

BRITISH CHEMICAL ABSTRACTS

Foreword.

The "A" section of the abstracts, dealing with pure chemistry, will be issued to Fellows of the Chemical Society and other subscribers at the end of each month, whilst the "B" section, covering applied chemistry, will appear each week, and will be circulated along with the *Journal of the Society of Chemical Industry* to members of that Society and to special subscribers.

The price of the "A" and the "B" sections is £3 13s. 6d. each per annum, post free (including joint Index), but Fellows of the Chemical Society may obtain the "B" abstracts for £1 10s. 0d., whilst Members of the Society of Chemical Industry may obtain the "A" abstracts for £2 0s. 0d. [The yearly membership subscriptions are £3 0s. 0d. in the case of the Chemical Society and £2 10s. 0d. in the case of the Society of Chemical Industry.] Copies of "A" or "B" abstracts printed on one side of the paper, and suitable for filing purposes, may be obtained at reasonable charges.

The general basis of classification adopted in the two sections is printed below. For the guidance of readers of "A" abstracts, it should be pointed out that abstracts of analytical papers may be found not only at the end of each section as tabulated below, but sometimes also, when the analytical method described has a very specialised object, in the body of the section, according to the material with which the analytical method deals.

A.—PURE CHEMISTRY.

General, Physical, and Inorganic Chemistry.

Sub-atomics.

- (a) Atomic spectra. Infra-red, visible, ultra-violet, X-ray emission and absorption spectra, Zeeman and Stark effects, Compton effect.
- (b) Electrical properties: Ionisation potentials of atoms, photo-electric and thermionic effects.
- (c) Properties of electrons and gaseous ions. Magnetic properties.
- (d) Isotopes—atomic weights.
- (e) Radioactive processes.
- (f) Other sub-atomic processes.
- (g) Theories of atomic structure and sub-atomic mechanism.
- (h) Atomic dimensions (except in solid state).

Molecular Structure.

- (a) Molecular spectra: Emission and absorption spectra of organic and inorganic substances. Fluorescence, luminescence, and phosphorescence. Raman effect.
- (b) Ionisation potentials. Photo-electric effect with compounds.
- (c) Conductivity. Dielectric constants. Dipole moment.
- (d) Molecular volumes.
- (e) Optical properties: Molecular refraction, dispersion, rotatory dispersion, optical activity, magnetic rotation.
- (f) Theories of molecular structure. Valency, secondary valency, including co-ordination, electronic and magnetic theories, constitutional formulæ of inorganic substances.
- (g) Molecular sizes and forces. Surface tension.

Crystal Structure.

- (a) X-Ray examination.
- (b) Crystal models.

- (c) Magnetic and electrical properties of crystals: Piezo-electricity; magnetostriction.
- (d) Optical properties. Rotatory dispersion.
- (e) Compressibility. Tensile strength.
- (f) Mesomorphic state.

Physical Properties of Pure Substances (not included above).

- (a) Molecular weights.
- (b) Electrical constants: Conductance, thermoelectric power, light-sensitivity, etc. Magnetic susceptibility.
- (c) Optical constants.
- (d) Thermal constants: Specific heats, heat of change of state, boiling points, freezing points, transition points.
- (e) Chemical constants.
- (f) Pressures and volumes: Density, vapour pressure, coefficient of expansion, equations of state, theory of corresponding states.
- (g) Compressibility.
- (h) Viscosity; fluidity; plasticity.
- (i) Diffusion.

Solutions and Mixtures.

- (a) Gaseous mixtures, liquid mixtures (excluding dilute solutions), solid solutions (including alloys), property-composition curves.
- (b) Miscibility of liquids and of solids. Solubility of gases and solids in liquids.
- (c) Distribution phenomena: Partition, absorption, adsorption, surface films, surface energy, membrane effects.
- (d) Dilute solutions: (i) Non-electrolytic solutions; (ii) Solutions of electrolytes. Colligative properties; non-colligative properties.
- (e) Disperse systems. Preparation and properties of suspensions, emulsions, smokes, foams, sols, gels, jellies. Coagulation, peptisation, ageing, cataphoresis, imbibition, etc.

Kinetic Theory. Thermodynamics.

- (a) Equilibrium in homogeneous systems; equilibrium, dissociation, ionisation constants, activity coefficients, etc.
- (b) Equilibrium in heterogeneous systems; uni- and multi-component systems, phase rule.
- (c) Thermochemistry.

Electrochemistry.

- (a) Electrical conductance.
- (b) Transport phenomena.
- (c) Electrode and diffusion potentials; e.m.f., concentration cells, etc.
- (d) Polarisation, overvoltage, passivity, etc.
- (e) Application of electrochemical methods.

Reactions.

- (a) Velocity studies in (i) Homogeneous systems; (ii) Heterogeneous systems.
- (b) Catalysed reactions: (i) and (ii) as above.
- (c) Electrode reactions.
- (d) Photochemical reactions.
- (e) Irradiated reactions.

New Methods of Preparing Substances arranged according to periodic table), etc.

Improved Methods of Preparing Substances, etc.

Analysis.

Apparatus.

Lecture Experiments.

Historical.

Geochemistry.

Organic Chemistry.

Aliphatic.

- Hydrocarbons.
- Halogen, nitro-, and nitroso-derivatives.
- Alcohols.
- Ethers.
- Alkyl salts.
- Sulphur compounds, including sulphonie acids.
- Acids.
- Thio- and sulpo-acids.
- Aldehydes.
- Aldoximes.
- Ketones and diketones.
- Ketoximes.
- Sugars, glucosides, and carbohydrates.
- Amines.
- Amino-alcohols.
- Amino-acids.
- Cyano-acids, thiocyno-acids.
- Amino-aldehydes and -ketones.
- Amides (including cyanic, cyanuric, and thiocyanic acids).
- Nitriles, carbylamines, metallic cyanides.
- Amidoximes, imino-ethers.
- Diazo-compounds.
- Phosphorus compounds.
- Arsenic, antimony, boron, silicon, etc. compounds.
- Aliphatic organo-metallic compounds.

Homocyclic.

- Hydrocarbons C_nH_{2n} to C_nH_{2n-6} .
- Halogen, nitroso-, and nitro-derivatives.
- Sulphonie acids.
- Hydrocarbons C_nH_{2n-2} to C_nH_{2n-4} . Derivatives under each.
- Amines. Includes anilides, carbamides, thiocarbamides, and sulphonie acids.
- Azoxy-compounds.
- Azo- "
- Hydrazo- "
- Diazo- "
- Diazoamino- "
- Phenols. Aminophenols, thiophenols, sulphides, sulphonie acids.
- Alcohols.
- Phenol-alcohols.
- Acids. Sulphonie acids and hydrazides under each member.
- Aldehydes. Derivatives under each.
- Ketones.
- Diketones and "oxyketones". "
- Quinones.
- Camphor group.
- Terpenes.
- Ethereal oils.
- Resins and balsams.
- Bitter principles and indifferent substances.
- Colouring matters (unclassified natural and artificial).
- Tannins.

Heterocyclic, etc.

- Furan group.
- Thiophen group (Se).
- Bases: N, N₂, N₃, etc.
- Alkaloids.
- Phosphorus compounds.
- As, Sb, Bi, B, Si compounds.
- Organo-metallic compounds.
- Proteins.

Analysis.

Biochemistry.

Respiration.

Blood: Gases; constituents; reactions (hæmolysis, anti-body formation, etc.).

Organs and their Proximate Constituents: Analytical data of constituents of organs: pure substances isolated from organs.

Secretions: Milk; lymph, etc.

Excretions: Urine; faeces; other excretions.

Diseases: Natural and experimental (in alphabetical order).

Metabolism: General; special; intermediary; fate of substances in the animal body.

Physiological Action: Variation of physiological conditions; action of drugs; toxicology.

Enzymes: General; specific.

Micro-organisms: Yeasts, moulds, protozoa, bacteria.

Hormones.

Vitamins.

Vegetable Physiology: General; reproduction and fertilisation; respiration; growth; proximate principles; diseases; poisons.

Analysis.

B.—APPLIED CHEMISTRY.

- I. General; Plant; Machinery.
- II. Fuel; Gas; Tar; Mineral Oils.
- III. Organic Intermediates.
- IV. Dyestuffs.
- V. Fibres; Textiles; Cellulose; Paper.
- VI. Bleaching; Dyeing; Printing; Finishing.
- VII. Acids; Alkalis; Salts; Non-Metallic Elements.
- VIII. Glass; Ceramics.
- IX. Building Materials.
- X. Metals; Metallurgy, including Electrometallurgy.
- XI. Electrotechnics.
- XII. Fats; Oils; Waxes.

- XIII. Paints; Pigments; Varnishes; Resins.
- XIV. Indiarubber.
- XV. Leather and Glue.
- XVI. Agriculture.
- XVII. Sugars; Starches; Gums.
- XVIII. Fermentation Industries.
- XIX. Foods.
- XX. Medicinal Substances; Essential Oils.
- XXI. Photographic Materials and Processes.
- XXII. Explosives.
- XXIII. Sanitation; Water Purification.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1932.

General, Physical, and Inorganic Chemistry.

Influence of pressure and foreign gases on the diminution of intensity of Balmer lines by weak magnetic fields. H. STAHL (*Z. Physik*, 1931, 72, 478—487).—The influence of pressure, and of N_2 , O_2 , and He, on the parallel components of H_β , H_γ , and H_δ from canal rays suggests that diminution in intensity caused by weak magnetic fields is partly due to Larmor precession and partly to external disturbance. A. B. D. CASSIE.

H discharge tube. E. LAU and E. REICHENHEIM (*Z. Physik*, 1931, 73, 31—32).—The construction of a discharge tube in which high concns. of H atoms may be obtained is described. The best results were obtained in the presence of a rare gas, particularly A. J. MEE.

Relation between the continuous and many-lined hydrogen spectra. IV. Y. HUKUMOTO (*Sci. Rep. Tôhoku*, 1931, 20, 599—607).—The continuous spectrum of the under-water spark resembles the continuous spectrum of H_2 , and is accompanied by the Fulcher bands; the intensity maxima occur in almost the same region of the ultra-violet. The under-water spectrum is therefore attributed to dissociation of H_2 . H. F. GILLBE.

Gas discharge wave-length list in extreme ultra-violet. J. M. MACINNES and J. C. BOYCE (*Physical Rev.*, 1930, [ii], 36, 368).—Published lines in the region 2500—100 Å. arising from discharges in H_2 , He, C, N_2 , O_2 , Ne, Na, Si, A, and Hg have been tabulated. L. S. THEOBALD.

Average life of the ionised helium atom. L. R. MAXWELL (*Physical Rev.*, 1931, [ii], 38, 1664—1686).—The theoretical average life vals. of energy levels of ionised He are 1/16 those of H, in agreement with experiment, and increase for higher quantum states. Respective vals. for the line 2733 Å. $6 \rightarrow 3$ are $1.1 \pm 0.2 \times 10^{-8}$ and 1.17×10^{-8} sec. for the sixth quantum state; average life became greater with increased voltage of the electron beam. Interpretation of results is uninfluenced by electron spin. N. M. BLIGH.

Anomalous dispersion of excited gases. VII. Anomalous dispersion in electrically excited helium. S. LÉVY (*Z. Physik*, 1931, 72, 578—586; cf. A., 1930, 1487).—A study of the dependence on pressure and current of the relative transition probabilities between different He levels, and of the influence of pressure on the excitation of singlet and triplet levels in He and Ne. A. B. D. CASSIE.

Colour of light from high-frequency discharges in helium. J. S. TOWNSEND and S. P. MCCALLUM (*Phil. Mag.*, 1931, [vii], 12, 1168—1175).

Magnetic rotation spectrum and heat of dissociation of the lithium molecule. F. W. LOOMIS and R. E. NUSBAUM (*Physical Rev.*, 1931, [ii], 38, 1447—1457).—The magnetic rotation spectrum of the green band system of Li_2 was measured, and intensities, quantum nos., and calc. and observed frequencies are tabulated. The heat of dissociation of the normal Li_2 mol. is 1.14 ± 0.03 volts. N. M. BLIGH.

Valency forces in lithium and beryllium. J. H. BARTLETT, jun., and W. H. FURRY (*Physical Rev.*, 1931, [ii], 38, 1615—1622).—For the Li_2 mol. in the ground state the calc. equilibrium distance of 2 normal atoms is 2.4 Å., and the heat of dissociation 1.09 volts. Two normal Be atoms repel each other. N. M. BLIGH.

Isotope effect in the band spectrum of lithium hydride. G. NAKAMURA (*Proc. Imp. Acad. Tokyo*, 1931, 7, 303—306).—A detailed account of work already noted (A., 1931, 1348).

Angular momentum of the Li^7 nucleus. L. P. GRANATH (*Physical Rev.*, 1930, [ii], 36, 1018).—Additional observations of hyperfine structure support the val. 3/2 for the angular momentum of Li (cf. A., 1930, 649). L. S. THEOBALD.

Second spark spectrum of carbon, C III. B. EDLÉN (*Z. Physik*, 1931, 72, 559—568).—52 singlet and 46 triplet lines were measured between 200 and 6500 Å.; the ionisation potential of the $2,1S$ level is 47.652 volts, and the 2^3P level is 6.465 volts above the ground level. A. B. D. CASSIE.

Jumping negative glow. W. A. LEYSHON (*Nature*, 1931, 128, 795—796).—The introduction of minute amounts of hexane and PhMe produces jumps in Ne tubes previously giving a steady negative glow. The jumping glow is probably related to the wavering positive column obtained in discharge tubes containing hydrocarbons. L. S. THEOBALD.

Transition probabilities and quenching in the $3P$ state of sodium. N. E. BERRY and G. K. ROLLEFSON (*Physical Rev.*, 1931, [ii], 38, 1599—1611).—An inert gas had no appreciable effect on the relative transition probabilities in the 3^2P state. With the addition of N_2 or H_2 the D light intensity variation followed that of the 3303 Å. line; He produced a marked increase in intensity. N. M. BLIGH.

Scattering of light in sodium vapour. S. A. KORFF (Physical Rev., 1930, [ii], 35, 435—436).—By using an artificial chromosphere the Na D lines have been shown to appear in absorption at lower v.d. than those for which they appear in emission.

L. S. THEOBALD.

Relative intensities in hyperfine structure multiplets. H. E. WHITE (Physical Rev., 1930, [ii], 36, 1800).

L. S. THEOBALD.

Wave-lengths in the spectra of the vacuum iron arc. K. BURNS and F. M. WALTERS, jun. (Pub. Allegheny Obs., Pittsburgh, 1931, 8, 39—64).—Accurate wave-lengths for lines of Fe I and Fe II between 3812 and 2157 Å. are recorded, and wave-lengths are computed for many lines.

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First spectrum of krypton. W. F. MEGGERS, T. L. DE BRUIN, and C. J. HUMPHREYS (Bur. Stand. J. Res., 1931, 7, 643—645).—By an improved method the total no. of lines recognised in the spectrum of neutral Kr atoms has been increased from 200 to 460.

E. S. HEDGES.

Aston's dark space in krypton and xenon and its gradual formation in helium. A. GUNTHER-SCHULZE and F. KELLER (Z. Physik, 1931, 72, 28—35).

A. B. D. CASSIE.

Spark spectrum of ruthenium. W. F. MEGGERS and A. G. SHENSTONE (Physical Rev., 1930, [ii], 35, 868).—Low terms of Ru II are tabulated.

L. S. THEOBALD.

Absorption of cadmium resonance radiation λ 2288 Å. and the life period of the Cd 2^1P_1 level. M. W. ZEMANSKY (Z. Physik, 1931, 72, 587—599).—Variation of absorption of resonance radiation with gas pressure indicates a life period of 1.99×10^{-9} sec. for the 2^1P_1 level.

A. B. D. CASSIE.

Deviations from Lambert's cosine law for glowing tungsten. E. SPILLER (Z. Physik, 1931, 72, 215—217).

A. B. D. CASSIE.

Existence of a new term in Hg I. E. D. MCALISTER (Physical Rev., 1930, [ii], 35, 1585—1586).—

L. S. THEOBALD.

Hyperfine structure and nuclear moments of mercury. H. SCHULER and J. E. KEYSTON (Z. Physik, 1931, 72, 423—441).—Hyperfine structure was examined in the 2537 Å. line, and in the region 7000—4000 Å. The isotopes 198, 200, 202, and 204 have zero nuclear spin, 199 has 1/2, and 201 has 3/2.

A. B. D. CASSIE.

Hyperfine structure and absorption of the 2537 mercury line. W. ZEHEND and M. W. ZEMANSKY (Z. Physik, 1931, 72, 442—446).—The relative intensities of hyperfine lines in the 2537 Å. line (cf. preceding abstract) are in agreement with absorption measurements (cf. Kopfermann and Tietze, A., 1929, 1119).

A. B. D. CASSIE.

Significance of mercury bands. H. KUHN (Z. Physik, 1931, 72, 462—471).—The energy of dissociation of Hg₂ is approx. 1 kg.-cal.

A. B. D. CASSIE.

Hyperfine structure of mercury. II. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 17, 1—5; cf. A., 1931, 1345).—The hyperfine

structure of the lines λ 4078, 4358, 5461, 2753, 2894, 3341, and 4916 is interpreted, and intensities and separations are given.

N. M. BLIGH.

Band spectrum of mercury hydride. R. RYDBERG (Z. Physik, 1931, 73, 74—86).—Results of a new study of the activated state of Hg hydride are given.

A. J. MEE.

Polarisation of mercury lines in stepwise radiation. A. C. G. MITCHELL (Physical Rev., 1930, [ii], 36, 1589—1590).—The polarisation of several Hg lines appearing in fluorescence when a mixture of N₂ and Hg vapour is subjected to a quartz-Hg arc is described and the significance discussed.

L. S. THEOBALD.

Appearances of the forbidden lines and the intensity modifications of the spectra of mercury, cadmium, and zinc under high-frequency excitation. J. OKUBO and E. MATUYAMA (Physical Rev., 1931, [ii], 38, 1651—1655).—Experimental.

N. M. BLIGH.

Influence of collisions on the formation of the Fraunhofer lines. A. PANNEKOEK (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 755—763).

W. R. ANGUS.

Chemical valency and properties of the spectral terms. A. T. WILLIAMS (Physikal. Z., 1931, 32, 870—875).—Theoretical. There is a connexion between the numerical differences of spectral terms and change of valency in certain groups of elements which have analogous electronic configurations: C, N, O, halogen, and Cu sub-groups.

A. J. MEE.

Spectra of two-electron systems. M. H. JOHNSON, jun. (Physical Rev., 1931, [ii], 38, 1628—1641).—Mathematical.

N. M. BLIGH.

Zeeman effect in intermediate coupling. D. R. INGLIS and M. H. JOHNSON, jun. (Physical Rev., 1931, [ii], 38, 1642—1647; cf. preceding abstract).—Mathematical. Energy level results for general two-electron configurations are applied to *g*-val. calculations in intermediate coupling.

N. M. BLIGH.

Hyperfine structure. S. GOUDSMIT (Physical Rev., 1930, [ii], 35, 436—437).—Attention is directed to an error which occurs in the application of the theory of hyperfine structure.

L. S. THEOBALD.

Distribution of chemical and thermal effects in a spark gap. H. TAKÔ (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 17, 57—67).—Measurements of temp. and of the amount of I liberated from KI by products formed at different positions along a spark gap indicate a parallelism between chemical and thermal effects.

F. L. USHER.

Band intensities. J. KAPLAN (Physical Rev., 1930, [ii], 36, 778).—Attention is directed to examples of band spectrum excitation which show marked deviations from the Franck principle.

L. S. THEOBALD.

Formation of helium molecular ion. E. MAJORANA (Nuovo Cim., 1931, 8, 22—28; Chem. Zentr., 1931, i, 3210).—The reaction $\text{He} + \text{He}^+ = \text{He}_2^+$ is examined from the energy point of view.

A. A. ELDRIDGE.

Theory of the double-crystal spectrometer. M. VON LAUE (Z. Physik, 1931, 72, 472—477).

A. B. D. CASSIE.

Prism spectrograph of large focal length. R. MANNKOPFF (Z. Physik, 1931, 72, 569—577).—A spectrograph built on one arm is described, several prisms refracting or reflecting the light through 180° , and so eliminating the radiation reflected from lens surfaces back to the photograph plate, as in the Littrow type.

A. B. D. CASSIE.

Total reflexion of X-rays. H. KIESSIG (Ann. Physik, 1931, [v], 11, 645—648).—Polemical against Edwards (A., 1931, 541), whose results do not agree with those of the author.

A. J. MEE.

X-Ray emission independent of temporary excitation. W. BAND (Physical Rev., 1930, [ii], 35, 1129).

L. S. THEOBALD.

Limited resolving power of a crystal grating. B. DAVIS (Physical Rev., 1930, [ii], 35, 209—210).

L. S. THEOBALD.

Multiple structure in the K X-ray absorption spectra of Cr, Mn, Fe, Co, Ni, and Cu. M. SAWADA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 229—250).—Photomicrographs and data for wide energy ranges are considered in relation to two hypotheses of the origin of extended multiple structure.

N. M. BLIGH.

X-Ray diagram lines strongly absorbed in the absorption spectra. S. KAWATA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 227—228; cf. A., 1931, 993).—The relative position of the emission line and corresponding absorption limit was determined from intensity diminution produced by an absorbing screen of the same element for L lines of W, Pt, Au, and Cu.

N. M. BLIGH.

Resolution of the $K\beta_1$ and $K\beta_2$ lines of the heavy metals. H. SEEMANN (Z. Physik, 1931, 73, 87—106).—A simple method for the resolution of the above doublets for the elements from Ta to U is described.

A. J. MEE.

Precision measurements in the K- and L-series of Cu, Sn, and Er to Re. I. WENNERLOF (Ark. Mat. Astron. Fysik, 1930, A, 22, No. 8, 20 pp.; Chem. Zentr., 1931, i, 3651).—L-Series of Re, Ta, Lu, "Ad," Er, and Sn and K-series of Cu were measured.

A. A. ELDRIDGE.

Ionisation potential of carbon. J. J. HOPFIELD (Physical Rev., 1931, [ii], 35, 1586—1587).—Using CO in He the spectrum of C I has been extended in the vac. region and new features have been observed. The new ultra-violet spectrum contains 3 series of multiplets which converge to the same three-fold limit, $^3P_{0,1,2}$, of the atom. These give an ionisation potential of 11.217 volts for the C atom from the 3P_0 lowest normal state.

L. S. THEOBALD.

Residual ionisation in nitrogen at high pressures. J. W. BROXON (Physical Rev., 1931, [ii], 38, 1704—1708; cf. A., 1931, 890).—Residual ionisation was greater at all pressures in nitrogen than in air. Results at high pressures are interpreted, and discussed in relation to earlier investigations in air, O_2 , N_2 , and CO_2 .

N. M. BLIGH.

Interpretation of the selective photo-electric effect from two-component cathodes. A. R. OLPIN (Physical Rev., 1931, [ii], 38, 1745—1757).—Evidence indicates that photo-electrically selective two-component cathodic surfaces are cryst. in nature. Computed vals. of the wave-lengths of light to which such a surface should respond are in good agreement for alkali hydride, oxide, and sulphide crystals. The hydrides exhibit 1 max., and the oxides 2 or 3 maxima in accordance with their cryst. types.

N. M. BLIGH.

Mass spectrograph analyses, and critical potentials for the production of ions by electron impact, in nitrogen and carbon monoxide. A. L. VAUGHAN (Physical Rev., 1931, [ii], 38, 1687—1695; cf. Bleakney, A., 1931, 10).— N_2^+ and N^+ ions appear at 15.8 ± 0.1 and 24.5 ± 0.1 volts, respectively, with increases of efficiency of production of the latter at 40.0 ± 1.0 and 47.0 ± 1.0 volts. Efficiency curves of total ionisation and of N_2 show max. at 100.0 ± 5.0 and 60.0 ± 5.0 volts, respectively. CO^+ , C^+ , and CO^{++} ions appear at 13.9 ± 0.2 , 22.5 ± 0.2 , and 43.0 ± 1.0 volts, respectively. O^- ions are formed between 9.5 ± 1.0 and 16.5 ± 1.0 and at 22.5 ± 1.0 to a max. at 33 volts. Results are interpreted as $N_2 \longrightarrow N^+ + N + e$; $CO \longrightarrow C^+ + O + e$; $CO^- \longrightarrow C + O^-$; $CO \longrightarrow C^+ + O^-$.

N. M. BLIGH.

Precise experimental determination of energy of excitation by electron impact in helium. J. E. ROBERTS and R. WHIDDINGTON (Phil. Mag., 1931, [vii], 12, 962—980).—Using a modification of the magnetic spectrum apparatus, excitation potentials in He were observed at 21.24 ± 0.03 , 23.19 ± 0.04 , and 23.84 ± 0.10 volts.

H. J. EMELEUS.

Diffraction of electrons by single crystals. J. J. TRILLAT and T. VON HIRSCH (Compt. rend., 1931, 193, 649—651).—A fine pencil of monokinetic electrons of 50 kv. impinging perpendicularly in vac. on Au leaf 0.1μ thick consisting of a single crystal gives a diffraction diagram, due to reflexion from planes passing through, or slightly inclined to, the [100] axis. When the pencil passes through a portion consisting of several crystals the ordinary Debye-Scherrer rings are produced, as is the case with X-rays.

C. A. SILBERRAD.

Certain effects accompanying electron diffraction. H. E. FARNSWORTH (Physical Rev., 1930, [ii], 35, 1131—1133).—In a repetition of previous work (A., 1929, 1212) with a second Cu crystal, all of the expected diffraction beams in the two principal azimuths and in the region below 325 volts have been observed.

L. S. THEOBALD.

Nuclear electrons. L. PAGE and W. W. WATSON (Physical Rev., 1930, [ii], 35, 1584—1585).—The hypothesis that nuclear electrons have no spin is discussed.

L. S. THEOBALD.

Electronic interference in the crystal lattice. F. KIRCHNER (Ann. Physik, 1931, [v], 11, 741—761).—The technique of electronic interference is improved and simplified. The method used was very accurate, and the wave-lengths determined in testing the de Broglie wave-mechanics relation $\lambda = h/mv$ do not agree with those calc. By spectral resolution of the

radiation after passing through a thin Al foil it is shown that the velocity loss in such a layer is not homogeneous. The same is found for radiation reflected from Au leaf. A. J. MEE.

Many-electron wave functions. J. H. BARTLETT, jun. (Physical Rev., 1931, [ii], 38, 1623—1627; cf. A., 1930, 390).—Mathematical. N. M. BLIGH.

Radiation from probe surfaces bombarded by electrons. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1931, 7, 751—764). E. S. HEDGES.

Photoelectrons and negative ions. J. L. HAMSHIRE (Nature, 1931, 128, 871).—Wellish's results (A., 1931, 1347) are discussed. L. S. THEOBALD.

Passage of H-canal rays through helium. R. DÖPEL (Physikal. Z., 1931, 32, 858—860).—The differences between electrons, protons, and neutral H atoms (neutrons) with regard to the excitation of He are investigated. In the first place the no. of protons in the total excitation of He by protons is determined. If a proton of 20—30 kv. excites He this excitation is not more than 0.1 of that by a neutron. The excitation by neutrons depends mainly on velocity and not on energy. A. J. MEE.

Motion of positive ions through gases. R. B. KENNARD (Physical Rev., 1930, [ii], 35, 1129—1131).—Previous results (A., 1928, 453; 1930, 269) for the scattering of alkali ions passing through gases are discussed. L. S. THEOBALD.

Ionisation of inert gases by slow alkali ions. II. Krypton and xenon. O. BEECK and J. C. MOUZON (Ann. Physik, 1931, [v], 11, 737—740; cf. A., 1930, 1494).—Xe is best ionised by Cs⁺. In general, a rare gas atom is most easily ionised by the ion of the alkali metal next to it in the periodic table. An exception is Kr, which is better ionised by K⁺ than by Rb⁺. A. J. MEE.

Determination of mobility of rare gas ions by the aid of negative layers. M. J. DUYVESTEYN (Z. Physik, 1931, 73, 33—44).—The negative layers in Ne, He, and A are described. In Ne the p. d. between the layers was 19 volts. The mobility of the positive ions was calc. from the concn. of the layer before the cathode for a small current. For a field of 1 volt per cm. and atm. pressure, the mobility of Ne ions was 9.8 cm. and of He ions 19 cm. per sec. A. J. MEE.

Emission of negative ions under the bombardment of positive ions. K. S. WOODCOCK (Physical Rev., 1931, [ii], 38, 1696—1703; cf. Sawyer, A., 1930, 835).—Li ions reflected from a metal surface gave a bundle at the specular angle, but not at the normal to the surface. A retarding field gave evidence of negative emission from the target, and this emission was analysed magnetically. Negative F, Cl, O, and S ions were obtained by bombarding NaF, CaF₂, NaCl, CaO, PbS, and oxide-coated vac.-tube filaments. Clean Pt, Au, Al, Ta, Ni, and W targets emitted electrons, and the ions H⁺, H₂⁺, OH⁺, and Cl⁺ with traces of probably N⁺ and LiOH⁺. N. M. BLIGH.

Doppler effect in the canal rays in neon. W. ROMA (Physical Rev., 1931, [ii], 38, 1709—1715).—The Ne spectrum in the ultra-violet between 2500 and

4000 Å. from a canal-ray tube showed Doppler effects in the 1st and 2nd spark lines, but, with two exceptions, not in the arc lines. Spectrograms and complete data are given. N. M. BLIGH.

Velocity spectrum of normal gaseous ions in air and the problem of ionic structure. L. B. LOEB and N. E. BRADBURY (Physical Rev., 1931, [ii], 38, 1716—1729; cf. A., 1931, 1107).—Theoretical. N. M. BLIGH.

Mass of positive ions in a glow discharge. O. LUHR (Physical Rev., 1931, [ii], 38, 1730—1738; cf. A., 1930, 1225).—Relatively large quantities of the ions N⁺, N₃₋₂⁺, O⁺, N₂⁺, O₂⁺, O₃⁺, SO₂⁺, and H₂SO₃⁺ were formed in a glow discharge in air, N₂, O₂, and SO₂. A mass spectrum analysis showed peaks corresponding with mol. wt. of 56—64, 76, 80, 96, 108, 138, 140, 168, and 200, indicating the presence of the ions 2N₂⁺, N₂O₂⁺, 2O₂⁺, N₂O₃⁺, and heavier combinations. The nature of aged air-ions is discussed. N. M. BLIGH.

Debye-Scherrer rings with material rays. M. VON LAUE (Naturwiss., 1931, 19, 951).—Preliminary experiments on the diffraction of rays of protons from crystals indicate that the rays penetrate the crystal so deeply as to necessitate the supposition of space lattice interference to account for the diffraction patterns (cf. Sugiura, A., 1931, 1107). W. R. ANGUS.

Systematics and statistics of nuclei. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 17, 6—9).—Any nucleus with an even or odd no. of protons satisfies the Bose and Fermi statistics, respectively, the proton in the nucleus satisfying the Fermi, and the electron in the nucleus satisfying the Bose statistics. N. M. BLIGH.

Classification of the elements. III. G. ODDO (Gazzetta, 1931, 61, 694—698).—A modification of the author's classification (A., 1925, ii, 623) and a discussion. H. F. GILLBE.

At. wts. of hydrogen and helium. R. T. BIRGE (Physical Rev., 1930, [ii], 35, 1015).—A discussion. L. S. THEOBALD.

Probable detection of an even-numbered isotope of mercury, Hg¹⁹⁸. H. SCHULER (Naturwiss., 1931, 19, 950—951).—From an examination of the hyperfine structure of the Hg green line (5461 Å.) the existence of the Hg¹⁹⁸ isotope is claimed. The evidence for this arises from the splitting up of the 6³P₂ term, since the 7³S term shows no splitting. W. R. ANGUS.

[Attempted] decomposition of the lead atom. IV. A. SMITS and (FRL.) J. M. A. KRUGER (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 866—874).—Discrepancies between the authors' previous results (cf. A., 1931, 16) and those of Pokrowski (A., 1930, 1086) were presumed to arise from impurities in the Pb. X-Ray irradiation of Pokrowski's Pb gives concordant results. Al plates are not influenced by irradiation. W. R. ANGUS.

Probable number of isotopes of eight metals as determined by a new method. F. ALLISON and E. J. MURPHY (Physical Rev., 1930, [ii], 36, 1097—1098).—The magneto-optic method of analysis (A.,

1930, 1541) indicates isotopes for Au (2), Pd (3), Pt (2), Rh (1), Ru (2), Ta (3), Tl (2), and Th (3).

L. S. THEOBALD.

Simple isotopic constitution of caesium. K. T. BAINBRIDGE (Physical Rev., 1930, [ii], 36, 1668).—Measurements with a Dempster mass spectrograph show that Cs has only one isotope. This indicates a packing fraction of -14.3 or an error of 0.077% in the accepted val., 132.81 , of the at. wt. Other possibilities are discussed.

L. S. THEOBALD.

Observed periodicity in the packing fraction. H. OLSON (Physical Rev., 1930, [ii], 35, 213—214).—A single oscillatory curve can be fitted to packing fraction data. Max. occur at mass no. 6, 10, 13, 17, 21, 25, . . . and min. are found for elements the mass no. of which is an integral multiple of 4. Periodicity in the heaviest elements is less certain. In atoms of mass no. $4n+1$ (n is an integer) the one proton is loosely connected to the core of the nucleus; in the $4n+2$ type the 2 protons are more firmly bound, and with the $4n+4$ type max. packing occurs, the 4 protons probably forming an α -particle which goes into the centre of the nucleus. L. S. THEOBALD.

Relation between uranium and radium. IX. Period of ionium. F. SODDY (Phil. Mag., 1931, [vii], 12, 939—945).—From the growth of Ra in U preps. purified in 1905—1909 the period of average life of Io was redetermined as 1.06×10^5 years, taking that of Ra = 2300 years.

H. J. EMELÉUS.

Simple apparatus for purifying radon. G. H. HENDERSON (Canad. J. Res., 1931, 5, 466—469).

R. S. CAHN.

Significance of the Compton effect in absolute γ -ray absorption measurements. L. H. CLARK (Phil. Mag., 1931, [vii], 12, 913—938).—The factors determining the amount of scattered radiation affecting electroscopic absorption measurements were investigated experimentally.

H. J. EMELÉUS.

Phosphorescent zinc sulphide screens and radioactivity under extremely high pressure. T. C. POULTER and H. McCOMB (Proc. Iowa Acad. Sci., 1930, 37, 311—312).—The intensity of phosphorescence of ZnS falls considerably under very high pressures. Radioactivity is scarcely affected by pressures up to 20,000 atm.

CHEMICAL ABSTRACTS.

Regularities in radioactive nuclei. H. C. UREY and H. JOHNSTON (Physical Rev., 1930, [ii], 35, 869—870).—Radioactive nuclei form a 4th cluster to be added to Barton's 3 non-radioactive clusters (A., 1930, 518).

L. S. THEOBALD.

Capture of electrons by α -particles. W. BAND (Physical Rev., 1930, [ii], 35, 1128—1129).—Theoretical.

L. S. THEOBALD.

α -Rays of long range from thorium- $C+C'$, and some determinations of velocities of α -rays. S. ROSENBLUM (Compt. rend., 1931, 193, 848—850).—On investigating by the magnetic method (cf. A., 1930, 837) the velocities of the 11.5-cm. group of α -rays of Th- $C+C'$ a new ray of velocity 1.098 times that of the α -ray of Th- C' has been observed, and probably another of relative velocity 1.037 belonging to the 9.7-cm. group. The velocities

of the α -rays of Ac and Ac- C' similarly determined by comparison with those of Ra- C' are respectively 1.782 and 1.893×10^9 cm. per sec.

C. A. SILBERRAD.

Transition probabilities for excited nuclei. M. DELBRUCK and G. GAMOW (Z. Physik, 1931, 72, 492—499).—Quantum mechanics gives an upper or a lower limit to the probabilities of emission of a long-range α -particle, a secondary β -ray, or γ -radiation, and these limits agree with experimental results.

A. B. D. CASSIE.

Specific ionisation of high-frequency radiation. W. KOLHORSTER and L. TUWIM (Naturwiss., 1931, 19, 917).—The energy of individual α - and β -particles can be calc. from an equation which is deduced for the sp. ionisation of high-frequency radiation.

W. R. ANGUS.

Calorimetry of absorption of γ -rays of radium. D. K. YOVANOVITCH and P. SAVITCH (Compt. rend., 1931, 193, 1006—1008).—By the method previously described (cf. A., 1926, 772; 1929, 116) the amounts of the heat evolved by 20.43 mg. of Ra which are absorbed by varying thicknesses of Pb, Ag, and Cu are determined, with results for Pb in agreement with the author's formula, but for Ag and Cu indicating probable non-absorption by these lighter elements of all the electrons produced. Of the 155.38 g.-cal. measured with the max. thickness of Pb, 129 are due to α -, 13.4 to β -, and 12.98 to γ -radiation; the last is, however, only partly absorbed.

C. A. SILBERRAD.

Cosmic-ray phenomena. L. M. MOTT-SMITH and G. L. LOCHER (Physical Rev., 1931, [ii], 38, 1399—1408).—A Wilson cloud expansion apparatus combined with Geiger-Müller electron-counters showed that the discharge of a counter due to cosmic radiation was accompanied by ion-tracks, indicating that the simultaneous discharge of two counters is due to ionising particles (high-energy electrons) and not to photons.

N. M. BLIGH.

Possibility of proof of electron spin by experiments on sharing of inelastic electron collisions. O. KLEMPERER (Physikal. Z., 1931, 32, 864—866).—Apparatus for determining the energy distribution of singly-scattered electrons is described. The results can be used to show the existence of electron spin.

A. J. MEE.

Spin of the photon. M. N. SANA and Y. BHARGAVA (Nature, 1931, 128, 870).—A discussion of results of previous investigators. Polarisation of light should not be explained by assuming a spin of the photon.

L. S. THEOBALD.

Constitution of the white dwarf stars. S. SUZUKI (Nature, 1931, 128, 838).—It is concluded that the heavy radio-elements are abundant in the white dwarfs.

L. S. THEOBALD.

Transition effects in cosmic rays. H. SCHINDLER (Z. Physik, 1931, 72, 625—657).—Cosmic rays, after traversing an absorbing layer, may have their ionising power increased on traversing a layer of another substance.

A. B. D. CASSIE.

Atomic stability as related to nuclear spin. W. D. HARKINS (Physical Rev., 1930, [ii], 35,

434—435).—All known data indicate that, in general, high nuclear stability is associated with zero nuclear angular momentum (zero spin). L. S. THEOBALD.

Quartz quarter-wave plate for the ultra-violet. Double refraction of amorphous silica and quartz caused by compression, and its dispersion. G. BRUHAT and J. THOUVENIN (Compt. rend., 1931, 193, 727—729, 843—845).—An arrangement consisting of superposed plates of left- and right-handed quartz of equal thickness ($107\ \mu$) cut perpendicular to the axis, which can be rendered quarter-wave for light of any wave-length by suitable inclination to the incident ray, has been used to determine for light of $\lambda\ 2700$ — 5780 the double refraction produced in plates of fused SiO_2 and of quartz by pressures of 30—200 kg. per sq. cm. Typical values of $(n_0 - n_e) \times 10^{13}$ for a pressure of 1 kg. per sq. cm. on a plate 1 cm. thick of fused SiO_2 are 3.79 for $\lambda\ 5780$ and 4.81 for $\lambda\ 2400$; those for quartz are substantially smaller. For a given wave-length the double refraction is proportional to the pressure. Havelock's formula (cf. A., 1929, 742) gives only a first approximation. C. A. SILBERRAD.

Ultra-violet absorption spectrum of ozone. R. RUYSSSEN (Natuurwetensch. Tijds., 1931, 13, 273—278).— O_3 at low concns. (0.38%) exhibits continuous absorption at wave-lengths below $2950\ \text{\AA}$; at higher concns. (4%) 10 bands appear at wave-lengths between 3152 and $3303\ \text{\AA}$. H. F. GILLBE.

Absorption spectra of salts in liquid ammonia. R. W. WOOD (Physical Rev., 1931, [ii], 38, 1648—1650).—Preliminary results for Nd NH_4 nitrate and KMnO_4 are reported. N. M. BLIGH.

Comparison of the reflexion spectra of $\text{SmCl}_6 \cdot 6\text{H}_2\text{O}$ at room temperature and at that of liquid air with its absorption spectra at low temperatures. S. FREED and F. H. SPEDDING (Physical Rev., 1930, [ii], 35, 212—213). L. S. THEOBALD.

Spectroscopical study of a bilirubin derivative with red fluorescence. C. DHÉRE (Ar. Int. Pharmacodyn. Ther., 1930, 38, 134—139; Chem. Zentr., 1931, i, 3572).—Compounds prepared by the action of (a) $\text{Zn}(\text{OAc})_2$ and I in KI on bilirubin in EtOH in presence of NH_3 (Auché, 1908), (b) $\text{Zn}(\text{OAc})_2$ and I in KI on bilirubin in pyridine, give in EtOH green solutions with a red fluorescence excited by ultra-violet radiation (particularly $3650\ \text{\AA}$). The fluorescence spectrum was examined. A. A. ELDRIDGE.

Absorption of ultra-violet light by lacquer films. W. P. DAVEY and D. C. DUNCAN (Physical Rev., 1930, [ii], 35, 1423).—Nitrocotton films, film solutions, and their individual ingredients have been investigated. No film showed selective absorption and all were opaque to wave-lengths $< 3300\ \text{\AA}$. L. S. THEOBALD.

Near infra-red absorption spectra of liquids determined by a photo-resistance cell. R. FREYMAN (Compt. rend., 1931, 193, 656—659).—Using a Rowland grating, a thalofide cell (cf. A., 1929, 145), and a valve amplifier the infra-red absorption spectra of 12 primary aliphatic and several aromatic alcohols,

6 aldehydes, and 7 alkyl halides have been determined between 0.85 and $1.15\ \mu$ with an accuracy of $\pm 3\ \text{\AA}$. The bands at 0.9 and $1\ \mu$ (cf. A., 1929, 736) are at least double, probably triple, with maxima moving towards greater wave-lengths as the series is ascended. New bands at $0.9631\ \mu$ in aliphatic and $0.978\ \mu$ in aromatic alcohols show no such variation and are probably the third harmonic of the $3\ \mu$ OH band. C. A. SILBERRAD.

Infra-red bands of slightly asymmetric molecules. H. H. NIELSEN (Physical Rev., 1931, [ii], 38, 1432—1441).—The general characteristics of the 3 types of bands are calc. N. M. BLIGH.

Absorption band in ethylene gas in the near infra-red. R. M. BADGER and J. L. BINDER (Physical Rev., 1931, [ii], 38, 1442—1446).—Investigations were made in the region $\lambda\lambda\ 6500$ — 9500 for C_2H_4 and C_2H_6 ; the latter showed no absorption. C_2H_4 showed a strong band at $\lambda\ 8720$ of structure resembling the predictions of Nielsen (cf. preceding abstract); provisional moments of inertia $\times 10^{40}$ are: A_x , u , v , 31, 27, and 3.8. N. M. BLIGH.

Infra-red absorption spectra of hydrogen carbonates and mercaptans. P. N. GOSH and B. D. CHATTERJEE (Z. Physik, 1931, 72, 542—552).—Absorption spectra due to Na_2CO_3 , K_2CO_3 , NaHCO_3 , KHCO_3 , and NaOH were determined between 5 and $12\ \mu$ with a prism spectrometer, and due to NaHCO_3 , NaOH , and EtSH between 1 and $5\ \mu$, with a grating spectrometer: bands near $2.94\ \mu$ are ascribed to O-H linkings, near $11.8\ \mu$ to Na-O linkings, and near 2.27 and $3.92\ \mu$ to the S-H linkings. A. B. D. CASSIE.

Infra-red absorption spectra of mixed organic liquids: electrolytic dissociation therein. R. FREYMAN (Compt. rend., 1931, 193, 928—930).—Determination of the infra-red absorption spectra of mixtures of EtOH or BuOH with CCl_4 enables about 1% of added alcohol to be detected by the intensity of the C-H bands (0.9 and $1\ \mu$). 0.1% is detectable by that of the OH band ($0.9631\ \mu$), this showing a max. for 10—20% and disappearing when there is less than 0.1% . This band behaves similarly when CCl_4 is replaced by BuBr , CHCl_3 , C_2Cl_4 , C_2HCl_3 , $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Br}$, or C_6H_6 . This behaviour is attributed to electrolytic dissociation of the alcohol, as in the case of HNO_3 (cf. A., 1930, 840). The displacement of this band, e.g., to 0.9778 in $\text{CH}_2\text{Ph}\cdot\text{OH}$, is associated with the presence of an ethylenic linking, gradually disappearing on dilution with, e.g., CCl_4 , whilst similar displacements are in some cases caused on adding an ethylenic compound to a saturated aliphatic alcohol. C. A. SILBERRAD.

Difference in the absorption spectrum of benzene in the liquid and vapour state. E. D. MCALISTER and H. J. UNGER (Physical Rev., 1930, [ii], 36, 1799).—Shifts towards higher frequencies are recorded for the absorption spectrum of the vapour in the 1.1 and $1.6\ \mu$ regions. L. S. THEOBALD.

Measurements on sodium and potassium chloride in the spectral region containing their normal vibrations. R. B. BARNES and M. CZERNY (Z. Physik, 1931, 72, 447—461).—Condensed layers of

NaCl and of KCl approx. $1\ \mu$ thick give the same optical consts. as plates split from a crystal. The principal vibration for NaCl is at $61.1\ \mu$, and for KCl at 70.7 ; subsidiary absorption maxima appear at 40.5 and $47\ \mu$, respectively. A. B. D. CASSIE.

Apparatus for Raman effect. B. ANAND (J. Sci. Instr., 1931, 8, 258—260).—A tube containing the liquid under investigation is placed at the common focus of four overlapping ellipses, and is illuminated by Hg lamps placed at the other foci.

C. W. GIBBY.

Molecular scattering of light from amorphous and crystalline solids. A. HOLLAENDER and J. W. WILLIAMS (Physical Rev., 1931, [ii], 38, 1739—1744).—Raman spectra are reported for several specimens of plate glass and for cryst. gypsum, BaSO_4 , and CuSO_4 , and aq. solutions of CuSO_4 , MgSO_4 , and K alum. The sulphates show lines corresponding with both the active and inactive frequencies of SO_4^{--} .

N. M. BLIGH.

Relative efficiency of the mercury-arc lines in exciting the Raman spectrum of benzene. M. WERTH (Physical Rev., 1930, [ii], 36, 1096).—Results obtained with suitable light filters are recorded. The 4th-power law is not confirmed for the region 3341 — $4358\ \text{\AA}$.; higher frequencies appear to be the more efficient in exciting the Raman lines.

L. S. THEOBALD.

Raman spectrum of the SO_4 ion. O. SPECCHIA (Atti R. Accad. Lincei, 1931, [vi], 13, 754—759).—Seven Raman lines excited by λ 4358.6 and $4046.8\ \text{\AA}$. in conc. H_2SO_4 (d 1.84) have been found. 4358 gives Raman frequencies corresponding with 24.3^* , 17.7^* , 14.7 , 11.2 , 9.5^* , 8.6^* , and $7.19\ \mu$. The asterisk indicates the fundamental frequencies of SO_4^{--} . Dilution of the acid causes displacement of the lines towards higher wave-lengths and variations in their relative intensity. Saturated solutions of MgSO_4 , MnSO_4 , and Li_2SO_4 all show the four SO_4 Raman lines.

O. J. WALKER.

Raman spectra from sulphur dioxide. R. G. DICKINSON and S. S. WEST (Physical Rev., 1930, [ii], 35, 1126—1127).—Recorded data for scattered lines from dry liquid SO_2 show three shifts with the average vals. $524.3\ \text{cm}^{-1}$, weak; $1145.9\ \text{cm}^{-1}$, strong; and $1340.1\ \text{cm}^{-1}$, medium. The last two shifts agree with the frequencies of the two strongest absorptions by gaseous SO_2 found by Coblentz.

L. S. THEOBALD.

Effect of dilution on the Raman spectra of nitric acid. E. L. KINSEY (Physical Rev., 1930, [ii], 35, 284—285).—Rao's main results and conclusions (A., 1930, 840) are confirmed.

L. S. THEOBALD.

Raman spectrum of hydrogenated derivatives of naphthalene. G. B. BONINO and P. CELLA (Atti R. Accad. Lincei, 1931, [vi], 13, 784—789).—The Raman spectra of deca- and tetra-hydronaphthalene have been measured. The structures of these mols. are discussed.

O. J. WALKER.

Raman spectrum of dichlorobromomethane. G. B. BONINO and L. BRÜLL (Atti R. Accad. Lincei, 1931, [vi], 13, 789—793).—The Raman spectrum of CHCl_2Br has been measured and compared with those

of CHCl_3 and CHBr_3 . The CHCl_2Br spectrum contains one more frequency than those of the other two mols. The calc. val. of the electric moment of CHCl_2Br is 1.25×10^{-18} .

O. J. WALKER.

Influence of substitution on frequency of [Raman] lines of ethylenic compounds. M. BOURGUEL (Compt. rend., 1931, 193, 934—937; cf. A., 1931, 284).—Of the strong ethylenic lines 1342 and $1623\ \text{cm}^{-1}$ changes in the former are difficult to follow, those in 1623 easy. In compounds $\text{C}_2\text{H}_3\text{R}$ the frequency corresponding with 1623 increases when R is an alkyl, becoming 1642 in all cases irrespective of mol. wt. of the alkyl. In disubstituted derivatives alkyls cause a further increase, greater in $\text{CH}_2\text{CR}'\text{R}''$ than in $\text{CHR}'\text{CHR}''$, and still greater in trisubstituted compounds. If R, R', or R'' is a halogen, and still more so if two or more are, there is a decrease. The following determinations are given: $\Delta^{\alpha}\text{-C}_n\text{H}_{2n}$ ($n=5-9$), $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}_2$, $\text{CPh}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, all 1642 ; $\text{CMeEt}\cdot\text{CH}_2$, 1652 ; $\text{CHEt}\cdot\text{CHMe}$, 1657 ; cyclohexane 1654 ; C_2HMe_3 , 1679 ; limonene 1647 and 1679 ; $\text{CPrBr}\cdot\text{CH}_2$, 1631 ; $\text{CH}_2\text{Ph}\cdot\text{CBr}\cdot\text{CH}_2$, 1631 .

C. A. SILBERRAD.

Raman effect in terpene compounds. I. Di-cyclic terpenes. G. DUPONT, P. DAURE, and J. ALLARD (Bull. Soc. chim., 1931, [iv], 49, 1401—1409).—Raman spectra of α - and β -pinene, carene, and camphene, and also of pinane, carane, and camphane, have been recorded. Mixtures of the terpenes give the spectra of all the constituents. They are easily distinguishable and may prove useful in the qual. or even quant. study of terpene mixtures.

M. S. BURR.

Doublets in the vibration spectrum of cyclohexane. J. W. ELLIS (Physical Rev., 1930, [ii], 35, 437—438).—The 3rd and 4th members of the C-H anharmonic series of cyclohexane have not been resolved. Data relating to the remaining members are discussed.

L. S. THEOBALD.

Raman spectra of geometric isomerides. C. F. FFOLLIOTT (Physical Rev., 1930, [ii], 36, 367).—The Raman spectrum of Et maleate has a broad, diffuse band at 4693 — $4699\ \text{\AA}$.; in Et fumarate this band is replaced by lines at 4692 and $4698\ \text{\AA}$. Frequency shifts are recorded.

L. S. THEOBALD.

Raman spectra of benzene and toluene. L. E. HOWLETT (Nature, 1931, 128, 796).—The line near $1000\ \text{cm}^{-1}$, characteristic of the C_6H_6 ring, has been resolved into 5 components in the case of C_6H_6 , and into 4 in that of PhMe. Other lines are complex, whilst several new lines have been observed in PhMe.

L. S. THEOBALD.

Light scattering in liquids. S. VENKATESWARAN (Nature, 1931, 128, 870—871).—Data for the Rayleigh scattering of the Hg arc in CS_2 , C_6H_6 , and PhMe agree with the depolarisation calc. on the theory of spinning electrons.

L. S. THEOBALD.

Measurement of fluorescence with a photo-electric cell. R. TOUSSAINT (Compt. rend., 1931, 193, 933—934).

C. A. SILBERRAD.

Energy transformations at surfaces. IV. Reciprocal action between excited dye molecules and oxygen. H. KAUTSKY and A. HIRSCH (Ber., 1931,

64, [B], 2677—2683; cf. A., 1931, 1374).—Exposure of tryptaflavine-SiO₂ adsorbate to minute mounts of O₂ immediately extinguishes the phosphorescence and greatly diminishes the fluorescence; the effect is reversible. The sensitiveness of the phosphorescence action is such that the change may be used for the detection of minute traces of O₂. All dye adsorbates examined resemble tryptaflavine with respect to phosphorescence, whilst showing individual action with regard to fluorescence. N₂, H₂, and CO₂ have no action. The influence of O₂ on dyes in solution is similar to but less marked than that on the adsorbates; the effects are slight in H₂O, noticeable in EtOH, and most marked in COMe₂. The behaviour of chlorophyll towards O₂ is the same in the presence or absence of isoamylamine. Diminution of fluorescence by O₂ is therefore not attributable to oxidation of the irradiated dye, but to transference of energy from the dye mol. to the O₂ mol. with activation of the latter.

H. WREN.

Sensitiveness of a copper grating photo-electric cell: comparison with optical absorption and photo-conductivity of cuprous oxide. L. DUBAR (Compt. rend., 1931, 193, 659—661).—A cell similar to that of Auger and Lapicque (cf. A., 1931, 1112), but with a Cu grating (+) in place of the Au layer (—), gives a photo-electric current proportional within wide limits to the incident light energy. Sensitiveness begins at λ 5750, is max. for 6200, and then declines. The internal resistance is 4000 ohms per sq. cm. The effect is probably localised in the Cu₂O next the Cu, which is of the semi-insulating type (cf. *ibid.*, 409). Curves compare for λ 5000—11,000 the current produced, with the light energy transmitted by a layer of Cu₂O, and with the photo-electric conduction current of semi-insulating Cu₂O.

C. A. SILBERRAD.

Crystal photo-cell. H. DEMBER (Physikal. Z., 1931, 32, 856—858).—It is shown that various specimens of cryst. Cu₂O from different sources all give the same photo-effect.

A. J. MEE.

Electronic conductivity of copper oxides. M. LE BLANC and H. SACHSE (Ann. Physik, 1931, [v], 11, 727—735).—The variation of sp. conductivity of Cu₂O and CuO with temp. was found over the range 20—400°, the specimens being comparable as regards particle size etc. The conductivity of Cu₂O is always below that of CuO, which, from the analogy with NiO and MnO, shows that Cu₂O is the normal oxide of Cu. If freshly-prepared Cu₂O is kept in vac. with O₂, there is an increase in conductivity, which is not reversed by removing the gas, but only by heating in vac. to 250°. The effect does not occur with H₂ or N₂.

A. J. MEE.

Photo-electric effect from thin films of alkali metal on silver. H. E. IVES and H. B. BRIGGS (Physical Rev., 1931, [ii], 38, 1477—1489).—The region of low reflecting power of Ag in the ultra-violet exerts a strong but indirect effect on the photo-emission of alkali metal films. Positions of max. and min. of photo-emission, and their variations with angle of illumination and plane of polarisation are found.

N. M. BLIGH.

Contact potential difference between iron and nickel and their photo-electric work functions. G. N. GLASOE (Physical Rev., 1931, [ii], 38, 1490—1496).—The equilibrium contact p.d. for electrolytic Fe and Ni, intensively outgassed, was Fe-Ni +0.21 ± 0.01 volt; the photo-electric long-wave limits were (Fe) 2620 ± 10 and (Ni) 2500 ± 10 Å. The corresponding work functions are (Fe) 4.71 ± 0.02, and (Ni) 4.93 ± 0.02 volts; the difference is the measured contact p.d.

N. M. BLIGH.

Dependence of photo-electric conductivity in crystals on potential. W. FLECHSIG (Physikal. Z., 1931, 32, 843—847).—The crystals used were of rock-salt which was completely transparent from the Schumann violet to the longer infra-red, and had developed a yellow colour by irradiation with X-rays. The characteristic curves for the crystals drawn between negative primary current and the field strength divided by the thickness of crystal show maxima indicating saturation. This can be explained by supposing that the electrons do not go right through the crystal, the quantum equivs. being supposed still to hold. An equation connecting saturation field strength and coloration of crystal is given.

A. J. MEE.

Conductivity and photo-effect at unidirectional layers. W. SCHOTTKY (Physikal. Z., 1931, 32, 833—842).—A summary of work on the unidirectional layer and photo-effect of Cu₂O. The unidirectional layer and rectifying layers occur only on substances having a negative temp. coeff. of resistance, and the direction of the current is always from the better to the worse conductor. The photo-effect associated with Cu₂O is considered, and it is stated that there is probably complete identity between the inner photo-electrons and the unidirectional-layer electrons, and that the unidirectional layer photo-effect is, in general, the same as the diffusion effect connected with the life-period of the inner photo-electrons.

A. J. MEE.

Increase of current in photo-cells by gas discharge. P. V. TIMOFEEV and N. S. CHLEBNIKOV (Z. Physik, 1931, 72, 658—668).—An empirical expression is given for the most efficient gas pressure for a given p.d. across the cell.

A. B. D. CASSIE.

Inner potential of a copper crystal. H. E. FARNSWORTH (Physical Rev., 1930, [ii], 36, 1799).

L. S. THEOBALD.

Temperature coefficient of the dielectric constant of water. R. T. LATTEY, O. GATTY, and W. G. DAVIES (Phil. Mag., 1931, [vii], 12, 1019—1025; cf. A., 1929, 1128).—The results of determinations made between 0° and 80° are expressed by the relation $\log_{10} D - 1.94361 - 0.0020045t$.

H. J. EMELÉUS.

Dipole moments of homologous alcohols, esters, and ketones. K. L. WOLF and W. J. GROSS (Z. physikal. Chem., 1931, B, 14, 305—325).—The dipole moments of various primary aliphatic alcohols, aliphatic ketones, and fatty acid esters have been determined. In ascending a homologous series the dipole moment alternately rises and falls, mols. with an even no. of C atoms generally having higher moments than mols. with an odd no. of C atoms.

With increase in the no. of C atoms in the chain, however, the dipole moment tends to a limiting val. An apparatus suitable for the measurement of the dielectric const. of such compounds is described.

R. CUTHILL.

Dipole moments of esters with hydrocarbon radicals having closed and branched chains. H. L. DONLE (*Z. physikal. Chem.*, 1931, B, 14, 326—338).—The dipole moments of various esters of aliphatic alcohols with branched chains, of alcohols with saturated ring systems, and of aromatic acids and phenols have been measured. From the moments of Me *p*-toluate and *p*-tolyl acetate it is calc. that in the benzoic and Ph esters the angles between the moments and the line joining the C atom of the ring to the adjacent atom of the substituent are 62° and 82°, respectively. These vals. have been successfully used to calculate the moments of the corresponding *m*-compounds, but with the *o*-compounds the calc. vals. differ from the experimental vals., possibly because of a restriction of the free rotation of the polar group in these compounds. R. CUTHILL.

General formula for calculation of dipole moments. O. FUCHS (*Z. physikal. Chem.*, 1931, B, 14, 339—345).—The calculation of the dipole moment of a C₆H₆ substitution product having two or more substituents from the moments of a mono-substituted compound and the other substituents is described. It is assumed that the substituents do not influence each other, and that substituents which are not rectilinear are freely rotatable. Comparison of the calc. with the experimental vals. indicates, however, that these assumptions are not always admissible.

R. CUTHILL.

Dipole moments of the chlorotoluenes and *o*-toluonitrile. K. L. WOLF and H. G. TRIESCHMANN (*Z. physikal. Chem.*, 1931, B, 14, 346—349).—The experimental vals. for the dipole moments of the above four compounds agree satisfactorily with the vals. calc. by vectorial addition (cf. preceding abstract). R. CUTHILL.

Electric moments of halogenonitrobenzenes. H. LÜTGERT (*Z. physikal. Chem.*, 1931, B, 14, 350—358).—The total polarisations of the chloro-, bromo-, and iodo-nitrobenzenes in C₆H₆ solution have been measured at 25° and 62—65° and used to calculate the dipole moments. The results show that the partial moments of the substituents in the *m*- and *p*-compounds do not influence each other.

R. CUTHILL.

Dielectric constant of liquids. IV. Aqueous solutions of potassium chloride. G. DEVOTO (*Gazzetta*, 1931, 61, 733—735).—The dielectric const. of KCl solutions at 17°, measured with undamped waves of 90 cm. wave-length, rises from 81.15 at zero concn. to 81.23 at a concn. of 0.001*M*.

H. F. GILLBE.

Change of dielectric polarisation of carbon disulphide with temperature. M. WOLFKE and J. MAZUR (*Nature*, 1931, 128, 871—872).—The dielectric polarisation of CS₂, calc. by the Clausius-Mossotti formula, decreases gradually from 0.2751 at -60° to 0.27372 at -90° and then falls rapidly to 0.2559 at -112°. The CS₂ mol. appears to

undergo a change in structure at -90° (cf. A., 1931, 1222).

L. S. THEOBALD.

Debye effect in viscous dielectrics. G. TODESCO (*Nuovo Cim.*, 1931, 8, 45—48; *Chem. Zentr.*, 1931, i, 3214—3215).

Anomalous variation of the electrical conductivity of quartz with temperature at the transformation point. H. SAEGUSA and S. SHIMIZU (*Nature*, 1931, 128, 835—836).—The electrical conductivity of quartz increases with a rise in temp.; anomalous variations appear at 573°.

L. S. THEOBALD.

Effect of a potential difference on acetone and ether. J. SAMBUSSY (*Compt. rend.*, 1931, 193, 855—856; cf. A., 1931, 410).—The limiting current through a column of COMe₂ follows Ohm's law accurately. The nature of the depolarisation current indicates electrolytic depolarisation, probably due to a trace of H₂O. Within the liquid the potential falls linearly with comparatively small drops at the electrodes. Et₂O behaves similarly unless dry, when the potential drops occur almost entirely at the electrodes. Dry Et₂O thus behaves as a semi-conducting substance.

C. A. SILBERRAD.

Effect of X- and γ-rays on the conductivity of paraffin. F. SEIDL (*Z. Physik*, 1931, 73, 45—61).—The sp. resistance of paraffin (m. p. 50°) was determined and the effect of X- and γ-rays on it investigated. There is an increase in conductivity, but this is due to secondary β-rays formed by the γ-rays, and not to absorbed β-rays. A. J. MEE.

Electrical conductivity of solid oxides of different valencies. M. LE BLANC and H. SACHSE (*Physikal. Z.*, 1931, 32, 887—889).—The electrical conductivity of many oxides was determined; in general it increases with the no. of free valencies.

A. B. D. CASSIE.

Electrical conductivity of powders. P. GUILLEMY (*Physikal. Z.*, 1931, 32, 891—892).—Preliminary. The electrical conductivity of powders is best determined from variation with frequency of the dielectric const. of an insulator in which the powder is embedded.

A. B. D. CASSIE.

Refractivities and optical dispersions of methane and its chloro-substitution derivatives. G. W. BRINDLEY and H. LOWERY (*Phil. Mag.*, 1931, [vii], 12, 945—954).—The refractivities and dispersions of MeCl, CH₂Cl₂, and CHCl₃ were measured between λ 6708 and λ 4358 Å. with a Jamin interferometer. The results agree with those calc. from vals. for C-H and C-Cl based on CH₄ and CCl₄, indicating the identity of the four C-H linkings in CH₄. The val. of the refractivity of HCl is 0.25 of that of CCl₄. The results are discussed.

H. J. EMELÉUS.

Theory of optical activity. K. SCHERINGA (*Chem. Weekblad*, 1931, 28, 665—666).—Polemical against Kuhn (A., 1931, 1214).

H. F. GILLBE.

Molecular polarisation and dissymmetry. R. DE MALLEMANN (*Compt. rend.*, 1931, 193, 651—654, 729—732).—Mathematical. An extension of the author's theories on optical rotatory power (cf. A., 1930, 981; 1931, 1215). The rotatory power of a

fluid of the simplest possible mols. would in general be expressed by the sum of 576 ternary products.

C. A. SILBERRAD.

Temperature of disappearance of anisotropy induced in the surface of glass by rubbing or drawing. H. E. VON GRONOW (Z. anorg. Chem., 1931, 201, 34—36).—When an unstrained surface of glass is rubbed in a certain direction the surface mols. become oriented parallel with that direction, and the resulting anisotropy can be detected by the action on polarised light of a thin film of methylene-blue deposited on the surface. In four glasses examined the temp. at which this anisotropy vanished was about 12° below that at which accidental double refraction was destroyed. A similar surface orientation was found in drawn glass threads.

F. L. USHER.

Double refraction and crystal structure. W. A. WOOSTER (Z. Krist., 1931, 80, 495—503).—All layer lattices not containing OH groups are optically negative; chain lattices parallel to the optic axis are positive. Strongly asymmetric groups doubly refract so that the electric vector of the more refracted ray is parallel to the shortest linkings; all symmetrical groups or three-dimensional lattices consisting of such have a low birefringence. Certain substances containing Fe or Ti have very high birefringence irrespective of crystal structure.

C. A. SILBERRAD.

Magnetochemistry. II. Magnetism of carbonyls and other complex compounds of the iron group. W. KLEMM, H. JACOB, and W. TILK. **III. Magnetism of carbides and nitrides.** W. KLEMM and W. SCHUTH. **IV. Magnetism of bivalent silver compounds.** S. KLEMM (Z. anorg. Chem., 1931, 201, 1—23, 24—31, 32—33).—II. Previous work is discussed, chiefly with reference to the distinction between "normal" and "penetration" complexes. The magnetism of complex compounds of Fe, Mo, Ni, Cu, and Pt belonging to both groups has been measured. The results, in general, support the views of Hieber on the constitution of the substances studied.

III. TiN, ZrN, TiC, ZrC, TaC, and WC are feebly paramagnetic and their susceptibilities are independent of temp. This, together with their high electrical conductivity and NaCl-type lattice, indicates their metallic character and distinguishes them from diamond (diamagnetic), BN, AlN, and SiC, which have the diamond- or Würzite-type of structure, low conductivity, and are typically non-metallic.

IV. Comparison of the magnetism of complex Ag compounds of C_6H_5N and phenanthroline with corresponding cupric compounds indicates the bivalency of Ag in them. The large difference observed between the magnetism of AgO and that of CuO is attributed to the partly metallic character of the latter.

F. L. USHER.

Magnetic birefringence of aqueous solutions of paramagnetic salts. C. HAENNY (Compt. rend., 1931, 193, 931—932).—The magnetic birefringence, b , of $PhNO_2$ under identical conditions being 100, the vals. of b_{546} for concns. of 1.314 (at 21°), 0.690 (at 22.6°), and 0.348 (at 22.2°) g. of $Ce(NO_3)_3$ per litre are respectively —59.52, —33.77, and —14.51;

b_{546}/b_{578} —1.080, 1.088, and 1.088; and b_{436}/b_{578} (at 21°, concn. 1.314 g. per litre)=1.57. Results for $Er(NO_3)_3$ (cf. A., 1911, ii, 81) are confirmed; b for both $Nd_2Mg_3(NO_3)_3$ and $Gd(NO_3)_3$ is very small.

C. A. SILBERRAD.

Magnetic susceptibility of complex compounds. L. CAMBI and L. SZEGO (Ber., 1931, 64, [B], 2591—2598).—Observations are recorded for a series of dithiocarbamates and xanthates of Fe, Ni, Co, and Mn of the Ni salts of α -dioximes, and of the acetylacetonates of these metals. The diamagnetic behaviour of $Ni(CN)_2$ and $K_2Ni(CN)_4$ is shared by a large class of Ni compounds. With Ni the formation of non-dissociated salts sol. in media of small dielectric const. is not sufficient to cause displacement of electrons into the third sphere. The electronic structure of the inner complex depends on the nature of the anion. The diamagnetic condition appears to be due to direct union of N or S with Ni and the direct union of Ni to N in the oximes and cyanide is rendered more probable. Co dithiocarbamates are diamagnetic, as are also Co acetylacetonate and oxalate. Diamagnetic compounds of Co are therefore formed with anions which afford paramagnetic complexes with Ni, Fe, and Mn, probably on account of the small at. vol. of the element. Fe dithiocarbamates appear uniformly to be structurally similar to the acetylacetonates and analogous salts. Their formation is not accompanied by passage of electrons into the third sphere. Dithiocarbamates with the residue $-NR'R''$ show marked weakening in action. With nitrosodithiocarbamates the transition of electrons into the third sphere occurs which is in harmony with the relatively greater stability of these substances in comparison with the Fe dithiocarbamates. The Mn dithiocarbamates have a magnetic susceptibility corresponding with that of the Mn ion; the acetylacetonate behaves similarly. Mn^{III} behaves similarly to Fe^{III} .

H. WREN.

Diamagnetism of liquid mixtures. S. R. RAO and G. SIVARAMAKRISHNAN (Nature, 1931, 128, 872).—The mass susceptibilities of mixtures of C_6H_6 with $PhCl$, C_6H_{14} , CCl_4 , and $PhNO_2$, of C_6H_{14} with $PhNO_2$, and of $COMe_2$ with $CHCl_3$ show no departure from the additive rule (cf. A., 1931, 900, 1000). Density-composition curves show deviations up to 6% in certain cases.

L. S. THEOBALD.

Chemical combination. F. HUND (Z. Physik, 1931, 73, 1—30).—Three theories of chemical combination are critically compared. That theory is the best which describes the state of the mol. by the characteristic functions of its single electrons. By an extension of Herzberg's theory, combination is said to have taken place when in the electron-characteristic function of the mol. two such functions of atoms are shared, and have added themselves in the space between the atoms. This theory gives an easier explanation of the theory of directed valency (Slater-Pauling) and other at. theories.

A. J. MEE.

Structure of organic molecules and modern atomic theory. G. BRUNI (Giorn. Chim. Ind. Appl., 1931, 13, 464—475).—A lecture.

Atoms and molecules as Fitzgerald oscillators. (SIR) C. V. RAMAN (Nature, 1931, 128, 795).—The

hypothesis that atoms and mols. may function as magnetic oscillators receives some experimental support. It is discussed as an explanation of the anomalous polarisation observed in light-scattering by liquids. L. S. THEOBALD.

Application of Van Laar's theory of the additive nature of b and \sqrt{a} to some tungsten and molybdenum compounds. J. A. M. VAN LIEMPT (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1032—1037).—Calculation of $\sqrt{a_k}$ for WCl_6 shows that the van der Waals attraction due to the central W atom is completely screened by the Cl atoms. The following consts. were calc. for W and Mo, respectively; b_k 236×10^{-5} , 180×10^{-5} , p_k 1675, 1405 atm., T_k 8635° , 5590° abs., $\sqrt{a_k}$ 50.2×10^{-2} , 35.5×10^{-2} .

H. J. EMELEÚS.
Co-ordination number of aluminium in aluminosilicates. J. S. HEY and W. H. TAYLOR (Z. Krist., 1931, 80, 428—441).—On the basis of previous (cf. A., 1929, 988; 1930, 528, 672) and additional data it is shown that the co-ordination no. of Al, and distances Al—O of the co-ordinated O atoms of cyanite, sillimanite, and andalusite are respectively 6, 1.9 Å., 4, 1.7 Å., and (probably) 5, <1.9 Å. C. A. SILBERRAD.

Domains of atoms and ions in crystals. E. HERLINGER (Z. Krist., 1931, 80, 465—480).—From a consideration of Pauling's and Goldschmidt's results (cf. A., 1927, 399; 1929, 247) it is deduced that the difference between corresponding at. and ionic radii is const. for each type of ion, and greatest, 0.8 Å., when the ion is of inert gas type. Consequently the thickness of the valency electron shell is independent of the no. of electrons therein, and differences in at. radii of different elements are due to compression of inner completed shells. Such a shell immediately next the valency electron shell is compressible to a thickness of 0.2 Å. C. A. SILBERRAD.

Ionic theory of organic reactions. II. C. PRÉVOST and A. KIRRMANN (Bull. Soc. chim., 1931, [iv], 49, 1309—1368).—A crit. consideration of the existing theories of org. reactions and a detailed discussion of the authors' ionic theory (A., 1931, 670).

M. S. BURR.
Oxidation and reduction as electronic processes. W. A. NOYES (Z. angew. Chem., 1931, 44, 893—896).—Résumé of an address. H. F. GILLBE.

Surface tension of solid silver at high temperature. M. MASIMA, S. SAKUI, and M. ISHII (Bull. Inst. Phys. Chem. Res. Tokyo, 1931, 10, 86—87).—Thin films of Ag deposited on quartz were heated until broken, and the surface tension was calc. from the known breaking stress. F. L. USHER.

Representation of crystal structure. E. B. BAILEY (Nature, 1931, 128, 869).—A new notation is suggested. L. S. THEOBALD.

Energy changes related to the secondary structure of crystals. F. ZWICKY (Physical Rev., 1930, [ii], 35, 378).—A secondary structure of large spacing superposed on the primary structure of crystals is postulated, with the atoms of the former being, in general, the more densely packed. The atoms of the latter are more easily removed from the crystals.

Physical processes involving crystals can be explained on this theory. A p.d. of approx. 0.001—0.01 volt should exist between the planes of each structure.

L. S. THEOBALD.
Inhomogeneities in crystals. R. H. CANFIELD (Physical Rev., 1930, [ii], 35, 114—115).—A criticism (cf. preceding abstract). L. S. THEOBALD.

Inhomogeneities in crystals. F. ZWICKY (Physical Rev., 1930, [ii], 35, 283—284).—A reply to criticism (cf. preceding abstract). L. S. THEOBALD.

Formation and characteristics of crystals of lead azide and some other initiating explosives. F. D. MILES (J.C.S., 1931, 2532—2542).—Two crystal forms of anhyd. PbN_3 were isolated, viz., α , orthorhombic ($a:b:c=0.586:1:1.433$; 12 mols. in unit cell; a 6.64, b 11.34, c 16.25 Å.), and β , monoclinic ($a:b:c=0.578:1:1.993$; 8 mols. in unit cell; a 5.10, b 8.83, c 17.60 Å.). A few measurements were made with the less stable α - and β - Hg^{II} azides. Hg^{II} fulminate was orthorhombic ($a:b:c=0.712:1:1.353$; 4 mols. in unit cell; a 5.48, b 7.71, c 10.43 Å.). Pb styphnate was monoclinic ($a:b:c=0.799:1:0.638$; 4 mols. in unit cell; a 10.02, b 12.54, c 8.00 Å.). Pb styphnate hydrate was isolated. The production and stability of these crystal forms are discussed. H. J. EMELEÚS.

[X-Ray] powder diagrams in relation to the physical and chemical purity of substances. G. R. LEVI (Atti III Cong. Naz. Chim. pura appl., 1929, 118—121; Chem. Zentr., 1931, i, 3211).—A comparison of results with hard and soft X-rays leads, under certain conditions, to approx. determination of the components of systems subject to oxidation, reduction, etc. A. A. ELDRIDGE.

Scattering of X-rays by metals. A. RUSTERHOLZ (Helv. Phys. Acta, 1931, 4, 68—121; Chem. Zentr., 1931, i, 3436—3437).—By means of Debye-Scherrer photographs with Cu $K\alpha$ -rays the at. scattering functions of Al, Cu, Ag, Au, and Pt were determined. A. A. ELDRIDGE.

Scattering of X-rays from paraffin, aluminium, copper, and lead. A. W. COVEN (Physical Rev., 1931, [ii], 38, 1424—1431).—The scattered intensities at angles in the range 30 — 120° with the primary beam were compared with those at 90° . Scattering from paraffin and Al was at an effective wave-length of 0.32, from Cu 0.26, from Pb 0.27 Å. The abs. vals. of the scattering per g. and per electron are calc. N. M. BLIGH.

Scattering of X-rays by water. E. AMALDI (Physikal. Z., 1931, 32, 914—919).—The difference in symmetry of H_2O from Hg makes a theoretical interpretation of X-ray patterns due to liquid H_2O uncertain. A. B. D. CASSIE.

Crystal structure of phosphorescent zinc sulphide. F. PREVET (J. Chim. phys., 1931, 28, 470—479; cf. A., 1931, 998).—The optimum concn. of flux and time of heating decrease as the temp. used in the prep. of phosphorescent ZnS is raised. The phosphorescence is displaced towards the red by CdS , and disappears with $>30\%$ CdS . Silicates in the Zn - S explosive mixture diminish the phosphorescence of ZnS , but H_3BO_3 increases the phosphorescence.

owing to the solvent action of B_2O_3 on ZnS at the high temp. attained. The phosphorescence of ZnS is related to the cryst. structure, and the intensity is directly proportional to the mean diameter of the grains.
J. G. A. GRIFFITHS.

Structure of the azide group. T. C. SUTTON (Nature, 1931, 128, 872—873).—The difference in structure of liquid and cryst. azides is discussed on electronic lines. The azide grouping takes the ring form when it is bound into a mol. by a non-polar linking, but may take a chain form when it is either an electronegative ion or is bound into a mol. by a polar linking.
L. S. THEOBALD.

Crystal structure of silver sulphate [and selenate]. K. HERRMANN and W. ILGE (Z. Krist., 1931, 80, 402—415).— Ag_2SO_4 has a 5.847, b 12.659, c 10.251; Ag_2SeO_4 , a 6.069, b 12.815, c 10.211 Å.; both have 8 mols. in the unit cell; space-group (probably) V_2^H . Their constitution is discussed in the light of Weissenberg's theory (cf. A., 1929, 247).
C. A. SILBERRAD.

Crystal structure of the series of barium and strontium carbonates. J. M. CORK and S. L. GERHARD (Amer. Min., 1931, 16, 71—77).—Mechanical mixtures gave the diffraction patterns of both $BaCO_3$ and $SrCO_3$; a pptd. mixture gave a single intermediate pattern, the relation of which to the parent patterns depended on the mol. fractions of the components present. New measurements were made on witherite.
CHEMICAL ABSTRACTS.

Crystal structure of thomsonite and natrolite. J. WYART (Compt. rend., 1931, 193, 666—668).—Thomsonite, from Bishopston (Scotland) and Vesuvius, has a 13.02, b 13.14, c 13.22 Å., with 10 mols. of $(CaNa_2)Al_2Si_2O_8 \cdot 2.5H_2O$ in the unit cell; space-group, probably C_{2v}^{10} , the crystal being pyroelectric. Natrolite has a 18.25, b 18.50, c 6.57 Å., with 4 mols. of $Na_2Al_2Si_3O_{16} \cdot 2H_2O$ in the unit cell; space-group C_{2v}^{10} . The structures of both are closely similar.
C. A. SILBERRAD.

Crystal structure of monoclinic pyroxenes. B. E. WARREN and J. BISCOE (Z. Krist., 1931, 80, 391—401).—The structures of augite, c 5.24 Å., acmite, c 5.26 Å., spodumene, a 9.50, b 8.30, c 5.24 Å., β 69° 40', 4 mols. in unit cell, hedenbergite, clinoenstatite, and jadeite are all closely similar to that of diopside (cf. A., 1929, 1223). Their composition is represented by $X_m Y_{2-m} (SiAl)_2 (O, OH, F)_6$, where $X=Ca$, Na , K , and $Y=Mg$, Fe , Al , Ti , Mn , and in spodumene Li , and m tends to be 1.0 or 0. The unit cell of wollastonite has a 7.88, b 7.27, c 7.03 Å., α 90°, β 95° 16', γ 103° 25', containing 6 mols. of $CaSiO_3$; that of pectolite a 7.91, b 7.08, c 7.05, α 90°, β 95° 10', γ 103° 0', with 2 mols. of $HNaCa_2(SiO_3)_3$. Their structures differ from those of diopside etc., being triclinic, and closely resembling that of the triclinic schizolite.
C. A. SILBERRAD.

Crystal structure of langbeinite, northupite, and hanksite. B. GOSSNER and I. KOCH (Z. Krist., 1931, 80, 455—464).—The dimensions of, and no. of mols., in the unit cell, and space-groups are: of langbeinite, $K_2Mg_2(SO_4)_3$, a 9.96 Å., 4, T_1^H ; northupite, $Na_2Mg(CO_3)_2 \cdot NaCl$, a 14.13 Å., 16, T_1^H ; hanksite, $9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$, a 10.52, c 21.25 Å., 2, C_{2v}^{10} .

The formula of hanksite is thus confirmed (cf. A., 1897, ii, 48).
C. A. SILBERRAD.

Spinel structure. F. MACHATSCHKI (Z. Krist., 1931, 80, 416—427).—At. distances between the atoms concerned can be deduced from intensities calc. by means of F curves for common spinel in satisfactory agreement with Goldschmidt's at. radii (cf. A., 1929, 747). Barth and Posnjak's results (cf. A., 1931, 1001) are criticised.
C. A. SILBERRAD.

Effect of electric field on X-ray diffraction pattern of a liquid. G. W. STEWART (Physical Rev., 1930, [ii], 36, 1413).—A discussion relating to $PhNO_2$ (cf. A., 1930, 1079).
L. S. THEOBALD.

Lattice constants of high-molecular saturated fatty acids and the K and L X-ray spectra of lower elements. A. KARLSSON (Ark. Mat. Astron. Fysik, 1930, A, 22, No. 9, 23 pp.; Chem. Zentr., 1931, i, 3651).—The following measurements were made: lattice const. of laurostearic, palmitic, stearic, and cerotic acids, $Pb(C_{31}H_{61}O_2)_2$, $Pb(C_{23}H_{45}O_2)_2$, Pb laurate, and Pb palmitate; L -series of Zn , Cu , Ni , Co , Fe , Mn , Cr , V ; $K\alpha$ -lines of Na , F , O , N .
A. A. ELDRIDGE.

Effect of general radiation in the diffraction of X-rays by liquids. W. C. PIERCE (Physical Rev., 1931, [ii], 38, 1409—1412).—The effects of general and characteristic radiation from a Mo tube were separated by balanced Sr and Zr filters, using n -hexyl alcohol as the scattering liquid.
N. M. BLIGH.

Higher order effects in the diffraction of X-rays by liquids. W. C. PIERCE (Physical Rev., 1931, [ii], 38, 1413—1419).—The X-ray diffractions of CCl_4 , $CHCl_3$, C_6H_6 , solutions of CCl_4 in C_6H_6 , o - and m - $C_6H_4Cl_2$ were determined for Mo- $K\alpha$ rays. The halogen compounds give additional max. in the intensity-angle curve at large angles, attributed to internal interference caused by scattering from the Cl atoms.
N. M. BLIGH.

Hall effect and lattice constant of gold-silver alloys. L. S. ORNSTEIN and W. C. VAN GEEL (Z. Physik, 1931, 72, 488—491).—A linear relation exists between the Hall coeff. and the lattice const.
A. B. D. CASSIE.

Permanent electric and magnetic moments of crystals. F. ZWICKY (Physical Rev., 1931, [ii], 38, 1772—1781).—Conditions for the existence of self-perpetuating electric moments in crystals and the analogous magnetic case are discussed.
N. M. BLIGH.

Magnetisation of electrolytic nickel films. E. P. T. TYNDALL and H. E. MALMSTROM (Proc. Iowa Acad. Sci., 1930, 37, 312—313).—Films of thickness approx. 130 m μ attain a magnetisation of about 380 c.g.s. in a field of 200 gauss.
CHEMICAL ABSTRACTS.

Structure sensitiveness of magnetism in metals. F. E. LOWANCE and F. W. CONSTANT (Physical Rev., 1931, [ii], 38, 1547—1551).—The magnetic susceptibility of Cu , Ag , Pt , and Bi was measured for the annealed state and after various degrees of cold work; the latter decreased the diamagnetism (Cu , Ag , Bi) or increased the para-

magnetism (Pt), explaining the variations in the measured susceptibilities (cf. Bitter, A., 1930, 1505) as due to a structure sensitiveness. N. M. BUGH.

After-effects with hysteresis loops at high temperatures. H. KUHLEWEIN (Physikal. Z., 1931, 32, 860—864).—The hysteresis loops become smaller with rise of temp. In the neighbourhood of the Curie point the saturation increase is reversible.

A. J. MEE.

Problem of the two Curie points. R. FORRER (J. Phys. Radium, 1931, [vii], 2, 312—320; cf. A., 1930, 529).—By choosing a substance for which the ferromagnetic Curie point (T_f) and that of the coercive force (T_h) are widely separated, the identity of the latter with the paramagnetic Curie point (T_p) has been established. A Cu-Ni alloy (70% Ni), having T_f at 70°, was used. For magnetite, T_h — T_f , and the latter is therefore considered to be coincident with T_p , which cannot be determined directly. Owing to a change in its magnetic state over a certain temp. range, T_h and T_p do not coincide in the case of ferrocobalt.

F. L. USHER.

Magnetostriction in ferromagnetic substances. M. KERSTEN (Z. Physik, 1931, 72, 500—504).—An inversion may occur in magnetostriction and electrical conductivity within the region of hysteresis.

A. B. D. CASSIE.

Magnetostriction of iron-nickel alloys. Y. MASIYAMA (Sci. Rep. Tohoku, 1931, 20, 574—593).—The magnetostriction of Fe-Ni alloys is anomalous throughout the interval 20—35% Ni. The transverse effect is approx. the reverse of the longitudinal effect, and the vol. change is the differential effect of the longitudinal and transverse changes.

H. F. GILLBE.

Magnetostriction and magnetic hysteresis. L. W. MCKEEHAN (Physical Rev., 1930, [ii], 36, 1670).—Akulov's conclusion (A., 1930, 1506) that the magnetostriction of a single crystal, expressed as a function of its magnetisation, is unaffected by the application of mechanical forces, is contested (cf. A., 1930, 1504).

L. S. THEOBALD.

Theory of ferromagnetism. T. HIRONE and T. HIKOSAKA (Z. Physik, 1931, 73, 62—73).

Physical concepts in theories of plastic flow. R. L. PEEK, jun., and D. A. MCLEAN (J. Rheology, 1931, 2, 370—384).—Theoretical. E. S. HEDGES.

Tensile strength of wetted salt crystals. II. Influence of different solvents and their dissolving forms. E. REXER (Z. Physik, 1931, 72, 613—620; cf. *ibid.*, 1931, 68, 591).—Increases in tensile strength and plasticity of NaCl and KI crystals in different solvents (H_2O , MeOH, 100% H_2SO_4 , and H_2SO_4 25% SO_3) are independent of the solvent.

A. B. D. CASSIE.

Dispersion theory of sound. H. O. KNESER (Ann. Physik, 1931, [v], 11, 761—776).—Theoretical. A theory for the propagation of sound in gases is derived from simple assumptions concerning the transference of quantised excitation energy by mol. collisions. The life period of the excitation energy is the only quantity involved that cannot be arrived at thermodynamically.

A. J. MEE.

Velocity of sound in oxygen. W. H. KEESOM, A. VAN ITTERBEEK, and J. A. VAN LAMMEREN (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 996—1003).—From measurements at 0° and —129° to —109° in O_2 , c_p , c_v , c_p/c_v , and $(c_p/c_v)_{p=0}$ (=1.400) were calc. The velocity of sound in O_2 (W) is related to the pressure (p) at —193° to —186° by $W^2 = N(1 + Pp + Qp^2)$. N , P , Q , and other derived consts. were calc.

H. J. EMELEUS.

Velocity of sound in hydrogen at liquid hydrogen temperatures. A. VAN ITTERBEEK and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 988—995).—Measurements with a wide resonator between 17.17° and 20.42° abs. at pressures from 0.1 to 1.0 atm. gave $(c_p/c_v)_{p=0} = 1.667$. The variation of the velocity of sound (W) with pressure (p) in H_2 over the same temp. range is given by $W^2 = N(1 + Pp + Qp^2)$. N , P , Q , and other derived consts. were calc.

H. J. EMELEUS.

Influence of pressure and tension on the specific resistance of bismuth single crystals. O. TRAPEZNIKOWA (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 840—843). W. R. ANGUS.

Relation between b. p. and chemical constitution. I. K. BILLIG (Svensk Kem. Tidskr., 1931, 43, 252—257).—The development of views regarding the relation between b. p. and constitution is outlined. In attempting to obtain a quant. relation, it is assumed that the b. p. $T = KfM$, where f is the degree of association at or near the b. p., M the mol. wt. in the vapour phase, and K a const. The lowest vals. of the "association factor" Kf , viz. 1—2, are found for the inert gases and certain halides. For homologous series Kf falls with increase of at. wt. and with increased branching of the chain. In general, the greater the tendency of a compound to polymerise, the greater is its Kf val.

H. F. GILLBE.

Thermal conductivity of inert gases. M. CURIE and A. LEFAPE (Compt. rend., 1931, 193, 842—843).—Using the thermometric method the thermal conductivity, K_0 ($\times 10^5$) g.-cal./sec./cm./degree, and coeff. A ($=K_0/\eta c_v$, where η is coeff. of viscosity and c_v sp. heat), K_0 for air being taken as 5.83×10^{-5} (cf. A., 1926, 231), have been determined as: He 33.63, 2.42; Ne 10.92, 2.49; A 4.06, 2.59; Kr 2.12, 2.54; X 1.24, 2.58, in good agreement as regards He, Ne, and A with previous results, and as regards the coeff. A near the theoretical val. 2.5.

C. A. SILBERRAD.

Variation of thermal conductivity of gases in electrical fields. W. BONWITT and G. GROETZINGER (Z. Physik, 1931, 72, 600—612).—Electrical fields may increase the thermal conductivity of gases, particularly of dipolar mols.

A. B. D. CASSIE.

Theory of thermal conductivity and diffusion. K. ULLER (Physikal. Z., 1931, 32, 892—897).—The potentials leading to thermal conductivity and diffusion need not be temp. and concn. respectively, but may be functions of these deduced from a wave-kinematical picture of the energy transfer.

A. B. D. CASSIE.

Exact measurement of the specific heats of iridium and ruthenium between 0° and 1604°

and a comparison of the calorimetric results obtained with the elements of the eighth group of the periodic system. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 808—822).—Pure Ir has d 22.81, m. p. 2360°. The sp. heat between 0° and 1700° is given by $c_p = 0.030725 + 0.000007404t$ and the at. heat by $C_p = 5.933 + 0.001429t$. Vals. for c_p , c_v , C_p , and C_v are tabulated. Pure Ru gave data which indicate its existence in at least 4 allotropic modifications. α -Ru, hexagonal, exists below 1035°, and has a_0 2.695 Å., c_0 4.273 Å., d_{calc} 12.71. The equations for c_p and C_p for the temp. intervals 0—1000°, 1000—1070°, 1070—1200°, 1200—1400°, and 1400—1604° are given. The c_p - t curve for Ru is given; β -Ru has the lowest temp. coeff. The allotropism of Ru and Fe is strikingly similar. C_p - t curves for the elements in group VIII are compared. Os, Ir, and Pt give straight lines. Ru shows static allotropism like Fe, whilst Rh shows dynamic allotropism. With increasing complexity of structure the tendency to form allotropic modifications is decreased. W. R. ANGUS.

Vapour density of hydrogen sulphide. R. H. WRIGHT and O. MAASS (Canad. J. Res., 1931, 5, 442—447).—An apparatus for measuring the v. d. of condensable gases at pressures above 1 atm. is described, and the v. d. of H_2S between 47° and -35°, and up to 4 atm. is recorded. The results are in agreement with theory (A., 1926, 233).

R. S. CAHN.

Entropy of polyatomic molecules. D. S. VILARS (Physical Rev., 1931, [ii], 38, 1552—1564; cf. A., 1931, 800).—Probabilities of the different symmetry varieties of NH_3 and CH_4 are derived; the calc. corresponding abs. entropies at 298.1° abs. are 51.5 and 50.1, respectively. N. M. BLIGH.

Densities of allyl alcohol, methyl ethyl ketone, and toluene at low temperatures. T. TONOMURA and K. UEHARA (Bull. Chem. Soc. Japan, 1931, 6, 255—258).—Measurements have been made at -80° to 0°.

R. CUTHILL.

Equivalence of the absolute gas constant and the molecular volume. G. SIBONI (Boll. Chim. farm., 1931, 70, 707—708).—A demonstration, based on the author's abs. temp. scale, that the gas const. R is numerically equal to the mol. vol.

H. F. GILLBE.

Vapour tensions of phosphorus trioxide. P. M. VAN DOORMAAL and F. E. C. SCHEFFER (Rec. trav. chim., 1931, 50, 1100—1104).—The v. p. of P_4O_6 , purified by Miller's method (A., 1929, 1155), has been determined directly, using a Hg manometer, over the range 56—178°. The results (mm. Hg) are expressed by the equation $\log p = 11.0516 - 2860.0/T - 0.00400T$. The m. p. is 23.8°. C. W. DAVIES.

Equation of state of gases and liquids, with reference to the variability of a and b with T and v . Hydrogen. III. Expressions for the critical magnitudes. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 977—987).—Mathematical; expressions for v_k and v_k/b_k are derived, and certain const. for H, calc. H. J. EMELEUS.

Viscosity of liquids. E. N. DA C. ANDRADE (Nature, 1931, 128, 835).—Vals. calc. for Hg, Cl, Br, I, O_2 , and H_2 from the formula $\eta_m = 7.82 \times 10^{-4} (AT_m)^{0.5} V_A^{0.15}$, where η_m is the viscosity at the m. p., T_m , A is the at. wt., and V_A is the vol. of a g.-atom at T_m , are in sufficiently close agreement with experimental vals. to support the view that at the m. p. liquids retain sufficient of the cryst. character of the solid state for the mols. to possess a frequency of vibration which is practically the same as that of the solid at the m. p. L. S. THEOBALD.

Fluidity of water in the vicinity of 20°. E. C. BINGHAM (J. Rheology, 1931, 2, 403—420).—A crit. report on published work. The need for accurate determinations of the fluidity of H_2O at 20° for use as a standard is emphasised. E. S. HEDGES.

Comparison of viscosity and molecular arrangement in 22 liquid octyl alcohols. G. W. STEWART and R. L. EDWARDS (Physical Rev., 1931, [ii], 38, 1575—1582; cf. A., 1930, 668).—The X-ray diffraction halos indicate periodicities interpreted as structural in the cybotactic groups. There is a correlation between the coeff. of viscosity and the perfection of grouping in the direction of the length of the chain mols.; the negative temp. coeff. of viscosity is accounted for. N. M. BLIGH.

Viscosity, heat conductivity, and diffusion in gaseous mixtures. XX. Viscosity of nitric oxide and its mixtures with nitrogen. M. TRAUTZ and E. GABRIEL (Ann. Physik, 1931 [v], 11, 606—610).—Data are recorded for NO between room temp. and 250° and for mixtures of NO and N_2 between room temp. and 100°. A. J. MEE.

Investigations of the vitreous state using a dilatometer. E. BERGER (Z. anorg. Chem., 1931, 201, 144).—Koerner and Salmang's conclusion (A., 1931, 1220) that a transformation interval for glass in the neighbourhood of 550° can be obtained only by heating rapidly is not in agreement with other observations. M. S. BURR.

Relation between solid solutions and mixed crystals and the conditions under which a true equilibrium between mixed crystals and solutions can be experimentally realised. V. CHLOPIN [with A. POLESSITSKY and (in part) A. RATNER and P. TOLMATSCHIEFF] (Ber., 1931, 64, [B], 2653—2666).—The systems BaBr_2 - RaBr_2 - H_2O , BaCl_2 - RaCl_2 - H_2O , $\text{Ba}(\text{NO}_3)_2$ - $\text{Ra}(\text{NO}_3)_2$ - H_2O , $\text{Ba}(\text{NO}_3)_2$ - $\text{Ra} \cdot D(\text{NO}_3)_2$ - H_2O , $\text{Pb}(\text{NO}_3)_2$ - $\text{Ra}(\text{NO}_3)_2$ - H_2O , $\text{Ba}(\text{NO}_3)_2$ - $\text{Pb}(\text{NO}_3)_2$ - $\text{Ra}(\text{NO}_3)_2$ - H_2O , $[\text{Ce}(\text{NO}_3)_3]_2\text{Mg}_3(+24\text{H}_2\text{O})$ - $[\text{Ra} \cdot E(\text{NO}_3)_3]_2\text{Mg}_3(+24\text{H}_2\text{O})$ - HNO_3 and BaCl_2 - RaCl_2 - $\text{Ra} \cdot \text{DCl}_2$ - H_2O , have been investigated. Two types of mixed crystals exist: (a) unstable, non-homogeneous products, not in equilibrium with the mother-liquor, obtained by spontaneous growth from scarcely supersaturated solutions, and (b) stable, homogeneous crystals in equilibrium with the mother-liquor, prepared from supersaturated solutions. Complete analogy exists between the distribution of a dissolved substance between two mutually insol. liquid phases and between a solid cryst. and a liquid phase. The course of redissolution of crystals from their saturated solutions at const. temp. has been followed photo-

graphically and kinematographically. A sensible velocity of recrystallisation is observed with naturally grown crystals; the rate of recrystallisation of the cryst. phase depends in the first place on its dimensions and surface development. The equilibrium const. in the formula of Doerner and Hoskins (A., 1925, ii, 381) is identical with the fractionation coeff. or the "partition factor" corresponding with the final equilibrium between Ba-Ra crystals and their dissolution at definite temp. In fractional crystallisation, the distribution of a dissolved substance between a cryst. and a liquid phase is governed by the Berthelot-Nernst law of distribution. The advantages of the use of radio elements in the experimental study of dil. solid solutions are detailed.

H. WREN.

Crystal structure and atomic properties of alloys containing transition elements. A. WESTGREN (J. Franklin Inst., 1931, 212, 577-599).—A survey of existing data concerning the composition and crystal structure of alloys of transition elements and of their hydrides, borides, carbides, and nitrides, which are metallic in character. Certain relations suggest that the different types are related to the at. radii and the no. of valency electrons of the constituents, but the present data are considered too incomplete to arrive at general conclusions.

D. R. DUNCAN.

Volumetric and dilatometric investigations of alloys. M. G. OKNOV (Metallurg. Leningrad, 5, 1-9).—Alloys [Cu-Sn, Cu-Sb, Cu-Zn (50%), Al-Zn] for which the volumetric and dilatometric analyses agree remain, after hardening, in the same condition as that assumed at high temp. With alloys [Fe-C, Cu-Al, Cu-Zn (75%)] exhibiting disagreement, the hardening is accompanied by auxiliary processes connected with a vol. change. In the Fe-C system hardening produces a tetragonal lattice.

CHEMICAL ABSTRACTS.

Physical properties, thermal analysis, and micro-structure of cast Al-Cu alloys with a copper content of 0-60%. G. P. KULBUSH (Trans. II Conf. Non-Ferrous Met., 1927, 1, 610-624).—A eutectic at 33% Cu (542°), a eutectic arrest in alloys of 2% Cu, a crit. point at 575° in alloys of 4-15% Cu, and absence of solid solutions in the neighbourhood of Al₂Cu (m. p. 590°) have been observed. The electrical conductivity and sp. gr. are directly proportional to the Cu concn. Mechanical properties are max. at 4.25% Cu. Alloys with 0.5% Mg have a eutectic at 527° (separation beginning with 5% Cu) and there is a crit. point at 505-570° in alloys with 4-15% Cu. CHEMICAL ABSTRACTS.

Thermodynamic study of the iron-carbon system in the solid and liquid states. I, II. [α -transition.] Y. CHU-PHAY (Trans. Faraday Soc., 1931, 27, 777-790, 790-797).—I. The f.-p. relations for binary systems showing solid solubility have been developed. The Fe-C system behaves as an ideal solution. The heat of fusion of γ -Fe and the heat of transition $\gamma \rightleftharpoons \delta$ are computed to be 66.4 and 2.2 g.-cal. per g., respectively; according to these data the true heat of fusion of Fe is 64.2, in good agreement with recent vals. Vals. calc. from

existing data for the δ -Fe liquids are widely divergent. The solute in the melt is C, but in the γ -field it is Fe₃C. The solute in austenite in true equilibrium with the melt is C.

II. The heat of the transition $\alpha \rightleftharpoons \gamma$ is 5.5 ± 0.2 g.-cal. per g. It is suggested that in an ideal system the heat of dissolution of a solid solute in a solid solvent, resulting in the destruction of the crystal structure of the former, is identical with the heat of dissolution of the solute in the melt. Reasons are given for the view that the solute in austenite is Fe₃C; its heat of dissolution is 5720 g.-cal. per mol. Anomalies are discussed.

J. G. A. GRIFFITHS.

Constitution of austenite and of the solid solution of carbon in δ -iron and of the liquid solution in equilibrium with these, examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1931, 27, 751-755).—The application of the author's equations (A., 1930, 406, 1360) to existing data for the Fe-C system shows that austenite, the solid solution of C in δ -Fe, and the coexisting liquid consist of solutions of monat. C in monat. Fe.

J. G. A. GRIFFITHS.

Diffusion of admixtures into steel, and the cellular theory of the structure of metals. N. AGEEV and M. ZAMOTORIN (Ann. Inst. Polytech. Leningrad, Sect. Math. Phys. Sci., 1928, 31, 15-28).—In the solid state the degree of penetration decreases as follows: 1000°, C, Pt, Fe-Mo, B, Fe-W, WC, Ni, Au, Mn, Fe-B, Co, Fe-Ti, Fe-Cr, Cr, V, Fe-Si, Fe-Mn, Fe-V, Si, W, Ti; 1200°, Fe-Si, Mo, Rh, Fe-Mn, Pd, Ru. In the liquid state at 1000° diffusion was observed with Al, Ce, and Sn, but not with Ag, Bi, Te, Pb, or Ca; at 1200° it was not observed with Ba or Li. At 750° diffusion of Zn, but not of Cd, was observed.

CHEMICAL ABSTRACTS.

Unit lattice made up of interpenetrating lattices [of chromium and nickel]. F. C. BLAKE (Physical Rev., 1930, [ii], 35, 660).—A synthetic interpenetrating lattice of 32 atoms of Ni and 64 of Cr has the unusual hardness of the many-atomed lattices of Cu-Al and Zn-Sn alloys. The first 16 lines expected to be strong in a powder photograph do not appear at all. The space-group is D_4^h .

L. S. THEOBALD.

Ferromagnetism and the phase state in the binary system Ni-Mn. S. KAYA and A. KUSSMANN (Z. Physik, 1931, 72, 293-309).—By suitable heat-treatment Ni-Mn alloys can be made ferromagnetic. Alloys containing up to 40% Mn are investigated. The saturation magnetisation of the 23% Mn alloy is raised about 20 times, its electrical conductivity is raised by 50%, and the magnetic transition point is raised to higher temp. Metallographic and X-ray data show that the transformation takes place without recrystallisation and at 23.7% Mn (Ni₃Mn) the distribution of the two at. species in the space lattice is regular.

J. FARQUHARSON.

Hall effect in tellurium amalgams. P. I. WOLD and J. M. HYATT (Physical Rev., 1930, [ii], 36, 375).—Amalgams containing approx. 30% Te are plastic when fresh but become hard and friable in a few hr. With the plastic amalgam the Hall effect is

small but increases 100- to 500-fold during 2—3 days. X-Ray photographs show that a cryst. structure persists throughout. The longitudinal effect resembles the Hall effect in behaviour.

L. S. THEOBALD.

Magnetic investigation of organic substances. H. BUCHNER (Z. Physik, 1931, 72, 344—349).—EtOH- CS_2 mixtures show a departure from additivity when χ is plotted against either wt. or vol.-% composition. CHCl_3 and COMe_2 mixtures (cf. A., 1931, 676) show additivity and no paramagnetic region. Also, $\text{CCl}_3\text{-CMe}_2\text{-OH}$ is diamagnetic and has a val. approx. the same as that computed from Pascals vals. $\text{PhOH-H}_2\text{O}$ and MeOH-CS_2 mixtures are additive in behaviour.

J. FARQUHARSON.

Influence of a common solute on the mutual solubility of two liquids. V. I. NESTEROVA and N. N. PETIN (J. Gen. Chem. Russ., 1931, 1, 272—278).—The mutual solubility of two liquids is affected by the addition of a solute only when the partition coeff. is infinitely great; thus, the addition of I has no effect, whilst conc. aq. NH_4CNS lowers the solubility of H_2O in Et_2O .

R. TRUSZKOWSKI.

Solubility of hydrogen in water under pressure. V. V. IPATIEV, jun., S. I. DRUSHINA-ARTEMOVITSCH, and V. I. TICHOMIROV (J. Gen. Chem. Russ., 1931, 1, 594—597).— H_2 dissolves in H_2O according to Henry's law at 20—140 atm. between 0° and 45° .

R. TRUSZKOWSKI.

Solubility of calcium gluconate. F. DE CARLI (Annali Chim. Appl., 1931, 21, 447—453).—The isotherm of the system $(\text{C}_6\text{H}_{11}\text{O}_7)_2\text{Ca-B}_2\text{O}_3\text{-H}_2\text{O}$ at 20° shows that H_3BO_3 increases considerably the solubility of Ca gluconate owing probably to the formation of $(\text{C}_6\text{H}_{11}\text{O}_7)_2\text{Ca}_x\text{B}_y\text{O}_z\cdot x\text{H}_2\text{O}$. A solution containing 10% of Ca gluconate at 20° is obtained by the addition of 1% H_3BO_3 .

O. F. LUBATTI.

Gas-solid equilibria. III. Pressure-concentration equilibria between silica gel and (a) water, (b) ethyl alcohol, directly determined under isothermal conditions. B. LAMBERT and A. G. FOSTER (Proc. Roy. Soc., 1931, A, 134, 246—264).—The $\text{H}_2\text{O-SiO}_2$ gel system behaves peculiarly and very differently from the $\text{C}_6\text{H}_6\text{-SiO}_2$ and EtOH-SiO_2 systems. The isothermals show hysteresis effects and rise more steeply from the concn. axis; they also show a persistent shift towards the pressure axis in successive experiments and are not reproducible, nor can they be followed experimentally up to the saturation pressures of pure H_2O . The isothermals for the EtOH-SiO_2 gel system resemble those of the $\text{C}_6\text{H}_6\text{-SiO}_2$ system; they show no hysteresis phenomena and are reversible. The EtOH isothermals, however, differ in shape from the C_6H_6 isothermals and display certain irregularities not shown by the $\text{C}_6\text{H}_6\text{-SiO}_2$ gel system.

L. L. BIRCUMSHAW.

Absorption of gas from a current of air. L. K. LEVIN and S. A. VOSNESSENSKI (J. Gen. Chem. Russ., 1931, 1, 233—234).—Polemical against Mecklenburg (cf. B., 1930, 884).

R. TRUSZKOWSKI.

Occlusion of hydrogen by platinum-black. A. SIEVERTS and H. BRUNING (Z. anorg. Chem., 1931, 201, 122—143; cf. A., 1930, 1246).—Pt-black

previously degassed in vac. at 200° takes up 26—44 vols. H_2 per vol. Pt at 0° . Sorption isobars have been measured between 200° and -120° , and also isotherms between 200° and -40° for a pressure range of 0—1 atm. The velocity of sorption has been determined at 25° and -20° . At 0° or below, sorption tends to stop before the normal val. is reached. This behaviour is probably associated with diffusion processes. The occluded H consists of 2 portions, one so firmly bound that it is not removed even in vac., and another the behaviour of which is represented by the usual equation of the adsorption isotherm, $x = ap^{1/n}$ ($1/n = 0.12$). Samples of Pt-black prepared by the formate method and also by pptn. with Mg were used.

M. S. BURR.

Effect of adsorbed hydrogen on the lattice constant of palladium-silver alloys. A. OSAWA (J. Study Met., 1930, 7, 243—253).—The max. absorption of H_2 takes place at 70% Pd, and the max. expansion of lattice at 75—80% Pd.

CHEMICAL ABSTRACTS.

Specific adsorption by activated charcoals. III. Porosity of charcoal and time taken for attainment of adsorptional equilibrium. M. M. DUBININ (J. Gen. Chem. Russ., 1931, 1, 289—294).—With large-pored C adsorption rapidly attains equilibrium, and the order of adsorption of homologous aliphatic and mineral acids does not undergo inversion with time, as is partly the case with finely-porous C, in which equilibrium is not attained after 40 days.

R. TRUSZKOWSKI.

Relation between gas content and adsorption of electrolytes by activated carbon. VII. Action of ozone on activated carbon. B. BRUNS and W. PYSCHOV (Z. physikal. Chem., 1931, 157, 57—64; cf. A., 1931, 904).—When dry C is treated with O_3 it gradually becomes unable to absorb acid from aq. solution, but acquires the power of adsorbing alkali. This change is apparently due to the formation of acid oxides on the C surface, for boiling H_2O extracts acidic substances. On prolonged treatment with O_3 the wt. of the C falls, owing to the formation of volatile oxides. On the other hand, the adsorption of H_2SO_4 from aq. solution by C is increased by treating the latter *in situ* with O_3 , the increase being greater than that occasioned by O_2 . The C which has been subjected to the action of O_3 under these conditions does not adsorb Na^+ from aq. NaOH. The first products of the action of O_3 on C are probably basic oxides, which in the dry state pass into more stable acid oxides, but are stabilised by H_2O .

R. CUTHILL.

Adsorptive capacity, catalytic activity, and crystalline structure of carbon. U. HOFMANN [with E. GROLL and W. LEMCKE] (Z. angew. Chem., 1931, 44, 841—845).—A lecture. A number of typical active charcoals give, after purification, the X-ray diagram of graphite when an improved technique is used. Increasing size of the crystals (calc. from the X-ray diagram) is accompanied by increasing hardness, decreasing adsorptive capacity for PhOH in aq. solution, and decreasing catalytic activity for the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$. Differences in the appearance of charcoal are dependent on

the conditions of deposition rather than on crystal size.

R. S. CAHN.

Selective adsorption of ionium by manganese dioxide. A. N. PILKOV (J. Gen. Chem. Russ., 1931, 1, 589—593).— MnO_2 pptd. by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ from a solution containing Ce and Io salts selectively adsorbs Io and U-X.

R. TRUSZKOWSKI.

Colloid chemistry of polonium. I. I. E. STARIK (Z. physikal. Chem., 1931, 157, 269—284).—The adsorption of Po from aq. solution by glass, parchment, dust, and various colloiddally dispersed substances has been observed, the amount adsorbed being, in general, greater in acid solution than in alkaline solution. These adsorption effects are most satisfactorily explained by supposing that in alkaline or neutral solution Po is colloiddally dispersed, but molecularly dispersed in acid solution.

R. CUTHILL.

Adsorption of iodine on films of barium chloride sublimed in vacuum, and the effect of temperature. J. H. DE BOER [with J. Broos] (Z. physikal. Chem., 1931, B, 14, 457—470).—The adsorption at room temp. and at 2.5° can be expressed by the same formula which holds for the adsorption by CaF_2 and BaF_2 (A., 1931, 1226), and the effect of variations in the amount of adsorbent is similar. With increase in the rate of sublimation, the adsorbing surface increases. The amount of I adsorbed by a given surface of adsorbent and under the same pressure of I vapour relative to the saturation v. p. is less at 2.5° than at room temp., from which it follows that the heat effect in the transition of solid I to the adsorbed state is negative. The effect of temp. on the consts. of the adsorption isotherm does not agree with the adsorption theory previously advanced (A., 1929, 875), apparently because the adsorbed film is unimol., not multimol.

R. CUTHILL.

Sorption process in the zeolite chabazite. M. G. EVANS (Proc. Roy. Soc., 1931, A., 134, 97—102).—The heats of adsorption for very small additions of NH_3 to chabazite crystals have been determined. The vals. of dh/ds (h being the heat in cal. and s the sorption in c.c.) rise rapidly to a max. and then slowly decrease with increase of s . If the unused chabazite is allowed to absorb the gas, then heated for 3 days to 350° , and the sorption re-measured, the vals. of dh/ds are initially large and gradually fall with increase of s . The adsorption of gas shatters the crystals. The structural changes during the sorption process are studied by means of X-rays.

L. L. BIRCUMSHAW.

Adsorption of bacteriophages by silicic acid. H. BECHHOLD and M. SCHLESINGER (Kolloid-Z., 1931, 57, 180—183).—Bacteriophages are adsorbed markedly by SiO_2 gel and strongly by "Silargel" (AgCl-SiO_2 gel) in acid buffer solutions. The process is a true, reversible adsorption equilibrium. The material is desorbed almost quantitatively in solutions of p_{H} 8.2.

E. S. HEDGES.

Adsorption of metallic salts by caseinogen. E. NEGRI (Arch. Farm. speriment., 1931, 53, 72—caseinogen from 100 c.c. of defatted cows'

milk adsorbs completely Pb (0.2—1.5 g.) from $\text{Pb}(\text{NO}_3)_2$ solutions. The adsorption is accompanied by decomp. of the salt into its ions, only the Pb being adsorbed. The compound formed is stable to washing.

T. H. POPE.

Surface films of insoluble substances on aqueous solutions. N. K. ADAM (Kolloid-Z., 1931, 57, 125—139).—A summary of published work.

E. S. HEDGES.

Experimental evidence in support of the balanced-layer theory of liquid film formation. C. W. FOULK and J. N. MILLER (Ind. Eng. Chem., 1931, 23, 1283—1288).—The theory is restated, and two new forms of apparatus have been devised to study film formation. The relation of the static and dynamic surface tensions of a solution to the surface adsorption is discussed. Tables are given to illustrate the relation of the difference between static and dynamic surface tension to foam formation and film formation in solutions.

J. W. SMITH.

Molecular forces at the boundaries of different phases. B. V. ILJIN (J. Gen. Chem. Russ., 1931, 1, 557—566).—If the dipole moment μ_A of a colloidal adsorbent exceeds that of a polar liquid μ_l in which it is immersed, the adsorbent is a lyophilic colloid, and if $\mu_l > \mu_s$, where μ_s is the dipole moment of a solute, this solute is not adsorbed by the colloid. In the case of lyophobic colloids ($\mu_A < \mu_l$) the solute is adsorbed if $\mu_s < \mu_l$, whilst in non-polar solvents the above effects are inverted. This mechanism of adsorption does not, however, apply also to adsorbents possessing a porous structure. Adsorbent C may be classified into a number of types, according to the nature of their surface and to their internal structure. The inversion of Traube's series in certain charcoals is possibly due to the existence of micropores impermeable to larger particles of solute.

R. TRUSZKOWSKI.

Calculation of molecular dimensions by means of an equation of state for surface films. P. P. KOSAKEVITSCH and E. S. USCHAKOVA (Z. physikal. Chem., 1931, 157, 188—202).—Surface tension measurements with aq. solutions of various capillary-active substances at room temp., taken in conjunction with existing data, show that with few exceptions Schofield and Rideal's equation of state for surface films on liquids (A., 1925, ii, 960) is valid over a considerable range of two-dimensional pressure, F . With low vals. of F , however, there are deviations similar to the deviations from Amagat's equation exhibited by gases under low pressures, and at very high vals. FA/RT passes through a max. with increase in F , and then falls rapidly. The val. of B is, in general, in satisfactory agreement with the val. for the cross-section of the active mol. obtained by X-ray methods. For an *iso*-alcohol the val. of B is greater than for the corresponding *n*-alcohol.

R. CUTHILL.

Membrane equilibrium and ion distribution. I. Dynamics of membrane permeability in relation to ion distribution. S. K. LUV (Kolloid-Z., 1931, 57, 139—152).—Mathematical.

E. S. HEDGES.

Effect of current strength on electro-osmosis through palmitic acid diaphragms. G. KOHLER

(Z. physikal. Chem., 1931, 157, 113—142).—The vol., v , of an acetate buffer solution of p_H 3.7—5.7 which passes through the membrane in unit time at 25° is related to the current strength, i , by the equation $v = ki - v_0 = k(i - i_0)$, where k , i_0 , and $v_0 = ki_0$ are consts. This equation may be deduced theoretically by supposing that a certain min. shearing strain must be applied to the electric double layer before any slip occurs, and on this assumption the streaming potential, ζ_0 , is given by the equation $\zeta = \zeta_0(1 - i_0/i)$, where ζ is the streaming potential calc. by applying the unmodified Helmholtz-Smoluchowski equation. v_0 should theoretically be proportional to the total cross-sectional area of the pores in the diaphragm. If ζ_0^2 is plotted against p_H^2 , the resulting graph consists of two intersecting straight lines. v_0 depends on the degree of dissociation of the buffer acid, and at $p_H < 4.0$ is practically zero. It appears that even when i is reduced below i_0 a minute electro-osmosis still persists.

R. CUTHILL.

Anomalies in cryoscopic use of benzene and nitrobenzene. (MLLE.) M. T. FRANÇOIS (Compt. rend., 1931, 193, 1008—1010).—The "consts.," K , for the normal fatty acids, C=2—12, 14, and 16, dissolved in C_6H_6 are respectively 29.7, 30.3, 30.5, 31.0, 31.8, 32.1, 32.8, 34.1, 34.2, 34.8, 36.3, 46.2, 46.3; dissolved in $PhNO_2$ they are (C_{16} omitted) 46.5, 46.5, 46.7, 47.0, 48.5, 48.6, 49.1, 52.8, 55.2, 61.9, 69.4, 86.2, showing that the idea that these solvents have two consts., a "normal" and an "abnormal," is incorrect (cf. B., 1929, 860). C. A. SILBERRAD.

Mutual effect of amino-acids in solution. M. FRANKEL (Biochem. Z., 1931, 241, 94—107).—For mixtures of glycine with *dl*-alanine, *l*-leucine, *l*-asparagine, *dl*-valine, and *d*-arginine, n is greater than that calc. from the components of the mixture, indicating a change of mol. condition on mixing. Since glycine in pure solution shows considerable intermol. attraction, the observed change represents probably a repression of association between the glycine mols. For mixtures of *dl*-alanine and *l*-leucine, *dl*-alanine and *dl*-valine, *dl*-alanine and *d*-alanine, *d*-alanine and *l*-leucine, *l*-leucine and *d*-leucine, the refractometric and cryoscopic data are additive, and no change of condition of the dissolved mols. occurs on mixing.

P. W. CLUTTERBUCK.

Hydrodynamics of disperse systems (rheology). M. REINER (Naturwiss., 1931, 19, 878—880).—Mathematical (cf. A., 1930, 145, 679).

E. S. HEDGES.

Determination of the size of colloidal particles from their viscosity. R. EISENSCHITZ and B. RABINOVITSCH (Ber., 1931, 64, [B], 2522—2529).—The viscosity of solutions of Bayer-cellulose in $COMe_2$, dioxan, $AcOMe$, and furfuryl alcohol converges in very dil. solution towards the val. of the solvent, and the behaviour approximates to that of the ideal solution. The modulus of elasticity depends less on the concn., but does not show even approx. the behaviour of an ideally dil. solution. In regard to their elastic properties cellulose solutions of concn. <1% must be regarded as swollen solute rather than as dil. solutions. If the ideal state is reached by further dilution the elastic modulus must previously pass through a

min. the incidence of which is a criterion of the transition of the gel to the sol condition. In the range of concns. investigated the dissolved particles cannot be regarded as having freedom of motion. Methods of measuring mol. wt. which have an osmotic or a viscosimetric basis are therefore inapplicable.

H. WREN.

Study of colloidal solutions by means of the polarisation of the light diffused by them. A. BOUTARIC and C. TOURNEUR (Compt. rend., 1931, 193, 1011—1012).—Changes in size of the particles of a colloidal solution can be followed by observing the degree of polarisation of light diffused perpendicularly to a beam incident on the solution. On diluting such a solution the polarisation, P , of the diffused beam increases, but its intensity, I , decreases according to the relation $P - a - b \log I$. The course of flocculation can thus be followed: on adding an electrolyte to a colloidal solution P at first increases then as flocculation proceeds decreases to a temporarily const. val., finally increasing when sedimentation begins.

C. A. SILBERRAD.

Constitution of molecular colloids. H. STAUDINGER (Bull. Soc. chim., 1931, [iv], 49, 1267—1279).—A lecture.

Diffusion of colloid particles. III. Significance of abnormally great diffusion velocities and new ion effect in hydrophilic sols. H. R. BRUINS (Kolloid-Z., 1931, 57, 152—166; cf. A., 1931, 561).—An examination of results formerly described with reference to electrostatic forces between ions and particles. The new ion effect and the electroviscous effect are parallel.

E. S. HEDGES.

Diffusion of colloidal electrolytes and other charged colloids. G. S. HARTLEY and C. ROBINSON (Proc. Roy. Soc., 1931, A, 134, 20—35).—Theoretical. The Stokes-Einstein equation is generally considered to give the relation between the diffusion of colloidal substances and their particle size, but the influence of electrical forces has been neglected. Since the ordinary Nernst equation for the diffusion of electrolytes must be extended to the case of multivalent ions to obtain a val. for the diffusion coeff. of a colloidal dye, it is impossible to deduce even qual. vals. for the particle size by this means. If electrolytes other than the diffusing one are present in the system, the potential gradient is reduced and a lower diffusion coeff. obtained. A method for determining particle size is indicated by the fact that agreement with the Stokes-Einstein equation is approached in the presence of excess of added electrolyte. The effect of added electrolyte suggests that the low vals. sometimes obtained for the diffusion velocity of dyes might be due to the presence of traces of electrolyte as impurity. The influence of electrical forces on the diffusion coeff. must also be taken into account in the case of charged colloids such as starch and gum-arabic (cf. A., 1931, 561).

L. L. BIRCHUMSHAW.

Diffusion of hæmoglobin in colloidal and molecularly disperse solutions. F. P. FISCHER (Kolloid-Z., 1931, 57, 166—173).—Colloidal solutions (starch, gelatin) retard the diffusion of hæmoglobin

in aq. solution. Aq. hæmoglobin solutions diffuse against blood-serum much more quickly than against H_2O , especially when the hæmoglobin is dil. In general, the diffusion velocity for a given quantity of added electrolyte increases as the concn. of hæmoglobin is reduced, and for a given concn. of hæmoglobin increases with decreasing concn. of electrolyte. Electrolyte solutions below a certain concn., which is characteristic for each electrolyte, accelerate the diffusion. Non-ionised substances (glycerol, sucrose, carbamide) reduce the diffusion velocity of hæmoglobin to a degree which is independent of the concn. of the added substance. The influence of serum and electrolytes is believed to be due to a solvation pressure of the hæmoglobin, which acts in addition to the driving force of diffusion. E. S. HEDGES.

State of division of dissolved substances at extreme dilutions. O. WERNER (Mikrochem., 1931, 10, 360—368).—In extremely dil. solutions Th-B and Th-C are present not as ions but as large complexes formed probably by adsorption on solid impurities in the solution. Evidence obtained by addition of electrolytes indicates that whereas Th-B behaves as a cation, Th-C behaves principally as an anion. H. F. GILLBE.

Coagulation of colloids by electrolytes. B. N. DESAI and P. M. BARVE (Nature, 1931, 128, 907—908). Results of measurements of the charge on colloidal $Fe(OH)_3$ diluted to different extents in the presence and absence of electrolytes are summarised. L. S. THEOBALD.

Coagulation of von Weimarn's formaldehyde-gold sols. III. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 17, 68—87; cf. A., 1930, 1249).—The coagulation vals. of NaCl and $BaCl_2$ for Au sols prepared by von Weimarn's method vary periodically with the p_H of the sol, as does also the duration of the red colour. F. L. USHER.

Influence of non-electrolytes, containing various numbers of hydroxyl groups, on the precipitation of thorium hydroxide from thorium nitrate solution by sodium hydroxide. G. M. NABAR, A. M. PATEL, and B. N. DESAI (Kolloid-Z., 1931, 57, 173—175).—The pptn. of $Th(OH)_4$ from $Th(NO_3)_4$ solutions by NaOH is prevented by glycol, glycerol, mannitol, fructose, maltose, glucose, lactose, and sucrose, in the presence of which colloidal solutions of $Th(OH)_4$ are formed. The min. quantity of org. substance required to prevent the pptn. is smaller the greater is the no. of OH radicals in the substance. The colloid particles are negatively charged. A slight excess of NaOH is necessary for stability and the particles are probably stabilised by simultaneous adsorption of the org. substance and OH ions. E. S. HEDGES.

Triple solvents and the stability of hydrosols. A. DUMANSKI, T. A. GRANSKAYA, and M. P. LONSKAYA (J. Gen. Chem. Russ., 1931, 1, 295—303).—Areas of turbidity, coagulation, etc. have been plotted using triaxial co-ordinates for the systems Fe hydrosol-EtOH, PrOH, or $COMe_2$ -org. solvent. The order of the coagulating effect in presence of alcohols is $PhMe < C_6H_4Me_2 < C_6H_5 < CCl_4 < Et_2O < AcOMe <$

$AcOEt$, and in presence of $COMe_2$, $C_6H_5 < PhMe < C_6H_4Me_2 < CCl_4 < Et_2O < AcOEt$.

R. TRUSZKOWSKI.

Colloidal sulphur. H. BASSETT and R. G. DURRANT (J.C.S., 1931, 2919—2956).—The stabilising ion in Odén's colloidal S is probably $S_6O_6^{2-}$ rather than $S_5O_6^{2-}$. During "ageing" the S becomes cryst. and at the same time the adsorbed $S_6O_6^{2-}$ is partly given up to the intermicellar liquid. An explanation of the mechanism of this change is put forward. The coagulating efficiency of cations depends, not only on the valency, but also on the solubility of the product formed with the stabilising ion. The coagulum always contains the coagulating ion in exact stoichiometric proportion to the adsorbed polythionate. F. L. USHER.

Triaxial co-ordinates in colloid chemistry. III. Peptisation of ferric hydroxide by alkaline solutions of mannitol. A. DUMANSKI and V. M. SIMONOVA. IV. Peptisation of ferric hydroxide by alkaline solutions of sodium tartrate. A. DUMANSKI and Z. P. TSCHESCHEVA. V. The system sucrose- $CaCO_3$ -NaOH. A. DUMANSKI and G. R. VISCHNEVSKAYA (J. Gen. Chem. Russ., 1931, 1, 209—218, 325—329, 620—624).—III. The system $Fe(OH)_3$ -aq. mannitol-aq. NaOH has been studied. Sharply-defined fields of total peptisation exist, and similar results are obtained for a no. of normally insol. substances, such as $CaCO_3$.

IV. The system $Fe(OH)_3$ -Na tartrate-NaOH has been studied. As the concn. of tartrate increases the state of $Fe(OH)_3$ changes from ppt. through hydrosol to ordinary solution.

V. $CaCO_3$ is peptised by alkaline aq. sucrose or mannitol, the particles being positively charged, in contradistinction to similarly prepared sols of heavy-metal hydroxides. Cryst. $CaCO_3 \cdot 6H_2O$ separates from the sol on keeping; this is formed from complex ions of the type $CaCO_3 \cdot CaC_{12}H_{21}O_{11}^+$, formed in the sol as a result of the adsorption of Ca saccharate on the $CaCO_3$ particles.

R. TRUSZKOWSKI.

Ageing and hysteresis in disperse systems. Sedimentational hysteresis of charcoal suspensions in dye solutions. B. V. ILJIN and Z. G. PINSKIER (J. Gen. Chem. Russ., 1931, 1, 569—583).—The stability of 4% suspensions of wood or animal charcoal in 0.025% Me-violet is 22—32% greater than in H_2O if sedimentation is measured immediately after preparing the system, and 6—22% greater when measurements are made 24 hr. later.

R. TRUSZKOWSKI.

Dissolution of gelatin in liquids. E. W. J. MARDLES (Kolloid-Z., 1931, 57, 183—194).—Measurements of the solubility of gelatin in H_2O have shown that the relations are similar to those of crystalloids, a limiting solubility being observed for a given temp., increasing with rise of temp. The solubility of gelatin increases rapidly above 26°. Hysteresis is observed in the sense that the solubility at a given temp. is higher for falling than for rising temp. After purification the solubility of gelatin is less. The hydrophilic properties of gelatin are enhanced by the addition of numerous org. compounds (e.g., $AcOH$, NH_4Et , $HCONH_2$), whilst other substances ($EtOH$, glycerol)

do not markedly diminish swelling and peptisation until their concn. reaches 30–40%. The surface tension of some gelatin organosols is greater than that of the pure dispersion media. E. S. HEDGES.

Absorption of water by gelatin. VI. Influence of the thickness and original concentration of the gel. D. J. LLOYD (Biochem. J., 1931, 25, 1580–1592).—The absorption of H_2O under varying conditions by discs of gelatin is influenced by the thickness of the disc. The swelling of both dried and undried gelatin gels in H_2O or salt solutions is not greatly influenced by the thickness. In acid or alkaline solutions swelling is a negative function of the logarithm of the thickness. The absorption of H_2O by gelatin is under all conditions an inverse logarithmic function of the original concn. at which the jelly was set. The amount of H_2O absorbed by gelatin from H_2O , solutions of salts, acids, or alkalis is a function of the square of the temp. as long as dissolution of the gel itself is inappreciable. The influence of the original concn. of the gel depends on the amount of H_2O in the system irrespective of whether the H_2O has penetrated into the jelly through the direct action of temp., p_H val. of the solution, or the nature of the salts present. At low temp. swollen gels in equilibrium with H_2O tend to approximate to a concn. of 10% regardless of the original concn. of the gel. In similar conditions gels which have been dried contain at equilibrium less H_2O than those which have not been dried. S. S. ZILVA.

Adsorption of organic liquids by gelatin gels without volume change. H. ERBRING (Kolloid-Z., 1931, 57, 195–196).—10% gelatin gels in the form of cubes were slowly dehydrated by immersing in EtOH– H_2O mixtures containing progressively increasing proportions of EtOH, finally in abs. EtOH, and drying in vac. The resulting mass contained numerous capillaries and when placed in org. liquids (hexane, CCl_4 , PhMe, C_6H_6 , Et_2O) took up large quantities without undergoing any change of vol. Clearly, a classification of gels according to whether they swell in the dispersion medium (gelatin in H_2O) or not (SiO_2 gel) is unsatisfactory. E. S. HEDGES.

Sol-gel transformation in gelatin. D. M. GREENBERG and M. A. MACKEY (J. Gen. Physiol., 1931, 15, 161–166).—The theory that the sol and gel structures are the same is said to be unacceptable. H. DAVSON.

Dilatometric measurement of protein hydration. K. H. GUSTAVSON (Ind. Eng. Chem., 1931, 23, 1298–1300).—The total vol. changes associated with gelatin–aq. solutions of various $[H^+]$ are not a measure of the degree of hydration of the gelatin. The removal of the H^+ and OH^- from the solutions by the protein influences the total vol. of the system. J. W. SMITH.

Plastic properties of casein gels. W. HALLER (Kolloid-Z., 1931, 57, 197–203).—The plasticity of certain colloidal products has been measured by forcing the substance under high pressure (2000 kg. per sq. cm.) through a fine orifice and determining the relation between velocity of flow and pressure. With casein gels structure viscosity was observed, the

flowing power increasing with the speed of flow in a way which can be represented accurately by the exponential equation of Ostwald and de Waele. The plasticity of casein gels depends on the presence of other substances, and particularly on the H_2O content, being small below 21% but rising rapidly with increasing amounts of H_2O . This is believed to be due to a transformation from a closed to an open gel structure, an explanation which is supported by dielectric measurements. E. S. HEDGES.

Gel formation and thixotropy in some Danish clays. A. JEPPESEN (Kolloid-Z., 1931, 57, 175–180).—The phenomena of setting and thixotropy in certain clays are described. E. S. HEDGES.

Swelling. III. Adsorption of neutral salts by cotton. A. LOTTERMOSER and W. HONSCH (Kolloid-Z., 1931, 57, 206–221).—Cotton adsorbs LiCl, NaCl, KCl, $CaCl_2$, and KCNS without changing the p_H of the solution. The adsorption is not strictly reversible and indicates the formation of compounds of the salts with cellulose. Adsorption of NaOH is irreversible. E. S. HEDGES.

Morphology of cellulose fibres. B. RABINOVITSCH (Kolloid-Z., 1931, 57, 203–206).—The changes in the fine structure of fibres of ramie trinitrate and tripalmitate produced by swelling in org. liquids are profusely illustrated by photomicrographs. In Et malonate longitudinal and spiral fibrils become visible, whilst transverse markings develop when the fibres swell in a mixture of Et malonate and cyclohexanone. By means of a needle micro-manipulator, these can be separated into constituent fibrils. On swelling, the long axis of the fibre contracts in the case of ramie trinitrate, but fibres of the tripalmitate increase in length. E. S. HEDGES.

Ionic activity in protein systems. A. BENE-
DIGNI and G. B. BONINO (Arch. Sci. biol., 1930, 14, 293–326; Chem. Zentr., 1931, i, 3573).—Electrometric measurements in the systems gelatin–HCl or $-H_2SO_4$ show that the difference in mean potential energy, $y_2 - y_1$, of the pair H^+, Cl^- (for 1g.-ion and unit wt. of gelatin) in solutions containing or free from protein is in dil. solution but little influenced by the HCl concn. In 1/16N-HCl the interionic forces in the protein medium are increased for both H^+ and for Cl^- ; on progressive dilution of the HCl the effects on the H^+ remain of the same order of magnitude and may even increase, whilst those on Cl^- gradually fall to the limiting val. in protein-free solution. f_{Cl^-} increases continuously with dilution, but f_{H^+} only at high HCl concns.; at low HCl concns., for the same original gelatin content, there is a gradual fall in f_{H^+} with dilution. The effects on the H^+ in H_2SO_4 solutions are greater than in HCl solutions, but the SO_4^{2-} effects are less than the Cl^- effects. For 1% gelatin solutions $\log f_{SO_4^{2-}}/\log f_{Cl^-}$ is for small H_2SO_4 concns. much lower than in corresponding protein-free solutions. In dil. H_2SO_4 solutions the gelatin appears not only to fix the SO_4^{2-} no more strongly than the Cl^- , but also to make it more free than in aq. H_2SO_4 of the same concn. Δy_H depends only on the p_H . Above p_H 1.5 the effects on the H^+ in protein systems suddenly increase. A. A. ELDRIDGE.

Effect of addition of salts on the isoelectric point of proteins. II. S. J. PRZYŁECKI and W. GIEDROYC (Biochem. J., 1931, 25, 1734—1735).—At concns. higher than the critical concns. (A., 1931, 1009), protein (gelatin or serum-albumin) particles may be supercharged at p_H other than that of the isoelectric point; protein solutions are thus obtained in which the particles behave as anions at p_H vals. lower than and as cations higher than that of the isoelectric point. S. S. ZILVA.

Electrokinetic potential of gelatin jellies. S. GLIXELLI and Z. STOLZMANN (Rocz. Chem., 1931, 11, 690—703).—The conductivity of gelatin solutions is unaffected by passage from sol to gel. The electrokinetic potential, ζ , of gelatin diaphragms diminishes with increasing concn. of gelatin from 1 to 12%, and with increasing p_H , up to the isoelectric point, p_H 4.85, at which ζ is 0. This apparent deviation from the Helmholtz-Smoluchowski theory is ascribed to binding of H_2O by gelatin, in accordance with Eggert and Reitstötter's theory. R. TRUSZKOWSKI.

Study of the electrophoresis of proteins by the moving boundary method. A. TISELIUS (Nova Acta Reg. Soc. Sci. Upsal., 1930, [iv], 7, No. 4, 107 pp.; Chem. Zentr., 1931, i, 3095—3096).—A modified Pauli-Engel apparatus has been used, the movement of the boundary being registered photographically. A buffer concn. of 0.02*N* for 0.3—0.4% of protein is necessary. The effect of diffusion is usually small, but is marked with Bence-Jones protein and albumin. Within certain limits (recorded for various proteins) the protein and buffer concns. do not affect the position of the isoelectric point. Movement of the protein in both directions in the neighbourhood of the isoelectric point does not occur with homogeneous materials. Near the isoelectric point the change in the velocity with p_H is characteristic for each protein, the velocity being a linear function of p_H . The components of protein mixtures have little mutual effect even in p_H regions where they are oppositely charged. Fibrinogen, lactalbumin, and globulin are heterogeneous. A. A. ELDRIDGE.

Cataphoresis of amino-compounds. H. R. KRUYT and J. J. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1007—1012).—Cataphoretic velocity measurements with $C_{10}H_8$, anthracene, and NH_2Ph sols in H_2O in presence of HCl indicate that the particles are negatively charged. Sols prepared from NH_2 -derivatives of these substances have a decreased negative charge or a positive charge, depending on the concn. of HCl .

H. J. EMELÉUS.

Magnetophotophoresis. E. REEGER (Z. Physik, 1931, 71, 646—657).—Apparatus for the study of magnetophotophoresis is described, and the movement of Fe and Sb particles suspended in N_2 has been examined. The ferromagnetic particles move only under intense illumination, show saturation with increasing magnetic fields, and do not reverse their direction of motion with reversal of the field; the diamagnetic particles do not show saturation, and behave arbitrarily when the field is reversed.

A. B. D. CASSIE.

Electrophotophoresis. P. SELNER (Z. Physik, 1931, 71, 658—665).—Rate of motion in electrophotophoresis reaches a limit with increasing field strength.

A. B. D. CASSIE.

Dependence of electrophotophoresis on light intensity and gas pressure. E. WILFLINGER (Z. Physik, 1931, 71, 666—677).—Electrophotophoretic forces increase proportionally to the light intensity, and show a max. variation at certain gas pressures usually between 300 and 400 mm. Hg.

A. B. D. CASSIE.

Electrostatic energy of dipole moments in different media. R. P. BELL (Trans. Faraday Soc., 1931, 27, 797—802).—The electrostatic energy of transfer of a spherical dipole mol. from one continuous medium to another is calc. This energy change is the determining factor for the distribution of dipole mols. only in extreme cases. Solubility data for H_2O and NH_3 agree semi-quantitatively with the equation. A previous error is corrected (A., 1931, 901).

J. G. A. GRIFFITHS.

Internal molecular potential between the substituent groups in a benzene ring as derived from the heats of combustion. H. A. STUART (Physical Rev., 1931, [ii], 38, 1372—1384).—Differences in the heats of combustion of isomeric C_6H_6 derivatives and between observed vals. and those calc. by the additivity rule for certain non-isomeric derivatives can be interpreted as the internal mol. potential between the substituent groups. Vals. of this are in good agreement with those calc. from the intermol. (van der Waals) forces. Deductions relative to the stability of valency angles are discussed.

N. M. BLIGH.

Osmotic pressure. J. J. VAN LAAR (Chem. Weekblad, 1931, 28, 662—665).—Theoretical. Expressions are derived for the thermodynamic potentials of the components of a binary mixture, for the osmotic pressure, and for the v. p. of a single substance and of a binary mixture. H. F. GILLBE.

Nernst heat theorem. H. J. BRENNEN (Physical Rev., 1930, [ii], 35, 121).—In view of certain discrepancies it is suggested (i) that U and T be regarded as independent variables and A as a dependent variable and (ii) that the Gibbs-Helmholtz equation should be written in the form $A - U = T(\partial A / \partial T) + KU(\partial A / \partial U)$, where K is a const.

L. S. THEOBALD.

Equilibrium $4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$. (MLLE.) A. E. KORVEZEE (Rec. trav. chim., 1931, 50, 1092—1099).—Measurements at 408°, 447°, and 520° by the method of von Falckenstein (A., 1907, ii, 19) lead to the expression $\log K_p = 5230/T - 5.86$. This is in good agreement with previous results over the range 350—650° except for some determinations of Lewis (A., 1906, ii, 843) in which, it is believed, equilibrium was not established. C. W. DAVIES.

Solutions of metals in non-metallic solvents; physical and chemical properties. C. A. KRAUS (J. Franklin Inst., 1931, 212, 537—562).—Published data on the physical and chemical properties of solutions of metals in NH_3 are discussed. It is suggested that in such solutions the metals are dissociated into cations, identical with those formed by the ordinary

salts of the metals, and anions consisting of free electrons.

D. R. DUNCAN.

Mode of action of solvents in chemical reactions. II. Salt formation by dimethylaminoazobenzene and trichloroacetic acid in indifferent media, and the effect of additions. A. WEISSBERGER and K. FASOLD (Z. physikal. Chem., 1931, 157, 65—95).—The equilibrium between Me-yellow, $\text{CCl}_3\cdot\text{CO}_2\text{H}$, and the salt formed by their interaction has been studied in C_6H_6 and CHCl_3 solutions by means of determinations of the extinction curves, the tendency to salt formation being greater in CHCl_3 than in C_6H_6 . A variety of acidic, basic, and neutral org. compounds displaces the equilibrium in C_6H_6 solution in favour of the free base, their efficiencies in this respect varying in much the same order as in the decomp. of Et diazoacetate (A., 1931, 1375). This is apparently the result of the formation of compounds, probably of the ammonium and oxonium types, by the added substances and $\text{CCl}_3\cdot\text{CO}_2\text{H}$.

R. CUTHILL.

Complex formation involving weak acids. II. Constitution of acetates in solution. H. T. S. BRITTON and F. H. MEEK (J.C.S., 1931, 2831—2840; cf. A., 1931, 1233).—The conductivities and p_H of solutions of the acetates of Pb, Cu, Be, Al, and Th containing varying proportions of AcOH have been determined. It is inferred that these acetates are largely hydrolysed in solution but give rise to a high concn. of AcO' . Measurements of the electrode potential of Pb in solutions of basic Pb acetates show that $[\text{Pb}^{++}]$ is very small in these.

F. L. USHER.

Compounds of bismuth nitrate with polyhydric alcohols. F. DE CARLI (Annali Chim. Appl., 1931, 21, 472—482).—Polarimetric measurements on solutions of mannitol and $\text{Bi}(\text{NO}_3)_3$ indicate that 1 mol. of alcohol reacts with 2 mols. $\text{Bi}(\text{NO}_3)_3$. The compound formed is not an additive product and does not contain the three NO_3 groups of the nitrate.

O. F. LUBATTI.

Debye-Hückel theory and its experimental testing. III. H. VAN VELDHUIZEN (Chem. Weekblad, 1931, 28, 621—625; cf. A., 1931, 168).—A survey of the results obtained by various workers in the experimental investigation, by means of e.m.f. measurements, of the validity of the Debye-Hückel expression for the activity coeff., together with some details of the more recent developments of the theory.

H. F. GILLBE.

Activity coefficient of the cupric ion in solutions of its sulphate. (MLLE.) M. QUINTIN (Compt. rend., 1931, 193, 846—848).—Debye's formulæ for the activity coeff., γ , of an ion of valency n in terms of concn., m , when the mean diameter of the ion, d , is or is not negligible, are respectively $\log \gamma = -(Ae^2n^2\sqrt{\Sigma mn^2})/2DKT$, and $-Ae^2\sqrt{\Sigma mn^2}/2DKT(1 + d\sqrt{\Sigma mn^2})$, where $A = 2e\sqrt{\pi N}/10\sqrt{10DKT}$, and N , k , e , and T have their usual meanings. These have been tested for solutions of CuSO_4 for vals. of m from 0.01 to 0.5625 by determining the e.m.f. of the cell $\text{Cu}|\text{CuSO}_4, m|[\text{NH}_4\text{NO}_3, \text{sat.}][\text{KCl}, \text{sat.}][\text{Hg}_2\text{Cl}_2]|\text{Hg}$. Except when m is < 0.16 d is practically const. = 3.8 Å., and Debye's theory holds when the factor depending thereon is taken into account. C. A. SILBERRAD.

Fusion of salts at high pressure. Mechanism of salt metamorphosis. A. GELLER (Fortschr. Min. Kryst. Petr., 1930, 14, 143—166; Chem. Zentr., 1931, i, 1086; cf. Kali, 1924, 18, 297; Tammann, A., 1929, 1137).—The method is subject to error at low pressures. For Na_2SO_4 earlier vals., and for bischofite Tammann's data, have been confirmed. The carnallite curve is modified. A. A. ELDRIDGE.

Velocity of crystallisation of different forms of dimethyl tartrate. G. RUMEAU (Compt. rend., 1931, 193, 1085—1087).—The ordinary varieties of *d*- and *l*-methyl tartrate, "m. p. 48°," both exist in two forms, but no certain method for obtaining these has yet been discovered. For α_1 (very unstable) and α_2 (stable) the m. p. are $< 48^\circ$ and $> 50^\circ$ and the velocities of crystallisation at 27° 0.66 and 3.20 mm. per min., respectively. Both forms give solutions of the same rotatory power with no indication of mutarotation (cf. A., 1931, 1113). The velocity of crystallisation of Patterson's β -methyl tartrate, m. p. 61° (cf. J.C.S., 1904, 85, 765), the existence of which is confirmed, is 0.275. It is very stable. C. A. SILBERRAD.

Topochemical change of solid substances in liquids. W. FEITKNECHT (Fortschr. Chem. Physik, 1930, 21, No. 2, 1—56; Chem. Zentr., 1931, i, 3533—3534).—A discussion. A. A. ELDRIDGE.

Vapour pressure of saturated salt solutions. V. KIREJEV (Z. anorg. Chem., 1931, 201, 221—224).—For low v. p. the equation $\log p_s = Q_s \log p_0 + C_s$ is deduced, where p_s and p_0 are the v. p. of a saturated salt solution and pure H_2O , respectively, at the same temp., Q_s is the quotient of the heat of formation of a saturated solution from 1 mol. of H_2O vapour and the mol. heat of vaporisation of H_2O , and C_s is the integration const. The equation is applicable to the data for solutions of Na_2CO_3 and Na_2SO_4 . From this equation and one derived previously (A., 1931, 793), a diagram for the system H_2O -NaCl has been constructed which agrees with the solubility and v. p. data. The relations may be applied to other solvents. M. S. BURR.

Thermodynamic investigations in the system iron-carbon-oxygen. W. KRINGS (Z. anorg. Chem., 1931, 201, 188—192).—Possible causes for the discrepancy between the observation of Dünwald and Wagner (A., 1931, 1128) and the author (A., 1929, 1230; 1930, 989) on the solubility of O_2 in Fe are discussed. M. S. BURR.

Equilibrium $4\text{CuCl}_2 + \text{O}_2 \rightleftharpoons 2\text{Cu}_2\text{OCl}_2 + 2\text{Cl}_2$. (MLLE.) A. E. KORVEZEE (Rec. trav. chim., 1931, 50, 1085—1091).—Measurements similar to those of Jellinek and Rudat (A., 1926, 909) have been made at 408° and 447°, using a stream of air in place of O_2 , and modifying the calculation to allow for the reaction vol. change. The expression $\log h_p = 6.131 - 6349/T$ is derived. C. W. DAVIES.

Polythermic field of crystallisation of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ in the system $2\text{NaCl} + \text{MgSO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$. V. P. ILJINSKI and A. F. SAGAJDATSCHNI (J. Gen. Chem. Russ., 1931, 1, 584—588).— $\text{NaCl} \cdot 2\text{H}_2\text{O}$ is said to separate between 0° and 20°. R. TRUSZKOWSKI.

Liquid area of carbamide-ammonia-carbon dioxide system. R. O. E. DAVIS and C. A. BLACK (Ind. Eng. Chem., 1931, 23, 1280—1282).—From the equilibrium data, the temp. which must be maintained in the outflow material of the autoclave, and the minimum temp. required at the base of the still in the recovery of the NH_3 , are deduced.

J. W. SMITH.

Calorimetric researches on standard substances. Heat of combustion of salicylic acid and naphthalene. L. J. P. KEFFLER (J. Chim. phys., 1931, 28, 457—469; cf. A., 1930, 702).—The isothermal heats of combustion of salicylic acid and C_{10}H_8 are 5235+1 g.-cal. (15°) per g. (weighed in vac.) and 9603, respectively. The former is preferred as a second calorimetric standard.

J. G. A. GRIFFITHS.

Heat of formation of fluorine oxide. H. VON WARTENBERG (Z. anorg. Chem., 1931, 200, 235—236).—Reconsideration of previous measurements yields a mean heat of formation of F_2O of $-9+2$ kg.-cal. per mol., compared with Ruff and Menzel's val. of -4.6 kg.-cal. The causes of the discrepancy are discussed; the author's val. is probably the more correct.

H. F. GILLBE.

Heats of dilution at 25° of certain uni-bivalent salts at high dilutions. II. Magnesium, calcium, strontium, and barium nitrates, and lithium, sodium, potassium, rubidium, caesium, magnesium, and calcium sulphates. E. LANGE and H. STREECK (Z. physikal. Chem., 1931, 157, 1—31).—The integral heats of dilution, V_m , and differential heats of dilution, Φ_m , have been obtained between 10^{-1} and $10^{-4}M$; the relation between these and the concn. (m) is similar to that already observed with other salts of the same type (A., 1931, 309). At the highest dilutions, V_m and Φ_m are positive, but with increase in m they rise and pass through a max. when m is still very small, ultimately becoming negative with several of the salts. For a group of salts having a common ion, the smaller is the radius of the variable ion in the non-hydrated state the more positive is V_m . Improvements in the differential calorimeter are described.

R. CUTHILL.

Heat of dissolution of sodium carbonate and specific heats of its solutions. J. C. SWALLOW and S. ALTY (J.C.S., 1931, 3062—3079).—An adiabatic calorimeter by means of which sp. heats of solutions can be determined quickly with an accuracy of 0.2% and heats of dissolution within 0.5% over the same temp. range is described. Full constructional details are given and the procedure is described. The apparatus is designed to work at temp. up to 500°. Sp. heats of solutions of Na_2CO_3 at 17.6°, 30°, 76°, and 98° and heats of dissolution of Na_2CO_3 at 30° are given.

F. L. USHER.

Thermochemistry of Portland cement. Heat of formation of alite and of jaeneckeite. O. F. HONUS (Chim. et Ind., 1931, 26, 1011—1022).—The mol. heat of formation of alite, $(3\text{CaO}, \text{SiO}_2)_4, 3\text{CaO}, \text{Al}_2\text{O}_3$, from CaCO_3 , SiO_2 , and Al_2O_3 is +116,150 g.-cal., and from its elements is +3,201,000 g.-cal. The mol. heat of formation of jaeneckeite, $8\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$, from

SiO_2 , Al_2O_3 , and CaO is +58,800 g.-cal. and from the elements is +1,861,000 g.-cal.

E. S. HEDGES

Independent mobility of ions and atoms in solid substances. K. FISCHBECK (Z. anorg. Chem., 1931, 201, 177—187).—Formation of Ag_2S or Cu_2S electrolytically at the surface of the respective metals by anodic polarisation and also non-electrolytically by the action of a polysulphide solution at the surface may go on independently, indicating that ionic transport through the layer of sulphide already formed is independent of mol. diffusion. By cathodic polarisation in a polysulphide solution the two processes may be made to oppose one another, and the calc. val. for the thickness of the sulphide layer formed is in good agreement with that measured by interference colours. Under the experimental conditions the sulphide does not act as a mixed conductor and conduction takes place in accordance with Faraday's law, contrary to earlier observations (A., 1927, 316). The conditions under which mixed electrolytic and metallic conduction might take place are discussed.

M. S. BURN.

Conductivity of acetone for continuous current. GARRIGUE (Compt. rend., 1931, 193, 925—926; cf. A., 1930, 1126).—The current variations obtained with various samples of COMe_2 and PhNO_2 appear to be due to irregularities in the distribution of potential, and these in turn to irregularly distributed changes in chemical composition, which are very little affected by light or change of temp. (cf. A., 1931, 410). Assuming change in current due to steady purification (cf. A., 1913, ii, 549) $\log(I-I_\infty)/\log I$ should be a linear function of time; this holds well for PhNO_2 , in many cases for COMe_2 , and occasionally for C_6H_6 .

C. A. SILBEREAD.

Conductivity of concentrated solutions in antimony trichloride. Z. KLEMENSIEWICZ and Z. BALOW (Rocz. Chem., 1931, 11, 683—689).—The conductivities of 1—3*N*-KCl, -KBr, -NH₄Cl, -NH₄Br, -RbCl, -TlCl, and -TlBr in SbCl_3 at 99° have been determined. The relation $\log \kappa = \eta \frac{1}{c}$, where η is the mol. concn., holds up to 0.5*N*; at higher concns. the slope of the curve becomes smaller for Tl salts and greater for the remaining salts studied. The curves connecting equiv. concn. with sp. conductivity exhibit a max. at about 2 *cN* for KCl and RbCl, but not for the other salts studied.

R. TRUSZKOWSKI.

Influence of cyclic α - and β -hydroxy-acids on the conductivity of boric acid and the configuration of these compounds. J. BOESEKEN, G. SLOOFF, and A. G. LUTGERHORST (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 932—940).—1-Hydroxy-cyclopentane-, -cyclohexane-, and -cycloheptane-1-carboxylic acids give an increased conductivity with boric acid, whilst 1-hydroxycyclobutane-1-carboxylic acid does not. Bornedicarboxylic acid (m. p. 102—103°) gives an increase, but the isomeric acid (m. p. 175°) gives none. The spatial arrangement of OH groups in these compounds is discussed on this basis.

H. J. EMELÉUS.

Volta effect in electrochemistry. O. SCARPA (Atti III Cong. Naz. Chim. pura appl., 1929, 83—94; Chem. Zentr., 1931, i, 3215—3216).

Electrolytic solution pressure, and the voltaic potentials metal/metal in the voltaic cell. H. HAMMERSCHMID and E. LANGE (Physikal. Z., 1931, 32, 958—964).—Theoretical. A. J. MEE.

Influence of temperature on the e.m.f. of separate half-elements. V. V. IPATIEV, jun., and S. I. JURIEV (J. Gen. Chem. Russ., 1931, 1, 549—556).—The temp. coeff. (18—90°) of the half-elements $\text{Hg}|\text{Hg}_2\text{SO}_4$, 0.1N- H_2SO_4 and $\text{Hg}|\text{Hg}_2\text{SO}_4$, 0.01N- H_2SO_4 , 0.09N- CdSO_4 are 0.00025 and 0.00032 volt, respectively; that of $\text{Cd}_{13.57\%}\text{Hg}|\text{0.01N-H}_2\text{SO}_4$, 0.09N- CdSO_4 rises with temp. The p.d. of the above half-elements at 90° in comparison with a H_2 electrode at 25° are 0.7046 ± 0.001 , 0.7080 ± 0.0005 , and 0.3613 ± 0.001 volt. The e.m.f. of the chain $\text{Hg}|\text{Hg}_2\text{SO}_4$, 0.01N- H_2SO_4 , 0.09N- $\text{CdSO}_4|\text{HgCd}_{13.57\%}$ is 1.069 at 90°, 1.061 at 100°, 1.054 at 110°, and 1.048 volts at 120°; this element is resistant to heating at 120° for 30 hr. R. TRUSZKOWSKI.

Temperature coefficient of the antimony electrode. G. P. AVSEEVITSCH and I. I. SHUKOV (J. Gen. Chem. Russ., 1931, 1, 199—208).—The p_{H} using an Sb electrode against a saturated Hg_2Cl_2 electrode is given by $p_{\text{H}} = \{E + 0.026 + (t^\circ - 18)0.00016\} / \{0.0542 + (t^\circ - 18)0.000275\}$. R. TRUSZKOWSKI.

Kinetics of the gas electrode. K. BENNEWITZ and W. SCHIEFERDECKER (Z. physikal. Chem., 1931, 157, 32—56).—Langmuir's adsorption theory has been applied to the processes occurring at a gas electrode in order to explain the passivity phenomena previously described (A., 1910, ii, 385). On the assumption that adsorbed H and O are both present on a Pt electrode in equilibrium with an aq. solution of an electrolyte the state of an electrode charged with H or O has been investigated. The conclusions arrived at are in qual. agreement with existing experimental data. R. CUTHILL.

Determination of equivalence potential in potentiometric titrations. Determination of dissociation constants of multivalent acids and bases, and isoelectric points of ampholytes. F. L. HAHN and R. KLOCKMANN (Z. physikal. Chem., 1931, 157, 209—212).—A method for the exact determination of the equivalence potential is described. From this val., together with the potential gradient and vol. of reagent added at the equivalence point, the equiv. wt. and both dissociation consts. of a bivalent acid or base or an ampholyte may be calc. R. CUTHILL.

Determination of glass-electrode potentials by means of a null ballistic valve electrometer. C. MORTON (J.C.S., 1931, 2977—2983).—If a resistance in the anode circuit of an electrometer triode valve is shunted by a galvanometer in series with a blocking condenser, an arrangement is obtained by means of which potentials operating through 1000 megohms can be easily determined with an accuracy of 0.01 mv. The device ensures complete zero stability. A modification of the method which permits the use of an ordinary receiving valve is described. F. L. USHER.

Determination of glass-electrode potentials by means of valve potentiometers. C. MORTON

(J.C.S., 1931, 2983—2991; cf. preceding abstract).—A thermionic valve potentiometer which may have a sensitivity of 38 micro-amp. per mv. is described. The sensitivity increases with the resistance of the source of e.m.f., and the instrument is especially valuable in conjunction with a glass electrode for differential potentiometric titration. F. L. USHER.

Polarisation capacity of mercury electrodes. T. ERDEY-GRUZ and G. G. KROMREY (Z. physikal. Chem., 1931, 157, 213—241).—Measurements of the polarisation of a Hg electrode in aq. $\text{Hg}_2(\text{NO}_3)_2$ have shown that at very high dilutions the polarisation effects are due solely to the Helmholtz double layer; as the solution becomes more conc., concn. polarisation plays a more and more important part and at the higher concns. this becomes entirely responsible for the observed effect. Measurements have also been made with Hg electrodes in solutions of salts of foreign metals. In general, the polarisation capacity in a solution containing an anion which forms a readily sol. Hg salt is smaller than that observed with an anion which forms a sparingly sol. Hg salt. The capacity of the double layer calc. from the polarisation data is, as a rule, much less than the capacity at the same potential calc. from the electrocapillary curve. With increasing electrolyte concn. the polarisation capacity increases, which is to be ascribed to an increase in the capacity of the double layer as a result of the diffuse portion becoming less and increasing nos. of ions passing into the Helmholtz double layer. R. CUTHILL.

Supersaturation phenomena in electrodeposition of metals. T. ERDEY-GRUZ and M. VOLMER (Z. physikal. Chem., 1931, 157, 182—187).—If a solution of metallic salt is electrolysed with a cathode of a foreign indifferent metal, the current density-voltage curve exhibits, in general, one or more discontinuities, which are due to the circumstance that the metal begins to separate, not at the equilibrium potential, but only when nuclei have been formed on the electrode, and this occurs at a more negative potential. R. CUTHILL.

Overvoltage of metals. T. ERDEY-GRUZ and M. VOLMER (Z. physikal. Chem., 1931, 157, 165—181).—If the slowest process involved in the separation of a metal by electrolysis is the discharge of the ions, the overvoltage, η , will be a linear function of $\log I$, where I is the current density. If, on the other hand, crystal growth at the electrode surface is the slowest process, then $1/\eta$ will be a linear function of $\log I$ if the rate of growth is determined by the rate of two-dimensional formation of nuclei on the crystal surface, $1/\eta^2$ will be a linear function of $\log I$ if the rate of growth depends on the rate of three-dimensional formation of nuclei, and η will be a linear function of I if the rate at which layers of metal spread over the crystal surface from the edges or corners is the determining factor. Measurements of the variation of η with I for various metals taken in conjunction with direct observation of the electrolytic growth of crystals show that η is a linear function of I . R. CUTHILL.

Semi-conducting cells of lead chloride. G. DECHENE (Compt. rend., 1931, 193, 922—925).—

Variations in discontinuities of potential at the electrodes, and in the conductivity of a cell consisting of compressed PbCl_2 , are discussed.

C. A. SILBERRAD.

Capillary-electrometer and electro-capillary curve. III. Influence of temperature on electro-capillary curve. F. O. KOENIG (Z. physikal. Chem., 1931, 157, 96—112; cf. A., 1931, 801).—The electro-capillary curve of 1M- KNO_3 containing 0.00545M- $\text{Hg}_2(\text{NO}_3)_2$ and 0.0064M- HNO_3 has been determined at 9.3°, 25°, 40°, and 55°. As the temp. rises, the max. on the curve is displaced in the direction of lower polarising potentials, an effect in which the dipole components of the Galvani potential play a part. At the same time, the interfacial tension corresponding with any given potential falls, except over the initial portion of the ascending branch of the curve, where it increases. This flattening of the curve is a consequence of the adsorption of the mercurous salt becoming more negative at all potentials as the temp. rises. The temp. coeff. of the max. interfacial tension increases numerically as the temp. rises and also as the concn. of KNO_3 falls, this effect being attributable to diminishing adsorption of KNO_3 .

R. CUTHILL.

Abnormal e.m.f. of filtration. L. RIETY and G. SALAGER (Compt. rend., 1931, 193, 854—855; cf. A., 1925, ii, 796).—When solutions of $\text{Hg}(\text{CN})_2$ of concns. varying from 1 to 200 g. per litre are forced through a tube drawn out at one end, by a difference of pressure of 745 mm., the p.d. decreases as the concn. increases. For varying pressures (p) the ratio p.d./ p is const. Results are the same for tubes of pyrex, ordinary glass, or quartz. HgCl_2 gives a p.d. which is about 0.25 of that given by $\text{Hg}(\text{CN})_2$.

C. A. SILBERRAD.

Passivity of metals. W. J. MÜLLER (Trans. Faraday Soc., 1931, 27, 737—751).—A lecture.

J. G. A. GRIFFITHS.

Couple iron-ferrous sulphide. Passivation of ferrous sulphide. A. TRAVERS and J. AUBERT (Chim. et Ind., 1931, 26, 1040).—In 1% Na_2SO_4 solution a difference of potential of 0.85 volt is set up between Fe and FeS, the FeS being cathodic. In oxidising agents, such as 5% $\text{H}_2\text{Cr}_2\text{O}_7$, the potential of FeS is raised by about 0.4 volt, and in dil. H_2SO_4 solution the potential is lowered by about 0.2 volt. This phenomenon seems to have some bearing on the passivity of metals and explains the need for a sufficient concn. of acid in preparing H_2S from FeS.

E. S. HEDGES.

Quantum mechanics of electrolysis. R. W. GURNEY (Proc. Roy. Soc., 1931, A, 134, 137—154).—Irreversible electrolytic phenomena are considered. The quantum-mechanical consideration of the neutralisation of the ions arriving at the electrodes affords an explanation of various well-known facts.

L. L. BIRCUMSHAW.

Flame temperatures. W. T. DAVID, W. DAVIES, and J. JORDAN (Phil. Mag., 1931, [vii], 12, 1043—1057).—Flame temp. in the explosion of H_2 -air and CO-air mixtures were measured by the change in resistance in Pt-Rh wires (0.0005 in. diam.) at the centre of the spherical explosion vessel. Observed vals. in dil. H_2 mixtures were higher than those

calc.; in all other cases they were lower. The results are discussed.

H. J. EMELÉUS.

Combination of hydrogen and oxygen on the surface of silica and its relation to the propagation of reaction chains in the gas. W. L. GARSTANG and C. N. HINSHELWOOD (Proc. Roy. Soc., 1931, A, 134, 1—7).—The kinetics of the surface reaction in SiO_2 vessels have been examined between certain pressure limits. The rate is directly proportional to the pressure of H_2 and almost independent of that of O_2 . Alyea's explanation of an upper explosion limit as being due to an abrupt change in the layer of gas adsorbed on the vessel wall (A., 1931, 688) is considered improbable, and the theory of gas phase deactivation is preferred. Experiments show that no low-pressure explosion occurs in an Al vessel; a vigorous surface reaction takes place.

L. L. BIRCUMSHAW.

Effect of frequency on the condensed discharge ignition of carbon monoxide-air detonating gas. G. I. FINCH and H. H. THOMPSON (Proc. Roy. Soc., 1931, A, 134, 343—351).—Experiments are described the results of which contradict the thermal theory of ignition, since they show that discharge oscillation frequency is a more potent factor in determining ignition than either the rate or amount of energy dissipation in the discharge. The electrical theory is consistent with all known facts relating to the ignition of gases.

L. L. BIRCUMSHAW.

Combustion of carbon disulphide in oxygen. H. W. THOMPSON and C. F. KEARTON (Z. physikal. Chem., 1931, B, 14, 359—370; cf. A., 1931, 45).—Investigation of the effect of variations in the dimensions of the reaction vessel on the crit. pressure range over which a mixture of CS_2 and O_2 ignites spontaneously has shown that the wall of the vessel promotes the reaction. C_2H_4 , Br, and, to a smaller extent, N_2 retard the reaction. O_3 markedly favours the propagation of the reaction chains, whereas CS_2 has the reverse effect. It is suggested that the reaction chains leading to inflammation involve a compound CS_2O_2 , probably formed on the wall. When a CS_2O_2 mol. meets an O_2 mol. the reaction chain proceeds to completion, but if the encounter is with a CS_2 mol. the chain is terminated. The wall also terminates the chain because it is covered with adsorbed CS_2 . Prolonged irradiation of mixtures of CS_2 and O_2 at 20—130° with ultra-violet light does not cause any reaction, even if a little NO_2 is present.

R. CUTHILL.

Slow combustion of hydrocarbons. R. SPENCE (Nature, 1931, 128, 873).—A discussion of reaction mechanism.

L. S. THEOBALD.

Kinetics of the decomposition, in carbon tetrachloride solution, of ozone and of ozone-chlorine mixtures. E. J. BOWEN, E. A. MOELWYN-HUGHES, and C. N. HINSHELWOOD (Proc. Roy. Soc., 1931, A, 134, 211—223).—The uncatalysed thermal decomp. of O_3 is unimol. in CCl_4 solution and is much faster than the bimol. gas reaction at ordinary pressures. The catalytic thermal reaction sensitised by Cl_2 proceeds in solution by a mechanism closely similar to the gas reaction, and the rate is nearly the same in each case. The photochemical reaction corresponds

closely with the gas reaction and gives a quantum yield of 2 in solution. These experiments establish CCl_4 as a normal solvent for purposes of comparison in the case of reactions which cannot be measured in the gas phase. L. L. BIRCUMSHAW.

Influence of the sulphur atom on the reactivity of adjacent atoms or groups. V. Comparative reactivities of nine homologous ω -hydroxy-sulphides. G. M. BENNETT and A. N. MOSSES (J.C.S., 1931, 2956—2962).—The reaction between HBr and the hydroxy-sulphides $\text{Ph}\cdot\text{S}(\text{CH}_2)_n\cdot\text{OH}$, where n is 2—10, in PhOH solution, is reversible and bimol. The reaction velocity alternates from $n=2$ to $n=4$, and thereafter falls to an approx. const. val. at $n=6$. Thus in the β - and δ -positions the OH group is very reactive, in the ε -position it is rather less reactive, and its reactivity ultimately falls to that of the OH group of cetyl alcohol; in the γ -position the reactivity is less than the normal. These results confirm the previous conclusions (A., 1927, 355), and their general significance is discussed. H. F. GILLBE.

Reactivity of the mercaptido-group. I. N. HELLSTROM (Z. physikal. Chem., 1931, 157, 242—268).—The reaction of secondary Na , K , or Ba glycolate with the corresponding chloro-, bromo-, or iodo-acetate in aq. solution at 25° , $\text{'O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{S'} + \text{CH}_2\text{X}\cdot\text{CO}_2 = \text{'O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2 + \text{X'}$ ($\text{X} = \text{Cl}$, Br , or I), follows the bimol. law. The velocity coeff., however, depends on the nature and concn. of the cation, the variation with concn. being in accordance with Bronsted's theory (A., 1925, ii, 681). Chloro-, bromo-, and iodo-acetamide also react with secondary Na glycolate in accordance with the bimol. law, $\text{'O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{S'} + \text{CH}_2\text{X}\cdot\text{CO}\cdot\text{NH}_2 = \text{'O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{X'}$, but the velocity coeff. is independent of the cation and greatest for the I compound and least for the Cl compound. R. CUTHILL.

Hydrolysis of starch by carbonic acid. M. A. DEWEY and N. W. KRASE (Ind. Eng. Chem., 1931, 23, 1436—1437).—The rates of hydrolysis of starch to reducing sugars by CO_2 in H_2O at 1000 lb. pressure at 156° , 186° , and 216° are linear functions of time, the rate being dependent on the temp. It is uncertain if the reaction be unimol. F. R. SHAW.

Halogenation of phenolic ethers and anilides. II. Velocity in 99% acetic acid. A. E. BRADFIELD and B. JONES. **III. "Phase and steric" factor.** A. E. BRADFIELD, W. O. JONES, and F. SPENCER (J.C.S., 1931, 2903—2906, 2907—2919).—II. The velocity coeffs. of the chlorination at 30° of various phenolic ethers and Ph esters in AcOH containing 1% H_2O have been determined. The results suggest that Holleman's "product rule" is inapplicable, but confirm the view that the energies of activation are compounded of terms characteristic of the groups attached to the nucleus. The following ethers have been prepared: *p*-bromophenyl Pr^a , b. p. $126^\circ/11$ mm.; *p*-bromophenyl *m*-nitrobenzyl, m. p. 89.3° ; *p*-chlorophenyl *m*-nitrobenzyl, m. p. 73.8° ; *o*-bromophenyl *p*-nitrobenzyl, m. p. 111.4° ; 2:4-dibromophenyl CH_2Ph , m. p. 67.8° .

III. Determinations of the velocity coeff. of the

chlorination of certain phenolic ethers at 35° and *p*-tolyl ethers at 20° and 35° show that of the 4 hypotheses previously suggested (A., 1929, 34), the correct one is that which requires α in the expression $k = \alpha e^{-1/RT}$ to be const., and the energy of activation E to be the sum of terms characteristic of the groups attached to the $\text{C}\cdot\text{H}_6$ nucleus. The influence of the alkoxy-group in the tolyl ethers, however, is somewhat different from that in the Ph series. When two similar positions are available for substitution the directive force of the groups is distributed symmetrically between them. The following ethers are described: 3-chloro-*p*-tolyl Pr^a , b. p. 106° ; 3-bromo-*p*-tolyl Pr^a , b. p. 115° ; 3-chloro-*p*-tolyl CH_2Ph , m. p. 50.5° ; 3-chloro-*p*-tolyl *p*-nitrobenzyl, m. p. 132° ; 3-bromo-*p*-tolyl CH_2Ph , m. p. 42.5° ; 3-bromo-*p*-tolyl *p*-nitrobenzyl, m. p. 131.5° ; 3-nitro-*p*-tolyl Pr^a , b. p. 154° ; 3-nitro-*p*-tolyl Pr^b , b. p. 134° .

H. F. GILLBE.

Rate of dissolution of oxygen in water. VI. Rate of absorption of oxygen by sodium sulphite solution. S. MIYAMOTO and T. KAYA (Bull. Chem. Soc. Japan, 1931, 6, 264—275; cf. A., 1931, 1016).—As the Na_2SO_3 concn. increases, the rate of absorption at 15° and 25° increases, then remains const. as the concn. rises from about 0.35 to 0.75*N*, and ultimately falls again. It is suggested that at low Na_2SO_3 concns. the Na_2SO_3 mols. are not brought to the surface sufficiently rapidly by diffusion to keep pace with the entry of O_2 mols., some of which therefore diffuse into the body of the liquid. In the period of const. absorption velocity there are sufficient Na_2SO_3 mols. in the surface to react with all the O_2 mols. which enter the surface, so that the O_2 concn. at the surface is zero. The diminution in absorption velocity at higher concns. is ascribed to increase in the min. val. of the velocity perpendicular to the surface required for penetration by an O_2 mol. to occur (*ibid.*, 437). R. CUTHILL.

Rate of dissociation of salt hydrates. Reaction $\text{CuSO}_4\cdot 5\text{H}_2\text{O} = \text{CuSO}_4\cdot\text{H}_2\text{O} + 4\text{H}_2\text{O}$. M. L. SMITH and B. TOPLEY (Proc. Roy. Soc., 1931, A, 134, 224—245).—"Static" and "flow" experiments were made in apparatus designed to meet the conditions imposed by the sensitivity to H_2O vapour. The rate of dehydration has been studied over the temp. range 0 — 43° , detailed measurements being made between 20° and 35° . The sensitivity to H_2O vapour at 0° is several hundred times that at 60° . The abs. reaction velocity coeff., unaffected by the reverse reaction or by H_2O vapour "poisoning" of the interface, is given by $\log_{10} K = 12.112 - (3982/T)$, where K is in mg. per sq. cm. per min. The empirical energy of activation is 18.250 g.-cal. per g.-mol. H_2O . The impedance effect of the monohydrate layer largely disappears when dehydration proceeds in the presence of H_2O vapour. L. L. BIRCUMSHAW.

Dissolution velocities of different faces of copper crystals. R. GLAUNER and R. GLOCKER (Z. Krist., 1931, 80, 377—390).—By exposing one face only of a Cu crystal to the attacking solution the relative velocities of dissolution of the faces and of polycryst. Cu in 21 different solutions were determined. Marked differences occurred, varying

from the case of $0.3N\text{-AsOH} + 0.1N\text{-H}_2\text{O}_2$ in which (111) dissolves thrice as quickly as (120), to that of $0.3N\text{-KCN}$, or $0.3N\text{-butyric}$, valeric, or benzoic acid $+ 0.1N\text{-H}_2\text{O}_2$ in which all faces dissolve at the same rate. Polycryst. Cu dissolves in most cases more quickly than any individual face of a single crystal.

C. A. SILBERRAD.

Theory of metallic corrosion in the light of quantitative measurements. V. Corrosion of iron and mild steel. G. B. BENGOUGH, A. R. LEE, and F. WORMWELL (Proc. Roy. Soc., 1931, A, 134, 308—343).—Using the O_2 absorption method of measuring corrosion (A., 1930, 712), two types of corrosion-time curves have been obtained for Fe and steel in KCl solutions, exponential for dil., linear for conc., solutions; each is associated with a distinct type of corrosion product. H_2 is evolved in all cases, and for solutions more conc. than $0.001N$ the proportion of corrosion due to this type of action is considerable. The H_2 -time curves are similar in general form to the corresponding O_2 -absorption curves. Micrographic observations indicate that the characteristic distribution of corrosion over completely immersed horizontal specimens is mainly determined by the distribution of a particular form of pptd. corrosion product, and not by any differential aeration that might occur or by the initial air-formed film of oxide. Neither the loose gelatinous FeOH nor the stable black Fe_3O_4 which constitutes the bulk of the "rust" formed under atms. of O_2 and air has any important retarding action on the access of O_2 to the metal in $0.1N$ and more conc. KCl solutions; they do not therefore behave as O_2 screens and stimulate corrosion by differential aeration, as usually assumed. In very dil. solutions in presence of O_2 , the rust builds up as mounds and does act as an O_2 screen, the corrosion rates being gradually reduced. Highly purified Fe gives nearly the same corrosion rate as mild steel in $0.1N\text{-KCl}$, but the rate of H_2 evolution is less. Both Fe and steel corrode more rapidly than Zn in conductivity H_2O , but much more slowly in $0.1N\text{-KCl}$.

L. L. BIRCUMSHAW.

Corrosion of metals. III. Dissolution. W. PALMER.—See B., 1931, 1099.

Corrosion rates of steel and composition of corrosion products formed in oxygenated water as affected by velocity. B. E. ROETHELI and R. H. BROWN.—See B., 1931, 1099.

Effect of oxygen concentration on corrosion rates of steel and composition of corrosion products formed in oxygenated water. G. L. COX and B. E. ROETHELI.—See B., 1931, 1099.

Mechanism of formation of aromatics from lower paraffins. V. SCHNEIDER and P. K. FROLICH (Ind. Eng. Chem., 1931, 23, 1405—1410).—By varying the rate of flow and extrapolating to 0% cracking, an attempt has been made to distinguish between primary and secondary reactions in the cracking of C_3H_8 . The secondary reactions have been analysed by repetition with the initial reaction products. Cracking reactions are approx. first order and homogeneous and there is no surface catalytic effect. C_3H_8 gives as a first step only propylene and

C_2H_4 , which gives a number of olefines and diolefines, any of which might yield aromatics, these being formed other than by simple polymerisation. Butylene is not a probable intermediate in the formation of butadiene from C_2H_4 . A mechanism of cracking of paraffins is suggested.

F. R. SHAW.

Oxidation of arsenites by atmospheric oxygen. N. A. SHILOV and S. M. PEVZNER (J. Chem. Ind., Russia, 1930, 7, 759—760).—I, H_2TiO_3 , and Cu, Fe, or Mn salts are ineffective, whilst chromates, molybdates, and Ce salts are slightly effective, in catalysing the oxidation of KH_2AsO_3 by O_2 . Complete oxidation is attained by passing air, N oxides (HNO_2), and gaseous HCl into a column down which are passing H_3AsO_3 and KI solutions. CHEMICAL ABSTRACTS.

Influence of neutral salts on the velocity of hydrolysis of ethyl acetate. W. WYCZAŁKOWSKA (Rocz. Chem., 1931, 11, 734—745).—The catalytic action of equiv. concns. of salts in the hydrolysis of AcOEt by HCl or HBr diminishes in the following series: $\text{SrCl}_2 > \text{CaCl}_2 > \text{BaCl}_2 > \text{NaCl} > \text{KCl} > \text{LiCl} > \text{SrBr}_2 > \text{CaBr}_2 > \text{BaBr}_2 > \text{NaBr} > \text{KBr} > \text{LiBr} > \text{Sr}(\text{NO}_3)_2 > \text{Ca}(\text{NO}_3)_2 > \text{NaNO}_3 > \text{KNO}_3$. The action of a given salt depends chiefly on its anion.

R. TRUSZKOWSKI.

Oxidation of thiol compounds by hydrogen peroxide. I. Catalysis of oxidation of cysteine and glutathione by iron and copper. N. W. PRIE (Biochem. J., 1931, 25, 1565—1579).—In the absence of added metal the rate of oxidation of cysteine by H_2O_2 is very small at p_{H} 2.1, but in the presence of Cu it is proportional to the concn. of Cu and H_2O_2 , although independent of that of cysteine. With Fe it is proportional to the concn. of Fe and cysteine and is slightly inhibited by H_2O_2 . At p_{H} 4.6 there is some metal-free oxidation and the rate in the presence of Fe is much increased; by Cu it is less markedly affected. Figures are given for the sp. rotations of cysteine and glutathione between p_{H} 2.1 and 9.0. Phosphate inhibits Fe and gives an inflected oxidation curve when the inhibition is incomplete. Pyrophosphate inhibits Fe stoichiometrically. At p_{H} 2.1 KCN activates Fe, but hardly Cu; at p_{H} 4.6 both are inhibited. $\text{Fe}(\text{CN})_6'''$ inhibits Cu and Fe, but $\text{Fe}(\text{CN})_6''''$ activates Fe and inhibits Cu only when oxidised. Haemocyanin has no catalytic effect, but at p_{H} 2.1 it is decomposed completely, giving catalytically active Cu. Haematin and haemoglobin are not stable. The rate of oxidation of glutathione in the presence of Cu is proportional to the concns. of Cu and H_2O_2 and independent of that of glutathione. In the presence of Fe the rate of oxidation is an inverse function of the glutathione concn. and is independent of H_2O_2 .

S. S. ZILVA.

Oxidations induced by sugars. I. Formation of barium peroxide. P. A. SHAFFER and B. K. HARNED (J. Biol. Chem., 1931, 93, 311—325).—Aeration of alkaline solutions of glucose activates O_2 with production of H_2O_2 . From $\text{Ba}(\text{OH})_2$ solutions so treated BaO_2 has been isolated. Its formation is favoured by low glucose and high $\text{Ba}(\text{OH})_2$ and O_2 concns. Under optimal conditions the BaO_2 formed is equiv. to not more than 0.2 of the absorbed O_2 . This is due to side reactions involving the oxidation of

sugar by H_2O_2 , BaO_2 , and a hypothetical sugar peroxide.

A. COHEN.

Lattice deformation and catalytic activity. N. PARRAVANO (*Atti III Cong. Naz. Chim. pura appl.*, 1929, 45—50; *Chem. Zentr.*, 1931, i, 3210).—A discussion. Change in the interat. distances is accompanied by change in the surface forces and therefore of catalytic activity.

A. A. ELDRIDGE.

Para-hydrogen transformation on tungsten and nickel. A. FARKAS (*Z. physikal. Chem.*, 1931, B, 14, 371—386).—The mechanism of the para-H transformation on W and Ni is the same as on Pt (A., 1931, 691), but with both catalysts O_2 acts as a poison. The curves representing the variation of the reaction velocity on Ni with temp. and pressure all exhibit a discontinuity, which is due to the formation at a certain temp. and H_2 pressure of a solid hydride on the Ni surface.

R. CUTHILL.

Influence of cerium oxide on the catalytic properties of thorium oxide. H. COPAUX (*Bull. Soc. chim.*, 1931, [iv], 49, 1397—1401).—The catalytic activity of ThO_2 containing 0—2% CeO_2 has been determined for mixtures of CO and air (2 : 5) at 455°. The oxide mixtures were obtained by calcination at different temp. of (a) nitrates, (b) oxalates, and (c) carbonates. In all cases except one sample of (b) the pure ThO_2 was a more effective catalyst for the oxidation of CO than the mixed oxides. A catalytic max. at 1% CeO_2 , corresponding with the max. for intensity of thermal luminescence, was obtained for (c) only. For mixed oxides from (a) a min. was obtained for 1% CeO_2 and neither max. nor min. for (b). Oxides from (a) calcined at 720° had a much lower catalytic activity than when calcined at 550°, but, in general, oxides prepared under apparently identical conditions had not necessarily the same activity.

M. S. BURR.

Kinetics of the contact process. E. BAUR (*Z. physikal. Chem.*, 1931, 157, 315—319).—It is calc. from the data of Taylor and Lenher for the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ on Pt (A., 1931, 1246) that the equilibrium const. is equal to the quotient of the velocity coeffs. of the opposing reactions in the vicinity of the equilibrium point.

R. CUTHILL.

Investigation of catalysis in the system palladium-hydrogen by means of resistance measurements. C. A. KNORR (*Z. physikal. Chem.*, 1931, 157, 143—163).—The rate at which H contained in Pd is removed by aq. solutions of various oxidising agents has been investigated by measurements of the resistance of the metal. With acid aq. $\text{K}_2\text{Cr}_2\text{O}_7$ the H is removed at an approx. const. rate until desorption is almost complete, and if the state of the Pd surface remains unchanged this rate is proportional to the concn. of $\text{K}_2\text{Cr}_2\text{O}_7$. These observations are interpreted as meaning that the velocity with which the H is removed is as a whole determined solely by the rate of the changes occurring at the interface, not by the rate at which H diffuses up to the interface, and a val. for the active surface of the Pd has been calc. by means of Nernst's theory of the velocity of heterogeneous reactions. Even small amounts of H_2S ,

AsH_3 , CS_2 , I, and thiophen poison the Pd surface, and markedly retard the removal of H.

R. CUTHILL.

Poisoning of platinum catalysts for oxidation of ammonia. J. Y. YEE and P. H. EMMETT.—See B., 1931, 1091.

Influence of pressure on some water-gas reactions. F. FISCHER and H. PICHLER.—See B., 1931, 1128.

Catalytic partial oxidation of alcohols in the vapour phase. III. W. L. FAITH and D. B. KEYES (*Ind. Eng. Chem.*, 1931, 23, 1250—1253).—A laboratory apparatus for the study of catalytic vapour-phase oxidations is described. The catalysts which have the highest coeff. of heat transfer yield the most efficient conversion of MeOH and EtOH into the aldehydes. Ag and Cu catalysts give more efficient conversion of EtOH into MeCHO than has been recorded previously.

J. W. SMITH.

Mechanism of catalytic hydrogenation of phenol under high pressure. S. ANDO.—See B., 1931, 1085.

Catalytic oxidation of *p*-cymene in the vapour phase. C. E. SENSEMAN and J. J. STUBBS.—See B., 1931, 1085.

Quantum mechanics of some photochemical processes. L. GOLDSTEIN (*Compt. rend.*, 1931, 193, 919—922; cf. A., 1931, 1393).—Mathematical. The probabilities of the dissociation of a diat. mol. irradiated by radiation of suitable frequency, resulting (a) in one of the atoms possessing a definite kinetic energy relative to the other and (b) in the production of one excited and one normal atom, are determined.

C. A. SILBERRAD.

Photolysis of potassium ferrioxalate solutions. III. A. J. ALLMAND and K. W. YOUNG (*J.C.S.*, 1931, 3079—3087).—The temp. coeff. of the photolysis of K ferrioxalate solutions (22—55°) rises from 1.029 at 3130 Å. to 1.060 at 4360 Å. The effect of two monochromatic radiations acting simultaneously is greater than that calc. additively. In contradiction to Kornfeld's report, the velocity of the photo-reduction of FeCl_3 by $\text{H}_2\text{C}_2\text{O}_4$ in aq. solution is proportional to the radiation intensity, and is not diminished by Fe^{++} ; the quantum efficiency is about 1. The probable mechanism of the reaction is discussed.

H. F. GILLBE.

Photochemical elementary process in single crystals and the electrical detection of the latent image. R. HILSCH and R. W. POHL (*Z. wiss. Phot.*, 1931, 30, 255—261).—A KBr crystal prepared in the dark shows no absorption of light from 210 mμ to the far infra-red. On irradiation with light (of normal photographic intensity) of 203 mμ a new absorption band appears at 630 mμ. On subsequent irradiation with light of 630 mμ this absorption is removed and electric disturbances measurable by an electrometer are induced. The corresponding second absorption band of AgBr is at 690 mμ, but the effect is more complicated.

J. LEWKOWITSCH.

Latent sensitivity of silver salts in solution. G. ZELGER (*Sci. Publ. Kodak Res. Lab.*, 1930, 14, 286—290).—A saturated solution of AgBr in 10%

aq. Na_2SO_3 shows a latent sensitivity to ultra-violet light. Unexposed solution, on development, remains clear for 5–7 min., the deposited Ag then being bluish-green, the Ag from exposed solution appearing immediately and being black. A trace of gelatin delays development and facilitates investigation. Graphs of $\log E$ against wt. of Ag pptd. in a given development time are very similar to the usual sensitometric curves for emulsions. NH_4Cl and KBr accelerate the speed of development. Warming the solution for 30 min. causes colloidal Ag to be formed, which, however, only feebly acts as development nuclei. Other Ag salts in dil. solution behave similarly. AgNO_3 is sensitive only if gelatin is added before exposure. J. LEWKOWITSCH.

Micellar theory of the latent photographic image. II. F. WEIGERT (Z. wiss. Phot., 1931, 30, 217–240; cf. *ibid.*, 1930, 29, 191).—Elementary micelles consisting of Ag halide, H_2O , gelatin, primary Ag, etc. are energised by light to form the latent image. Development is the activation of developer mols. by this energy. The latent image occurs in two forms, an anisotropic “form factor” and an isotropic “activation factor.” The S-form of the density curve is due to development of Ag halide within the micelle by gelatin on strong exposure. The theory is fully discussed in relation to photo-dichroism, the Albert effect, solarisation, and other photographic phenomena. J. LEWKOWITSCH.

Photographic unit of intensity. ANON. (J. Opt. Soc. Amer., 1931, 21, 654–676).—A report of a committee of the Society. C. W. GIBBY.

Photographic sensitivity. A. CHARRION (J. Chim. phys., 1931, 28, 556–571).—A lecture on published work, particularly the Ag_2S theory of sensitisation. E. S. HEDGES.

Mechanism of photolysis of alkyl iodides. G. EMSCHWILLER (Compt. rend., 1931, 193, 1003–1005).—The applicability to the fact that photolysis of alkyl iodides gives yields sometimes in excess, sometimes in defect, of the quantum equiv. (cf. A., 1931, 694), of the alternate theories of dissociation followed by recombination, and of activation by deactivation, is discussed. In view of the facts that HI and C_3H_6 combine directly to Pr^2I , that C_2H_4 and HI interact only in the light of the Hg lamp to yield H_2 and $\text{C}_2\text{H}_4\text{I}_2$, on which HI then further acts in the cold and dark to form EtI and I ; and that HI in the cold and dark does not act on an alkyl iodide, whilst EtI and HI in the light give C_2H_6 and no C_2H_4 , it is concluded that either theory is applicable. C. A. SILBERRAD.

Photosynthesis of carbohydrates in vitro. J. BELL (Trans. Faraday Soc., 1931, 27, 771–777).—Full details of a repetition of the work of Balv and co-workers are given. Negative results were obtained. J. G. A. GRIFFITHS.

Decomposition of nitrous oxide by cathode rays. G. R. GEDYE (J.C.S., 1931, 3016–3022).— N_2O is decomposed by cathode rays according to the equation $4\text{N}_2\text{O} = 3\text{N}_2 + 2\text{NO} + \text{O}_2$; each mol. decomposed requires 7–9 electron-volts (cf. A., 1931, 320), and the number of mols. which react per ion-pair is

thus about 4. The ionic reaction follows the same course as the photochemical reaction. The first stage after recombination of the ions or absorption of the quantum is probably dissociation of the N_2O into N_2 and O , and possible subsequent stages are $\dot{\text{O}} + \text{N}_2\text{O} = 2\text{NO}$, and thermal dissociation of two further mols. of N_2O by collision with the activated products of this reaction. H. F. GILLBE.

Combined photographic effects of cathode rays, X-rays, and other radiations. V. DOLEJŠEK and A. NEMEJCOVA (Coll. Czech. Chem. Comm., 1931, 3, 536–547).—Cathode rays, like X-rays, when combined with white light cause at a certain density of darkening of a photographic plate an “inversion,” i.e., a smaller effect than the sum of the single effects. The sequence X-rays–heat, or cathode rays–heat, also causes inversion. Under the combined action of cathode rays and X-rays, inversion occurs within a certain range of densities of blackening, but is independent of sequence. E. S. HEDGES.

Reduction of sodium hydroxide. P. VILLARD (Compt. rend., 1931, 193, 681–685; cf. A., 1930, 1006).— NaOH and Mn in a current of N_2 or H_2 at 600° (rapidly at 700°) yield Na (KOH behaves similarly); at the same time NaH is volatilised and deposited further along the tube. Ferromanganese, Cr (at 800°) and W act similarly, as also does Fe in N_2 at 750° . With a little H_2 added to the N_2 Fe yields only NaH ; with more, fumes of Na are still produced, but there is no deposit. This is due to H_2O from decomp. of the Fe_2O_3 first formed, and explains the bad yield of Gay Lussac and Thenard’s process, which would be improved by substituting H_2 by N_2 , when a lower temp. would suffice. Co and Ni at 600 – 750° cause evolution of Na vapour, but no metal is deposited, and the Co and Ni are not oxidised. Zn has no action. Co and Ni reduce ZnO at 700° and 750° , respectively. C. A. SILBERRAD.

Behaviour of ultramarine towards sodium iodoazide. J. HOFFMANN (Z. anorg. Chem., 1931, 201, 175–176).—The evolution of N_2 which occurs when Na iodoazide reacts with different kinds of ultramarine has been investigated qualitatively, and the bearing of the results on the question of the structure of the different ultramarines is discussed. M. S. BURR.

Conversion of potassium formate into oxalate. W. DOMINIŁ and S. JANCZAK (Rocz. Chem., 1931, 11, 746–752).—80% yields of $\text{K}_2\text{C}_2\text{O}_4$ are obtained by heating HCO_2K on Al plates at 460 – 500° ; with Fe plates the yields are only 55%, and a very impure product is obtained. The yields are smaller in an atm. of CO_2 than of air. R. TRUSZKOWSKI.

Dehydration of salts. M. COPISAROW (Nature, 1931, 128, 838).— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and salts of Mg , Fe , Ni , and Co can be successfully dehydrated by distilling a neutral liquid of high v. p. containing the salt or its aq. solution. Decomp. and oxidation or reduction are practically eliminated. Dehydration by means of Ac_2O (A., 1931, 182) has limitations. L. S. THEOBALD.

Beryllium ferrite and ferric oxide from its decomposition. H. FORESTIER and M. GALAND (Compt. rend., 1931, 193, 733–736).—Beryllium fer-

rite, BeFe_2O_4 , was prepared as other ferrites (cf. A., 1925, ii, 1159). When dried at 100° it has the structure of lepidocrocite, space-group V_1 (cf. A., 1931, 1390); at 360° it decomposes into $\text{BeO} + \text{Fe}_2\text{O}_3$; the Fe_2O_3 is the unstable magnetic form with cubic (diamond) structure (Malaguti's oxide), and changes to ordinary Fe_2O_3 with evolution of heat at 630° . BeO in the ferrite thus plays the part of H_2O in lepidocrocite. C. A. SILBERRAD.

Corrosion of magnesium in various salt solutions. I. H. ENDO and K. MIYAZAKI (J. Study Met., 1930, 7, 283—301).—A quant. study of corrosion in H_2O and in solutions of CO_2 , NaCl , Na_2SO_4 , NaNO_3 , Na_2CO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, and K_2CrO_4 .

CHEMICAL ABSTRACTS.

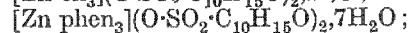
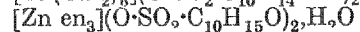
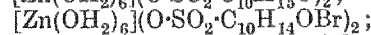
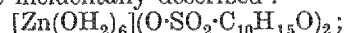
Action of sulphur dioxide on phosphates of calcium. A. E. HUGHES and F. K. CAMERON (Ind. Eng. Chem., 1931, 23, 1262—1271).—The v. p. of SO_2 - H_2O mixtures have been measured between 0° and 90° . Below -2.6° solid $\text{SO}_2 \cdot 7\text{H}_2\text{O}$ is stable. The v. p. is lowered by contact with solid $\text{Ca}_3(\text{PO}_4)_2$ and under these conditions the hydrate is stable only below -4.2° . When $\text{Ca}_3(\text{PO}_4)_2$ is treated at 25° with H_2O kept saturated with SO_2 , complete dissolution of the H_3PO_4 is slowly attained. The action of a two-phase mixture of SO_2 and H_2O at 100° gives rise to a complicated series of reactions and equilibrium is attained slowly. Almost all the H_3PO_4 can then be extracted with H_2O but much SO_2 is decomposed, rendering the process uneconomical. SO_2 and a little H_2O at 65° gradually convert $\frac{2}{3}$ of the H_3PO_4 into the available form. When Ca_3PO_4 is heated in a current of SO_2 at 450° again about $\frac{2}{3}$ of the H_3PO_4 is rendered available. None of the procedures is more economical than that utilising H_2SO_4 .

J. W. SMITH.

Preparation and purification of salts by means of zeolites. G. AUSTRERWEIL (Compt. rend., 1931, 193, 1013—1016).—The course of base exchange by means of zeolites is analogous to that of extraction. Thus by the action of a quantity of zeolite saturated with 1 equiv. of K^+ on a solution of 1 equiv. of $\text{Ca}(\text{NO}_3)_2$ 0.42 equiv. of K^+ enters the solution in exchange for the equiv. amount of Ca^{++} . On successive repetitions with fresh K^+ -saturated zeolite the same fraction (0.42, the "coeff. of exchange") of the remaining Ca^{++} is exchanged for K^+ . Generally if a be the coeff. of exchange, T the permissible residual amount of the ion to be removed, and n the no. of lots of zeolite required, $n = \log T / \log(1 - a)$. Experimental results with K^+ and Ca^{++} agree with the formula, which is of general application. C. A. SILBERRAD.

New effect in solutions of optically active substances. I. P. PFEIFFER and K. QUEHL (Ber., 1931, 64, [B], 2667—2671).—Addition of phenanthroline (3 mols.) to aq. solutions of Zn β -camphor- or α -bromo- π -camphor-sulphonate causes marked diminution or increase respectively in optical activity. With Zn quinate a smaller change is observed. Dipyrindyl behaves similarly to but less pronouncedly than phenanthroline, whereas NH_3 , pyridine, and ethylenediamine are inactive. Addition of ZnSO_4 to an aq. solution of cinchonine hydrochloride scarcely affects the optical activity, which diminishes

very greatly on subsequent addition of phenanthroline; addition of NaOH gives unchanged cinchonine, leaving an optically inactive solution from which the salt $[\text{Zn phen}_2]\text{Br}_2 \cdot 7\text{H}_2\text{O}$ is readily isolated. Strychnine sulphate behaves similarly. The changes in optical activity are attributed to the formation of new asymmetric centres, presumably the octahedrally constructed tridipyrindyl- and triphenanthroline-Zn ions containing asymmetric Zn atoms. The following salts are incidentally described:



$[\text{Zn phen}_3]\text{Br}_2 \cdot 7\text{H}_2\text{O};$ $[\text{Zn phen}_3](\text{NO}_3)_2 \cdot 7\text{H}_2\text{O};$ Zn quinate dehydrate. H. WREN.

Reduction of mercuric cyanide by tin in presence of certain metallic salts. J. GOLSE (Compt. rend., 1931, 193, 1016—1018).—Although Sn has no action on a pure solution of $\text{Hg}(\text{CN})_2$, in presence of many sol. chlorides, nitrates, or sulphates, but not of bromides or iodides, Hg and $\text{Sn}(\text{OH})_2$ are pptd. and HCN is formed. This is due to intermediate formation of compounds such as $\text{Na}_2\text{Hg}(\text{CN})_4$, HgCl_2 , yielding Hg^{++} , which reacts with Sn, the final result being $\text{Hg}(\text{CN})_2 + \text{Sn} + 2\text{H}_2\text{O} = \text{Sn}(\text{OH})_2 + \text{Hg} + 2\text{HCN}$. With an iodide the Hg appears as an iodo-mercuric ion, $\text{Hg}(\text{CN})_2 + 4\text{KI} = \text{K}_2\text{HgI}_4 + 2\text{HCN}$, and similarly in the case of bromides. C. A. SILBERRAD.

Thermal decomposition of alunite. W. L. FINK, K. R. VAN HORN, and H. A. PAZOUR (Ind. Eng. Chem., 1931, 23, 1248—1250).—By X-ray diffraction methods and chemical analysis it has been shown that alunite, $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$, is transformed into small or imperfectly formed crystals of dehydrated alum when heated at 500 — 600° . This is decomposed at 700 — 800° into Al_2O_3 and K_2SO_4 . At 1200 — 1400° the Al_2O_3 reacts with part of the K_2SO_4 to give $\text{K}_2\text{O} \cdot 10\text{Al}_2\text{O}_3$. J. W. SMITH.

Halides of the rare earths. V. Halides of ytterbium. G. JANTSCH, N. SKALLA, and H. JAWUREK (Z. anorg. Chem., 1931, 201, 207—220).—Pure, white, anhyd. YbCl_3 , m.p. $854 \pm 3^\circ$, is obtained by heating the hydrated salt in a current of gaseous HCl at a temp. which is slowly raised to 350° . When heated in vac. at 870 — 900° , YbCl_3 sublimes, and a small quantity of YbCl_2 is formed with evolution of Cl_2 . YbCl_2 is obtained as a greenish-yellow compound by reducing YbCl_3 in H_2 at 600 — 700° . It dissolves readily in H_2O to a clear, wine-yellow solution which slowly evolves H_2 and becomes turbid. The solution is decolorised by acids, and strong acids cause a violent evolution of H_2 . When heated, the salt begins to decompose into Yb and YbCl_3 before fusion takes place. The electrolytic conductivity of aq. YbCl_3 falls with time, due to oxidation to a basic salt. White YbBr_3 is obtained by heating the mixture $\text{YbBr}_3 \cdot 6\text{H}_2\text{O} + 6\text{NH}_3 \cdot \text{Br}$ in a stream of HBr with very slow rise of temp. Most of the H_2O has been removed when 250° is reached, but the mixture must be heated at 600° to sublime NH_4Br . Fusion does not take place even at 940° . On heating in vac. Br is evolved at 700° and about 90% YbBr_3 is obtained at 850° , whilst some YbBr_3 volatilises and Yb is also formed.

Reduction of YbBr_3 with H_2 is apparently a more satisfactory method of obtaining YbBr_2 . YbI_3 cannot be obtained from the hydrated salt, but must be prepared by heating YbCl_3 in a current of HI . It forms black lustrous crystals exhibiting dichroism and dissolving to a colourless solution. Chloride is always present. On heating, decomp. to I and YbI_2 is already marked at 700° and is complete before fusion takes place. In vac. evolution of I from YbI_3 begins at 250° and becomes stronger at 450 – 460° . At 600° golden-yellow YbI_2 is left and partly sublimes. At 700° it is very volatile and fuses at approx. 820° . Decomp. of YbI_2 into Yb and I also takes place. The clear yellow aq. solution of YbI_2 is more stable than that of YbCl_2 , but it also slowly evolves H_2 . Conductivity data are given. M. S. BURR.

Rare earths. J. KENDALL (Proc. Roy. Phil. Soc. Glasgow, 1931, 59, 1–11).—A lecture giving an account of the application of the ionic migration method to an attempted separation of isotopes, and to separations of rare earths. C. W. GIBBY.

Alleged thalious thioper-rhenate. H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDART (J.C.S., 1931, 2976–2977).—The existence of TiReS_4 and TiReSO_3 described by Feit (A., 1931, 1255), is regarded as improbable. H. F. GILLBE.

Preparation and properties of cyanogen fluoride. V. E. COSSLETT (Z. anorg. Chem., 1931, 201, 75–80).—By the action of ICN on AgF at 220° , CNF is obtained in a yield of 20–25% as a colourless gas condensable to a white powder subliming at -72° (760 mm.); mol. wt. from vapour density, 45. V. p. have been measured between -140° and -30° , and the coeff. of viscosity has been determined. CNF is almost insol. in H_2O . F. L. USHER.

Reactions of titanium. B. V. HEATH (J. Soc. Chem. Ind. Victoria, 1931, 31, 531–533).—The prep. and analytical uses of TiCl_3 are described.

N. H. HARTSHORNE.

Alkali salts of hydrofluotitanic acid. III. H. GINSBERG and G. HOLDER (Z. anorg. Chem., 1931, 201, 193–206).—All the alkali metals form well-defined *fluotitanates* of the general formula M_2TiF_6 . In moist air or aq. solution these are readily hydrolysed. $\text{Li}_2\text{TiF}_6 \cdot 2\text{H}_2\text{O}$ loses practically all the H_2O of crystallisation below 50° . $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ loses H_2O of crystallisation still more readily (A., 1931, 446). Like the K salt (*loc. cit.*), the Rb and Cs salts form stable oxyfluorides, MTiOF_4 , when heated at 400 – 600° , but the Li and Na salts pass directly into TiO_2 and alkali fluoride. All the compounds lose TiF_4 above 600° . $(\text{NH}_4)_2\text{TiF}_6$ is decomposed when heated at 300° and TiO_2 only is left.

M. S. BURR.

Hydrolysis of nitrosyl chloride and of nitrogen tetroxide by potassium hydroxide. A. PERRET and R. PERROT (Compt. rend., 1931, 193, 937–939).—Known wts. of NOCl and aq. KOH (1.5–17N) interact in vac.; pure NO is evolved. Results are similar for $N \gg 8$, the % of N appearing as NO , NO_2 , and NO_3 , being respectively 31.3–42.3, 39.4–52.0, and 15.0–18.3, but with 17N-aq. KOH the figures are 9.4, 86.0, and 4.6. The ratio of NO N to NO_3 -N

averages 2.07. Decomp. does not therefore occur solely according to $\text{NOCl} + 2\text{KOH} = \text{KNO}_2 + \text{KCl} + \text{H}_2\text{O}$, but also according to $\text{NOCl} + \text{KOH} = \text{KCl} + \text{HNO}_2$, and $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$. 2–3% of the Cl appears as chlorate. N_2O_4 and aq. KOH interact similarly, but the amount of N appearing as NO never exceeds 10%, and for 17N-aq. KOH is 3%; its amount is always double that appearing as NO_3 . It is suggested that there are two isomeric forms of HNO_2 having different velocities of neutralisation.

C. A. SILBERRAD.

Compounds of tervalent vanadium. A. ROSENHEIM, E. HILZHEIMER, and J. WOLFF (Z. anorg. Chem., 1931, 201, 162–174).—The following internal complex compounds of V^{III} have been prepared: *salicylates*, $\text{M}[\text{V}(\text{C}_6\text{H}_4 \cdot \text{OCO}_2)_2]_n \cdot n\text{H}_2\text{O}$ (M is Ca, Sr, or Ba, and n is 4, 6, or 4, respectively); *pyrocatecholoxides*, $\text{M}_3[\text{V}(\text{C}_6\text{H}_4\text{O}_2)_3]_n \cdot n\text{H}_2\text{O}$ (M is NH_4 , CN_3H_6 , or $\text{C}_2\text{N}_4\text{H}_7\text{O}$, and n is 2, 4, or 2, respectively), and also $\text{C}_5\text{H}_5\text{N}[\text{V}(\text{C}_6\text{H}_4\text{O}_2)_2]_3 \cdot 5\text{H}_2\text{O}$; a *benzhydroxamate*, $\text{V}(\text{OH})(\text{C}_7\text{H}_5\text{O}_2\text{N})_2$; and the existence of an *acetyl-acetate*, $\text{V}(\text{C}_5\text{H}_7\text{O}_2)_3$, has also been confirmed. A pyridine thiocyanate derivative, $\text{C}_5\text{H}_5\text{N}[\text{V}(\text{C}_5\text{H}_5\text{N})_2(\text{CSN})_2]$, has been prepared and also *vanadium triglycollate*, $\text{V}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 4\text{H}_2\text{O}$, and polynuclear *formates*, $\text{V}(\text{HCO}_2)_3$ and $\text{V}_5(\text{HCO}_2)_{12}(\text{OH})_3 \cdot 6\text{H}_2\text{O}$, and *acetates*, $\text{V}(\text{OAc})_3 \cdot \text{H}_2\text{O}$ and $\text{V}(\text{OH})(\text{OAc})_2 \cdot \text{H}_2\text{O}$. The properties of these compounds have been compared with those of the corresponding iron compounds. The following new internal complex compounds, derivatives of ferric diglycollic acid, $\text{H}[\text{Fe}(\text{C}_2\text{H}_2\text{O}_3)_2]$, have been prepared: $\text{M}[\text{Fe}(\text{C}_2\text{H}_2\text{O}_3)_2]_n \cdot n\text{H}_2\text{O}$ (M is CN_3H_6 or Li, and n is 3 or 1.5, respectively), and $\text{M}[\text{Fe}(\text{C}_2\text{H}_2\text{O}_3)_2]_2 \cdot n\text{H}_2\text{O}$ (M is Ba, Sr, or Cd, and n is 4, 10, or 4, respectively). An earlier observation on V^{III} sulphates is corrected.

M. S. BURR.

Theory of the displacement of the metals of group V from solutions of the salts by hydrogen. I. V. V. IPATIEV, jun. (Ber., 1931, 64, [B], 2725–2733).—Mainly a theoretical treatment of the results recorded for the displacement of As, Sb, and Bi by H (cf. A., 1931, 1242, 1243). It is shown that with 20 c.c. of solution in tubes of 25–30 mm. diam. the reaction proceeds uniformly through the whole vol. of solution. The displacement of metals from solutions of the salts is an ionic reaction. Increase in $[\text{H}^+]$ retards the pptn. of Bi and Sb and accelerates that of As.

H. WREN.

Chloroantimonates. III. L. I. SAUCIUC (Bul. Soc. Chim. Romania, 1931, 13, 23–26).—The prep. of the following compounds is described: $\text{Zn}(\text{SbCl}_6)_2 \cdot 5\text{H}_2\text{O}$, unstable; $17\text{CdCl}_2 \cdot \text{SbCl}_3 \cdot 18\text{H}_2\text{O}$, relatively stable, colourless; $17\text{CoCl}_2 \cdot \text{SbCl}_3 \cdot 32\text{H}_2\text{O}$, violet; $\text{AlCl}_3 \cdot 3\text{SbCl}_3 \cdot 6\text{H}_2\text{O}$, very hygroscopic, unstable.

D. R. DUNCAN.

Complex compounds of tartaric acid with tervalent metals. E. E. WARK and J. W. WARK (Z. physikal. Chem., 1931, 157, 310–314).—Structures for the complex tartrates of Sb^{III} , Cr^{III} , and Fe^{III} alternative to those suggested by Jelinek and Gordon (A., 1924, ii, 836) are proposed and shown to be reconcilable with these authors' experimental data.

R. CUTHILL.

Double sulphates of bismuth with alkali metals. II. Double sulphates of bismuth and lithium. L. MALOSI (Atti R. Accad. Lincei, 1931, [vi], 13, 775—779; cf. A., 1929, 1408).—The system $\text{Bi}_2(\text{SO}_4)_3\text{--Li}_2\text{SO}_4\text{--H}_2\text{O}$ has been studied at 25°. The double sulphates $\text{Li}_3\text{Bi}(\text{SO}_4)_3\cdot 2\text{H}_2\text{O}$ and $\text{Li}(\text{BiO})\text{SO}_4\cdot \text{H}_2\text{O}$ were obtained. O. J. WALKER.

Oxidation of sulphur in relation to its composition. G. A. MOROZOVA (Khlopk. Nezavis., 1931, no. 3, 74—77).—When kept in 15% H_2O_2 at 60° for 5 hr., amorphous S was transformed into the cryst. form. Very little H_2SO_4 was formed. The polythionic acid state is intermediate. In alkaline medium the reaction is more rapid and much H_2SO_4 is formed. CHEMICAL ABSTRACTS.

Preparation [and properties] of manganese dioxide. Y. KATO and T. MATSUHASHI.—See B., 1931, 1091.

Anhydrous and hydrated manganous sulphate. I. J. H. KŘEPELKA and B. REJHA (Coll. Czech. Chem. Comm., 1931, 3, 517—535).—The following compounds are recognised: MnSO_4 , $\text{MnSO}_4\cdot \text{H}_2\text{O}$, $(\text{MnSO}_4\cdot \text{H}_2\text{O})_2$, $\text{MnSO}_4\cdot 4\text{H}_2\text{O}$, $\text{MnSO}_4\cdot 5\text{H}_2\text{O}$, and $\text{MnSO}_4\cdot 7\text{H}_2\text{O}$. The hemi-, di-, tri-, and hexahydrates, and a second form of the tetrahydrate mentioned in the literature do not exist. The conditions of formation of all the existing hydrates have been investigated. The anhyd. and more highly hydrated forms change to $\text{MnSO}_4\cdot \text{H}_2\text{O}$ on exposure to the atm. The eutectic mixture contains 32.3% MnSO_4 and 67.7% H_2O . E. S. HEDGES.

What manganese compound is formed in the oxidation of manganous hydroxide? D. KOSZEGI (Z. anal. Chem., 1931, 86, 346—352).—The composition of the product formed by oxidising $\text{Mn}(\text{OH})_2$ in alkaline solution with O_2 or H_2O_2 varies with the conditions from that of a substance containing rather more O than Mn_2O_3 to that of one with rather less than MnO_2 . F. L. USHER.

Rhenium pentoxide. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (J.C.S., 1931, 3087—3088).—Reduction of Re_2O_7 vapour with Re yields the purplish-red *pentoxide*, which is insol. in H_2O , and in HCl , H_2SO_4 , and KOH solutions, but sol. in warm dil. HNO_3 and in fused KOH . It is stable in air, in O_2 up to 300°, and in S up to 190°. At 300° in vac. it sublimes with decomp. H. F. GILLBE.

Constitution of Prussian blue and Turnbull's blue. E. JUSTIN-MUELLER (Bull. Soc. chim., 1931, [iv], 49, 1285—1289).—The action of aq. $\text{H}_2\text{C}_2\text{O}_4$ on Prussian blue to form "sol. blue," $[\text{Fe}^{\text{II}}(\text{CN})_6\cdot \text{Fe}^{\text{II}}]\text{H}$, which, when treated with $\text{Fe}(\text{CN})_3$, gives Prussian blue once more, is best explained by assigning to the latter the formula $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6\cdot \text{Fe}^{\text{II}}]_3$, i.e., ferric tri-ferrocyanide. It can also be formulated as a closed chain. Similarly Turnbull's blue, which gives with aq. $\text{H}_2\text{C}_2\text{O}_4$ the same sol. blue and can be reconstituted by the action of $\text{Fe}(\text{CN})_3$ on the latter, is a ferrous diferriferrocyanide, $\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6\cdot \text{Fe}^{\text{III}}]_2$, also represented as a closed chain. The action of aq. KOH or NaOH in forming a ferrocyanide in the first case and a ferricyanide in the second is explained by the

complete elimination of Fe^{III} from Prussian blue and of Fe^{II} from Turnbull's blue. M. S. BURR.

Heat treatment of the γ -monohydrate of ferric oxide. R. D. WILLIAMS and J. THEWLIS (Trans. Faraday Soc., 1931, 27, 767—771).—X-Ray powder photographs show that $\text{Fe}_2\text{O}_3\cdot \text{H}_2\text{O}$ (crystals, 10^{-5} cm. diam.), prepared by adding $\text{Ca}(\text{OH})_2$ to dil. FeCl_3 and subsequent atm. oxidation, has the same structure as lepidocrocite. Conversion of the γ -hydrate into cubic Fe_2O_3 (5×10^{-7} growing to 10^{-6} at 500°) occurs chiefly between 250° and 300° and the transformation of the latter into rhombohedral Fe_2O_3 (10^{-4} cm.) occurs mainly between 500° and 600°.

J. G. A. GRIFFITHS.

Dithiocarbamates and nitrosodithiocarbamates of iron. L. CAMBI and A. CAGNASSO (Atti R. Accad. Lincei, 1931, [vi], 13, 809—813; cf. A., 1931, 1382).— Fe^{III} N-ethylthiocarbamate, $\text{Fe}(\text{NHEt}\cdot \text{CS}_2)_3$, and its NO-derivative, $\text{NO}\cdot \text{Fe}(\text{NHEt}\cdot \text{CS}_2)_2$, and Fe^{II} N-benzylthiocarbamate and its NO-derivative are described. The Fe^{III} compounds are orange-red and the NO-compounds green and with low dielectric consts. T. H. POPE.

Behaviour of iron pentacarbonyl towards alkalis. H. HOCK and H. STUHLMANN (Chem.-Ztg., 1931, 55, 874—875).— $\text{Fe}(\text{CO})_5$ combines with NaOH in EtOH to give the colourless, cryst., H_2O -sol. $\text{Fe}(\text{CO})_5\cdot \text{NaOEt}$, which reacts with more NaOEt and produces $\text{CO}(\text{OEt})_2$ and $\text{Fe}(\text{CO})_4\text{Na}_2$. The latter is analogous to the authors' Hg compound (A., 1929, 412; 1930, 47) and is converted by acid into the red, Et_2O -sol. $\text{Fe}(\text{CO})_4\text{H}_2$, which decomposes in the presence of conc. mineral acid into H_2 and $\text{Fe}(\text{CO})_4$ (green). The production of $\text{Fe}(\text{CO})_4\text{H}_2$ and CO_2 from $\text{Fe}(\text{CO})_5$ may be regarded as a form of hydrolytic water-gas reaction taking place at room temp. Priority is claimed over Hieber (A., 1931, 810).

J. GRANT.

Rhodium dioxide. L. WOHLER and K. F. A. EWALD (Z. anorg. Chem., 1931, 201, 145—161).— RhO_2 cannot be obtained anhyd. When prepared by the action of free Cl_2 on a strongly alkaline Rh solution the dioxide hydrate contains a considerable quantity of the oxychloride, RhOCl , as an impurity. Contrary to the statements of other investigators, fusion with oxidising agents, such as Na_2O_2 or KNO_3 , gives only Rh_2O_3 . Hydrated RhO_2 may be obtained pure by the electrolysis of a solution prepared by treating aq. Na_3RhCl_6 with aq. KOH . The dark green hydrated RhO_2 separates at the anode and the solution becomes dark blue, probably due to the formation of colloidal RhO_2 . There is no evidence of the formation of RhO_3 . Attempts to dehydrate the product always result in the formation of Rh_2O_3 . The proportion of combined H_2O to 1 mol. RhO_2 apparently lies between 1 and 2 mols.

M. S. BURR.

Univalent stage in group VIII of the periodic system. W. MANCHOT and H. SCHMID (Ber., 1931, 64, [B], 2672—2677).—When warmed with 90% NaH_2PO_2 solution and NaOH , $\text{K}_2\text{Pd}(\text{CN})_4$ evolves H_2 with production of univalent Pd, but reaction is less marked than with Na-Hg. With PdCl_2 the metal is rapidly produced. $\text{K}_2\text{Pt}(\text{CN})_4$ is unaffected.

$K_2Ni(CN)_4$ is readily reduced to $NiCN$, whilst $NiSO_4$ and $Ni(OAc)_2$ easily react with conc. NaH_2PO_2 in absence of $NaOH$. $RuCl_3$ solution is rapidly decolorised by warm NaH_2PO_2 in absence of alkali without production of metal. Since the resulting solution reduces more strongly than NaH_2PO_2 , the formation of Ru^I is postulated. The presence of HCl or $NaOH$ increases or decreases the action of NaH_2PO_2 . $K_4Ru(CN)_6$ is not reduced by NaH_2PO_2 , $Na-Hg$, or Al . $RhCl_3$ solution is more slowly decolorised by NaH_2PO_2 with probable formation of Rh^I , whereas $K_3Rh(CN)_6$ appears stable. $K_3Ir(CN)_6$ is not affected whilst $IrCl_3$ and (non-alkaline) NaH_2PO_2 feebly evolve H_2 without giving a solution with pronounced reducing properties. The behaviour of $K_4Os(CN)_6$ and $OsCl_3$ is similar to that of the corresponding Ir compounds. H. WREN.

Precipitation of platinum-black. A. SIEVERTS and H. BRÜNING (Z. anorg. Chem., 1931, 201, 113—121).—For the quant. pptn. of Pt-black at least 2 mols. each of HCO_2Na and Na_2CO_3 are necessary to 8 of H_2PtCl_6 . With this proportion of HCO_2Na a gas-free product is obtained, but with excess the ppt. contains adsorbed formate which cannot be removed by washing and gives CO and H_2 when the ppt. is heated in a stream of CO_2 . With a smaller proportion of HCO_2Na than 2 mols. to 1 of H_2PtCl_6 , Pt hydroxides are pptd. with the Pt. With smaller proportions than 2 mols. of both Na salts bright particles of Pt are obtained and the pptn. is not complete. Excess of HCO_2Na gives a more finely divided product. The amount of CH_2O necessary to ppt. Pt-black depends on temp., 2 mols. CH_2O to 1 mol. H_2PtCl_6 being required at low temp. and 1:1 at high. Side reactions occur so that the reduction is not quant. M. S. BURR.

Colour in the mineral world. R. M. CAVEN (Proc. Roy. Phil. Soc. Glasgow, 1931, 59, 109—118).—A lecture. C. W. GIBBY.

Present limits of microchemical knowledge and measurements. F. L. HAHN (Mikrochem., 1931, 10, 313—321).—A review, describing especially the application to microchemistry of catalytic and induced reactions and research on complex metallic compounds. H. F. GILLBE.

Value of fluorescence analysis in microchemistry. M. HAITINGER, F. FEIGL, and A. SMON (Mikrochem., 1931, 10, 117—128).—The sensitivity of the fluorescence method renders it of particular value in microanalytical work. Of 207 compounds examined, a great number exhibited an indeterminate reddish-violet fluorescence which was of no value for the purpose of identification; 62 compounds showed a definite fluorescence. Compounds of metals in a lower valency state gave a more characteristic fluorescence than those of the same metal in a higher valency state. Very few coloured compounds, other than U salts, fluoresce, and identification by this method is thus in general applicable only to compounds other than those usually prepared or sought in microchemical analysis. The examination of a spot of solution on filter-paper is fruitless, owing to the characteristic fluorescence of the paper. The

results obtained with a large number of compounds are tabulated. H. F. GILLBE.

Determination of the potential gradient in potentiometric titration when the reagent is added in large amounts at once. F. L. HAHN and R. KLOCKMANN (Z. physikal. Chem., 1931, 157, 206—208).—A graphical method of determining the slope of the titration curve at the equivalence point when the reagent is added in large amounts at once is described. An approx. val. for the equilibrium const. of the reaction can thus be obtained very rapidly. R. CUTHILL.

Characterisation of experimentally determined quantities in potentiometric titration. F. L. HAHN and R. KLOCKMANN (Z. physikal. Chem., 1931, 157, 203—205).—A scheme for the recording of potentiometric titrations together with a system of symbols are described. R. CUTHILL.

Application of azeotropy to the determination of small quantities of impurities. W. SWIENOSLAWSKI (Rocz. Chem., 1931, 11, 714—718).—The content of impurities in liquids can be determined with an accuracy of 0.003—0.005% by adding a third liquid with which the liquid under examination and the impurity form a ternary azeotropic mixture, and comparing the b. p. with that of a binary azeotropic mixture of the pure liquid and the third liquid added. R. TRUSZKOWSKI.

Use of indicators. A. THIEL (Z. angew. Chem., 1931, 44, 863—864).—The Na salt of Me-red (E. Merck) is readily sol. (25%); it gives an orange ppt. in H_2O containing CO_2 and its solutions should therefore be prepared with boiled distilled H_2O or H_2O containing a trace of Na_2CO_3 . *p*-Xylenolphthalein (Merck) is superior to thymolphthalein, since the H_2O -solubility is 35 times as great, whilst both indicators have similar absorption spectra and behaviour to alkalis. A. J. HALL.

Indicators. P. F. THOMPSON (J. Soc. Chem. Ind. Victoria, 1931, 31, 536—544).—Advantages are claimed for a solution of dimethylglyoxime in aq. NH_3 as an indicator in place of $K_3Fe(CN)_6$ in the titration of Fe by $K_2Cr_2O_7$. A modified indicator for the titration of Zn with $K_4Fe(CN)_6$ is proposed. A solution of $K_4Fe(CN)_6$ and NH_4 molybdate gives with acids a brown colour, the depth of which increases with $[H^+]$, and is sensitive to 0.1 pH . N. H. HARTSHORNE.

Colorimetric determination of chlorates by the use of aniline hydrochloride. R. A. JONES (Analyst, 1931, 56, 807).—A sample of $NH_4Ph.HCl$ reagent gave only a transient blue colour with ClO_3^- . Conc. $KClO_3$ solution was added to the diluted solution until a slight permanent blue colour appeared; dilution was then completed, the reagent being kept for at least 18 hr. and filtered. T. McLACHLAN.

Determination of fluorine as calcium fluoride. P. MOUGNAUD (Compt. rend., 1931, 193, 738—740).—Carrière and Janssens' results (cf. A., 1931, 1384) are due to two sources of error approx. cancelling each other, the excess wt. of "lime" due to presence of CO_2 in the aq. NH_3 and air being compensated for by loss of CaF_2 through dissolution (cf. *ibid.*, 1023).

Using aq. NH_3 of various origins the method gave errors up to 3.2%. C. A. SILBERRAD.

Apparatus for determination of peroxides. E. STATHIS (Z. anal. Chem., 1931, 86, 303—304).—An improved apparatus for the determination of peroxides by Bunsen's method is described. R. CUTHILL.

Ceric sulphate as a volumetric oxidising agent. R. JANSSENS (Natuurwetensch. Tijds., 1931, 13, 257—270).—When $\text{Ce}(\text{SO}_4)_2$ is employed for potentiometric titration, equilibrium is established more rapidly than when $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 is used, and the potential change at the end-point is somewhat sharper. If an indicator is used the colour change is invariably sharper. Details are given of the determination of H_2O_2 , Fe^{2+} , $\text{Fe}(\text{CN})_6^{4-}$, Sn^{2+} , and Ti^{3+} with $\text{Ce}(\text{SO}_4)_2$ solution. H. F. GILLBE.

Micro-volumetric determination of sulphates. S. BALACHOVSKI and F. GINSBURG (Z. anal. Chem., 1931, 86, 344—346; cf. A., 1930, 1544).—After pptg. sulphates with Ba^{2+} , excess of the latter is titrated with either K_2CrO_4 or $\text{Na}_4\text{P}_2\text{O}_7$ in aq.-alcoholic solution, using an indicator such as bromothymol-blue. As little as 1 c.c. of solution may be used. F. L. USHER.

Micro-determination of nitrogen by Dumas' method. A. FRIEDRICH (Mikrochem., 1931, 10, 355—359).—Removal of air from the CuO is effected in the combustion tube, and entry of air into the Kipp CO_2 apparatus is prevented by a device which bubbles CO_2 through the acid in the upper vessel; the CaCO_3 is degassed by evacuation in contact with H_2O . A method of preventing condensed H_2O from blocking the tube between the combustion tube and the nitrometer is described. H. F. GILLBE.

Direct determination of nitrogen in gases. H. R. AMBLER (Analyst, 1931, 56, 804—807).—All combustible constituents of the gas are burnt in a regulated stream of electrolytic O_2 in the presence of 40% KOH . If CH_4 is present above 2 or 3%, the Pt wire is kept at a yellow heat; if not, a dull red heat is used. Excess of O_2 is absorbed by the addition of 25% alkaline pyrogallol, equal in vol. to the KOH present. N_2 , including A etc., is measured. An apparatus is described. T. MCLACHLAN.

Wet separation of phosphate ion as bismuth phosphate. J. BOUGAULT and E. CATTELAINE (J. Pharm. Chim., 1931, [viii], 14, 417—418).—The conditions under which phosphate may be separated as Bi phosphate have been determined, but the method presents no advantage over that in which the Pb salt is pptd. (A., 1931, 1142). H. F. GILLBE.

Determination of phosphoric acid and molybdenum as ammonium phosphomolybdate. S. KITAJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 285—327).—Conditions for the quant. pptn. of NH_4 phosphomolybdate have been fully worked out with respect to concns. of MoO_4^{2-} , HNO_3 , and NH_4NO_3 . The influence of various nitrates has been studied. By using suitable concns. of NH_4NO_3 , Mo can also be quantitatively pptd. F. L. USHER.

Micro-determination of phosphoric and arsenic acids by the ceruleomolybdate method. C. ZINZADZE (Ann. Agron., 1931, No. 3, 321; Proc. Internat. Soc. Soil Sci., 1931, 6, 95—103; cf. A., 1931, 725).—Improvements are recorded. The reagent is prepared by heating 120 c.c. of H_2SO_4 (d 1.785) with 6.02 g. of MoO_3 until dissolved, cooling, adding 70 c.c. H_2O , cooling and diluting to 200 c.c. To 100 c.c. of this solution is added 0.28 g. of powdered MoO_3 ; the mixture is boiled for 10 min., cooled, decanted, and diluted to 100 c.c. (2.51 c.c. = 0.2 c.c. N-KMnO_4). The solution to be examined (1—30 c.c.) is neutralised with Na_2CO_3 or H_2SO_4 in the presence of 3 drops of 2:6-dinitrophenol to produce a faint yellow colour, diluted to 40 c.c., and treated with the reagent (0.6 c.c. for 0.1—0.5 mg. P; 0.3 c.c. for <0.1 mg. P). The mixture is boiled 4—5 min., cooled, diluted to 50 c.c., and the colour compared with standard preps. A more rapid method consists of adding to the test solution, prepared as above, 2 c.c. of a solution containing 3.01 g. MoO_3 in 60 c.c. H_2SO_4 (d 1.785) diluted to 400 c.c. 5 c.c. of a solution of SnCl_2 (0.51 g. in 100 c.c. H_2O) are added and the colour is compared with standards after 5 min. The colour fades after 2 hr., whereas that of the first method is stable for 7—10 days. A. G. POLLARD.

Determination of phosphoric acid in phosphorites and apatites. S. N. ROSANOV and E. N. ISSAKOV (Z. anal. Chem., 1931, 86, 352—359).—The established methods of determining PO_4^{3-} have been tested comparatively on 20 mineral specimens. The "citrate" process is the most accurate, but all (of the 5 tried) are trustworthy if proper working conditions are observed. F. L. USHER.

Colorimetric determination of silicic acid especially in water. O. LIEBKNECHT, L. GERB, and E. BAUER (Z. angew. Chem., 1931, 44, 860—863).—Thayer's method (A., 1930, 1145) may give low results owing to absorption of SiO_2 in the FePO_4 ppt., but an alternative method free from this error consists of adding to 50—100 c.c. of the H_2O 3 c.c. of aq. Na_2HPO_4 (18.6 g. of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ per 200 c.c.), 3 c.c. of aq. CaCl_2 (20 g. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ per 100 c.c.), and 1 g. CaCO_3 (this gives ppts. which are more easily filtered than when MgCO_3 is used), heating in a boiling water-bath for 10 min., then filtering hot, washing once with hot H_2O , and determining SiO_2 in the filtrate colorimetrically as described by Thayer. A correction is made for the small amount of SiO_2 dissolved from the glass flask used by performing a blank experiment using H_2O containing a known small amount of SiO_2 . A. J. HALL.

Quantitative analysis of complex cyanides. V. OPOTZKI (J. Chem. Ind., Russia, 1930, 7, 1632—1633).—The substance is heated with 5 parts of Na in an Fe tube in a current of H_2 and steam, the NH_3 evolved being determined acidimetrically.

CHEMICAL ABSTRACTS.

Colorimetric determination of potassium with cobaltinitrite. E. M. EMMERT (J. Assoc. Off. Agric. Chem., 1931, 14, 573—575).—The filtrate or supernatant solution after pptn. of K with excess of NaNO_2 —Na cobaltinitrite reagent is compared colori-

metrically with a standard. Errors of 8.4 to -5% are recorded for 0.3—15.9 mg. K. H. R. JENSEN.

Direct and indirect determination of potassium by means of sodium potassium cobalt-hexanitrite. E. REMY (Arch. Pharm., 1931, 269, 678—683).—Small quantities of K, *e.g.*, that present in 0.5 c.c. of blood-serum, can be determined within 0.5% gravimetrically as $K_2NaCo(NO_2)_6 \cdot 6H_2O$ or by decomp. of this salt by dil. H_2SO_4 and colorimetric determination of the resulting $CoSO_4$. R. S. CAHN.

Adsorption method for the micro-detection of silver. G. ETTISCH and J. TAMCHYNA (Mikrochem., 1931, 10, 92—96).—A thin flat collodion membrane is cut into strips which are immersed for about 18 hr. in a solution of an amphoteric substance such as albumin or aminoacetic acid and then washed thoroughly with H_2O . In carrying out the test for Ag, a piece of the treated membrane, of about 0.5 sq. cm. in area, is immersed in 10 c.c. of the solution under test for at least 24 hr. and is then washed and transferred to a test-tube containing 0.5 c.c. of H_2O ; 1 drop of a saturated EtOH solution of *p*-dimethylaminobenzylidenerhodanine and 1 drop of dil. HNO_3 are added, when, in presence of Ag, a red colour appears on the membrane. The yellow colour produced by the reagent may be removed by washing the membrane with Et_2O . The limiting dilution is $1:4 \times 10^7$, compared with $1:5 \times 10^6$ by the usual procedure. The test serves to demonstrate the dissolution of Ag by distilled H_2O after contact for 4 days. H. F. GILLBE.

Application of *p*-dimethylaminobenzylidenerhodanine in spot analysis. H. HOLZER (Mikrochem., 1931, 10, 60—63).—A reply to Feigl (A., 1931, 590), reaffirming the author's view that the reaction is not sp. for Ag (cf. A., 1930, 1150).

H. F. GILLBE.

Application of *p*-dimethylaminobenzylidenerhodanine in spot analysis. F. FEIGL (Mikrochem., 1931, 10, 64—65).—A reply. H. F. GILLBE.

Spectral analysis by sensitive lines within the range of the glass spectrograph. W. KRAEMER (Z. Elektrochem., 1931, 37, 862—874).—With a special small spectrograph described elsewhere the following elements have been detected in various steels and hard alloys by their persistent lines in the visible spectrum by reference to the international wave-lengths for Fe and Ne: Ca, Mg, Cu, Al, C, Si, Ti, Zr, Ni, Co, Cr, Mn, Mo, W, V, S, P, and As. Lines suitable for the purpose are recorded for each element.

M. S. BURR.

Micro-determination of calcium. F. P. MAZZA and A. ROSSI (Diagnost. Tecn. Lab., 1931, 1, 147—149; Chem. Zentr., 1931, i, 3492).—The [body] liquid (1 c.c.) is neutralised, heated at 100° for 3 min. with 20% Na_2CO_3 (1 c.c.) and 95% EtOH (1 c.c.), and centrifuged; the ppt. is twice centrifuged with 2 c.c. of 50% EtOH and then with cold H_2O . The ppt. is added to 0.01N-I acidified with dil. HCl, the solution then being titrated with 0.01N- $Na_2S_2O_3$.

A. A. ELDRIDGE.

Quantitative analysis using X-ray absorption spectra. G. E. MUCHIN [with Z. I. STADNIK] (Ukrain. Chem. J., 1931, 6, [Sci.], 147—160).—

Glocker and Frohnmayer's method (A., 1925, ii, 270) has been verified for mixtures containing Ba and Cd.

R. TRUSZKOWSKI.

Iodometric micro-determination of magnesium in organic liquids. C. BOMSKOV (Z. physiol. Chem., 1931, 202, 32—36).—The Mg is pptd. with 8-hydroxyquinoline in EtOH, the ppt. is separated by centrifuging, dissolved in HCl, and brominated. The excess of Br is determined iodometrically.

J. H. BIRKINSHAW.

Quantitative spectral analysis. I. Quantitative analysis by means of emission spectra with reference to the determinations of tin in lead and of small amounts of titanium, silicon, and iron in high-grade aluminium. A. SCHLEICHER and J. CLERMONT (Z. anal. Chem., 1931, 86, 191—216).—The principle of homologous pairs of lines has been applied to the analysis of Pb containing small amounts of Sn, and the data of Gerlach and Schweitzer have been amplified. Tables showing the characteristics of a large no. of convenient pairs of lines for Ti (0.005—0.3%) in Al, using Cu as reference substance, are given.

F. L. USHER.

Quantitative spectrum analysis. Quantitative analysis by means of emission spectra with special reference to determination of tin in lead and determination of small amounts of titanium, silicon, and iron in aluminium. II. A. SCHLEICHER and J. CLERMONT (Z. anal. Chem., 1931, 86, 271—288; cf. preceding abstract).—The spectro-analytical determination of Si and Fe in "pure" Al is described.

R. CUTHILL.

Application of piperidinium piperidyldithioformate to the colorimetric determination of copper. R. G. HARRY (Analyst, 1931, 56, 736—737).—Addition of piperidinium piperidyldithioformate in EtOH solution to a nearly neutral solution of a Cu salt gives a yellowish-brown coloration, which is approx. proportional to the amount of Cu present. Cd, Hg, and Bi do not affect the colour, but Fe interferes and must be removed. Org. matter may be removed by alternate charring at 400° and oxidation with HNO_3 .

T. McLACHLAN.

Determination of mercury by Deniges' cyanide method. J. EURY (Bull. Sci. pharmacol., 1930, 37, 599—603; Chem. Zentr., 1931, i, 3705).—By using a quantity of KCN almost exactly corresponding with the quantity of Hg present, and by employing 0.05N solutions, the use of a correction factor is avoided.

A. A. ELDRIDGE.

Reduction of ferric salts by mercury. F. H. CAMPBELL and R. H. HOOK (J. Soc. Chem. Ind. Victoria, 1931, 31, 544—547).—A simplification of a previous method (A., 1922, ii, 217) is described; the reduced solutions may be left for several days before titrating.

N. H. HARTSHORNE.

Analysis of aluminosilicates. E. DELFELD.—See B., 1931, 1091.

Determination of permanganate in presence of manganate. A. I. MALKOV, I. U. MISHUSTIN, and I. A. KAZARNOVSKI (J. Chem. Ind., Russia, 1930, 7, 601—602).—The mixture is titrated with $H_2C_2O_4$ in presence of H_2SO_4 and H_3PO_4 ; the total Mn is

determined by reducing to MnO_2 with $0.1N\text{-HCO}_3\text{Na}$, adding KI, acidifying, and titrating with $\text{Na}_2\text{S}_2\text{O}_3$.

CHEMICAL ABSTRACTS.

Iodometric determination of ferric salts. E. RUPP (Z. anal. Chem., 1931, 86, 217—219).—Ferric salts are readily converted into ferricyanide by boiling for a short time with KCN if H_3PO_4 and aq. NH_3 have been previously added. The resulting mixture, after oxidising with KMnO_4 in presence of H_2SO_4 and removal of excess of the former with $\text{H}_2\text{C}_2\text{O}_4$, is treated with KI and ZnSO_4 and titrated with $\text{Na}_2\text{S}_2\text{O}_3$. Accurate results are obtained except when Cu^{++} , Cd^{++} , Ni^{++} , or Zn^{++} are present in the original sample.
F. L. USHER.

Behaviour of 1-phenyl-2:3-dimethylpyrazol-one with cobalt solutions. K. WOYNOFF (Chem.-Ztg., 1931, 55, 914).—A delicate test for Co consists in the addition of a drop of 20—30% solution of antipyrine to a filter-paper soaked in the Co solution and subsequently dried. After a few min. a blue ring is obtained (improved by warming) with concns. of Co >0.000416 g. of CoCl_2 per c.c.

J. W. BAKER.

Determination of chromium, vanadium, and manganese in a mixture by titration with a ferrous salt, and analysis of steel. R. LANG and F. KURTZ (Z. anal. Chem., 1931, 86, 288—303).—The methods described depend on the titration with 0.02 or 0.1N- FeSO_4 of the Mn as MnO_4^{--} , the Cr as CrO_4^{--} , and the V as VO_3^{--} , NHPh_2 being used as indicator in the last two titrations. The mixed solution is oxidised with $\text{K}_2\text{S}_2\text{O}_8$ in presence of HPO_3 and AgNO_3 and the CrO_4^{--} , VO_3^{--} , and MnO_4^{--} are titrated. By treatment of the resulting mixture with $\text{K}_2\text{S}_2\text{O}_8$ and HCl, the V and Cr are again oxidised, and then titrated. Finally, this mixture is treated with KMnO_4 so as to oxidise the V and titrated a third time. Alternatively, the initial oxidation may be effected with $\text{K}_2\text{S}_2\text{O}_8$ and HCl, the VO_3^{--} and CrO_4^{--} being titrated, after which the V is re-oxidised with $\text{K}_2\text{Cr}_2\text{O}_7$ and titrated. The V and Mn are then determined together in a second sample of solution by the method previously described (A., 1929, 1032). If the solution for analysis contains Cl⁻, the second method should be employed, the first oxidation, however, being made with KMnO_4 and HCl. Both methods are suitable for the analysis of steel, but if W is present it must be converted into fluoride by addition of NaF, otherwise it interferes with the titrations.
R. CUTHILL.

Analytical chemistry of tantalum, niobium, and their mineral associates. XX. Separation of tin from tantalum and niobium. W. R. SCHOELLER and H. W. WEBB (Analyst, 1931, 56, 795—801).—Fusion of the mixture with alkali has been shown to be unsatisfactory, as low results are obtained. Schoeller and Powell's process is serviceable. The mixture is fused with NaHSO_4 , leached with tartaric acid, and treated with a little HgCl_2 and H_2S . SnO_2 is ignited and the earth acids are recovered by pptn. with tannin (cf. A., 1931, 814). When much Sn is present, it is reduced by H_2 at a moderate red heat and dissolved in dil. HCl. SiO_2 , when present, is removed by H_2SO_4 and HF.

T. McLACHLAN.

Quantitative spectral analysis of alloys. H. TOPELMANN and W. SCHUHKNECHELT.—See B., 1931, 1100.

Vacuum thermocouples. J. JAFFRAY (Compt. rend., 1931, 193, 926—927).—The relation between Δ , the deviation on the scale of a Moll galvanometer, and I , the intensity of current traversing the heating resistance of a vac. thermocouple used to measure a feeble a.c. is $\Delta = KI^n$. For old and new model thermocouples K is respectively 0.06318 and 0.07478; n 2.006 and 1.962.
C. A. SILBERRAD.

Application of differential ebullioscopes to the examination of the purity of individual liquids. W. SWIENTOSLAWSKI, J. USAKIEWICZ, and A. ZMACZYNSKI (Rocz. Chem., 1931, 11, 704—713).—Liquids of the highest purity exhibit a difference of $<0.040^\circ$ between their b. p. and the condensation point of their vapours, using a differential ebullioscope fitted with a rectifying column 1 m. in length. The same temp. difference is observed for "fairly pure" liquids, using a reflux condenser 25—27 cm. in length in place of the rectifying column, whilst liquids with a difference of $0.2\text{—}1.0^\circ$ are classified as "technically pure."
R. TRUSZKOWSKI.

M. p. apparatus. P. MULLER (Ann. Chim. Analyt., 1931, [ii], 13, 322—323).—The apparatus consists of an electrically heated Al plate. The absence of flame or fumes permits observation of the melting through a lens, and the determination may be carried out with very small amounts of material.

E. S. HEDGES.

Sensitive thermostat with thermionic relay. R. E. SUMMERS (J. Soc. Chem. Ind. Victoria, 1931, 31, 535—536).—The instrument is described and figured.
N. H. HARTSHORNE.

Control of humidity of air currents. W. H. J. VERNON and L. WHITEBY (Nature, 1931, 128, 837).—Any method (cf. A., 1931, 1264) of saturating a stream of air which depends on its passage vertically through a column of H_2O is subject to doubt.

L. S. THEOBALD.

Control of humidity of air currents. P. A. BUXTON (Nature, 1931, 128, 837).—Precautions to be taken in humidifying air by means of $\text{H}_2\text{SO}_4\text{—H}_2\text{O}$ mixtures are discussed.
L. S. THEOBALD.

X-Ray camera for powder diagrams at any temperature. N. W. TAYLOR (Rev. Sci. Instr., 1931, [ii], 2, 751—755).—The cylindrical brass camera, 57 mm. diam., can be used from 1000° to -180° . The film is placed round the outside. For high temp. the specimen is coated on an axial electrically heated wire. For low temp. a narrow metal tube, through which liquid air flows, is substituted for the wire.

C. W. GIBBY.

Fixed points of a colorimetric system. J. GUILD (Trans. Optical Soc., 1931, 32, 1—36).—A discussion of the constns. involved in the specification of colour on the trichromatic system.

C. W. GIBBY.

Simple micro-Baly tube for absorption spectrum analysis. C. S. HICKS (Austral. J. Exp. Biol., 1931, 8, 199—200).—The apparatus is described and figured.
A. LAWSON.

Colorimeter for use with disc mixture. (Miss) D. NICKERSEN (*J. Opt. Soc. Amer.*, 1931, 21, 640—642).—A 12-in. square sample of the substance under test, and standard comparison discs, are brightly illuminated. The light reflected from both passes through a photometric cube, and that from the latter is mixed by a revolving wedge. Matching is carried out through an eyepiece. The instrument was devised especially for use with agricultural products.

C. W. GIBBY.

Electric furnace for elementary micro-analysis without hollow bomb. W. FUNER (*Mikrochem.*, 1931, 10, 66—69).—The furnace described consists essentially of a centrally-bored Fe block wound externally with nichrome wire. It has the advantage over furnaces employing the vapour of a boiling liquid (cf. A., 1931, 638) that the danger of contamination by vapour in the air is obviated. For the initial heating 0.5 amp. is required, and 0.35 amp. suffices to maintain the temp., which is const. to within 2°.

H. F. GILLBE.

Application of the electromagnetic micro-balance to residue determinations and electrolytic analysis. E. WIESENBERGER (*Mikrochem.*, 1931, 10, 10—26).—Full details are given of the construction of an electromagnetic compensation balance capable of detecting 0.005—0.01 microg. and having a period of swing of about 17 sec. Illustrations are given of the use of the balance for the determination of metals by conversion into sulphate. Electrolytic determination of quantities of metals of the order of 10 microg. presents difficulties, but satisfactory results for Cu were obtained by using a Pt dish, holding 10—15 cu. mm., as the cathode, and a Pt wire, 0.1 mm. in diameter, as the cathode.

H. F. GILLBE.

Construction and operation of capillary mercury arcs. R. H. CRIST (*J. Opt. Soc. Amer.*, 1931, 21, 690—697).—The tube is cooled by H₂O flowing over gauze surrounding it. The usual deposit does not form on the cold part.

C. W. GIBBY.

Electro-filtration. R. LADENBURG (*Naturwiss.*, 1931, 19, 987—988).—The validity of the Deutsch exponential formula for electro-filtration does not prove that the "electric wind" plays no essential part in the process (cf. Mierdel and Seeliger, A., 1931, 1263).

E. S. HEDGES.

Lindemann electrometer. F. MÜLLER and K. GEISSLER (*Z. Elektrochem.*, 1931, 37, 857—861).—The sources of error in the use of the Lindemann electrometer for the determination of the e.m.f. of cells of comparatively high resistance, and the possibility of improvements in the construction of the instrument, are discussed. When the electrometer is used as a null instrument the experimental error can, under favourable conditions, be reduced to 0.1 mv.

M. S. BURR.

Filters for small quantities of substances. E. EIGENBERGER (*Mikrochem.*, 1931, 10, 57—59).—The filter described is suitable for use with up to about 10 mg. of ppt. or crystal, and filters rapidly and without loss. An arrangement is described in which substances may be recrystallised from, e.g., Et₂O at -70°. An evacuated double-walled vessel,

filled with a mixture of solid CO₂ and Et₂O, contains a tube carrying a filter at the bottom and fitted with a glass plunger half-way from the top; the upper half of the tube is widened and holds the solution of the substance to be recrystallised. After recrystallisation has been effected the plunger is raised and the crystals and mother-liquor fall on to the filter, filtration being aided by suction. H. F. GILLBE.

Vessel for vacuum evaporation. A. REZEK (*Mikrochem.*, 1931, 10, 97—98).—A conical flask is fitted with a ground hollow stopper to which is sealed at the lower end a narrow glass tube bent up at the end. When the apparatus, containing the solution to be conc., is placed in a vac. desiccator, evaporation proceeds smoothly and without loss of solute.

H. F. GILLBE.

Microdistillation. K. LINDENFELD (*Mikrochem.*, 1931, 10, 90—91).—The traces of substances evolved during the heating of certain materials may be examined if the heating is carried out in a small flask of which, after filling, the neck is drawn out to a capillary and bent down at an angle. The material which distils into the capillary is collected at the end by centrifuging the tube after cutting it off. The material evolved from 1 g. of a substance which lost only 1% on drying at 100° has been thus collected for examination.

H. F. GILLBE.

Greaseless and chemically inert valve for high vacua. H. C. RAMSFERGER (*Rev. Sci. Instr.*, 1931, [ii], 2, 738—749).—A small cup-shaped vessel containing fused AgCl is pressed down on an internal glass jet by a screw attached to the outside of the glass tubing. The cup is fixed to one end of a cylindrical Ag bellows, about 2 in. in length, the other end of which is fixed to the outer end of the glass tubing. The pyrex glass-Ag seal is made by first platinising the former and then sealing the two together with AgCl. Detailed directions are given.

C. W. GIBBY.

Controlling the flow of gas into a vacuum system. H. P. KNAUSS (*Rev. Sci. Instr.*, 1931, [ii], 2, 750).—A wire is placed inside a length of rubber pressure tubing, the pores of which have been closed by soaking in castor oil, and squeezed in a clamp.

C. W. GIBBY.

Automatic regulation of the concentration of solutions. O. TEUFERT (*Chem. Fabr.*, 1931, 4, 445—446).—In the apparatus described a valve controlling the inflow of water is regulated by the movements of a float as the sp. gr. of the solution changes.

D. R. DUNCAN.

Portable apparatus for the complete analysis of technical gases. E. OTT.—See B., 1931, 1125.

Microscope warm stage for observations and m. p. determinations by transmitted and reflected light. C. WEYGAND and W. GRUNTZIG (*Mikrochem.*, 1931, 10, 1—9).—The electrically heated stage described is readily fitted to the ordinary polarising microscope; screws are provided for rectilinear movement in two directions. A micro-manipulator for use with the stage is also described. Details are given of the determination of m. p., especially in reflected polarised light; the use of a

heated stage obviates errors due to the difficulty of bringing the thermometer and object into sufficiently close contact. H. F. GILLBE.

Piston areometer. I. Effect of pressure on the balance constant. J. A. BEATTIE and W. L. EDEL (Ann. Physik, 1931, [v], 11, 633—644).—The instrument is described, and its accuracy determined. A. J. MEE.

Protective coatings for mineral and rock specimens. R. W. CLARK (Science, 1931, 74, 439—440).—A solution of a photographic film in BuOAc

forms an invisible, protective coating for friable specimens. L. S. THEOBALD.

International scale of high temperatures. J. MENDOUSSE (Ann. Physique, 1931, [x], 16, 209—310).—An experimental and theoretical investigation of radiation pyrometry, especially in relation to precision. The methods described permit an accuracy of 0.1° at 1100°, 0.5° at 1600°, and 1° at 2500°. E. S. HEDGES.

Probable error. J. F. TOCHER (Inst. Chem., 1931, 63 pp.).—A lecture. N. H. HARTSHORNE.

Geochemistry.

Sulphur content of Polish mineral gases. H. BURSTIN and J. WINKLER (Przemysł Chem., 1931, 15, 354—355).—Galician mineral gases contain 2—5 mg. S per cu.m. R. TRUSZKOWSKI.

Radioactivity of natural waters. J. A. HOOTMAN (Amer. J. Sci., 1931, [v], 22, 453—463).—Apparatus suitable for measuring the radioactivity of natural waters and its calibration are described. Some results on flowing artesian wells in N.E. Mississippi are given. N. H. HARTSHORNE.

Seasonal variation of iron and manganese in water of Takasuka-numa [lake], Saitama. S. YOSHIMURA (Japan. J. Geol., 1931, 8, 269—279).

CHEMICAL ABSTRACTS.

Chemical analysis of the subthermal spring at Sutiusko near Podsused. S. S. MIHOLIC (Bull. Soc. Chim. Yugoslav., 1931, 2, 157—162).—The mineral constituents are almost exclusively $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. The temp. is 19.3°, the average temp. of the surroundings being 11.2°.

N. H. HARTSHORNE.

Determination of the density [of sea-water]. R. DE BUEN (Mem. cons. oceanogr. Ibero-Amer., 1930, No. 3, 3—20).—A review. Conductometric or refractometric methods are preferred to chemical methods. CHEMICAL ABSTRACTS.

Solubility of calcium carbonate in sea-water. H. WATTENBERG (Naturwiss., 1931, 19, 965).—The surface layers of sea-water in the warm zone are supersaturated solutions of CaCO_3 which are very stable in the absence of seed crystals. The deeper layers contain more CO_2 (which is a stronger acid under pressure) and are not saturated with CaCO_3 . P. G. MARSHALL.

Black tourmalines. G. W. WARD (Amer. Min., 1931, 16, 145—190).—Optical and chemical properties are tabulated and discussed. A simple formula cannot be found. There is no marked difference in composition for tourmalines from different geological sources. CHEMICAL ABSTRACTS.

"Zebra" rock. D. W. TRAINER, jun. (Amer. Min., 1931, 16, 221—225).—Quartz, chlorite, hæmatite (dark areas), and limonite (light areas) are present in the banded rock from Argyle Station, East Kimberley, W. Australia; the banding may be due to leaching or reduction of Fe. CHEMICAL ABSTRACTS.

Fervanite. F. L. HESS and E. P. HENDERSON (Amer. Min., 1931, 16, 273—277).—Fervanite, from Gypsum Valley, San Miguel Co., Colorado, has n_a 2.186, n_β 2.222, n_γ 2.224, and contains insol. 9.40, Fe_2O_3 34.46, V_2O_5 37.92, H_2O —11.40, CaO 2.40, SO_3 (calc.) 3.42, total 99.00%, corresponding with $2\text{Fe}_2\text{O}_3 \cdot 2\text{V}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. CHEMICAL ABSTRACTS.

Amphibole group. A. N. WINCHELL (Amer. Min., 1931, 16, 250—266).—A discussion. CHEMICAL ABSTRACTS.

Composition of the alkali amphiboles. H. BERMAN and E. S. LARSEN (Amer. Min., 1931, 16, 140—144).—The range of replacement is comparatively limited. Between the few types there is limited miscibility, but within the type there may be complete isomorphism of Mg and Fe^{II} and of Al and Fe^{III} . The deduced formula is $(\text{Ca}, \text{Na})_2\text{Na}_{0-1}\text{Mg}(\text{Mg}, \text{Al})_4(\text{Al}, \text{Si})_2\text{Si}_6\text{O}_{22}(\text{O}, \text{OH}, \text{F})_2$, the elements within parentheses being completely replaceable. CHEMICAL ABSTRACTS.

Clarkeite. C. S. ROSS, E. P. HENDERSON, and E. POSNJAK (Amer. Min., 1931, 16, 213—220).—"Clarkeite," from Spruce Pine, N.C., has d 6.39, H 4—4.5, n_a 1.997, n_β 2.098, n_γ 2.108, and contains: CaO 1.10, PbO 3.70, K_2O 1.42, Na_2O 2.61, BaO 0.04, UO_3 82.76, $(\text{Fe}, \text{Al})_2\text{O}_3$ 0.50, rare earths 1.12, H_2O 5.22, SiO_2 0.30, insol. 1.20, total 99.97%, corresponding with $\text{RO}_3\text{UO}_3 \cdot 3\text{H}_2\text{O}$. CHEMICAL ABSTRACTS.

Syngenite. R. D. TERZAGHI (Amer. Min., 1931, 16, 309).—Syngenite, $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, from the crater of Haleakala, Maui, Hawaii, has n_a 1.500, n_β 1.520, n_γ 1.520. CHEMICAL ABSTRACTS.

Veins of cobalt, nickel, and native silver in the Kongsberg district. R. STØREN (Tidsskr. Kjemi Berg., 1931, 11, 95—97; cf. A., 1931, 331).—Ni and Co minerals are associated with Ag in certain of the Kongsberg veins, and their presence, together with that of small amounts of Sb, has sometimes given rise to difficulties in connexion with the refining of the Ag. They occur as secondary minerals (erythrite etc.) the original minerals having probably been dissolved when the Ag was pptd., and subsequently redeposited; up to the present they have not been found in the veins carrying argentite and secondary wire Ag. The Kongsberg Ag deposits thus exhibit full analogy with those of Temiskaming, and the statements of Vogt and others that Ni and Co do not occur at Kongsberg are consequently incorrect. H. F. HARWOOD.

Specific heat of certain radioactive minerals.

A. DORABIALSKA, T. NIWINSKI, and E. TURSKA (Rocz. Chem., 1931, 11, 727—733).—The sp. heats in g.-cal. per g. degree at 18—21° are: uraninite 0.0999, johannite 0.1674, blomstrandite 0.1502, thorianite 0.0880, orangite 0.1637, thorite 0.1516, and fergusonite 0.1122. R. TRUSZKOWSKI.

Artificial formation of lithiophilite [LiMnPO₄].

F. ZAMBONINI and L. MALOSI (Z. Krist., 1931, 80, 442—454).—(1) Equal parts of LiCl and MnCl₂ are heated for 4 hr. at 850°, a stream of POCl₃ vapour and of vapour from aq. HF being admitted at opposite ends of the tube; besides LiMnPO₄ small black crystals of a higher Mn oxide are formed. (2) Equal parts of LiCl and Li₃PO₄ are heated with 1.5 parts of Mn₂(PO₄)₂. The clear brown crystals of LiMnPO₄ are rhombic, $d_{100} 3.334$ — 3.4 , $a : b : c = 0.4522 : 1 : 0.5834$; Li₃PO₄, of which good crystals are obtained by the second method, is likewise rhombic, $a : b : c = 0.4709 : 1 : 0.5852$. Intergrowths of the two substances are also obtained. C. A. SILBERRAD.

Dacites of Lassen Peak and vicinity, California, and their basic inclusions. H. WILLIAMS (Amer. J. Sci., 1931, [v], 22, 385—403).—Mainly geological. Chemical compositions are given.

N. H. HARTSHORNE.

Glauconite and foraminiferal shells.

F. A. BURT (Science, 1931, 74, 457—458; cf. A., 1931, 1028).—Details of occurrences of glauconite found in fossil-bearing concretions from the Cook Mountain formation of Brazos County, Texas, are recorded.

L. S. THEOBALD.

Production of coal seams. G. STADNIKOV (Kolloid-Z., 1931, 57, 221—225).—A discussion on colloid-chemical grounds. E. S. HEDGES.

Occurrence of germanium in coal and its products. V. M. GOLDSCHMIDT (Nachr. Ges. Wiss. Göttingen, 1930, 398—401; Chem. Zentr., 1931, i, 3445).—H₂O-sol. GeO₂ is reduced by C and adsorbed as Ge^{II}; many coals contain 0.001—0.01% Ge, the quantity in the ash being 0.01—0.5%. Ge is also present (0.01—0.1%) in light ash and soot.

A. A. ELDRIDGE.

Chemical modifications of certain calcareous specimens preserved in wooden cases. F. TABOURY (Bull. Soc. chim., 1931, [iv], 49, 1289—1291).—An efflorescence of crystals of Ca(OAc)₂·2H₂O, formed on the surface of calcareous specimens kept in oak cases, was due to the presence in the atm. of AcOH which came apparently from the wood. Calcite proved more resistant to the acid than aragonite and, of the latter, coarse-grained specimens were less readily attacked than the fine-grained ones.

M. S. BURR.

Origin and nature of the peaty soils of Travancore. T. R. N. PILLAI and V. SUBRAMANIAN (J. Indian Inst. Sci., 1931, 14A, 99—117).—The org. matter in the Kari soils of Travancore is probably derived mainly from kathira, a grass which grows in the surface H₂O. The high H₂O content of the air-dried soil is due to resinous coatings round the particles, which prevent the movement of H₂O and plant nutrients. The chief mineral constituents, particularly FeSO₄·Al₂(SO₄)₃·24H₂O, are thought to

be formed by reactions (for which mechanisms are suggested) between Fe and Al sulphates washed down from higher lands, org. acids from plant decomp., and salts washed in by tidal rises. The free H₂SO₄ in the soil suggests the possibility of fertilising it by insol. phosphates. N. H. HARTSHORNE.

Tropical soils. II. Some characteristic igneous rock soil profiles in British Guiana.

F. HARDY and R. R. FOLLETT-SMITH (J. Agric. Sci., 1931, 21, 739—761).—The formation of tropical red-earth and sandy-earth soils is examined. Basic and intermediate igneous rocks give rise to a "primary gibbsitic laterite" which, subsequently, is re-silicated forming kaolinitic earths highly coloured with hydrated oxides of Fe. Acid igneous rocks directly generate kaolinitic earths which are but slightly coloured with Fe. These changes are shown by the distribution of free and combined SiO₂ and of gibbsitic Al₂O₃, methods for the determination of which are described.

A. G. POLLARD.

Formation of arable soils from the loess of Dutch Limburg. J. VAN BAREN (Z. Pflanz. Düng., 1931, 22A, 359—373).—Chemical and mineralogical examinations of a loess soil profile are recorded and the soil formation process is discussed in relation to the weathering factors, SiO₂/Al₂O₃ and (CaO+Na₂O—K₂O)/Al₂O₃ (Harrassowitz).

A. G. POLLARD.

Sulphur cycle in a high moor and an alder peat soil in comparison with a garden soil.

H. SZIMMAT (Bot. Archiv., 1931, 33, 136—171).—Seasonal variations in the H₂S content of soils are recorded. Controlling factors are soil aeration and the activities of H₂S-producing and H₂S-oxidising bacteria. H₂S exists free in high moor and alder bog soils, but in garden soils is mainly combined with Fe. Bacteria producing H₂S by sulphate reduction are active only in soils rich in sulphates. *Thiobacillus thioparus* is less frequent and *T. oxidans* more frequent in acid than in neutral soils.

A. G. POLLARD.

Classification of water soils.

J. O. VEATCH (Michigan Agric. Exp. Sta. Bull., 1931, 14, 20—23).—The complete H₂O soil consists of three horizons, (1) aq. surface, (2) subaq. or sedimental, (3) basal geological substratum. (1) is of prime importance in the differentiation of these soils, the significant criteria being depth, chemical nature of solutes, reaction, and the nature and quantity of suspended matter. A scheme of classification of soils on this basis is suggested.

A. G. POLLARD.

Soils of Australia in relation to vegetation and climate. J. A. PRESCOTT (Bull. Counc. Sci. Ind. Res. Austral., 1931, No. 52, 71 pp.).

Soil survey of the swamps of the Lower Murray River. J. K. TAYLOR and H. G. POOLE (Bull. Counc. Sci. Ind. Res. Austral., 1931, No. 51, 43 pp.).—A special system of classification of these soils is suggested. The growth of lucerne in certain very acid soils is ascribed to their abnormally large Ca contents. Burning of clays renders some of the bases non-exchangeable, Ca being affected more than Mg. The NaCl content of this soil is the principal cause of infertility.

A. G. POLLARD.

Soil study of the Mont Alto state forest. J. T. AUTEN (Pennsylvania Dept. of Forests and Waters Res. Bull., 1930, No. 4, 64 pp.).—In the forest soils examined, the clay content was a relatively unimportant factor in the vol.-growth of timber. The % of total N in the soils varied little, but that of Ca and P was greatest in ridge soils where growth was least. Nitrates were absent from nearly all

soils, but an accumulation of org. N in surface layers suggests symbiotic N fixation even in these acid soils. Soil moisture is an important factor controlling growth of timber and may to some extent influence the distribution of species. In peaty horizons the ratio loss on ignition:N was 50:1. Of micro-organisms present *Actinomyces* predominated and fungi outnumbered bacteria. A. G. POLLARD.

Organic Chemistry.

Gaseous products from action of cathode rays on hydrocarbons. C. S. SCHOEFFLE and C. H. FELLOWS (Ind. Eng. Chem., 1931, 23, 1396—1398).—When bombarded with cathode rays saturated hydrocarbons give large amounts and unsaturated small amounts of gas consisting of H_2 and CH_4 and saturated hydrocarbons of lower mol. wt. than the original compound. Aromatic hydrocarbons give negligible amounts of gas and branched-chain give more gaseous saturated hydrocarbons than do straight-chain compounds. The reaction is similar to that of hydrocarbons under the influence of corona discharge or α -particles. F. R. SHAW.

Free organic radicals in the gaseous phase. II. Preparation of free ethyl. III. Mechanism of the reactions of free radicals. F. PANETH and W. LAUTSCH (Ber., 1931, 64, [B], 2702—2707, 2708—2718; cf. A., 1929, 788).—II. Under conditions closely similar to those described (*loc. cit.*), the thermal decomp. of $PbEt_4$ leads to the disengagement of free Et , which behaves towards mirrors of As, Sb, Zn, and Cd in the same manner as Me. The radical is identified by the isolation of $ZnEt_2$ and by conversion of the latter substance into EtOH.

III. Investigation of the relationship between the rate of disappearance of radicals in metal-free tubes, the pressure of the transport gas and its nature (H_2 and Ne+He), the concn. of the radical, and the diameter of the tube shows that each radical is retained at the first contact by a reactive metal mirror such as Zn or Pb; as soon as by surface diffusion the necessary no. of radicals has accumulated at an individual metallic atom, definite chemical products result which, if volatile, are removed by the current of gas. A small proportion, of the order 0.1%, of the incident radicals remains attached to glass, quartz, or Fe. The coeff. of attachment (accommodation) coeff. depends on the temp. of the glass and its individual properties but is practically const. for a given glass tube. The observed unimol. rate of disappearance of the radicals is thus explained. Secondary changes at the glass surface result in the transformation of the radicals into inert hydrocarbons. H. WREN.

Olefine series. I. Synthesis of Δ^{α} -olefines. R. WILKINSON (J.C.S., 1931, 3057—3062).—The n - Δ^{α} -olefines from pentene to nonene are synthesised according to the reaction: $CH_3R \cdot MgBr + CH_2Br \cdot CH:CH_2 \rightarrow CH_2R \cdot CH_2 \cdot CH:CH_2 + MgBr_2$ (cf. A., 1904, i, 872); they are purified by addition of the calc. amount of Br below -5° and regeneration from

the resulting dibromides by interaction with Zn-Cu in 95% EtOH. The b. p., d_4^{25} , and n_D^{25} of the olefines and their dibromides, and the crit. solution temp. of the olefines and NH_2Ph , are determined.

H. A. PIGGOTT.

Abnormal decomposition of β -substituted allyl radicals. C. PRÉVOST and G. RICHARD (Bull. Soc. chim., 1931, [iv], 49, 1368—1372).—When Δ^{β} -pentenyl bromide (2 mols.) is treated with Mg (1 atom), the incomplete reaction yields unchanged material; a fraction, b. p. $75-83^\circ/120$ mm., containing mainly hydrocarbons with a little Br; $\gamma\delta$ -diethyl- $\Delta^{\alpha\alpha}$ -hexadiene, b. p. $88-89^\circ/120$ mm., d^{25} 0.7526 (tetrabromide, m. p. 35°); γ -ethyl- $\Delta^{\alpha\alpha}$ -octadiene, b. p. $97^\circ/120$ mm., d^{25} 0.754; $\Delta^{\gamma\gamma}$ -decadiene, b. p. $63^\circ/19$ mm., d^{25} 0.7559 (tetrabromide, m. p. $70-71^\circ$); and a fraction distilling above $90^\circ/19$ mm., probably condensed hydrocarbons. The three diene hydrocarbons are obtained in yields up to 80—90% and result from the formation of the abnormal Mg derivatives $CH_2:CH \cdot CHEt \cdot MgBr$ and $CHEt(MgBr) \cdot C(MgBr):CH_2$ and their decomp., e.g., $(CHEt:CH \cdot CH_2)_2MgBr + CHEt:CH \cdot CH_2Br = MgBr_2 + (CHEt:CH \cdot CH_2)_2$.

R. BRIGHTMAN.

Acetylene polymerides and their derivatives. I. Controlled polymerisation of acetylene. J. A. NIEUWLAND, W. S. CALCOTT, F. B. DOWNING, and A. S. CARTER (J. Amer. Chem. Soc., 1931, 53, 4197—4202).—A low-temp. catalytic polymerisation of C_2H_2 is described producing vinylacetylene (I), divinylacetylene (II), b. p. $83.5^\circ/760$ mm., and a tetrameride (probably $\alpha\epsilon\eta$ -octatrien- γ -ine), b. p. $40^\circ/20$ mm., $82^\circ/100$ mm. (with polymerisation), 156° (violent decomp.); the method involves passing C_2H_2 into an aged mixture of Cu_2Cl_2 , NH_4Cl , Cu, and aq. HCl. V.-p. data are given for (I) and (II). (I) is reduced to C_4H_{10} and converted by H_2SO_4 in presence of $HgSO_4$ into Me vinyl ketone; at -10° , (I) forms a hydrate, probably $C_4H_4 \cdot 2H_2O$. (II) is reduced to hexane and adds 6 atoms of Br; it absorbs O_2 from the air, giving a highly explosive peroxide (or ozonide) which detonates spontaneously on keeping. (II) is extremely dangerous to handle. Reaction mechanisms for the formation of the polymerides are suggested. C. J. WEST (b).

Preparation and physical properties of ethyl- and methyl-acetylenes. F. R. MOREHOUSE and O. MAASS (Canad. J. Res., 1931, 5, 306—312; cf. A., 1928, 732).—An improved apparatus is described for the prep. of Δ^{α} -propinene, m. p. -101.5° , b. p. $-23.3^\circ/760$ mm., and Δ^{α} -butinine, m. p. -122.5° , b. p. $8.6^\circ/760$ mm. A. A. LEVI.

Action of α -olefinic bromides on magnesium organo-bromides. C. PRÉVOST (Bull. Soc. chim., 1931, [iv], 49, 1372—1381).—The action of cinnamyl bromide on MgEtBr in Et_2O affords 0.14 mol. of EtBr , 0.025 mol. of allylbenzene, b. p. $164^\circ/749$ mm., d^{18}_4 0.8849, and 0.025 mol. of propenylbenzene, b. p. $176^\circ/760$ mm., d^{18}_4 0.8975; 0.5 mol. of ω -propylstyrene and 0.23 mol. of α -ethylallylbenzene, 0.045 mol. of α - δ -diphenyl- $\Delta^{\alpha\delta}$ -hexadiene, b. p. 187 — $188^\circ/13$ mm., d^{18}_4 0.9986, 0.045 mol. of dicinnamyl, m. p. 81 — 82° , and some undistillable condensation products. These observations are explained by assuming the functional exchange: $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Br} + \text{EtMgBr} \longrightarrow \text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{MgBr} + \text{EtBr}$, since the yield of dicinnamyl is not due to the presence of excess of undissolved Mg , being unchanged with reagents free from metal. A similar explanation is advanced for the complex mixture of products obtained by the action of α - ξ -dibromo- $\Delta^{\alpha\delta}$ -hexadiene on MgEtBr . The former, obtained from PBr_3 and divinyl glycol (yield 50%), thus affords about 5% of a hydrocarbon, b. p. 88 — $90^\circ/120$ mm., d^{21}_4 0.7541, probably γ - δ -diethyl- $\Delta^{\alpha\delta}$ -hexadiene; about 25% of γ -ethyl- $\Delta^{\alpha\delta}$ -octadiene, b. p. $96^\circ/120$ mm., $153^\circ/760$ mm., d^{14}_4 0.7609, with possibly a little ϵ -ethyl- $\Delta^{\alpha\gamma}$ -octadiene; a fraction b. p. 110 — $118^\circ/120$ mm., d 0.794, probably $\Delta^{\alpha\delta}$ -decadiene; a fraction b. p. 130 — $150^\circ/12$ mm., containing a mixture of isomeric hydrocarbons, probably $\text{C}_{16}\text{H}_{26}$, e.g., b. p. 132 — $134^\circ/12$ mm., d^{21}_4 0.7888; and a residue amounting to about 50% of the total which is probably a mixture of hydrocarbons of high mol. wt. R. BRIGHTMAN.

Colour reactions of organic nitro-derivatives with alkalis. L. DESVERGNES (Ann. Chim. Analyt., 1931, [ii], 13, 321—322).—The colour reactions given by 132 org. NO_2 -derivatives with solutions of KOH or NH_3 in EtOH or COMe_2 are listed.

E. S. HEDGES.

Determination of small amounts of alcohol. E. WIDMARK (Svensk Kem. Tidskr., 1931, 43, 245—251)—Polemical. It is shown that L. Smith's modification of the author's method (A., 1931, 990) has no advantages over the original process either as regards simplicity of manipulation or accuracy.

H. F. HARWOOD.

Alkyl α -chloroethyl ethers. H. R. HENZE and J. T. MURCHISON (J. Amer. Chem. Soc., 1931, 53, 4077—4079).—The following alkyl α -chloroethyl ethers are prepared by saturating a well-cooled mixture of equimol. quantities of paracetaldehyde and the appropriate alcohol with dry HCl : Me , b. p. 72 — $73^\circ/751$ mm.; Et , b. p. $97.5^\circ/750$ mm.; Pr , b. p. $47.5^\circ/40$ mm.; Bu , b. p. 48.9 — $50.3^\circ/11$ mm., and amyl , b. p. 63.3 — $66.3^\circ/8$ mm. All b. p. are corr. These ethers are hydrolysed rapidly in presence of moisture, yielding the original materials; when kept, they polymerise (to tars).

C. J. WEST (b).

Ethyl ethers of α -glycols. D. BARDAN (Bull. Soc. chim., 1931, [iv], 19, 1426—1434).—The following Et ethers of α -glycols are obtained by the action of Grignard reagents on the corresponding Et α -ethoxycarboxylate: γ -ethoxy- β -methylbutan- β -ol (yield 79%), b. p. 141° (phenylurethane, m. p. 226°); δ -ethoxy- γ -ethylpentan- γ -ol (yield 75%), b. p. 179 —

182° (phenylurethane, m. p. 231°); β -ethoxy- γ -propylhexan- γ -ol (77%), b. p. 102 — $104^\circ/19$ mm.; β -ethoxy- γ -butylheptan- γ -ol (75%), b. p. 123 — $124^\circ/15$ mm. (phenylurethane, m. p. 237°); β -ethoxy- γ -isoamyl-octan- γ -ol (76%), b. p. 133 — $134^\circ/14$ mm.; β -ethoxy- α -diphenylpropan- α -ol (50%), b. p. 150 — $154^\circ/4$ mm. (phenylurethane, m. p. 243°); δ -ethoxy- γ -ethylhexan- γ -ol (76%), b. p. 193 — 195° ; γ -ethoxy- δ -propylheptan- δ -ol (75%), b. p. 109 — $110^\circ/15$ mm. (phenylurethane, m. p. 246°); γ -ethoxy- δ -butyloctan- δ -ol (75%), b. p. 130 — $132^\circ/14.5$ mm. (phenylurethane, m. p. 242°); β -ethoxy- α -diphenylbutan- α -ol, b. p. 188 — $193^\circ/15$ mm.; α -ethoxy- α -phenyl- β -ethylbutan- β -ol (73%), b. p. 143 — $147^\circ/23$ mm. (phenylurethane, m. p. 236°); α -ethoxy- α -phenyl- β -propylpentan- β -ol (80%), b. p. 154 — $156^\circ/19$ — 20 mm. (phenylurethane, m. p. 241°); α -ethoxyl- α -phenyl- β -butylhexan- β -ol (74%), b. p. 173 — $174^\circ/14.5$ mm. (phenylurethane, m. p. 244°), and β -ethoxy- α - β -tri-phenylethan- α -ol, m. p. 136 — 136.5° . Et α -ethoxypropionate, b. p. 66 — $68^\circ/27$ mm., is obtained (yield 65%) from Et α -bromopropionate, b. p. $62^\circ/24$ mm., prepared from α -bromopropionyl chloride (from propionyl chloride, b. p. 79 — 80° , and Br). The following, similarly obtained, are also described: butyryl chloride, b. p. 99.5 — 101° ; α -bromobutyryl chloride, b. p. 151 — 153° ; Et α -bromo-, b. p. 177 — 179° , and α -ethoxy-butyrate (65% yield), b. p. 67 — $68^\circ/16$ mm.; α -bromophenylacetyl chloride; Et α -bromo-, b. p. 165 — $166.5^\circ/30$ mm., and Et α -ethoxyphenylacetate, b. p. 155 — $157^\circ/26$ mm. R. BRIGHTMAN.

Preparation, properties, and uses of glycerol derivatives. III. Chlorohydrins. G. P. GIBSON (Chem. and Ind., 1931, 949—954, 970—975).—The prep. of glycerol mono- and di-chlorohydrins from glycerol and HCl , both with and without AcOH as a catalyst, has been systematically investigated and the various by-products formed have been determined, isolated, and their properties tabulated. Treatment of glycerol containing 2% of AcOH with a limited quantity of HCl at 100° and re-treatment of the residual glycerol from various batches gives an overall yield of mono- (I) (mainly α , containing 5% of the Ac derivative) 85.6, and di- (II) 3.6, -chlorohydrins, polyglycerol chlorohydrins (III) 9.7, and unchanged glycerol, 1.1%. With 4% AcOH at 130° the whole of the HCl may be used if the reaction vessels are in series, but the (II) formed increases rapidly at the expense of the (I) (containing 10.3% of the Ac derivative), which, however, is completely miscible with H_2O (f. p.-composition curve plotted). Without AcOH , glycerol and HCl at 100° give (I) free from acetates, but this process is uneconomical and further reaction to (II) is slow. With excess of HCl and 4% AcOH at 130° the yield of (II) is good and the HCl may be used economically if the reaction vessels are in series, whilst formation of (III) is small. Crude soap-lye or 40% glycerol "foots" may be used, the inorg. salts separating in a readily filterable form. With 4% AcOH at 100° formation of (III) is reduced to a min., but the HCl is not used economically, repeated treatment giving 88.5, 9.0, and 2.5%, respectively, of (II), (I), and (III). (II) forms const.-b. p. mixtures with H_2O and aq. HCl and miscibility and f.-p. diagrams for the systems

(II)-H₂O, (II)-H₂O-HCl [crit. point at 25°, 52% of (II), HCl 12%], and (II)-H₂O-AcOH [crit. point at 25°, (II) 43%, H₂O 9.7%] are plotted. From a study of the distillation of the dichlorohydrin in steam containing HCl it is found that this product may be formed continuously and simultaneously volatilised in steam by treatment of glycerol with fuming HCl at 160°, the final product containing (II) 83.2, (I) 5.8, (III) 9.3, and unchanged glycerol, 1.7%. The following were isolated in the course of the investigation: dichlorohydrin, b. p. 108—110°/40 mm.; diglycerol dichlorohydrin di-, b. p. 159—160°/3 mm., monochlorohydrin tri-, b. p. 179—181°/3 mm., and diglycerol tetra-, b. p. 194—197°/3 mm., -acetate.

J. W. BAKER.

Reactions relating to carbohydrates and polysaccharides. XXVIII. Preparation, separation, and identification of the isomeric bromoethylideneglycerols. H. HIBBERT and E. HALLONQUIST (Canad. J. Res., 1931, 5, 428—435).—Oily bromo-paracetaldehyde (modified prep. for cryst. or oily material) with glycerol and a little H₂SO₄ gives a mixture of bromoethylideneglycerols, which with HCl, pyridine, and BzCl affords α -bromoethylideneglycerol β -benzoate (I), m. p. 109°, and impure β -bromoethylideneglycerol α -benzoate (II), an oil, b. p. 170°/16 mm. The constitution of (II) is proved because on hydrolysis it yields α -bromoethylideneglycerol, b. p. 151°/23 mm., giving the γ -Me ether, b. p. 117.5—119°/22 mm., also obtained from glycerol α -Me ether. (I) gives similarly α -bromoethylideneglycerol, b. p. 144—145°/22 mm. (β -Me ether, b. p. 128—129°/21 mm., also obtained from glycerol β -Me ether). The ratio of the amounts of (I) and (II) formed, 1:15, is changed to 1:8 by 1% of dry HCl at 25°. These results are in agreement with the theory that increase in ease of "semi-acetal" formation involves decrease in ease of cyclic acetal formation.

R. S. CAHN.

Sugar-alcohols. F. VALETIN (Coll. Czech. Chem. Comm., 1931, 3, 499—513).—In agreement with Helferich's rule (A., 1925, i, 9) CPh₃Cl reacts to form ethers with all the primary alcohol groups in sugar alcohols but not with secondary alcohol groups, and thus are obtained the CPh₃ ethers of *l*-rhamnitol, m. p. 132—135°, [α]_D +3.95° in C₆H₆; fucitol, m. p. 138—142°, [α]_D -5.0° in C₆H₆; *epi*-rhamnitol, m. p. 68—72°, [α]_D -4.2° in C₆H₆; *l*- α -rhamnohexitol (alcohol, m. p. 180—183°; lit., m. p. 170—173°), m. p. 122—125°, [α]_D -2.0° in C₆H₆-MeOH (3:1); (CPh₃)₂ ethers of mesoerythritol, m. p. 182—184°; adonitol, m. p. 141—145°; xylitol, m. p. 152—156°; *l*-arabitol, m. p. 111—113°, [α]_D -3.5° in C₆H₆; mannitol, m. p. 98—103°, [α]_D -3.5° in C₆H₆; sorbitol, m. p. 83° (softens at 72°), [α]_D -7.8° in C₆H₆; α -glucoheptitol, m. p. 117—123°; glycol, m. p. 191° (cf. A., 1923, i, 331; crystallographic data by NOVÁČEK); and the (CPh₃)₃ ether of pentaerythritol, m. p. above 350°. CHPh₂ or CMe₂ derivatives of these ethers could not be obtained. J. W. BAKER.

Determination of anhydrides of organic acids in the presence of acids not corresponding with these anhydrides. V. O. LUKASHEVITSCH (J. Chem. Ind. Russ., 1931, 8, 1086—1087).—A 1-g.

sample is dissolved in 10 c.c. of CO₂-free H₂O, and the total acidity is determined by titration with NaOH (phenolphthalein), whilst another 1 g. is boiled under reflux for 30 min. with MeOH, after which H₂O is added, and the solution is also titrated with NaOH. The anhydride content is calc. from the difference between the no. of c.c. of NaOH used in the two titrations, according to the equation (R·CO₂)₂O + MeOH \rightarrow R·CO₂Me + R·CO₂H. R. TRUSZKOWSKI.

Simple and complex ferrous carboxylates. W. FRANK (Annalen, 1931, 491, 30—51).—The following salts are prepared from *M* solutions of FeSO₄ and the appropriate Na salt under light petroleum: Fe⁺⁺ formate (+2H₂O), glycollate (+2H₂O), salicylate (+2H₂O), oxalate (+2H₂O), succinate (+4H₂O), fumarate (+3H₂O), *r*-malate (+2H₂O), and *d*-tartrate (+2H₂O). Fe⁺⁺ malonate (+2H₂O) and Fe⁺⁺ citrate (+H₂O) are prepared by the action of Ferrum reductum on the acids in aq. solution. The air dried salts are not particularly sensitive (except salicylate and succinate) to O₂. The degrees of dissociation of the above salts do not correspond with the strengths of the corresponding acids, but are probably dependent on structural factors. Thus, the order oxalate < malonate < succinate can be correlated with the increasing distance apart of the CO₂H groups and, hence, the suppression of co-ordination with the O atoms of the ·CO· groups. The α -OH group lowers the degree of dissociation (malate and tartrate < succinate), probably owing to increased tendency of co-ordination. Addition of the corresponding Na salts to solutions (*M*/200) of the Fe⁺⁺ salts causes, in each case, considerable depression of the degree of dissociation. The dissociation consts. of various complex salts, formed when aq. solutions of, e.g., Na formate, K oxalate, are shaken with an excess of, e.g., Fe⁺⁺ formate, Fe⁺⁺ oxalate, in N₂, are calc. from solubility data and the concns. of undissociated Fe⁺⁺ salt and anions. The salts Na₂Fe(HCO₂)₆·5H₂O, K₂Fe(C₂O₄)₂·2H₂O, and Na₂Fe[CH₂(CO₂)₂]₂·2H₂O are isolated. The views of Scholder (A., 1927, 855) on the structure of complex Fe⁺⁺ oxalates are criticised.

H. BURTON.

Reduction of fatty acid bromides. W. KIMURA (J. Soc. Chem. Ind., Japan, 1931, 34, 355—356B).—5*N*-H₂SO₄ in MeOH is more convenient than HCl in the Rollet reduction of fatty acid bromides. High yields of neutral esters are obtained from linoleic and linolenic bromides; reduction of clupanodonic decabromide proceeds less smoothly and the yield (53%) is smaller than by the original method.

E. LEWKOWITSCH.

A low-melting, easily-soluble fatty acid octabromide. H. RUDY and I. H. PAGE (Naturwiss., 1931, 19, 774—775).—In the separation of unsaturated fatty acids of a cephalin from a human brain a fraction of "octabromide," m. p. 163—164°, differing from the usual octabromide was obtained. The reasons for the appearance of two modifications of octabromide are discussed. It is suggested that the insol. should be called α -octabromide, the sol. β -octabromide.

W. R. ANGUS.

Decomposition of esters by alcohols in feebly alkaline medium. E. M. BELLET (Compt. rend.,

1931. 193, 1020—1023).—The interaction of a variety of alcohols in large excess with a variety of esters in presence of a small amount of NaOH is studied. The displaced alcohols are separated and determined, after fractional distillation, as allophanates. It is found that the higher alcohols are displaced by the lower, the extent of replacement being the greater the higher is the temp. and the greater the difference in mol. wt. of the alcohols. *tert.*-Alcohols are displaced (by primary) more readily than primary alcohols.

H. A. PIGGOTT.

Catalytic decomposition of ortho-esters by aluminium oxide. F. SIGMUND and S. HERSCHDORFER (Monatsh., 1931, 58, 280—288).—When $\text{CMe}(\text{OEt})_3$ and $\text{CtEt}(\text{OEt})_3$ are passed over heated Al_2O_3 , EtOAc and EtCO_2Et , respectively, are formed, with the elimination of Et_2O in each case. The reaction is complete at 180° and has also been examined at 250° . No reaction is observed at room temp., but a considerable amount takes place at 75° and 90° . When $\text{CMe}(\text{OBu}^t)_3$ mixed with some $\text{CMe}(\text{OBu}^t)_2\cdot\text{OEt}$ is passed over clay catalyst at 200° , instead of the more active Al_2O_3 , a corresponding mixture of EtOAc and MeOAc is obtained. An attempt to prepare $\text{CtEt}(\text{OBz})_2\cdot\text{OEt}$ for treatment resulted in decomp. into Bz_2O and EtCO_2Et on distillation without the aid of a catalyst. The keten formation, observed in the catalytic decomp. of similar substances by other investigators, did not take place in the substances examined.

M. S. BURR.

Purification of sodium ricinoleate. T. H. RIDER (J. Amer. Chem. Soc., 1931, 53, 4130—4133).—The total fatty acids obtained by hydrolysis of castor oil are dissolved in an equal vol. of 95% EtOH and the solution is kept at -15° for 4 days, whereby the solid acids (2.5—3% of total) separate completely, and consist of dihydroxystearic and stearic in the ratio 2:1. The mixed Me esters of the liquid acids are distilled and the fraction, b. p. $188\text{--}193^\circ/4\text{ mm.}$, is acetylated. The resultant *Me acetylricinoleate*, b. p. $195^\circ/1\text{ mm.}$, is hydrolysed by EtOH-KOH to ricinoleic acid, m. p. 5° , from which the Na salt is prepared.

C. J. WEST (b).

Composition of linseed oil. H. P. KAUFMANN and M. KELLER (Chem. Umschau, 1931, 38, 294—296).—The criticisms of van der Veen and of van Loon (A., 1931, 1395) are refuted. The zero thiocyanogen vals. found for pure stearolic and behenolic acids (9—24 hr.) are reaffirmed.

E. LEWKOWITSCH.

Mechanism of the reaction between ethyl carbonate and Grignard reagents. D. IVANOV (Compt. rend., 1931, 193, 773—776).—According to previous theory (A., 1928, 417; 1929, 1049), the action of MgXR on Et_2CO_3 should give RCO_2Et and $\text{Mg}(\text{OEt})\text{X}$. The ester could not be isolated by extraction with light petroleum; it may, however, combine with $\text{RO}\cdot\text{MgX}$ to give the oxonium compound $\text{RO}\cdot\text{C}(\text{O})\cdot\text{O}\cdot\text{MgX}$, which is insol. in light

petroleum, but may be distilled to give the ester [this would not result from the more stable $\text{CR}(\text{OEt})_2\cdot\text{OMgX}$, (I)]. From a mixture of Et_2CO_3 , $\text{CH}_2\text{Ph}\cdot\text{MgX}$, and MgPrBr , C_3H_8 and Et xy-di-

phenylacetoacetate are obtained, showing that before hydrolysis $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$ must be formed, and not a complex of type (I).

F. R. SHAW.

Ketoperoxide of ethyl laevulate. F. FICHTER and S. LURIE (Helv. Chim. Acta, 1931, 14, 1445—1448).— Et laevulate and 94.5% H_2O_2 at 0° to room temp. give the *ketoperoxide*, $[\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{O})\cdot\text{O}]_n$, m. p. $71\text{--}72^\circ$, which when heated at 100° (bath)/12 mm. decomposes into CO_2 , propionic acid, Et propionate , and a trace of succinic acid.

H. BURTON.

Determination of configuration in the terpene series. V. J. VON BRAUN and W. KELLER (Ber., 1931, 64, [B], 2617—2621; cf. A., 1929, 819, 1424).—The method adopted for the determination of the configurative relationships of *d*- β -methyl-adipic and -succinic acids is not available for the Pr^t acids, since the Bz_2 derivative of isopropyltetramethylenediamine does not react smoothly with PBr_5 . The converse process also appears inapplicable, since racemisation occurs during the reduction of isopropylsuccinic esters by Na and EtOH or by H_2 and Cu chromite.

β -isoPropyladipic acid in conc. H_2SO_4 is transformed by N_3H in CHCl_3 and subsequently by alkali into $\alpha\delta$ -diamino- β -isopropylbutane, b. p. $88\text{--}90^\circ/16\text{ mm.}$ (picrate, m. p. 218° ; hydrochloride; Bz_2 derivative, b. p. $274^\circ/0.2\text{ mm.}$), converted by Me_2SO_4 and alkali followed by KI into the diquaternary iodide, $\text{C}_{13}\text{H}_{22}\text{N}_2\text{I}_2$, m. p. 240° (corresponding chloroplatinate, decomp. $305\text{--}310^\circ$). The Bz_2 compound is transformed by PBr_5 in C_6H_6 or PhCl into $\alpha\delta$ -dibromo- β -isopropylbutane, b. p. $110^\circ/15\text{ mm.}$, in 5% yield. The above diquaternary iodide is converted by successive treatment with Ag_2O and conc. KOH into (?) a mixture of unsaturated bases $\text{C}_9\text{H}_{10}\text{N}$, b. p. $145\text{--}150^\circ$ (picrate, m. p. $108\text{--}120^\circ$), and β -isopropyl- $\Delta^{\alpha\gamma}$ -butadiene, b. p. $86\text{--}87^\circ$. With Br in CS_2 the unsaturated hydrocarbon affords $\alpha\delta$ -dibromo- β -isopropyl- Δ^{β} -butene, b. p. $106\text{--}107^\circ/15\text{ mm.}$, which loses HBr when acted on by $\text{Pd}+\text{H}_2$ and is converted by NaOPh into $\alpha\delta$ -diphenoxy- β -isopropyl- Δ^{β} -butene, b. p. $220^\circ/15\text{ mm.}$; hydrogenation of the last-named compound in presence of Pd is accompanied by loss of NaOPh and production of a mixture of mono- and di-ethers. The constitution of the butadiene is determined by treating the unsaturated dibromide with NMe_3 in C_6H_6 , hydrogenation of the product, and final conversion into the diquaternary iodide described above.

H. WREN.

Iodometric determination of citric acid. P. A. KOMETIANI (Z. anal. Chem., 1931, 86, 359—366).—A solution containing 5—40 mg. of citric acid is treated at $40\text{--}45^\circ$ with KMnO_4 in presence of H_2SO_4 and KBr . The resulting pentabromoacetone is filtered, dissolved in EtOH , and treated with excess of NaI , each mol. of citric acid yielding 6 equivs. of I. The method is more exact and rapid than those hitherto in use and is suitable for routine analyses.

F. L. USHER.

Acetyl derivatives of the lactones of monobasic sugar acids. F. W. UPSON and Q. R. BARTZ (J. Amer. Chem. Soc., 1931, 53, 4226—4227).—Acetyl-

ation of *d*- γ -gluconolactone in presence of $ZnCl_2$ gives a liquid *Ac*₄ derivative, whilst *d*- δ -gluconolactone affords a *tetra-acetylgluconic acid monohydrate*, m. p. 114—117°, $[\alpha]_D -1.21^\circ$, which when heated at 100°/vac. gives 2:3:4:6-*tetra-acetyl-d*- δ -gluconolactone, a glassy solid, $[\alpha]_D +64.35^\circ$ (after 6 min.) $\rightarrow 0^\circ$ (42 hr.). The *Ac*₄ derivatives of α -*d*-glucoheptonolactone (γ), *d*- γ -mannonolactone, and *l*- γ -mannonolactone have m. p. 128°, 119°, and 119°, respectively.

C. J. WEST (b).

Determination of gluconic acid. F. DE CARLI (Annali Chim. Appl., 1931, 21, 465—471).—The determination is based on the measurement of the optical rotation produced by complex compounds formed by gluconic acid and Ca gluconate with $Bi(NO_3)_3$.

O. F. LUBATTI.

Preparation of *d*-galacturonic acid. K. P. LINK and R. NEDDEN (J. Biol. Chem., 1931, 94, 307—314).—A detailed account is given of the isolation of *d*-galacturonic acid from citrus pectic acid (cf. A., 1930, 744, 1021).

H. BURTON.

Mesohydry. IV. Constitution of acids substituted with sulphur, nitrogen, etc. in the carbonyl group. G. ODDO (Gazzetta, 1931, 61, 699—704).—Substances containing a CO_2H group substituted with $\cdot SH$, $\cdot NH_2$, $\cdot NH\cdot NH_2$, $\cdot NH\cdot OH$, etc. exist only in one form, which is regarded as the mesohydric form, $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C \\ \diagdown \quad \diagup \\ S \end{array} \cdot H$ or $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C \\ \diagdown \quad \diagup \\ NH \end{array} \cdot H$, but give, on replacement of the mesohydric H atom by alkyl groups, two series of compounds $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C \\ \diagdown \quad \diagup \\ SR \end{array}$, $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C \\ \diagdown \quad \diagup \\ S(OR) \end{array}$, derived from the ionisable form, $\begin{array}{c} O \\ \diagup \quad \diagdown \\ C \\ \diagdown \quad \diagup \\ OH \end{array}$.

E. E. J. MARLER.

Limpricht-Piria reaction for the preparation of aldehydes. B. ZAAR (J. pr. Chem., 1931, [ii], 132, 163—168).—Distillation of mixtures of Ba laurate and formate gives dodecaldehyde (I), laurionone, dodecyl alcohol, m. p. 21.6°, b. p. 114°/2 mm., Me laurate, *dodecyl laurate*, m. p. (synthetic) 27°, b. p. 226°/4.5 mm., and *formate*, b. p. 120°/4.5 mm. CH_3O is assumed to be an intermediate product, which partly reduces and partly oxidises (I). (I) forms an additive compound, m. p. 44.5—45.5°, with 1 mol. of dodecyl alcohol, and a similar compound, m. p. 35.5—36°, with decyl alcohol; these decompose slowly into their components when distilled.

R. S. CAHN.

Catalytic decomposition of acetals by aluminium oxide. II. F. SIGMUND and S. HERSCHDORFER (Monatsh., 1931, 58, 268—279).—When heptaldehyde di-*n*-propylacetal is passed over pure Al_2O_3 at 250°, $PrOH$ is removed and Pr heptenyl ether is obtained, just as by the action of a clay catalyst (cf. A., 1929, 539). With citronellal diethylacetal, 2 mols. of $EtOH$ are eliminated and a mixture of unsaturated hydrocarbons, $C_{10}H_{16}$ and $C_{10}H_{18}$, is formed. It has not been possible to determine the structure of these compounds. The attempted prep. of citral diethylacetal resulted in decomp. with the formation of an unsaturated ether $C_{10}H_{15}\cdot OEt$, which combines with an amount of Br corresponding with two double linkings, suggesting ring formation. Although it takes up 6H, the last two atoms react

much more slowly than the others, apparently due to the breaking of the ring. The hydrogenated product is *Et $\gamma\gamma$ -dimethyloctyl ether*, b. p. 206—208°. On passing the unsaturated ether, $C_{10}H_{15}\cdot OEt$, over Al_2O_3 at 250° $EtOH$ is removed and *p*-cymene is formed.

M. S. BURR.

Dodecaldehyde. B. ZAAR (J. pr. Chem., 1931, [ii], 132, 169—174).—Dodecaldehyde has m. p. 11—11.7°, but sometimes a second form, m. p. 44.5° (cf. Kraft, A., 1880, 866), is obtained. These are regarded as ketonic and enolic forms, respectively, since the latter is largely converted into the former when distilled. Both are unimol. and yield the same oxime and semicarbazone [m. p. 105—106.5° (lit. 101.5—102.5°)].

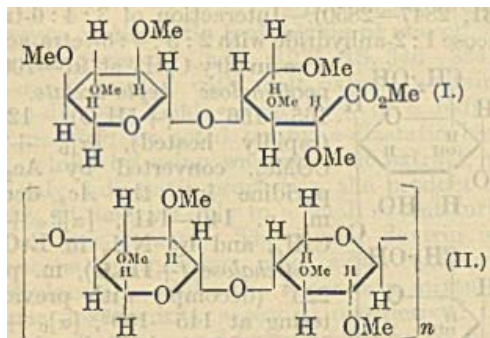
R. S. CAHN.

Friedel-Crafts syntheses in the aliphatic and hydroaromatic series. H. HOPFF (Ber., 1931, 64, [B], 2739—2748).—Saturated aliphatic and hydroaromatic hydrocarbons are almost as well adapted to the Friedel-Crafts synthesis as benzenoid hydrocarbons. Wieland's assumption of the primary addition of the acid chloride to the ethylenic linking (A., 1922, i, 1033) is not therefore universally valid. *n*-Pentane, $AlCl_3$, and $AlCl_3$ yield *Me β -amyl ketone*, b. p. 136—140° (oxime, b. p. 101—105°/20 mm.; *semicarbazone*, m. p. 114°). Under similar conditions, CH_4 , C_2H_6 , and C_3H_8 do not react, whereas *cyclohexane* gives a comparatively good yield of *cyclohexyl Me ketone* (semicarbazone, m. p. 168°). *cyclohexane*, $AlCl_3$, HCl , and CO at 150 atm. and room temp. afford hexahydrobenzaldehyde (*semicarbazone*, m. p. 185°) and *cyclohexanecarboxylic acid* (corresponding *amide*, m. p. 182°). Similarly, *n*-butane yields $COMePr^s$ and acidic products, whilst *n*-pentane gives α -methylvaleric acid, b. p. 190—208° (*amide*, b. p. 231—232°, m. p. 94°), and $COEtPr^s$ (*oxime*, b. p. 73—75°/11 mm.), reduced to $CH_3EtPr^s\cdot OH$, b. p. 129—130° (*phenylurethane*, b. p. 175°/12 mm.). Oxidation of the carbinol affords the ketone, b. p. 115—116°, which is further oxidised to $AcOH$ and $EtCO_2H$. Treatment of the carbinol with 90% H_3PO_4 at 220° gives a hexene, b. p. 65—69°, reduced to β -methylpentane, b. p. 61.5—62°/750 mm. $COEtPr^s$ and Br give a substance, $C_6H_{10}OBr_2$, b. p. 95—100°/14 mm., whereas PCl_5 yields the compound $C_6H_{11}Cl$, b. p. 115—116°. Ketones of higher b. p. are also obtained by the reaction of $AlCl_3$ with *n*-pentane. *n*-Hexane, $AlCl_3$, and CO at 50—60°/118 atm. analogously afford a mixture of carboxylic acids, $COPr^sPr^s$, b. p. 135—137°, and higher ketones. β -Methylbutane yields $COEtPr^s$ in place of the expected aldehyde. CH_4 , C_2H_6 , and C_3H_8 do not react with CO , whereas $MeCl$ affords $AcCl$ or $AcOH$ and $EtCl$ yields $EtCOCl$ or $EtCO_2H$.

H. WREN.

Polysaccharides. IX. Evidence of pyranose structure of xylan. W. N. HAWORTH and E. G. V. PERCIVAL (J.C.S., 1931, 2850—2854).—Acetolytic degradation of dimethylxylan at 0°, followed by deacetylation, oxidation with aq. Br in presence of $Ba(OBz)_2$, and exhaustive methylation of the oxidation product gives *Me hexamethylidixylobionate*, b. p. about 170°/0.06 mm., $[\alpha]_D +10.4^\circ$ in H_2O . This has the

structure (I) in consequence of its hydrolytic fission (2% HCl) to α -2:3:4-trimethylxylopyranose and

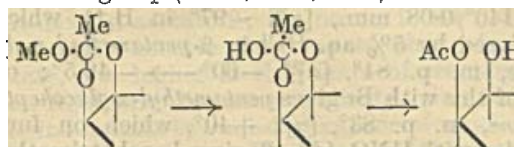


2:3:5-trimethylxylonolactone; xylan therefore has formula (II). H. A. PIGGOTT.

Sugar derivatives containing sulphur. M. GEHRKE and W. KOHLER (Ber., 1931, 64, [B], 2696—2702).—Acetobromoxylose is transformed by K_2S_2 in MeOH at 0° into *dixylosyl disulphide hexa-acetate*, m. p. 142° , $[\alpha]_D^{25} -254.6^\circ$ in $CHCl_3$, hydrolysed by MeOH- NH_3 to *dixylosyl disulphide* ($+1H_2O$), m. p. $188-191^\circ$ (decomp.), $[\alpha]_D^{25} -283.6^\circ$ in H_2O , and reduced by Zn dust and Ac_2O in presence of NaOAc to *thioxxylose (xylothiose) tetra-acetate*, m. p. 99° , $[\alpha]_D^{25} -6.88^\circ$ in $CHCl_3$, prepared also from acetobromoxylose and K thioacetate in boiling EtOH. *Et triacetylxylosyl xanthate*, m. p. $105-106^\circ$, $[\alpha]_D^{25} +17.30^\circ$ in $CHCl_3$, from acetobromoxylose and K Et xanthate in EtOH or thioxxylose tetra-acetate is transformed by KOEt in EtOH into the K salt, m. p. 160° (decomp.), $[\alpha]_D^{25} -16.5^\circ$ in H_2O , converted by HCl into the mutarotatory thioxxylose (not isolated). Acetobromoxylose and KSet in MeOH yield *ethylthioxxyloside triacetate*, m. p. 101° , $[\alpha]_D^{25} -83.5^\circ$ in $CHCl_3$, hydrolysed by aq. $Ba(OH)_2$ to *ethylthioxxyloside*, m. p. 117° , $[\alpha]_D^{25} -78.1^\circ$ (equilibrium). By analogous processes the following are prepared: *diarabinosyl disulphide*, m. p. $190-193^\circ$ (decomp.), $[\alpha]_D^{25} -228^\circ$ in H_2O (*hexa-acetate*, m. p. 152° , $[\alpha]_D^{25} -215.2^\circ$ in $CHCl_3$); *thioarabinose tetra-acetate*, m. p. 79° , $[\alpha]_D^{25} +41.8^\circ$ in $CHCl_3$; *thioarabinose* and its Na derivative, m. p. 155° (decomp.), $[\alpha]_D^{25} +57.8^\circ$ in H_2O ; *benzylthioarabinoside triacetate*, m. p. 148° , $[\alpha]_D^{25} -44.6^\circ$ in $CHCl_3$, and non-cryst. *benzylthioarabinoside*. Acetobromoglyceraldehyde and K thioacetate in boiling MeOH yield *dimeric thioglycerol diacetate*, m. p. 158° , hydrolysed by Na in MeOH to the Na derivative of thioglycerol, $(C_3H_5O_2SNa, 2H_2O)_x$, decomp. $230-235^\circ$, from which the compound $(C_3H_5O_2SAu)_x$, *dimeric ethylthioglyceride*, m. p. 110° , and the *disulphide* $(C_6H_{10}O_4S_2)_x$, decomp. $200-205^\circ$, are obtained. Acetobromoglyceraldehyde and K Et xanthate afford the compound $(C_7H_{12}O_4S_2)_x$, m. p. $142-143^\circ$. Bromoglycollaldehyde affords a similar series of dimeric compounds, viz., $(C_4H_6O_2S)_2$, m. p. 139° (with K thioacetate), whence $(C_4H_3OSNa, 2H_2O)_x$, decomp. $>300^\circ$; $(C_4H_6OS)_2$, m. p. $40-41^\circ$, and $(C_4H_6O_2S_2)_x$, decomp. $223-225^\circ$. Bromoglycollaldehyde and K Et xanthate in MeOH yield the substance $(C_5H_8O_2S_2)_x$, m. p. 112° . The process is not applicable to acetobromorhamnose, which in MeOH affords γ -methylrhamnoside tri-

acetate; in EtOH, BuOH, or amyl alcohol products free from S are obtained. H. WREN.

Third variety of triacetylmethylrhamnoside. W. N. HAWORTH, E. L. HIRST, and H. SAMUELS (J.C.S., 1931, 2861—2864).—The prep. of γ -triacetylmethylrhamnoside is improved. The relative (but not complete) stability of γ -acetylmethylrhamnoside to alkalis, and the removal of the Ac group by Me_2SO_4 and alkali (cf. A., 1930, 68), are confirmed. Both it and its Me_2 derivative, although stable in aq. solution, are extremely labile in 0.01N-HCl at room temp., the hydrolysis proceeding in two stages; the first, recognised by the production of reducing sugar, is very rapid, and probably consists in hydrolysis of the methylglucosido-group, and is followed by the second and slower reaction of disruption of the orthoacetate group (cf. A., 1930, 1024):

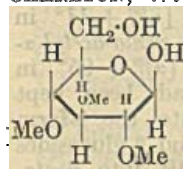


H. A. PIGGOTT.

Reactions relating to carbohydrates and polysaccharides. XXXVII. Formation of dextran by *Leuconostoc mesenteroides*. H. L. A. TARR and H. HIBBERT (Canad. J. Res., 1931, 5, 414—427; cf. A., 1931, 1276).—Four strains of *L. mesenteroides* produced dextran from sucrose in a suitable medium, two produced it from glucose, but none from melezitose, raffinose, fructose, galactose, lactose, maltose, xylose, or glycerol. A method for the prep. of relatively large amounts of dextran is described.

R. S. CAHN.

Structure of 2:3:4-trimethylglucose. W. CHARLTON, W. N. HAWORTH, and R. W. HERBERT (J.C.S., 1931, 2855—2857).—The annexed formula is assigned to 2:3:4-trimethylglucose on account of its oxidation by HNO_3 ("conc." or d 1.26) to *i*-xylotrimethoxyglutaric acid and 2:3:4-trimethyl- δ -saccharolactone. An improved method of prep. of 2:3:4-trimethyl- β -methylglucoside is given. H. A. PIGGOTT.

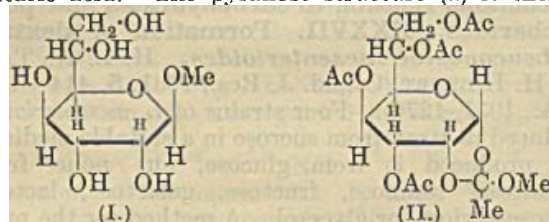


Conversion of 2:3:4-triacetyl- α -methylglucoside into 3:4:6-triacetyl-2-methyl- α -methylglucoside. W. N. HAWORTH, E. L. HIRST, and (Miss) E. G. TEECE (J.C.S., 1931, 2258—2260; cf. A., 1930, 1023).—Methylation (MeI and Ag_2O) of 2:3:4-triacetyl- α -methylglucoside gives 3:4:6-triacetyl-2-methyl- α -methylglucoside, m. p. 120° , $[\alpha]_D^{25} +145^\circ$ in $CHCl_3$, identified by deacetylation with NH_3 in MeOH to 2-methyl- α -methylglucoside, m. p. $147-148^\circ$, $[\alpha]_D^{25} +155^\circ$ in H_2O , further hydrolysed by 7% HCl to 2-methyl- β -glucose. A migration of Ac from position 2 to 6 has therefore occurred during acetylation. The conversion of 2-methylglucose into phenylglucosazone (cf. A., 1929, 1043) is incomplete, some normal phenylhydrazone being also formed. H. A. PIGGOTT.

Products of oxidation of *d*-mannose with ammoniacal copper oxide in presence of air at room temperature. J. PARROD and (Mlle.) Y.

GARREAU (Compt. rend., 1931, 193, 890—891).—*d*-Mannose is oxidised by ammoniacal $\text{Cu}(\text{OH})_2$ to $\text{H}_2\text{C}_2\text{O}_4$ and 4-*d*-arabinotetrahydroxy-*n*-butylglyoxaline, the products being the same as those obtained from *d*-glucose (cf. A., 1931, 852). F. R. SHAW.

Walden inversion in α -glucoheptose series. Preparation of new derivatives and determination of structure of methyl- α -glucoheptoside. W. N. HAWORTH, E. L. HIRST, and M. STACEY (J.C.S., 1931, 2864—2872).— α -Glucoheptose (improved prep.) is converted into β - and α -methyl- α -glucoheptosides by HCl in MeOH ; the former is formed in preponderating amount and is readily separated in a cryst. state, but the yield of the latter is improved by reduction of HCl concn. from 5% to 3%. Further methylation of the former with Me_2SO_4 and alkali gives *pentamethyl- β -methyl- α -glucoheptoside*, b. p. $140^\circ/0.08$ mm., $[\alpha]_D^{20} -97^\circ$ in H_2O , which is hydrolysed by 5% aq. HCl to β -*pentamethyl- α -glucoheptose*, m. p. 84° , $[\alpha]_D^{19} -60^\circ \rightarrow -42.5^\circ$; oxidation of this with Br gives *pentamethyl- α -glucoheptono- δ -lactone*, m. p. 83° , $[\alpha]_D^{19} +40^\circ$, which on further oxidation with HNO_3 (*d* 1.42) gives *l*-arabotrimethoxyglutaric acid. The pyranose structure (I) is there-



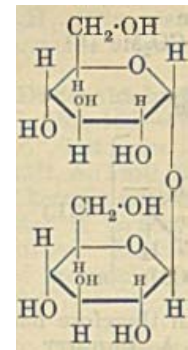
fore assigned to β -methyl- α -glucoheptoside. α -Pentaacetyl- α -glucoheptosidyl bromide, prepared by a modification of Levene and Raymond's method (A., 1931, 336), is converted into β -*penta-acetyl- α -glucoheptosidyl chloride*, m. p. 125° , $[\alpha]_D^{20} +11^\circ$ in CHCl_3 , by activated AgCl , and into α -*penta-acetyl- α -glucoheptosidyl chloride*, m. p. 97° , $[\alpha]_D^{20} +95^\circ$ in CHCl_3 , by activated AgCl that had been kept some weeks; the α - is converted into the β -form by fresh activated AgCl . These α - and β -glucosides are converted by dry Ag_2O in MeOH into *penta-acetyl- β -*, m. p. 150° , $[\alpha]_D^{19} -28^\circ$ in COMe_2 , and α -*methyl- α -glucoheptosides*, m. p. 169° , $[\alpha]_D^{19} +91^\circ$ in CHCl_3 , respectively. These were also obtained by action of Ac_2O and pyridine on the corresponding methyl- α -glucoheptosides. A third cryst. " γ "- Ac_5 derivative, m. p. 112° , $[\alpha]_D^{19} +43^\circ$ in CHCl_3 , is obtained from β -penta-acetyl- α -glucoheptosidyl chloride, MeOH , and quinoline at 40° ; on hydrolysis with cold 0.1*N*- NaOH four Ac groups were readily removed, but the last was completely resistant. The structure (II) is therefore assigned (cf. A., 1930, 1024), and the name "*tetra-acetyl- α -glucoheptose 1:2-orthomethylacetate*" is suggested.

H. A. PIGGOTT.

Preparation of polysaccharide anhydrides. P. KARRER and H. FRIESE (Helv. Chim. Acta, 1931, 14, 1317—1318).—Hepta-acetylcellobiosidodimethylamine (A., 1929, 174) and MeI in MeOH give the corresponding quaternary iodide, converted by the method previously described (A., 1921, i, 766) into *cellobiose anhydride*.

H. BURTON.

Synthesis of a new disaccharide, neotrehalose. W. N. HAWORTH and W. J. HICKINBOTTOM (J.C.S., 1931, 2847—2850).—Interaction of 3:4:6-triacetylglucose 1:2-anhydride with 2:3:4:6-tetra-acetylglucose in at -100° gives



neotrehalose hepta-acetate, m. p. $155\text{--}156^\circ$, $(+1\text{H}_2\text{O})$ $122\text{--}130^\circ$ (rapidly heated), $[\alpha]_D^{20} +78^\circ$ in COMe_2 , converted by Ac_2O and pyridine into the Ac_8 derivative, m. p. $140\text{--}141^\circ$, $[\alpha]_D^{20} +90^\circ$ in C_6H_6 , and by NH_3 in EtOH into *neotrehalose* ($+1\text{H}_2\text{O}$), m. p. $210\text{--}220^\circ$ (decomp.) with previous sintering at $145\text{--}150^\circ$, $[\alpha]_D^{20} +95^\circ$ in H_2O ; this is hydrolysed to glucose by dil. HCl . The $\alpha\beta$ -structure (annexed formula) is assigned on the grounds of its synthesis, but it differs in $[\alpha]_D$ from the $\alpha\beta$ -neotrehalose previously described (A., 1928, 1224).

H. A. PRIGOTT.

Sweet principle of Kaa-he-e (*Stevia rebaudiana*, Berton). III. Steviol and isosteviol produced by hydrolysis with enzymes and acids, respectively. M. BRIDEL and R. LAVIEILLE (J. Pharm. Chim., 1931, [viii], 369—379; cf. A., 1931, 1100).—Hydrolysis of stevioside with hot 5% H_2SO_4 gives a phenol, *isosteviol*, $\text{C}_{26}\text{H}_{30}\text{O}_3$, m. p. 234° , $[\alpha]_D^{20} -78^\circ$, 24 in 95% EtOH , also obtained by treatment of the isomeric steviol with H_2SO_4 . *iso*Steviol is thus a secondary product; on treatment with KMnO_4 it gives a substance, m. p. 315° , in poor yield. Stevioside does not contain a free phenolic group.

R. S. CAHN.

Sugar-beet sapogenin. V. PRELOG (Chem. Listy, 1931, 25, 393—398).—This sapogenin possesses ethylenic linkings, not reducible by Na in BuOH , but giving a positive reaction with $\text{C}(\text{NO}_2)_4$, and a CO_2H group attached to a *tert.* C atom; decarboxylation with evolution of CO and CO_2 takes place at $80\text{--}130^\circ$ in the presence of conc. H_2SO_4 . A secondary OH group is present, and oxidation with CrO_3 yields a *keto-acid*, $\text{C}_{31}\text{H}_{48}\text{O}_3$, m. p. $160\text{--}200^\circ$ (*semicarbazone*, m. p. 270° ; *Me* ester, m. p. $184\text{--}185^\circ$, and its *semicarbazone*, m. p. 235°), which on further oxidation gives a *hydroxyketolactone*, $\text{C}_{31}\text{H}_{46}\text{O}_4$, m. p. 273° . It follows that beet sapogenin possesses two readily oxidisable *tert.*-C atoms, of which one is α and the other γ to the CO_2H group.

R. TRUSZKOWSKI.

Highly-polymerised compounds. LVI. Alterations of the micellar theory of Mayer. H. STAUDINGER (Ber., 1931, 64, [B], 2721—2724).—A reply to Mayer and Mark (A., 1931, 1276).

H. WREN.

Colloidal properties of starch as an expression of its constitution. M. SAMEC (Arh. Hemiju, 1931, 5, 265—280).—The physical properties of starch are profoundly affected by the presence of even such minimal quantities of protein as are usually present in it. The colorations given with *I* indicate that the surfaces of the mols. or mol. aggregates of amylo- and erythro-dextrins are different in type; this difference depends either on a

difference in the nature of the O linkings, or on a different mode of packing of the constituent mols.

R. TRUSZKOWSKI.

Products of diastatic hydrolysis of starch. A. TYCHOWSKI (Przemysł Chem., 1931, 15, 346—354).—Potato-starch treated with malt extract containing α - and β -diastase yields about 30% of a reducing dextrin not further acted on by α -diastatic barley extract, whilst by using warmed malt extract, possessing only β -diastatic properties, the product contains 90% of dextrans only to a small extent further acted on by α -diastase. The former dextrin is of homogeneous composition, and arises exclusively from amylopectin, whilst the latter is a mixture of this same dextrin with a second one derived from amylose; only the second form is acted on by barley extract. The above results indicate that potato-starch contains 30% of amylopectin and 70% of amylose.

R. TRUSZKOWSKI.

Hemicelluloses. II. Composition of hemicellulose from cotton-seed hulls. E. ANDERSON and S. KINSMAN (J. Biol. Chem., 1931, 94, 39—47).—Hydrolysis of the hemicellulose (cf. A., 1931, 884) with N -H₂SO₄ gives *l*-xylose (I) (74%), *d*-glycuronic acid (II) (9.7%), and an insol. substance (19%). The aldobionic acid (*loc. cit.*) is derived from 1 mol. of (I) and 1 mol. of (II). A partial structure is suggested for the hemicellulose.

H. BURTON.

Intermediate products in the formation of cellulose. M. LÜDTKE (Cellulosechem., 1931, 12, 307—310).—A lecture.

R. S. CAHN.

Acetolysis of cellulose. IV. Relation between cellulose and cellulose-dextrans. Preparation of crystalline cellulose acetate II. K. DZIENGEL, C. TROGUS, and K. HESS (Annalen, 1931, 491, 52—106).—The crude product (A) obtained by acetolysis of cellulose, using the method previously described (A., 1927, 44), but increasing the reaction time from 2.5 to 3 days, is separable into a MeOH-sol. fraction (B) (about 30%), m. p. 130—150°, $[\alpha]_D^{25} +4.7^\circ$ in CHCl₃, and a MeOH-insol. fraction, m. p. 255—265°, $[\alpha]_D^{25} -16.2^\circ$ in CHCl₃; the latter corresponds with biosan acetate (*loc. cit.*). Fractional pptn. of A in hot CHCl₃ with hot MeOH gives ultimately a product (C) (termed limit-dextrin acetate I) (after method I) with m. p. 290° (decomp.), $[\alpha]_D^{25} -18.8 \pm 0.1^\circ$ in CHCl₃, AcOH content 62.8 \pm 0.4%, which can be crystallised by concentrating a solution (0.3—1%) in MeOH-CHCl₃ (1:1) during 2—4 days at 58—64° (bath). Extraction of a crude product obtained when reaction is carried out during 2.5 days with hot MeOH containing increasing amounts (up to 30%) of CHCl₃ gives a residue which had const. similar to those of C but could not be crystallised. B is separable by pptn. with MeOH from a solution in MeOH-CHCl₃ into fractions with $[\alpha]_D^{25} -10.31^\circ$ to $+24.5^\circ$. Crystallisation of the fractions with $[\alpha]_D^{25} -3.3^\circ$ to $+3.6^\circ$ gives a product, $[\alpha]_D^{25} -14.6^\circ$, which after further fractionation ultimately affords a fraction resembling C. Crystallisation (as above) of dextrin acetates with $[\alpha]_D^{25} -8.8^\circ$ to -19° gives products which, without exception, show the same Röntgen diagram as cellulose acetate II (cf. A., 1930, 750), indicating that these products contain the same

cryst. substance admixed with differing proportions of an amorphous substance. The Röntgen diagrams of the materials obtained when fibrous cellulose acetate, C, and limit-dextrin acetate 2 (see below) are dissolved in Et malonate, MeOH-CHCl₃, and pyridine, respectively, and the solutions evaporated at various temp., show that transformation (cf. *loc. cit.*) of the diagrams for cellulose acetate I into those for cellulose acetate II occurs between 35° and 45°, 30° and 45°, and 60° and 75°, respectively. The Röntgen diagrams for various dextrin acetate fractions (obtained from A by method I) recovered from solutions in Et malonate at various temp. indicate the production of a substance (termed acetate III) at temp. of 60° (for fraction of $[\alpha]_D^{25} -10.8^\circ$) to 85° ($[\alpha]_D^{25} -17.7^\circ$); the change cellulose acetate II \rightarrow acetate III is not complete in the latter case even at 160°, and does not occur at any temp. with C or limit-dextrin acetate 2; the nearer is the rotation of the dextrin acetate fractions to that of cellulose acetate, the higher is the temp. of rearrangement. The Röntgen diagrams indicate that cellulose-dextrans contain two substances, one of which appears to be cellulose acetate II. Acetate III is considered to be an additive compound of cellulose acetate II and a substance formed during acetolysis, which is not a glucose acetate or cellobiose acetate, but may be an Ac derivative of the H₂O-sol. carbohydrate described by Klages (A., 1931, 827). The H₂O-insol. carbohydrate of Klages (*loc. cit.*) is readily acetylated by Ac₂O and KOAc; subsequent fractionation of the Ac derivative by method I gives ultimately limit-dextrin acetate 2, m. p. 288°, $[\alpha]_D^{25} -23.0^\circ$ in CHCl₃, AcOH content 62.6%, which can be crystallised (as above).

[By E. GARTHE.] The mol. wts. of limit-dextrin acetates 1 and 2 are 500—800 and 700—2400, respectively; the lower vals. are found with small concns. Similar variations are found for other fractions, and the average mol. wts. of fractions containing acetate III decrease with increase in its concn.

H. BURTON.

Optical rotation of cellulosic materials. II. Optical rotation of two fractions of alkali-soluble oxidised cellulose. T. F. MURRAY, jun., C. J. STAUD, and H. LEB. GRAY (J. Amer. Chem. Soc., 1931, 53, 4021—4028; cf. A., 1930, 750).—Oxidation of long-fibre cotton with KMnO₄ (available O=2 equivs. per C₆H₁₀O₅ group) in *N*-H₃PO₄ at 53° is apparently complete in 1 hr. (or less), as indicated by the wt. of oxidised cellulose (A) recovered, the amounts dissolved in 17.5% NaOH, the sp. rotations of the alkaline extracts, and the uniformity of the ratio of β - to γ -oxycellulose (approx. 1:4) in the alkali-sol. fraction of A. Removal of the β -oxycellulose approx. 2 hr. after acidification of the 17.5% NaOH extract of A with AcOH gives rather less material than after 15 hr. The sp. rotations of the γ -oxycellulose in neutral solutions are approx. $\frac{1}{2}$ to $\frac{3}{4}$ of those in 9% NaOH, whilst the sp. rotations of β - and γ -oxycelluloses are apparently equal (within experimental error) in the NaOH solutions used. C. J. WEST (b).

Replacement of copper in copper-ethylenediamine-cellulose solutions by cobalt. W. TRAUBE

and V. SCHENK-THIEKOTTER (Cellulosechem., 1931, 12, 301—307).—Cellulose-ethylenediamine-CuO solution does not react with Fe or Ni. Zn replaces the Cu and ppts. the cellulose. Co ppts. the Cu partly as Cu and partly as Cu_2O ; the cellulose is unchanged, but now readily pptd. by warming or acidification. Co exists in the solution as $[\text{Co en}_2]^{++}$, forming a salt or an alcoholate with the cellulose. In presence of air the colour of the solution changes from pink to claret, $[\text{Co en}_2]^{++}$ becomes $[\text{Co en}_2]^{+++}$, the viscosity falls greatly owing to induced oxidation of the cellulose, and the stability of the solution is greatly increased; acidification or warming slowly ppts. a mauve substance, approx. $\text{Co}, 1.5\text{—}2.0 \text{ en}_2, 3\text{C}_6\text{H}_{10}\text{O}_5$. R. S. CAHN.

Conversion of primary into secondary cellulose acetate. E. ELON and A. SCHRODT (Z. angew. Chem., 1931, 44, 933—935).—The reduced mol. wt. ($M_{\text{rel}}^p - K \times \eta_{\text{sp}}/c \times F_c$, where K =viscosity-mol. wt. const.= 6.25×10^2 , η_{sp} =sp. viscosity, c =concn., F_c = $288/M_{\text{rel}}$, 288 being the mol. wt. of the monomeric triacetate and M_{rel} its reduced mol. wt. calc. on the basis of the Ac content) of the polymeric primary (insol. in COMe_2) and secondary (sol. in COMe_2) cellulose acetates, determined by viscosity measurements, is approx. const., so that conversion of the primary into the secondary product (by heating with 95% AcOH at 100°) occurs without appreciable change in the degree of mol. aggregation. Moreover, when the true wt. of cellulose in either the primary (cellulose 39.4; AcOH 60.6%) or the secondary (cellulose 43.0; AcOH 57.0%) acetate is plotted against the viscosity of the sample all the points lie on the same curve. Hence the cellulose residue in both substances is identical. The change in properties on conversion depends only on the fission of AcOH, i.e., in the proportion of polar and non-polar groups in the mol. (cf. B., 1926, 188).

J. W. BAKER.

Formation of methylamines by catalytic dehydration of the system ammonia-methyl alcohol. E. BRINER and J. GANDILLON (Helv. Chim. Acta, 1931, 14, 1283—1307).—The effects of catalysts, temp., contact time, and composition of the gaseous mixture on the formation of NH_2Me , NHMe_2 , and NMe_3 from NH_3 and MeOH are studied. The effectiveness of the catalysts used decreases in the following order: Al_2O_3 , ThO_2 , SiO_2 gel, kaolin, blue W_2O_5 . With Al_2O_3 , the optimum temp. for conversion of MeOH into amines is 405° , whilst the no. of mols. of amines formed from 100 mols. of MeOH is a max. at 457° ; the majority of the experiments are, therefore, carried out at 430° . Decrease in the mol. ratio NH_3/MeOH for a fixed contact time causes an increase in the percentage of NH_3 converted into amines (and a corresponding decrease for MeOH) and inverts the proportions of NH_2Me and NMe_3 (higher with lower ratios) formed; the amount of NHMe_2 increases slightly. Diminished contact time increases the amount of NH_2Me at the expense of the NHMe_2 . The catalytic dehydration of the systems NH_2Me -MeOH and NHMe_2 -MeOH are studied briefly. The method used for the determination of mixtures of NH_3 , NH_2Me , NHMe_2 , and NMe_3 is a modification of Weber and Wilson's (A., 1918, ii, 377). NMe_3

reacts with HNO_2 at 100° (bath) but not in the cold; at 100° , the change $\text{NMe}_3 + \text{HNO}_2 \rightarrow \text{NO} \cdot \text{NMe}_2 + \text{MeOH}$ probably occurs. Modern theories of contact catalysis are also discussed. H. BURTON.

Decomposition of quaternary ammonium hydroxides. J. VON BRAUN and E. R. BUCHMAN (Ber., 1931, 64, [B], 2610—2617).—Examination of the decomp. of methylethyl-, ethyl-*n*-propyl-, methyl-*n*-butyl-, methyl-*n*-hexyl-, and methyl-*n*-octyl-piperidinium hydroxides in glycerol and by KOH confirms the previous theories (cf. A., 1929, 1046). The following compounds are incidentally described: methyl-*n*-butylpentenylamine, b. p. $74\text{—}76^\circ/20$ mm. (hygroscopic methiodide; picrate, m. p. 80°), hydrogenated to methyl-*n*-butyl-*n*-amylamine, b. p. 182° (picrate, m. p. 87° ; methiodide, m. p. 112°); 1-*n*-hexylpiperidine, b. p. $110^\circ/22$ mm. (hydrochloride, m. p. 200° ; picrate, m. p. 106° ; methiodide, m. p. 124°); methyl- Δ^5 -pentenyl-*n*-hexylamine, b. p. $108\text{—}109^\circ/21$ mm. (picrate, m. p. 61.5° ; non-cryst. methiodide), hydrogenated to methyl-*n*-amyl-*n*-hexylamine, b. p. $113\text{—}114^\circ/25$ mm. (picrate, m. p. 64° ; very hygroscopic methiodide); 1-*n*-octylpiperidine, b. p. $135^\circ/18$ mm. (hydrochloride, m. p. 189° ; picrate, m. p. 70° ; hygroscopic methiodide, m. p. 131°); methyl- Δ^5 -pentenyl-*n*-octylamine, b. p. $139\text{—}140^\circ/22$ mm. (non-cryst. picrate and methiodide; very hygroscopic hydrochloride), hydrogenated to methyl-*n*-amyl-*n*-octylamine, b. p. $132^\circ/15$ mm. H. WREN.

Quaternary ammonium salt in which the hydrogen is completely replaced by aldehydic residues. II. T. G. LEVI (Gazzetta, 1931, 61, 665—672; cf. A., 1930, 227).— CH_2O condenses with NH_4 salts of dithioacetic, dithiobenzoic, thioacetic, ethylxanthic, and butylxanthic acids, thiolbenzthiazole, and thiophenol giving corresponding quaternary dimethyleneammonium salts. The condensation occurs only with salts having the NH_4 group directly linked to S. E. E. J. MARLER.

Action of dilute formaldehyde solution on amino-acids. H. F. HOLDEN and M. FREEMAN (Austral. J. Exp. Biol., 1931, 8, 189—198).—Using the Van Slyke method for determining the decrease in $\text{NH}_2\text{-N}$, the rate of reaction of histidine, tyrosine, alanine, lysine, cystine, glycine, and glutamic acid (1%) in 0.1*N*-NaOH with 0.5% CH_2O at 37° decreases in the above order. In the above list, only histidine reacts in neutral solution. Very small changes in the optical rotations occur during the reactions. The course of the reactions of a proteose and a peptone is similar to, the rate less than, that of histidine, and the reaction with a metaprotein is reversible. The effect of change of p_{H} on the solubility of the isolated formolised tyrosine which contains neither free CH_2O nor $\text{NH}_2\text{-N}$ is described. Rise of temp. gives increased vals. in the Van Slyke determination of $\text{NH}_2\text{-N}$ in tyrosine. A. LAWSON.

Sarcosine anhydride and sarcosylsarcosine. F. SIGMUND and E. LIEDL (Z. physiol. Chem., 1931, 202, 268—280).—Sarcosine Et ester, b. p. $39\text{—}41^\circ/9$ mm., with H_2O , or better on heating in a sealed tube, yields sarcosine anhydride (I), m. p. $147\text{—}148^\circ$. (I) is hydrolysed by aq. NaOH or Ba(OH)_2 giving

sarcosylsarcosine (II), m. p. 184—185°. On heating (II) in vac., (I) sublimes. Carbomethoxymono- and -di- and chloroacetyl-sarcosylsarcosine are syrups; the β -naphthalenesulphonyl derivative is cryst., m. p. 173° (softens 167°). Disarcosylsarcosine and the ester of (II) could not be obtained.

J. H. BIRKINSHAW.

Preparation of iminodicarboxylic acids from amino-acids and halogeno-fatty acids. E. ABDERHALDEN and E. HAASE (Z. physiol. Chem., 1931, 202, 49—55).—*L*-(+)-Alanine and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ in presence of dil. NaOH or $\text{Ba}(\text{OH})_2$ yield iminoacetic- α -propionic acid, m. p. 220° (hydrochloride, decomp. 212°, $[\alpha]_{\text{D}}^{25} +1.4^\circ$; Cu salt). Similarly *dl*-valine gives *dl*-iminoacetic- α -isobutyric acid (hydrochloride), glycine and *L*-bromopropionic acid give *d*-(-)-iminoacetic-propionic acid (hydrochloride) $[\alpha]_{\text{D}}^{25} -2.2^\circ$, *L*-(+)-alanine and *L*-(-)- α -bromopropionic acid give $\alpha\alpha$ -iminodipropionic acid (hydrochloride, optically inactive).

J. H. BIRKINSHAW.

Action of mercuric salts on cystine. D. G. SIMONSEN (J. Biol. Chem., 1931, 94, 323—328).—When cystine is treated with HgSO_4 in dil. H_2SO_4 the reaction $3(\text{SR})_2 + 3\text{H}_2\text{O} \rightarrow \text{R}\cdot\text{SO}_3\text{H} + 5\text{SHR}$ (cf. A., 1931, 754, 1026) occurs to the extent of 75%; cysteic acid is isolated in 68% of the theoretical amount. The intermediate formation of a hydro-sulphoxylic acid is postulated.

H. BURTON.

Resolution of inactive cystine and isolation of *d*-cystine. L. HOLLANDER and V. DU VIGNEAUD (J. Biol. Chem., 1931, 94, 243—252).—Acetylation of inactive cystine, prepared by a slight modification of the method of Hoffman and Gortner (A., 1922, i, 429), with Ac_2O in aq. NaOH gives the Ac_2 derivative [*Et* ester, m. p. 122—123° (corr.)], resolved by brucine into the Ac_2 derivatives of *d*-, $[\alpha]_{\text{D}}^{25} +212^\circ$, and *L*-cystines; the presence of *d*-cystine in the original product is thus established. The *Et* ester, m. p. 124.5° (corr.), $[\alpha]_{\text{D}}^{25} -96^\circ$ in EtOH, and brucine salt, m. p. 148—150° (corr.), $[\alpha]_{\text{D}}^{25} -66^\circ$ in H_2O , of diacetyl-*L*-cystine, and the brucine salt, m. p. 162—164°, $[\alpha]_{\text{D}}^{25} +21^\circ$ in H_2O , of diacetyl-*d*-cystine are described.

H. BURTON.

Ketimine-enamine tautomerism. II, III. **Chemical and spectrochemical methods for the determination of structure.** K. VON AUWERS and H. WUNDERLING (Ber., 1931, 64, [B], 2748—2758, 2758—2767; cf. A., 1930, 897).—II. Spectrochemical data are recorded for Pr *n*-butyrate, *Et* diethyl-acetoacetate, *Et* diallylmalonate, Me and *Et* crotonate, *Et* β -ethoxycrotonate, *Et* acetoacetate, *Et* β -aminocrotonate, and *Et* β -piperidinocrotonate when homogeneous and dissolved, e.g., in MeOH, EtOH, hexane, 1-methylnaphthalene, COMe_2 , and AcOEt . The consts. of the first six compounds in 1-methylnaphthalene are almost without exception higher than those of the homogeneous materials, particularly with regard to dispersion, so that this solvent is less suitable for aliphatic than for aromatic compounds (cf. loc. cit.). The other solvents have little influence on the consts. of saturated substances. This is also the case for unsaturated compounds with *n*-hexane, whereas the alcohols behave similarly to 1-methylnaphthalene. *n*-Hexane is (spectroscopically) a strongly enolising

agent and is approached in this respect by 1-methylnaphthalene. With the amino- and piperidinocrotonates, the alcohols and COMe_2 , increase the already high sp. exaltation of refraction and dispersion, whereas the other solvents have feeble action. *n*-Hexane induces no trace of enolisation, thus confirming the conclusion that these compounds and their allies are homogeneous or nearly homogeneous enamines. Optical data are recorded for Me β -methylaminovinyl ketone, Me β -dimethylaminovinyl ketone, Me β -dimethylamino- α -methylvinyl ketone, Me β -piperidinovinyl ketone, 5-methoxy-2-methylphenyl α -amino- Δ^4 -propenyl ketone, and the corresponding 5-OH-compound. Spectrochemical observations are not generally suitable for investigation of possible tautomerism of substances of the type $\text{CH}_2\text{R}\cdot\text{C}(\text{NH})\cdot\text{CO}\cdot\text{R}'$ and $\text{CHR}\cdot\text{C}(\text{NH}_2)\cdot\text{CO}\cdot\text{R}'$. The compound considered by Mumm and Bergell (A., 1912, i, 936) to be the α -imide of *Et* acetylpyruvate is shown to be *Et* α -amino- β -acetylacrylate. It is considered that no tendency has been observed towards the formation of imines with the group $\text{O}:\text{C}:\text{C}:\text{C}:\text{N}$ —, but that enamines $\text{O}:\text{C}:\text{C}:\text{C}:\text{N}$ — occur in their stead. These compounds should therefore be designated and formulated uniformly as enamines.

III. Spectroscopic examination has been made of the following substances homogeneous or in quinoline: diaceto- and dipropio-nitrile; *Et* α -cyano- β -amino- γ -phenylcrotonate; β -amino- and β -diethylaminocinnamonnitrile; *Et* β -diethylaminocinnamate; *Et* 1:3-diamino- and 1:3-dihydroxy-2-naphthoate; 1-amino-2-cyanoindene; 1-cyano-2-hydroxy- and -2-methoxy-indene; 1-cyano-1-methylhydind-2-one; *Et* α -aminoglutaconate. According to spectroscopic

evidence the structure $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_2\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{CO}-\text{CH}\cdot\text{CO}_2\text{Et} \end{matrix}$ adopted

by Thorpe is untenable; the compound is a true naphthalene derivative and must be regarded as *Et* 1:3-dihydroxy-2-naphthoate. The colour is so slight that search for an alternative formulation is unnecessary. Similar observations apply to the

substance $\text{C}_6\text{H}_4\begin{matrix} \text{CH}_2-\text{C}\cdot\text{NH} \\ \diagdown \quad \diagup \\ \text{C}(\text{NH})\cdot\text{CH}\cdot\text{CO}_2\text{Et} \end{matrix}$ Thorpe's classi-

fication of substances into imines or compounds with longer imine phase, amines, and amines with short imine phase is not supported by optical evidence, and the compounds examined are to be regarded and designated uniformly as enamines. The difference in chemical behaviour of the individuals is not a consequence of different structure, but of influences attributable to the substituents.

H. WREN.

Reductions with lead-sodium [alloys]. II. A. GOLDACH (Helv. Chim. Acta, 1931, 14, 1436—1444).—Investigation of the Pb compounds formed during the reduction of COMe_2 with a Pb-Na alloy (A., 1931, 1274) shows the presence of Pb tri- and tetra-*iso*-propyls.

H. BURTON.

Reactions catalysed by metallic halides. I. **Action of aluminium chloride on halogen compounds in presence of cycloparaffins.** C. D. NENITZESCU and C. N. IONESCU. II. **Mechanism of the Friedel-Crafts reaction.** C. D. NENITZESCU, D. A. ISACESCU, and C. N. IONESCU (Annalen, 1931, 491, 189—210, 210—220).—I. *cyclo*Hexyl chloride (I)

(365 g.) is stirred with a mixture of AlCl_3 (400 g.) and cyclohexane (II) (1300 c.c.) at room temp.; after 3 days the reaction mixture has separated into two layers and 96% of the theoretical amount of HCl has been evolved. The top layer consists of (II) and a mixture of saturated hydrocarbons, separable into fractions of b. p. 200—230° (*A*; 190 g.) and b. p. 178—186°/23 mm. (*B*; 63 g.). *A* affords a mixture (*C*) of hydrocarbons, $\text{C}_{12}\text{H}_{22}$, b. p. 213—215°/755 mm., separable by cooling in Et_2O and CO_2 into solid, m. p. 46·5°, and liquid, b. p. 212°/757 mm., constituents; *C* is not dehydrogenated with Pt-asbestos at 300—308° and may contain 2:2'-dimethyldicyclopentyl. When *B* is kept, a small amount of a hydrocarbon, m. p. 216°, having the same composition ($\text{C}_{18}\text{H}_{32}$) as *B*, separates. The bottom layer contains all the *Al* and after decomp. with ice gives a mixture (75 g.) of unsaturated hydrocarbons, probably formed by polymerisation of the intermediate cyclohexene, arising (by loss of HCl) from (I). Mixtures of *B* and *C* (in varying proportions) are also formed from (II), AlCl_3 , and EtBr , PrCl , Pr^nCl , Bu^nCl , CHCl_3 , CCl_4 , AcCl , PrCOCl , and BzCl ; the inactive halides (CHCl_3 , CCl_4) give *C* only. *B* and *C* are not formed from (II) and AlCl_3 alone or in presence of HCl , PhNO_2 , or olefines; the chlorides are probably H acceptors in processes involving dehydrogenation of (II). A hydrocarbon, $\text{C}_{14}\text{H}_{26}$, b. p. 237—239°, is formed from (I), AlCl_3 , and methylcyclohexane, whilst S-containing compounds are produced from (I) and AlCl_3 in CS_2 . AcCl , (II), and AlCl_3 also give 2-methylcyclopentyl Me ketone (semicarbazone, m. p. 158°) (isolated from the bottom layer of the reaction mixture), oxidised by alkaline NaOBr to 2-methylcyclopentanecarboxylic acid, b. p. 113°/13 mm. [chloride (III), b. p. 171—172°/758 mm.; amide, m. p. 147—148°]. The acid isolated from Russian petroleum by Aschan (A., 1890, 737) and by Markownikoff (A., 1899, i, 800) is probably 1-methylcyclopentane-1-carboxylic acid. 2-Methylcyclopentyl *Pr* ketone, b. p. 75—80°/9 mm. (semicarbazone, m. p. 112°), is similarly obtained using PrCOCl . Decomp. of the lower layer from (II), BzCl , and AlCl_3 gives PhCHO (probably formed by reduction of BzCl), a small amount of a substance, not melted at 200°, and *Ph* 2-methylcyclopentyl ketone, b. p. 160—162°/36 mm. (oxime, m. p. 110°; semicarbazone, m. p. 104—106°), also prepared from (III), C_6H_6 , and AlCl_3 .

II. CH_2PhCl heated with Ph_2 , C_{10}H_8 , PhOMe , and mesitylene gives 4-benzylidiphenyl, 1-benzyl naphthalene, *p*-methoxydiphenylmethane, and 2:4:6-trimethyldiphenylmethane, respectively. Similarly, BzCl and Ph_2 , C_{10}H_8 , and anthracene (in presence of PhNO_2) give *Ph* *p*-diphenyl ketone, *Ph* α -naphthyl ketone, and 9-benzoylanthracene (almost quant. yield), respectively. Similar condensations could not be effected between these chlorides and C_6H_6 . AlCl_3 appears to be a good catalyst for reactions similar to the above. Styrene and AlCl_3 in a large excess of C_6H_6 at room temp. give a little CHMePh_2 and much polystyrene. Styrene is not an intermediate in the reaction between $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Cl}$, C_6H_6 , and AlCl_3 ; dibenzyl is isolated in 85% yield. H. BURTON.

Action of aluminium chloride on benzylidene and benzyl chlorides. E. WERTPOROCH and A.

FARNIK (Annalen, 1931, 491, 265—273).— CHPhCl_2 (320 g.) and AlCl_3 (4 g.) at -15° after 2 hr. stirring give a little (4·2 g. of crude) chloro-*m*-dichloromethyl-diphenylmethane (I), b. p. 165°/0·11 mm., 212° (slight decomp.)/13 mm., hydrolysed by H_2O and CaO at 160° to dimeric *m*-aldehydobenzhydrol (unimol. phenylhydrazones, formed in hot AcOH), oxidised by CrO_3 in $\text{AcOH}-\text{H}_2\text{SO}_4$ to *m*-benzoylbenzoic acid (II), also obtained by similar oxidation of (I). (I) is reduced by red *P* and *HI* (*d* 1·7) at 140° to phenyl-*m*-tolymethane [also formed by similar reduction of dichloro-*m*-trichloromethyldiphenylmethane (A., 1930, 1028)], also oxidised to (II). CH_2PhCl (126 g.) and AlCl_3 (2 g.) in PhNO_2 (500 g.) similarly give a mixture (4 g.), b. p. 139°/0·14 mm., of *o*- and *p*-chloromethyldiphenylmethanes, oxidised directly (or after conversion into the corresponding alcohols) to a mixture of *o*- and *p*-benzoylbenzoic acids. H. BURTON.

Nitration of benzyl chloride. T. VAN DER LINDEN (Rec. trav. chim., 1931, 50, 1105—1110).—Nitration of CH_2PhCl gives 15·3% of the *m*-isomeride (cf. A., 1928, 747). R. S. CAHN.

Tetraphenyldi-*tert*-butylethynylethane. J. G. STAMPELL and C. S. MARVEL (J. Amer. Chem. Soc., 1931, 53, 4057—4065).—Tetraphenyldi-*tert*-butylethynylethane (I), m. p. (tube) 120—125°, m. p. (block) 141—142°, is obtained when diphenyl-*tert*-butylethynylmethyl bromide (II) is treated with 40% $\text{Na}-\text{Hg}$ in Et_2O and the resultant solution then treated with a 10% solution of $(\text{CMe}_2\text{Br})_2$ in Et_2O . When (I) is heated slowly it rearranges to the hydrocarbon (III), $\text{C}_{38}\text{H}_{38}$, previously obtained (A., 1928, 1365) from (II) and Ag . (I) absorbs O_2 rapidly but a cryst. peroxide could not be isolated; (I) also absorbs Br in CCl_4 , whilst (III) does not. (I) is also isomerised to (III) when heated in heptane or COMe_2 or when dissolved in Et_2O at room temp. Diphenyl-*tert*-butylethynylacetic acid, m. p. 171—172°, is obtained from (II), Mg , and CO_2 or from Na diphenyl-*tert*-butylethynylmethyl (IV), prepared by the action of 40% $\text{Na}-\text{Hg}$ on (I) or (II). (IV) is hydrolysed by H_2O to the methane derivative, which, when distilled, isomerises to α -diphenyl- δ -dimethyl- Δ^2 -pentadiene, b. p. 115—118°/0·55 mm.; a dimeride, m. p. 178·8—179·8°, is also formed. The pentadiene is oxidised by O_3 to COPH_2 and $\text{CMe}_3\text{CO}_2\text{H}$. The Na derivative from (III) and H_2O gives a compound, $\text{C}_{38}\text{H}_{40}$ (?), m. p. 162·8—163·8°, which decolorises Br .

C. J. WEST (b).

Reaction between halogenoacetanilides and phenylhydrazine. W. RENNER (J. pr. Chem., 1931, [ii], 131, 342—345; cf. A., 1895, i, 521; Ber., 1894, 28, Ref., 130).—Both bromo- and chloro-acetanilides react with $\text{NHPh}\cdot\text{NH}_2$ to give mainly α -, m. p. 149° (A., 1895, i, 521), with some β -phenylhydrazinoacetanilide, m. p. 137°. The latter is identified by its oxidation by yellow HgO in EtOH to glyoxylanilide-phenylhydrazones, (I), m. p. 171°; hitherto it has been erroneously described as (I) (*loc. cit.*).

H. A. PIGGOTT.

Reduction of dinitro-compounds with alkali sulphides. Preparation of *m*-nitroaniline. I. I. VORONTZOV (J. Chem. Ind., Russia, 1930, 7, 2145—2147).—The yield (80%) of *m*-nitroaniline from

m-dinitrobenzene is improved by addition of NaHCO_3 . A procedure is described. CHEMICAL ABSTRACTS.

Optical activity of phenylethylamine. Correction. E. OTT (Annalen, 1931, 491, 287—289).—When optically active α -phenylethylamine (I) contains a small amount of its methylol compound [from (I) and CH_2O], its rotation is much increased; distillation of such a mixture gives a product still contaminated with CH_2O and thus possessing a high rotation. The high rotation of the "residual amine" previously obtained (A., 1931, 1050) from (I) is due to contamination with CH_2O , which is present in small amount in the Et_2O used for extraction.

H. BURTON.

Preparation of methyl derivatives of α - and β -naphthylamine. V. M. RODIONOV and V. E. VEDENSKI (J. Chem. Ind., Russia, 1930, 7, 11—16).—Me *p*-toluenesulphonate (33 g.) when heated with β -naphthylamine (25 g.) yields β -naphthylamine sulphate (13.5 g.), β -naphthyldimethylamine (7 g.), and (by acetylation) β -naphthylacetmethylamide (13 g.); the reactants in the ratio 3:1 afford 80% of β -naphthyldimethylamine. β -Naphthyltrimethylammonium *p*-toluenesulphonate, m. p. 241—242°, gives with KI a methiodide, $\text{C}_{13}\text{H}_{19}\text{NI}$, m. p. 189—190°. Diazotised sulphanilic acid and α -naphthyldimethylamine yield a dye, $\text{C}_{10}\text{H}_6(\text{NMe}_2)\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ (1:4) (red on wool in acid bath); $\text{C}_{10}\text{H}_6(\text{NMe}_2)\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{SO}_3\text{Na}$ (from *p*-nitroaniline-*o*-sulphonic acid) dyes wool violet in an acid bath. CHEMICAL ABSTRACTS.

Action of phenylmethylhydrazine on dithioacids. H. WUYTS and M. GOLDSTEIN (Bull. Soc. chim. Belg., 1931, 40, 497—503).—As with $\text{NH}_2\cdot\text{NHPh}$ (A., 1930, 453), dithiocarboxylic acids in which the $\cdot\text{CS}_2\text{H}$ group is not attached to an aromatic nucleus react with $\text{NH}_2\cdot\text{NPhMe}$ in Et_2O to form thiohydrazides $\text{RCS}\cdot\text{NH}\cdot\text{NPhMe}$ and thus are obtained the *as-phenylmethylhydrazides* of dithiophenylacetic, m. p. 80—81°, dithio-*n*-valeric, m. p. 122—123°, and dithiocyclohexoic, m. p. 100—107°, acids. When the $\cdot\text{CS}_2\text{H}$ group is directly attached to an aromatic nucleus the sole product is the hydrazone $\text{CHR}\cdot\text{N}\cdot\text{NPhMe}$, dithio-benzoic, -*p*- and -*o*-toluic, and - α -naphthoic acids giving the phenylmethylhydrazone of PhCHO , *p*- and -*o*- (accompanied by *o*-toluthioaldehyde, which distilled with Cu powder affords *oo'*-dimethylstilbene) tolualdehyde, and α -naphthaldehyde, respectively. At -15° the initial salts were isolated in several cases.

J. W. BAKER.

Basic properties of hydrazones. IV. R. CIUSA and G. OTTOLINO (Gazzetta, 1931, 61, 729—732; cf. A., 1931, 957).—The green resin, m. p. 235°, obtained by the action of gaseous HCl and air on benzaldehydephenylhydrazone or dibenzylidene-*pp'*-dihydrazinotriphenylmethane or by boiling benzaldehydephenylhydrazone with HCl and PhCHO is $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{HCl})\cdot\text{N}\cdot\text{CHPh}$. Benzaldehydephenylmethylhydrazone (2 mols.) and PhCHO (1 mol.) on boiling with conc. HCl in presence of air give a green compound, m. p. 170°, probably $\text{CHPh}\cdot\text{N}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{NMeCl}\cdot\text{N}\cdot\text{CHPh}$.

E. E. J. MARLER.

Hypothesis of deformation of tervalent nitrogen. W. SWIENTOSLAWSKI (Annalen, 1931, 491, 273—283).—A reply to Meisenheimer and Theilecker (A., 1929, 566) and Hantzsch (A., 1930, 1032); the author's deformation hypothesis is defended.

H. BURTON.

Hypothesis of deformation of nitrogen in oximes and diazo-hydrates. A. HANTZSCH (Annalen, 1931, 491, 284—287).—Various points discussed by Swientoslawski (see preceding abstract) are criticised. The deformation hypothesis does not give conclusive results.

H. BURTON.

Action of dehydrating catalysts in the cracking and hydrogenation of phenols. A. KLING and D. FLORENTIN (Compt. rend., 1931, 193, 859—860; cf. A., 1926, 381).— PhOH at 470 — 480° in H_2 at 200 atm., in presence of a dehydrating catalyst (Al_2O_3 , ThO_2 , Cr_2O_3) yields a considerable amount of C_6H_6 . The activity of such catalysts is greatly increased by previous heating to about 750° , e.g., Al_2O_3 dried at 150° in 4 hr. at 485° converted 45% of PhOH into C_6H_6 ; when previously heated to 750° it yielded 75%. Mo_2O_5 prepared at a low temp. yields mainly cyclohexane and hexane, when prepared at a high temp. C_6H_6 is the chief product. It is recommended that PhOH be heated with such a catalyst with about 9% (by wt.) of H_2 , at about 300 kg. per sq. cm. and 485° for times varying from 0.5 hr. (with Mo_2O_5) to 3 hr. (with Al_2O_3).

C. A. SILBERRAD.

Nitration in presence of mercury salts. A. I. ZAKHAROV (J. Chem. Ind., Russia, 1931, 8, 30—37).—The formation of dinitrophenols from C_6H_6 is an oxidising function of dil. HNO_3 , and not the result of catalytic action by $\text{Hg}(\text{NO}_3)_2$. Nitration of C_6H_6 with 10% excess of 60% HNO_3 and 4—5% $\text{Hg}(\text{NO}_3)_2$ at 60 — 65° affords mainly PhNO_2 and 15—20% of $\text{C}_6\text{H}_4(\text{NO}_2)_2$, whilst at 20 — 25° for 5—6 hr. and then at 60 — 65° it affords 7—8% and 70—75%, respectively. Formation of OH-compounds is typical of C_6H_6 and its homologues, but not of its derivatives. C_{10}H_8 , anthracene, and naphthol afford only NO_2 -derivatives; PhOH , even with 10—20% $\text{Hg}(\text{NO}_3)_2$, also does not give $(\text{NO}_2)_2$ -derivatives. Salicylic acid gives the 4- and 6- NO_2 -derivatives (5:1). Treatment of C_{10}H_8 in CCl_4 with N_2O_4 in presence of $\text{Hg}(\text{NO}_3)_2$ gives the 1:8- $(\text{NO}_2)_2$ -derivative (65—70%; subsequently 90%); in CHCl_3 the $(\text{NO}_2)_3$ -derivative (73—75%) is obtained. CHEMICAL ABSTRACTS.

Halogenation of phenolic ethers and anilides.

II. A. E. BRADFIELD and B. JONES. III. A. E. BRADFIELD, W. O. JONES, and F. SPENCER.—See this vol., 26.

Migration of acyl groups in *o*-aminophenols.

II. F. BELL (J.C.S., 1931, 2962—2967).—Acetylation of 2-benzamidophenol affords 2-acetamidophenyl benzoate (I), m. p. about 140° , and benzylation of 2-acetamidophenol gives 2-benzamidophenyl acetate (II), m. p. about 140° (cf. Raiford, A., 1920, i, 156); (II) is converted into (I) when molten, (I) remaining unchanged. 2-Acetamidophenyl α -naphthoate and 2- α -naphthamidophenyl acetate are interconvertible; 2- α -naphthamidophenyl benzoate and 2-benzamidophenyl α -naphthoate are unchanged after melting,

but each is converted into 2- α -naphthamidophenol on alkaline hydrolysis. 3-Acetamidophenyl benzoate, m. p. 140°, is hydrolysed to 3-acetamidophenol, no migration occurring. 3-Acetamidophenol α -naphthoate, m. p. 153°, and β -naphthoate, m. p. 141°, are hydrolysed by warm NaOH to *m*-aminophenol. It is suggested that hydrolytic migration involves the intermediate formation of a benzoxazole and depends on the arrangement of the NH₂ and OH groups in space. A theory based on electronic conceptions is advanced to account for the diverse ways in which the benzoxazole breaks down under the hydrolytic action of alkalis.

F. R. SHAW.

Interaction of amines and phenols with arylsulphonyl chlorides. F. BELL (Analyst, 1931, 56, 802—804).—As a rule *p*-toluene- and *m*-nitrobenzenesulphonyl chlorides give sharply melting, easily crystalline sulphonanilides and sulphonates with arylamines and phenols. Polynitroamines may be recovered unchanged, *o*-nitroamines may form mixtures of mono- and di-sulphonanilides, and halogens present in the nucleus diminish the reaction velocity and render the process unsuitable for characterisation. Nitroaminophenols are best characterised by the prep. of acetamidophenols.

T. McLACHLAN.

Primary additive products in indirect substitution in the benzene nucleus. IV. J. VAN ALPHEN (Rec. trav. chim., 1931, 50, 1111—1116; cf. A., 1931, 954).—The presence of alkoxy-groups in the 4 and 4' positions is necessary for the formation of additive products of Ph₂ derivatives and HNO₃, and other substituents must be absent. The following Ph₂ derivatives do not form such additive compounds: 4-OH-; 4-OMe-, m. p. 88° (lit. 90°); 4-iodo-4'-hydroxy- (from diazotised 4-iodo-4'-aminodiphenyl), m. p. 193° (*Ac* derivative, m. p. 150°; *Me* ether, m. p. 183°); 4:4'-I₂-; 4:4'-Me₂-; 3:3'-Me₂-; 2:2'-Me₂- (from *o*-iodoanisole or 2:2'-dihydroxydiphenyl); 2:2'-dinitro-4:4'-diethoxy- (from *p*-iodo-*m*-nitrophenetole), m. p. 113.5°.

R. S. CAHN.

Reaction between phenylcarbimide and ω -anilino-phenyl-1- β -hydroxynaphthylmethane. A. NERI (Gazzetta, 1931, 61, 681—684; cf. A., 1901, i, 81).— ω -Anilino-phenyl-1- β -hydroxynaphthylmethane reacts with PhNCO to give *s*-diphenyl(phenyl-1- β -hydroxynaphthylmethyl)carbamide, NHPH·CO·NPh·CHPh·C₁₀H₆·OH, m. p. 118°, which when boiled with HCl gives PhCHO, *s*-diphenylcarbamide, and anhydrophenyldi- β -hydroxynaphthylmethane, CHPh(C₁₀H₆)₂O (A., 1887, 494).

E. E. J. MARLER.

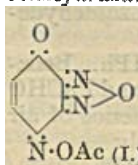
***o*-Alkoxybenzhydramines possessing local anæsthetic powers.** (MLE.) Y. BONNARD and J. M. OULIF (Bull. Soc. chim., 1931, [iv], 49, 1303—1309).—Eight *o*-alkoxybenzhydramines, RO·C₆H₄·CHPh·NH₂, where R = Me, Et, Prⁿ, Prⁱ, Bu, Bu^s, heptyl, and CH₂Ph, have been obtained by reducing the oximes of the corresponding benzophenones with Na-Hg or Na and EtOH. The benzophenones were obtained by alkylation of *o*-hydroxybenzophenone (yield 80—88%), prepared in 30—40% yield by demethylation of *o*-methoxybenzophenone with 48% HBr. The anæsthetic power of the amines and their hydrochlorides for the cornea of rabbits

increases with mol. wt. of the alkyl group up to C₄. The anæsthetic power for the lingual nerve of the dog is a max. when R = Et and then decreases regularly to R = heptyl. The following are described: *o*-methoxy-, m. p. 39°, b. p. 210°/27 mm. (oximes, m. p. 150° and 130°); *o*-ethoxy-, m. p. 40°, b. p. 199°/20 mm. (oxime, m. p. 159°; semicarbazone, m. p. 159—160°); *o*-propoxy-, b. p. 204°/20 mm. (oxime, m. p. 114°; semicarbazone, m. p. 110°); *o*-isopropoxy-, b. p. 193°/14 mm. (oxime, m. p. 111°); *o*-butoxy-, b. p. 205°/19 mm. (oxime, m. p. 69°; semicarbazone, m. p. 113—114°); *o*-isobutoxy-, b. p. 193°/144 mm. (oxime, m. p. 64°; semicarbazone, m. p. 114—115°); *o*-heptoxy-, b. p. 208°/21 mm. (oxime, m. p. 175°; semicarbazone, m. p. 175°), and *o*-benzyloxy-benzophenone, m. p. 62°, b. p. 264°/20 mm. (oxime, m. p. 96°; semicarbazone, m. p. 60°). *o*-Methoxybenzhydramine has b. p. 185—187°/23 mm. (hydrochloride, m. p. 250°); *o*-ethoxy- (hydrochloride, m. p. 245°; tartrate, m. p. 90°; acetate, m. p. 135°), *o*-propoxy-, b. p. 180°/19 mm. (hydrochloride, m. p. 240—250°), *o*-isopropoxy-, b. p. 188°/18 mm. (hydrochloride, m. p. 255—260°); *o*-butoxy-, m. p. 199°/21 mm. (hydrochloride, m. p. 250°); *o*-isobutoxy-, b. p. 195°/18 mm., m. p. 265°; *o*-heptoxy-, b. p. 187°/19 mm. (hydrochloride, m. p. 254°), and *o*-benzyloxy-benzhydramine, b. p. 150°/19 mm. (hydrochloride, m. p. 188°), are also described.

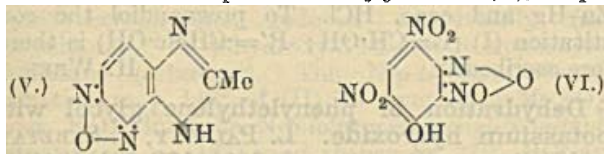
R. BRIGHTMAN.

Tetranitrosopyrocatechol and derivatives. J. FREJKA, J. ŽIKÁ, and H. HAMERSKY (Coll. Czech. Chem. Comm., 1931, 3, 550—560).—Nitrosation of pyrocatechol in aq. AcOH gives tetranitrosopyrocatechol [the salts NaHA, PbA, CdH₂A₂, CaH₂A₂, BaH₂A₂ (A = C₆O₆N₄), and also NH₄, Ag, and Cu salts, and the Ac₂ and Bz₂ derivatives are described]. The free acid and many of its salts are explosive. It is reduced by Sn and HCl to tetra-aminopyrocatechol (hydrochloride; sulphate). H. A. PIGGOTT.

Nitrosoresorcinol and related tetraketocyclohexene oximes. W. BORSCHKE and H. WEBER (Annalen, 1931, 489, 270—295).—The Ac₂, m. p. 120°, and Bz₂, m. p. 150—151°, derivatives of nitrosoresorcinol, and the Ac₃, m. p. 119—120°, and Bz₂, m. p. 182—184°, derivatives of dinitrosoresorcinol, are described. Oximation of dinitrosoresorcinol gives an inseparable mixture (A+B) of trioximinocyclohexenones [Na₂H₂O, and Na₃H₂O salts; Ac₃, m. p. 118—162° (Ac₂O in the cold), and Bz₃, m. p. 184° (BzCl and Na₃ compound), derivatives] both in acid and alkaline solutions (cf. A., 1897, i, 218); only by prolonged action of NH₂OH·HCl in acid solution at 100° could the tetraoxime, decomp. 210°, be obtained. By heating the Ac₃ derivatives (A+B) with MeOH or Ac₂O a mixture of the two possible acetylbenzofurazan-quinonemonoximes (C) results, from which acetylbenzofurazan-4:7-quinone-7-oxime (I), m. p. 142—143° (decomp.) (Ac-free oxime, m. p. 172°), can be isolated. The Ac₄ derivative, m. p. 178—179°, of the tetraoxime (Ac₂O at 0°) is dehydrated by Ac₂O at the b. p. to diacetylbenzofurazan-4:7-quinonedioxime (II), m. p. 178° (or 188°?) [hydrolysed by dil. NaOH at room temp. to the dioxime (III), m. p. 225—226°], and

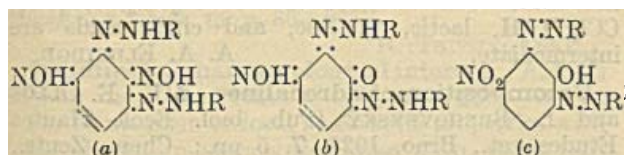


a little benzodifurazan. Oximation of (C) and acetylation of the mixture gives (II) and vic-benzodifurazan (IV), m. p. 62°. Reduction of (III) with H_2 and Pd at 160°/1 atm. yields 4:7-diaminobenzofurazan, m. p. 193—194° (Ac_2 derivative, decomp. 320°); (IV) similarly gives 4:5-diaminobenzofurazan, m. p. 151° [Ac_2 derivative, m. p. 217—218°, converted by MeOH and HCl at the b. p. into the glyoxaline (V), m. p.



285° (decomp.). Oxidation of (A+B) with HNO_3 gives, not 2:3:4:6-tetranitrophenol (*loc. cit.*), but 4:6-dinitro-7-hydroxybenzofuroxan (VI), m. p. 145—146° ($+C_6H_9$, m. p. 132—133°; *K*, pyridine, m. p. 215°, and $NPhEt_2$, m. p. 176°, salts); similarly, (C) gives 4:6-dinitro-7-hydroxybenzofurazan, m. p. 156° (decomp.) (*K*, pyridine, m. p. 182—184°, and NEt_2Ph , m. p. 158°, salts). Oxidation of the tetraoxime or of (III) (?) with HNO_3 (*d* 1.4) gives 4:7-dinitrobenzofuroxan, m. p. 182°.

Nitrosoresorcinol gives a 2:4-dinitrophenylhydrazone, m. p. 205° (by reaction in the quinoneoxime form), converted by HNO_3 in AcOH into 2:4:2':4'-tetranitro-5-hydroxyazobenzene, m. p. 228—229°. Dinutrosoresorcinol gives dihydrazones of type (a) with 2:4-dinitrophenylhydrazine and of type (b) with *o*- and *p*-nitrophenylhydrazines; both are converted into azo-compounds (c) by HNO_3 . The *di-p*-, m. p.



272°, and *di-o*-, m. p. 273°, -nitrophenylhydrazones of type (b), the bis-2:4-dinitrophenylhydrazones, type (a), m. p. 266°, 2:6(?) -dinitrodi-(*o*-nitrobenzeneazo)-, m. p. 264° (decomp.), 2:6-dinitrodi-(*p*-nitrobenzeneazo)-, m. p. 325°, and 2:6-(?) -dinitrobis-(2:4-dinitrobenzeneazo)-phenol, m. p. 172°, are described. The nitrophenylhydrazones of (A+B) are oxidised by HNO_3 to nitrobenzeneazo-derivatives of 7- or 5-nitrobenzofurazan. The *o*-nitrophenylhydrazone, m. p. 210—211° (oxidation product, m. p. 197—198°), *p*-nitrophenylhydrazone, m. p. 220—222° (oxidation product, m. p. 243—244°), and 2:4-dinitrophenylhydrazone, m. p. 226° (oxidation products, m. p. 192° and 212°), of the trioxime (A+B) are described.

Interaction of 2:3:4:6-tetranitrophenol with $NPhEt_2$ and *p*-toluenesulphonyl chloride gives 2:3:4:6-tetranitrodiphenyldiethylammonium chloride, m. p. 125—126°, and with pyridine an additive compound, decomp. 310°. H. A. PIGGOTT.

Catalytic hydrogenation under pressure of 4:4'-dihydroxydiphenylmethane. J. VON BRAUN and G. IRMISCH (Ber., 1931, 64, [B], 2621—2629).—Catalytic hydrogenation under pressure of 4:4'-dihydroxydiphenylmethane in presence of Ni with or without Mn or Co or Fe affords 4:4'-dihydroxydicyclohexylmethane, m. p. 123—127° (Ac_2 derivative

m. p. about 80°), in almost quant. yield; formation of cyclohexanol or 4-methylcyclohexanol could not be detected. The compound is oxidised by CrO_3 to the corresponding diketone, $C_{13}H_{20}O_2$, m. p. 94—95° (oxime, m. p. 202—203°; semicarbazone, m. p. 243°; phenylhydrazone, transformed by short treatment with dil. H_2SO_4 into methylenebis-tetrahydrocarbazole, m. p. 85—95°). Oxidation of the diol with hot conc. HNO_3 gives methylene- $\beta\beta'$ -diadipic acid, $CH_2[CH(CH_2\cdot CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H]_2$, m. p. 185—187°, in 30% yield (Et_4 ester, b. p. 205°/0.1 mm.). Treatment of the acid in conc. H_2SO_4 with N_3H in $CHCl_3$ at 30° yields methylene- $\beta\beta'$ -ditetramethylene-diamine, $CH_2[CH(CH_2\cdot NH_2)\cdot CH_2\cdot CH_2\cdot NH_2]_2$, isolated as the Bz_4 derivative, m. p. 225°, and converted by successive treatment with alkali and Me_2SO_4 , KI, AgCl, and $PtCl_4$ into the chloroplatinate, $C_{21}H_{12}N_4Cl_{12}Pt$, m. p. 270—272°. Et methylene-diadipate is converted by Na wire and a little $EtOH$ at 100—120° into *Et* methylenediketopentamethylene-carboxylate, $CH_2(CH<\frac{CH_2\cdot CH\cdot CO_2Et}{CH_2\cdot CO})_2$, transformed

by boiling 2*N*- H_2SO_4 into methylene-3:3'-dicyclopentanone, m. p. 63—64°, b. p. 150—160°/0.2 mm. (slight decomp.) (semicarbazone, m. p. 258°). $\alpha\alpha$ -Di-4-hydroxycyclohexylethane is not smoothly oxidised by HNO_3 to the corresponding tetracarboxylic acid, the esterified product corresponding more closely with the diglutaric ester, $CHMe[CH(CH_2\cdot CO_2Et)\cdot CH_2\cdot CO_2Et]_2$. The corresponding diketone is oxidised with loss of C.

[With G. MANZ.] 4:4'-Dihydroxytriphenylmethane is readily hydrogenated at 220—230° to phenyldi-4-hydroxycyclohexylmethane, b. p. 225—230°/0.1 mm., transformed by CrO_3 in AcOH into the corresponding diketone, $C_{19}H_{24}O_2$, m. p. 125°, b. p. 210—220°/0.5 mm. (semicarbazone, m. p. 195—197°; non-cryst. oxime). 1:1'-Di-4-hydroxyphenylcyclohexane is reduced to a mixture of stereoisomeric 1:1-di-4-hydroxycyclohexylcyclohexanes, m. p. 165—170° (non-cryst. Ac derivative, b. p. about 200°/0.1 mm.), oxidised by CrO_3 in AcOH to the diketone, $C_{18}H_{22}O_2$, m. p. 166° (semicarbazone, m. p. 239°; oxime, m. p. 196°). The two diols last described are oxidised by HNO_3 beyond the adipic acid stage. H. WREN.

Action of cyanogen bromide on ethers of phenols. G. BARGELLINI and F. MADESANI (Gazzetta, 1931, 61, 684—694).—CNBr reacts in presence of $AlCl_3$ with hydroxyquinol trimethyl ether, giving cyano-2:4:5-trimethoxybenzene, m. p. 112—114°, and 1-bromo-2:4:5-trimethoxybenzene; with 1:2:3:5-tetramethoxybenzene giving a *Br*- (m. p. 72—74°) and a *CN*- (m. p. 114°) derivative (tetramethoxybenzoic acid, m. p. 149—150°); with thymol Me ether, giving a mixture containing small amounts of a *Br*-derivative and yielding on hydrolysis the amide of methyl-*p*-thymotic acid, m. p. 160°, and with veratrole, giving 4-bromoveratrole and cyanoveratrole. Karrer (A., 1919, i, 591; 1920, i, 389) obtained only nitriles by this method. E. E. J. MARLER.

Substituted phenylstyrylcarbinols. H. WILLSTAEDT (Ber., 1931, 64, [B], 2693—2695).—Under very mild conditions cinnamaldehyde is converted by Mg *p*-anisyl bromide in Et_2O into γ -phenyl- α -*p*-anisyl-

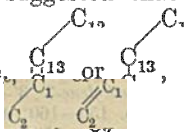
Δ^8 -propenyl alcohol, m. p. 106—107° (*p*-nitrobenzoate, m. p. 105°; dibromide, m. p. 164°). Under similar conditions Mg *p*-bromophenyl bromide gives γ -phenyl- α -*p*-bromophenyl- Δ^8 -propenyl alcohol, m. p. 100°.

H. WREN.

Constitution of cholesterol. III. Bromo-derivatives of cholesterol. R. DE FAZI and F. PIRRONI (Gazzetta, 1931, 61, 735—753).—Wieland's formula for cholesterol (Z. angew. Chem., 1929, 42, 421) indicates the possible existence of 16 stereoisomeric forms, giving rise to 64 halogeno-derivatives. Previous work on the bromination of cholesterol is summarised, the effects of various methods of bromination on the different forms of cholesterol are described, and the existing Br₂-derivatives tabulated.

E. E. J. MARLER.

Constitution of cholesterol. IV. isoCholesterols. R. DE FAZI (Gazzetta, 1931, 61, 753—758).—It is suggested that one of the two alternative

formulæ, , suggested by Windaus (A., 1927, 557) for allocholesterol may represent the β -cholesterol of Diels and Linn (A. 1908, i, 263).

E. E. J. MARLER.

Isomerisation of ergosterol. W. STOLL (Z. physiol. Chem., 1931, 202, 232—236).—Heating ergosterol with *p*-toluenesulphonyl chloride in pyridine gives ergotetraeno B (A., 1930, 203). The latter combines with 1 mol. of CCl₃·CO₂H, and hydrolysis of the product with NaOH gives "isoergosterol" which gives a ppt. with digitonin, forms an acetate, m. p. 131—132°, [α]_D -84°, and on hydrogenation gives ergostenyl acetate. It may be a mixture of isomerides.

J. H. BIRKINSHAW.

Pregnandiol, a sterol derivative from the urine of pregnancy. II. A. BUTENANDT [with F. HILDEBRANDT and H. BRÜCHER (Ber., 1931, 64, [B], 2529—2539; cf. A., 1930, 633)].—Further analyses of pregnandiol, pregnandioneoxime, and the ketodicarboxylic acid, m. p. 270°, confirm the mol. formula C₂₁H₃₆O₂ for the diol. It gives no ppt. with digitonin and is indifferent to NaOMe at 200°. Oxidation of the diol by CrO₃ in AcOH affords the dicarboxylic acid (III), m. p. 270°, [α]_D²⁵ +125.2° in pyridine, and an

the isomeric acid) is distilled at 270—285°/15 mm. the ketone (IV), m. p. 147°, is obtained (dioxime, decomp. 263°). Pregnandione (II) is reduced by Clemmensen's method to pregnan (I; R=H₂; R'=Et), m. p. 83.5°, [α]_D +20° in CHCl₃. The hydrocarbon is identical with that prepared from Et cholanate by the steps followed by Wieland (A., 1927, 247) to aetiocholyol Me ketone, which affords pregnan when acted on by Zn-Hg and conc. HCl. To pregnandiol the constitution (I) (R=CH·OH; R'=CHMe·OH) is therefore ascribed.

H. WREN.

Dehydration of phenylethylene glycol with potassium hydroxide. L. PALFRAY, S. SABETAY, and D. SONTAG (Compt. rend., 1931, 193, 941—944).—Phenylethylene glycol is converted by KOH at 250°/partial vac. (cf. A., 1929, 441 *et seq.*) into α -phenylethyl alcohol (phenylurethane, m. p. 88.5—89°; allophanate, m. p. 181—182°) and BzOH. Oxidation-reduction processes similar to those described by Lock (A., 1930, 597) probably occur.

H. BURTON.

Decomposition of adrenaline. I—V, VIII. T. VACEK (Pub. biol. Ecole Hautes Études vet., Brno, 1927, 6, 7, 4, 10, 5 pp.; 1928, 7, 6, 5 pp.; 1929, 8, 9 pp.; Chem. Zentr., 1931, i, 3696).

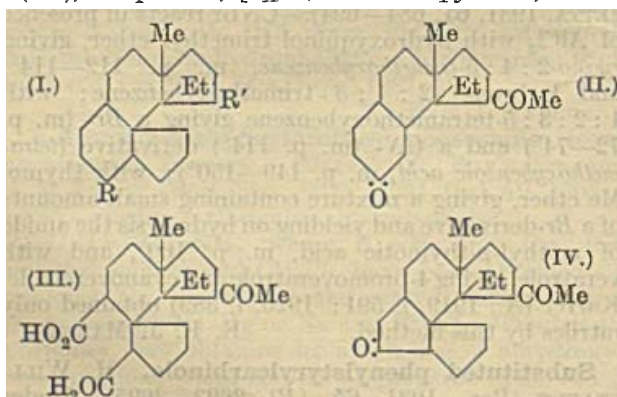
Decomposition of adrenaline. VI. J. KOLDA (Pub. biol. Ecole Hautes Études vet., Brno, 1928, 7, 5 pp.; Chem. Zentr., 1931, i, 3696).—Solutions containing H₂SO₄ are most, and those containing H₃PO₃ least, resistant to oxidation by H₂O₂. Photo-oxidation is least in solutions containing H₂SO₄ and greatest in those containing NaOBz; H₃PO₄, H₃PO₂, CCl₃·CO₂H, lactic, tartaric, and citric acids are intermediate.

A. A. ELDRIDGE.

Decomposition of adrenaline. VII. E. ÖLLOS and L. BREHOVENSKY (Pub. biol. Ecole Hautes Études vet., Brno, 1928, 7, 5 pp.; Chem. Zentr., 1931, i, 3696).—Oxidation of adrenaline is promoted by the presence of COMe₂-CHCl₃.

A. A. ELDRIDGE.

Synthesis of pharmacologically important amines. III. Synthesis of adrenaline and related compounds. K. KINDLER and W. PESCHKE (Arch. Pharm., 1931, 269, 581—606).—Aroyl cyanides, prepared by Mauthner's method (A., 1909, i, 160) or by oxidation of araldehyde cyanohydrins with CrO₃ in AcOH, are reduced catalytically (Pd-black) in AcOH (cf. A., 1931, 616) to ω -aminoacetophenones and thence to β -hydroxy- β -arylethylamines; the following are prepared: ω -aminoacetophenone [sulphate, m. p. 182° (decomp.); picrate, m. p. 182° (decomp.)]; ω -amino-*p*-methoxyacetophenone (I) [sulphate, m. p. 168° (turning red); Bz derivative, m. p. 118°]; ω -amino-3:4-dimethoxyacetophenone (II) [sulphate, m. p. 193° (decomp.); picrate, m. p. 188° (lit. 177°)]; ω -amino-3:4-methylenedioxyacetophenone [sulphate, m. p. 201°; hydrochloride, m. p. 210°; picrate, m. p. 177° (decomp.); Bz derivative, m. p. 163°]; β -hydroxy- β -phenyl-, m. p. 57° (+H₂O, m. p. 43—44°); β -hydroxy- β -*p*-methoxyphenyl-, m. p. 70° [hydrochloride, m. p. 188° (decomp.) (lit. 171—172° and 202°)]; β -hydroxy- β -3:4-dimethoxyphenyl-, m. p. 77° [hydrochloride, m. p. 170° (lit. 163°)]; ON-Bz₂ derivative, m. p. 141°; N-3:4-dimethoxy-



isomeric acid, m. p. 259° (decomp.), [α]_D²⁵ +115.3° in pyridine. When the acid of m. p. 270° (and, probably,

benzoyl derivative, m. p. 127—128° (lit. 124°); β -hydroxy- β -3:4:5-trimethoxyphenyl-, m. p. 144° (hydrochloride, m. p. 203°; picrate, m. p. 206°; ON-Bz, derivative, m. p. 143°), and β -hydroxy- β -3:4-methylenedioxyphenyl-ethylamines, m. p. 75° (hydrochloride, m. p. 192°, decomp. 210°; N-Bz, m. p. 157°, and N-Bz-O-Ac, m. p. 109°, derivatives). (II) is demethylated by 37% HCl at 160—165° to ω -amino-3:4-dihydroxyacetophenone, reduced catalytically (as hydrochloride) to β -hydroxy-3:4-dihydroxyphenyl-ethylamine (arterenol). The N-*p*-toluenesulphonyl derivative, m. p. 148°, of (II) is converted by Me_2SO_4 in aq. KOH into the N-*p*-toluenesulphonyl-N-methyl derivative, m. p. 137°, and thence by 37% HCl at 150—160° into adrenalone, reduced catalytically (as hydrochloride) to *dl*-adrenaline. The N-*p*-toluenesulphonyl derivative, m. p. 126°, of (I) is similarly converted by way of the N-*p*-toluenesulphonyl-N-methyl derivative, m. p. 93°, into ω -methylamino-*p*-hydroxyacetophenone and thence into β -hydroxy- β -*p*-hydroxyphenylethylmethylamine (sympathol).

H. BURTON

Action of hydrogen sulphide on acid chlorides.

IV. Hydrogen sulphide and toluoyl chlorides. L. SZPERL [with J. PENDOLA, W. WIOROGÓRSKI, M. TOMASZEWSKA, T. FAJNER, and L. PODWYSOCKA] (Rocz. Chem., 1931, 11, 753—762).—The following substances have been prepared by passing H_2S through *o*-, *m*-, or *p*-toluoyl chlorides, alone, or in xylene solution: *di-o*-, m. p. 58—59°, and *di-p*-toluoyl sulphide, m. p. 87—89°, *di-o*-, m. p. 88—89°, and *di-p*-toluoyl disulphide, m. p. 115—116°, and *di-m*-toluoyl disulphide, m. p. 86—87°.

R. TRUSZKOWSKI.

Amidines of pharmacological interest. A. P. T. EASSON and F. L. PYMAN (J.C.S., 1931, 2991—3001).—For comparison of local anæsthetic properties with "anæsthesin," *p*-aminobenzamidine, m. p. about 125° (decomp.) [dihydrochloride, m. p. about 320° (decomp.); monohydrochloride, m. p. 225—226°; monopicate, m. p. 231—232° (decomp.)]; *m*-aminobenzamidine dihydrochloride, m. p. 265—266°, monohydrochloride (+2 H_2O , m. p. 79—85°; anhyd., m. p. 162—163°); 3:4-dimethoxybenz-amidine, m. p. 110—120° [hydrochloride, m. p. 237° (decomp.); picrate, m. p. 217—218°], from *iminoether* hydrochloride, m. p. 142—143° (efferv.), have been prepared, but possess no similar activity. *p*-Carbethoxybenz-amidine hydrochloride, m. p. 217—218° (from *iminoether* hydrochloride, m. p. 179°), and *p*-carbethoxyphenylguanidine, m. p. 162—163° [hydrochloride, m. p. 166—167°; picrate, m. p. 224—225°; nitrate, m. p. 201—202° (decomp.)], prepared from *p*-carboxythio-carbamide, m. p. above 330°, through *S*-methylisothiocarbamide hydriodide, m. p. 238—239° (decomp.), have slight activity. *p*-Hydroxyphenyl-*S*-methylisothiocarbamide hydriodide, m. p. 176—181°, and -guanidine hydrochloride, m. p. 197—198° (picrate, m. p. 235—236°; nitrate, m. p. 205—206°), are similarly prepared. Benzveratrylamidine, m. p. 121° (hydrochloride, m. p. 217—218°; picrate, m. p. 217—218°), from benzoyl-veratrylamine, PCl_5 , and NH_3 , has strong anæsthetic properties; a similar product could not be obtained from veratrylveratrylamine, m. p. 192—183°.

o-Hydroxybenz-amidine [sulphate, m. p. 285°

(decomp.); picrate, m. p. 245—246°], prepared from *iminoether* hydrochloride, m. p. 150—151° (decomp.), has weaker antiseptic properties than salicylic acid. *p*-Hydroxyphenyl-acetiminioether hydrochloride, m. p. 145—148° (efferv.); -acetamidine hydrochloride, m. p. 253—254°, picrate, m. p. 212—213°, nitrate, m. p. 175—176°; -*N*-methylacetamidine hydrochloride, m. p. 229—230°, picrate, m. p. 167—168°; *m*-hydroxybenz-iminoether hydrochloride, m. p. 161—164° (decomp.), -amidine sulphate, m. p. 245° (decomp.), picrate, m. p. 260—261°, have been tested for pressor effect.

The hypoglycæmic properties of some of the following have been tested: *p*imelamidine hydrochloride, m. p. 218—219°, picrate, m. p. 249—250° (decomp.); azelamidine sulphate, m. p. 310—315° (decomp.), picrate, m. p. 260—261°; sebacamidine picrate, m. p. 249—250°; nonane-1:9-dicarboxylic acid chloride, b. p. 191—192°/22 mm., -diamidine picrate, m. p. 245—246°; decane-1:10-diamidine hydrochloride, m. p. 174—175°, picrate, m. p. 227—228°; undecane-1:11-diamidine picrate, m. p. 192—193°; and valeramidine sulphate, m. p. 272—274° (decomp.), picrate, m. p. 195—196°.

F. R. SHAW.

Addition of bromine to substituted cinnamic acids. H. WILLSTAEDT (Ber., 1931, 64, [B], 2688—2693).—Addition of Br to cinnamic acid is impeded by the presence in the *ortho* position of a F, Cl, Br, or I atom in order of increasing effect. The influence is still more pronounced in the cases of 2-chloro-6-fluoro- and 2:6-dichloro-cinnamic acids. Cl in the *meta* or *para* position somewhat diminishes the rate of addition of Br. The following are described: $\alpha\beta$ -dibromo-*o*-fluoro-, m. p. 183°; $\alpha\beta$ -dibromo-*o*-chloro-, m. p. 183°; $\alpha\beta$ -dibromo-*o*-bromo-; $\alpha\beta$ -dibromo-*o*-iodo-, m. p. 186° (decomp.) - β -phenylpropionic acid. 2-Chloro-6-fluorotoluene, b. p. 153—154°, from the chlorotoluidine hydrochloride through the diazonium fluoroborate, decomp. 141°, is converted by CrO_2Cl_2 into 2-chloro-6-fluorobenzaldehyde, b. p. 104—105°/20 mm. (semicarbazone, m. p. 213°), which affords 2-chloro-6-fluorocinnamic acid, m. p. 212°, when heated with $\text{CH}_2(\text{CO}_2\text{H})_2$ and AcOH. 2:6-Dichlorocinnamic acid, m. p. 192—193°, $\alpha\beta$ -dibromo- β -2:6-dichloro-, m. p. 192°, $\alpha\beta$ -dibromo- β -*m*-chloro-, m. p. 183°, and $\alpha\beta$ -dibromo- β -*p*-chloro-, m. p. 191°, -phenylpropionic acids are described.

H. WREN.

Cinnamylideneacetic acid. E. FRIEDMANN and H. MAI (Helv. Chim. Acta, 1931, 14, 1213—1214).—Cinnamaldehyde and pyruvic acid in aq. EtOH-NaOH give 64% of cinnamylidenepyruvic acid (as Na salt), oxidised by H_2O_2 to cinnamylideneacetic acid (90% yield).

H. BURTON.

Syntheses in the hydroaromatic series. XI. "Dien" syntheses with cyclopentadiene, cyclohexadiene, and butadiene and acetylenedicarboxylic acid and its esters. O. DIELS and K. ALDER [with H. NIENBURG] (Annalen, 1931, 490, 236—242).—cyclopentadiene (I) and Me acetylenedicarboxylate (II) combine readily to give Me 3:6-endomethylene-3:6-dihydrophthalate, b. p. 134—135°/10—11 mm. [free acid (III), m. p. 170°, prepared from (I) and acetylenedicarboxylic acid in Et_2O], reduced catalytically (colloidal Pd) in COMe_2 to Me 3:6-endomethylene- Δ^1 -tetrahydrophthalate, b. p. 132—

133°/12 mm. [the free acid (cf. A., 1930, 472) (*Me H* ester, m. p. 131°), is also obtained by catalytic reduction of (III)]. Dehydration (with AcCl) of the acid obtained by successive reduction and hydrolysis of the adduct from cyclohexadiene and (II) gives 3:6-endoethylene- Δ^1 -tetrahydrophthalic anhydride (*loc. cit.*), whilst the acid prepared similarly from the adduct from butadiene and (II) is dehydrogenated by Br at 200° to phthalic acid. H. BURTON.

Addition of maleic anhydride to *as*-diphenylethylene. T. WAGNER-JAUREGG (Annalen, 1931, 491, 1—13).—The compound (I), $\text{C}_{22}\text{H}_{16}\text{O}_6$, previously obtained (A., 1931, 198) from 1 mol. of *as*-diphenylethylene (II) and 2 mols. of maleic anhydride (III), behaves as a saturated substance except towards alkaline KMnO_4 , and when heated to 330° (bath) gives (III) and resinous material. Hydrolysis of (I) with warm 2*N*- NaOH or conc. HCl in AcOH affords an anhydride-dicarboxylic acid, $\text{C}_{22}\text{H}_{18}\text{O}_7$, m. p. 277.5° (all m. p. are corr.; decomp.), reduced only slowly (Adams' method) in AcOH to a substance, $\text{C}_{22}\text{H}_{24}\text{O}_6$, m. p. 279° (decomp.). (I) is converted by HBr (*d* 1.78) in AcOH into 1-phenyl-1:2:3:4-tetrahydronaphthalene-3:4-dicarboxylic acid (IV), m. p. 178—185° (decomp.) (according to rate of heating) [also formed from (I), HI (*d* 1.9), and red P in AcOH], and a small amount of a substance, m. p. 305—309° with darkening after previous sintering. Dry distillation of (IV) gives 1-phenyldihydronaphthalene, b. p. 302°, and an acid, m. p. 261.5—263.5°, whilst distillation with anhyd. $\text{Ba}(\text{OH})_2$ and Zn dust affords 1-phenylnaphthalene. Oxidation of (IV) with alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ and CrO_3 in AcOH gives 1-phenylnaphthalene-3(or 4)-carboxylic acid, m. p. 171.5—173.5°, and *o*-benzoylbenzoic acid, respectively. The production of (I) is considered not to involve a 1:4-addition of (III) to (II); addition is probably similar to that occurring with (III) and pyrrole (Diels and Alder, A., 1931, 849). Di(diphenylene)butadiene is recovered unchanged after 11 hr. heating with (III) in tetrahydronaphthalene. H. BURTON.

Synthesis of phenolic aporphines. I. Introduction and preparation of nitro-derivatives of 3:4-dihydroxyphenylacetic acid. J. M. GULLAND (J.C.S., 1931, 2872—2880).—A discussion of the methods of protection of OH groups in the synthesis of phenolic aporphines is given. 2-Nitro-3:4-dimethoxyphenylacetic acid (I) is demethylated to give a mixture of 2-nitro-4-hydroxy-3-methoxy- (II), m. p. 161°, and -3:4-dihydroxy-phenylacetic acid (III), m. p. 171°. (II) is converted by ClCO_2Et and NaOH into 2-nitro-3-methoxy-4-ethylcarbonato-, m. p. 132—133° (+0.5 C_6H_6 , m. p. 110—118°), and by CH_2PhCl into 2-nitro-4-benzoyloxy-3-methoxy-phenylacetic acid, m. p. 144° (CH_2Ph ester, m. p. 80° or 101°). 2-Nitro-3:4-diethylcarbonato-, m. p. 115° or 127—128°, and 2-nitro-3:4-dibenzoyloxy-phenylacetic acid, m. p. 85°, are similarly obtained from (III). Hydrolysis of (I) with *N*- NaOH affords 5:6-dimethoxyanthranilic acid, m. p. 175° (decomp.). 6-Nitro-3:4-dimethoxy- is demethylated with HBr in poor yield to 6-nitro-3:4-dihydroxy-phenylacetic acid, m. p. 212°, and with NH_2Ph gives 6-nitro-3:4-dimethoxyphenylacetanilide, m. p. 201—202°. F. R. SHAW.

Stereoisomerism of derivatives of 1:1'-dinaphthyl. A. CORBELLINI (Atti R. Accad. Lincei, 1931, [vi], 13, 702—704).—1:1'-Dinaphthyl-8:8'-dicarboxylic acid may be resolved into its optical antipodes by fractional crystallisation or pptn. of its brucine, cinchonine, or strychnine salt.

T. H. POPE.

Perkin synthesis. E. MÜLLER (Annalen, 1931, 491, 251—265).—Homophthalic anhydride (I) and NaCPh_3 in C_6H_6 give a *Na* enolate (II), converted by AcOH into (I) and by I in C_6H_6 into the dianhydride ($\text{o}-\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO-O} \\ \text{CH-O} \end{smallmatrix}\rangle$), m. p. 160—161°, and a trace of a compound, $\text{C}_{18}\text{H}_{12}\text{O}$, m. p. 216—217° (decomp.). (II) and PhCHO at room temp. afford 85% of the lactone of β -hydroxy-*o*-carboxy- $\alpha\beta$ -diphenylpropionic acid, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH} \\ \text{CO} \end{smallmatrix}\rangle\text{CO}_2\text{H}\rangle\text{CHPh}$, m. p. 185—186° (*Me* ester, m. p. 138—139°), converted by boiling Ac_2O into the benzylidene derivative of (I). These results afford further confirmation for the views that an intermediate OH-acid is formed during the Perkin reaction, and that the acid anhydride reacts in its enol form (cf. Kalnin, A., 1929, 63; Kuhn and Ishikawa, A., 1931, 1413). The complex mechanism suggested by Kalnin (*loc. cit.*) for the interaction of the aldehyde and enolate is not in agreement with the observation that BzCN , which contains no mobile H atom, reacts with Ac_2O and NaOAc at 180°, forming COMePh ; the mechanism of this reaction is: $\text{BzCN} + \text{Ac}_2\text{O} \longrightarrow \text{OH}\cdot\text{CPh}(\text{CN})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{OAc} \longrightarrow \text{CH}_2\text{Bz}\cdot\text{CO}_2\text{H} \longrightarrow \text{COMePh}$.

Et homophthalate when treated successively with NaCPh_3 , CH_2PhBr , and EtOH-KOH gives benzylhomophthalic acid. The enolate from AcOEt and NaCPh_3 reacts with I giving a trace of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$. Inconclusive results were obtained using Ac_2O and NaCPh_3 or $(\text{CH}_2\text{Ph}\cdot\text{CO})_2\text{O}$ and Na or NaCPh_3 .

H. BURTON.

Additive power of glycocholic acid and a new reaction of this acid. S. MINOVICI and M. VANGHELOVICI (Bull. Soc. Chim. România, 1931, 13, 5—10).—Like cholic acid (A., 1930, 1435), glycocholic acid (cholylamidoacetic acid), m. p. 144°, forms crystalline compounds with NH_2Ph , m. p. 90°; PhCHO , m. p. 81°; PhNO_2 , m. p. 105° (fluorescent: the formation of this compound can be used to detect this acid in the presence of other bile acids); $\text{CH}_2\text{Ph}\cdot\text{OH}$, m. p. 87°; *n*-amyl alcohol, m. p. 75°; and glyceryl trioleate, m. p. 145°, when the components are heated together with rigid exclusion of H_2O . All are decomposed by H_2O . J. W. BAKER.

Condensation products from 4:6-dinitro-*m*-xylene and aldehydes. P. RUGGLI, A. ZIMMERMANN, and R. THOUVAY (Helv. Chim. Acta, 1931, 14, 1250—1256).—4:6-Dinitro-*m*-xylene (I) (1 mol.), PhCHO (2 mols.), and piperidine at 145—160° (bath) give 75% of 4:6-dinitro-1:3-distyrylbenzene (II) and a little 2:4-dinitro-5-styryltoluene, m. p. 142° (lit. 145°); NaOEt cannot be used as the condensing agent owing to its action (resinification) on (I). Similar treatment of a mixture of (I) and 2:4-dinitro-*m*-xylene, such as is obtained during the isolation of (I) from the product of dinitration of *m*-xylene, also gives

(II). (I) and 2 mols. of anisaldehyde afford 4 : 6-dinitro-1 : 3-di-*p*-methoxystyrylbenzene, m. p. 179°, whilst with 0.5 mol. of the aldehyde, impure 2 : 4-dinitro-5-*p*-methoxystyryltoluene, m. p. 148°, results. 4 : 6-Dinitro-1 : 3-di-(β-2'-furylvinyl)benzene, m. p. 235°, and impure 2 : 4-dinitro-5-β-2'-furylvinyltoluene, m. p. 138°, are similarly prepared using furfuraldehyde. Anthraquinone-2-aldehyde (2 mols.) gives only α-4 : 6-dinitro-m-tolyl-β-2-anthraquinonylethylene, m. p. 277°, which probably contains traces of the double condensation product. Condensation products were not obtained from C₆H₅Me, C₆H₅Ph, CCl₂Ph₂, benzil, *o*-nitrobenzaldehyde, and heptaldehyde; resinification occurred with *p*-NMe₂·C₆H₄·CHO and cinnamaldehyde (or its Br-derivative). H. BURTON.

Complex internal salts of copper and nickel with the condensation product of *o*-hydroxybenzaldehyde and ethylenediamine. J. V. DUBSKY and A. SOKOL (Coll. Czech. Chem. Comm., 1931, 3, 548—549).—The prep. of di-*o*-hydroxybenzylidene-ethylenediamine, and its complex salts with Ni, C₁₆H₁₄O₂N₂Ni, m. p. 330° (decomp.), and Cu, m. p. 322° (decomp.), is described. H. A. PIGGOTT.

***p*-Methoxymethylbenzaldehyde.** R. QUELET (Compt. rend., 1931, 193, 939—941).—*p*-Xylylene glycol Me₂ ether, AcCl, and a little ZnCl₂ in CCl₄ give crude *p*-methoxymethylbenzyl chloride (cf. A., 1931, 955), oxidised by hexamethylenetetramine in aq. EtOH to *p*-methoxymethylbenzaldehyde, b. p. 125°/16 mm. (semicarbazone, m. p. 182°), converted by conc. aq. KOH into *p*-xylylene glycol Me ether and *p*-methoxymethylbenzoic acid, m. p. 123°. H. BURTON.

Optical resolution of racemic aldehydes. II. M. BETTI and P. PRATESI (Atti R. Accad. Lincei, 1931, [vi], 13, 646—649; cf. A., 1930, 916).—Treatment of *p*-methylhydratropaldehyde with phenyl-β-hydroxy-naphthylmethylamine yields a mixture of compounds which show different solubilities in EtOH and yield the optically active aldehydes, [α]_D +1.51° and -1.69° (semicarbazone [α]_D +2.09°), respectively, on hydrolysis. T. H. PORR.

Dioximes. LXXXI. G. PONZIO (Gazzetta, 1931, 61, 704—719).—A summary of work in this series on the prep. of aminoarylglyoximes and their reactions with HCN, acylating agents, and Br leads to the conclusion that the so-called α- and β-forms are structural rather than stereoisomerides, the "β" form being the true glyoxime, CPh(NOH)·C(NOH)·NH₂ (I), derived from formamidoxime and giving a ureide with KCN, whilst the "α" form is a derivative of formhydrazonamide, CPh(NOH)·C(NH)·NH·OH (II), giving a carbamate with KCN. The following are described: a carbamate, NH₂·CO₂NH·C(NH)·CPh·NOH, from (II) and KCN; phenylureidoglyoxime, CPh(NOH)·C(NOH)·NH·CO·NH₂, m. p. 185° (decomp.), from (I) and KCN; a Bz₃ derivative, CPh(N·OBz)·C(N·OBz)·NHBz, m. p. 167—168°, obtained by prolonged heating with BzCl of the 1-*O*-Bz or the *OO*-Bz₂ derivative of (I), or of the 2-*O*-Bz or the *ON*-Bz₂ derivative of (II), and giving with NaOH a Bz derivative, m. p. 148°, of aminophenylfurazan; an *ON*-Bz₂ derivative, C₆H₄Me·C(N·OBz)·C(NBz)·NH·OH, m. p. 199—200°, from the *p*-Me homologue (IV) of (II), giving a Bz derivative, m. p. 163—164°, of amino-*p*-tolylfurazan; a carbamate from (IV) and KCN; amino-*p*-tolylglyoxime, C₆H₄Me·C(NOH)·C(NOH)·NH₂ (III), m. p. 174° [Ni salt, [C₉H₁₀O₂N₃]₂Ni; ureide, m. p. 195—196° (decomp.)], from chloro-*p*-tolylglyoxime and NH₃. E. E. J. MARLER.

Constitution of lignin. XV. Chemical formula of the lignin of conifers. P. KLASON (Ber., 1931, 64, [B], 2733—2739; cf. A., 1931, 1401).—During the sulphite boil the aldol H₂O is lost from α-lignin in such a manner that the product must be regarded as the hydrosulphonic acid of a trimeric conifer aldehyde, whereas from β-lignin H₂O is lost from the nucleus only, which then combines with SO₂, the complex (OH)₂C₆H₃·CH(OH)·CH₂·CHO remaining unaffected. The cause of the polymerisation of β-ligninsulphonic acid does not lie in the CHO or SO₃H groups, which appear unaffected. Apparently the free phenolic OH groups determine the polymerisation and the colour is darkened by a desmotropic form of the polymeric β-acid. Under analogous conditions α-ligninsulphonic acid does not appear to be darkened or polymerised. The technical "black boil" is due to the production of H₂SO₄ or polythionic acid, which combines with the Ca necessary to neutralise the ligninsulphonic acids formed, thus allowing the development of free β-ligninsulphonic acid. The isolation of melaligninsulphonic acid establishes the formula of β-ligninsulphonic acid and hence of β-lignin. Total lignin behaves as if the components are united according to the scheme

OH·R·CH(OH)·O·R·CH(OH)·O · · · R·CHO, leaving a free aldehydic group; such lignin is present only in minor amount in wood, in which the chain must be regarded as closed or the aldehydic group united as glucoside to a carbohydrate. On the assumption that α-lignin, (C₁₀H₈O₄)₆, and β-lignin, C₁₀H₁₂O₄(C₉H₈O₄Ac)₂ are present in the simplest possible ratio in lignin, the formula C₉₂H₁₀₈O₃₈ is assigned to the latter compound. Since the sulphite boil involves the loss of aldol H₂O and the Ac group, the lignin obtained thereby has the composition C₈₈H₉₀O₂₉. These formulae agree with the results of elementary analysis and determinations of OMe and Ac. High concn. of H₂SO₄ and high temp. cause alterations in the α- and β-ligninsulphonic acids, particularly in the former: the primary acid, (C₁₀H₁₀O₃)₃·H₂SO₃, can pass into the acid (C₁₀H₁₀O₃)₂·H₂SO₃. Determination of the ratio S : OMe in the solid ligninsulphonic acids yields figures almost identical with those calc. from the formula of lignin in wood, thus indicating that α- and β-lignin are chemically united therein. The two forms of lignin are therefore considered to be chemically united to a single individual in wood: the individuality of the α- and β-ligninsulphonic acids is observed only after the treatment with H₂SO₄ whereby the two acids pass into solution. H. WREN.

Orientation phenomena among the cyclohexanones. V. Transposition in alkylation of cyclanones by Haller's method. R. CORNUBERT, C. BORREL, and H. LE BIHAN (Bull. Soc. chim.,

1931, [iv], 49, 1381—1397).—The max. yield of tetrahydropyrone derivative is obtained with 2 mols. of PhCHO and 1 mol. of 2-methylcyclohexanone at -18° , saturating with HCl, but the experimental conditions affect the orientation too much for a comparison of different ketones. 2-Methylcyclohexanone is obtained in 20% yield, together with products distilling up to $275^\circ/14$ mm., by decomposing the benzylidene compound in EtOH-KOH for $1\frac{1}{2}$ hr. Since the liquid benzylidene compound obtained in presence of HCl gives a semicarbazone, m. p. 171° , and on hydrogenation a fraction, b. p. $171^\circ/16$ mm., from which the tetrahydropyrone of 2-methyl-6-benzylcyclohexanone, m. p. 190° , is obtained, the benzylidene derivative probably contains about 65% of true benzylidene derivative, m. p. 60° , and another substance of the same b. p. giving the semicarbazone. The liquid benzylidene compound obtained in the crystallisation of benzylidenedimethylcyclohexanone on hydrogenation similarly yields about 68% of the tetrahydropyrone of 2-methyl-6-benzylcyclohexanone. 2:2-Dimethylcyclohexanone has been obtained pure by agitating the alkylation product with NaHSO_3 , conversion into semicarbazone, and hydrolysis with 10% H_2SO_4 (yield 28%), and in 20% yield by treating its benzylidene compound with EtOH-KOH. Pure 2:6-dimethylcyclohexanone is obtained from the oxime, m. p. 118° (yield 70%), by hydrolysis with 10% H_2SO_4 at 60° . No transformation of 2:2 into 2:6-dimethylcyclohexanone is effected with HCl, NaOH, H_2SO_4 , dil. NH_3 , or NaHSO_3 . Fractionation of the methylation product without NaHSO_3 yields a similar mixture of 2:2- and 2:6-dimethylcyclohexanone, and methylation with MeI yields a mixture of 89.5% of 2:2- and 10.5% of 2:6-dimethyl derivative.

Benzylation of 2-methylcyclohexanone in Et_2O with NaNH_2 and CH_2PhBr affords a mixture of 2-methyl-2-benzylcyclohexanone (benzylidene compound, m. p. 82°) and 2-methyl-6-benzylcyclohexanone (tetrahydropyrone, m. p. 191°) in the proportion 92—94% and 8—6%, respectively, together with 2-methyl-2:6-dibenzylcyclohexanone, m. p. 105° , and 2-methyl-6:6-dibenzylcyclohexanone, b. p. $230\text{—}232^\circ/15$ mm. With CH_2PhCl the proportions of 2-methyl-2-benzyl- and 2-methyl-6-benzylcyclohexanone are 90—89% and 10—11%, respectively.

R. BRIGHTMAN.

Carbon rings. XVII. Derivatives of 8-, 15-, and 30-membered rings: molecular refraction increment of some ring systems. L. RUZICKA and H. A. BOEKENOOGEN (Helv. Chim. Acta, 1931, 14, 1319—1335).—Reduction of cyclooctanone with Na and aq. NaHCO_3 in Et_2O (cf. A., 1928, 65) gives cyclooctanol (I) and about 15% of 1:1'-dihydroxy-1:1'-dicyclooctyl (II), m. p. $92\text{—}94^\circ$. (I) is dehydrated by $\beta\text{-C}_{10}\text{H}_7\text{-SO}_3\text{H}$ at 190° to cyclooctene, converted by Darzens' method (A., 1910, i, 322) into cyclooctenyl Me ketone, b. p. about $110^\circ/16$ mm. (not characterised), which is reduced catalytically (Pt-black) in AcOEt to cyclooctyl Me ketone (semicarbazone, m. p. $180\text{—}181^\circ$). (II) is dehydrated by aq. oxalic acid at 130° to dicyclooctenyl, b. p. $115\text{—}116^\circ/0.25$ mm., reduced to dicyclooctyl, b. p. about $140^\circ/1$ mm. cycloOctanone, $\text{CH}_2\text{Cl-CO}_2\text{Et}$, and NaOEt

give the ester, $\text{C}_7\text{H}_{14}>\text{C}(\text{O})\text{-CH-CO}_2\text{Et}$, b. p. $125^\circ/2.5$ mm.; distillation of the free acid furnishes cyclooctylformaldehyde, b. p. $76\text{—}78^\circ/16$ mm. [semicarbazone, m. p. about 140° (not sharp)]. cycloOctanone, $\text{CH}_2\text{Br-CO}_2\text{Et}$, and Zn in C_6H_6 afford, after dehydration with PBr_3 in C_6H_6 and subsequent hydrolysis with EtOH-KOH, cyclooctenylacetic acid, b. p. $135\text{—}137^\circ/1.2$ mm., reduced catalytically (Adams) to cyclooctylacetic acid, b. p. $130^\circ/1$ mm. [Et ester (III), b. p. $119\text{—}126^\circ/14$ mm.].

[With M. HURBIN.] Reduction of (III) with Na and EtOH gives β -cyclooctylethyl alcohol, b. p. $125\text{—}127^\circ/12$ mm., when regenerated from the H phthalate.

cycloPentadecanone is reduced with Na and EtOH to cyclopentadecanol (IV) and some 1:1'-dihydroxy-1:1'-dicyclopentadecyl (V), m. p. $147\text{—}147^\circ$. (V) is dehydrated by dil. H_2SO_4 in presence of PhMe to impure dicyclopentadecenyl, b. p. $265\text{—}270^\circ/1.3$ mm., reduced (Adams) to dicyclopentadecyl, m. p. 44° . (IV) is dehydrated by $2\text{-C}_{10}\text{H}_7\text{-SO}_3\text{H}$ at $150\text{—}210^\circ$ in CO_2 to cyclopentadecene, b. p. $122\text{—}123^\circ/1.2$ mm., m. p. $36\text{—}37^\circ$. Reduction of cyclotriacontane-1:16-dione with Na and EtOH gives cyclotriacontane-1:16-diol, m. p. $96\text{—}98^\circ$, dehydrated by KHSO_4 at 180° to Δ^1 -cyclotriaconten-16-ol, b. p. about $270^\circ/0.3$ mm., m. p. $68\text{—}69^\circ$, which is dehydrated further by $2\text{-C}_{10}\text{H}_7\text{-SO}_3\text{H}$ at $200\text{—}210^\circ$ to $\Delta^{1:15(\text{or } 16)}$ -cyclotriacontadiene, b. p. $240^\circ/0.4$ mm., m. p. $50\text{—}52^\circ$, reduced (Adams) to cyclotriacontane. The diol from the dione and MgMeI in isoamyl ether is dehydrated by 95% HCO_2H to 1:16-dimethyl- $\Delta^{1:15(\text{or } 16)}$ -cyclotriacontadiene, b. p. about $250^\circ/1$ mm., m. p. $64\text{—}65^\circ$, reduced catalytically (Pt-black) in AcOEt to 1:16-dimethylcyclotriacontane, m. p. 52° . The above dione, $\text{CH}_2\text{Br-CO}_2\text{Et}$, and activated Zn give Et 1:16-dihydroxycyclotriacontane-1:16-diacetate, m. p. $117\text{—}118^\circ$.

Mol. refraction data (at 20°) for the above and other compounds show that the increments for 5-, 7-, 8-, and 15-membered rings are $+0.04$, -0.10 , -0.47 , and -0.62 , respectively; the 6-ring is assumed to be "normal."

[With G. A. VAN KLINKENBERG.] The diketone, $\text{C}_{23}\text{H}_{44}\text{O}_2$, m. p. $75\text{—}76^\circ$, previously described (A., 1928, 642) is probably impure tricosane-8:16-dione, m. p. $88\text{—}89^\circ$ (disemicarbazone, m. p. $141\text{—}142^\circ$), now synthesised from azelalyl chloride and Zn n-heptyl iodide. H. BURTON.

Alcoholic, phenolic, and hydrolytic fission of organic compounds by catalysts. II. J. HOUBEN and W. FISCHER (Ber., 1931, 64, [B], 2636—2645; cf. A., 1931, 486).—*m*-Nitrophenyl CCl_3 ketone is converted by a little NaOMe in MeOH into Me *m*-nitrobenzoate, m. p. $78\text{—}79^\circ$, whilst *m*-aminophenyl CCl_3 ketone hydrochloride affords Me *m*-aminobenzoate hydrochloride, m. p. 215° (decomp.). Ethanolysis of the trichloroacetyldimethylpyrrole affords Et 2:4-dimethylpyrrole-5-carboxylate, m. p. 125° , whilst 3-trichloroacetyl-3-methylindole yields Et 2-methylindole-3-carboxylate, m. p. $134\text{—}135^\circ$. Trichloroacetone, Na, and *n*-octyl alcohol yield *n*-octyl acetate, b. p. $94^\circ/13$ mm., in 70% yield. Cetyl benzoate is derived from ω -trichloroacetophenone,

cetyl alcohol, and NaOMe in Et₂O. PhOH, KOAc, and ω -trichloroacetophenone at 120° give BzOPh, m. p. 70—71°; *p*-tolyl, m. p. 70°, *o*-tolyl, b. p. 177—180°/18 mm., and menthyl, b. p. 178—185°/14 mm., benzoates are similarly prepared. The following alcoholyses of ω -trichloroacetophenone are described: by MeOH in presence of HCO₂K, HCO₂K and HCO₂H, KOAc, KOAc and AcOH, KOBz and Mg(OH)₂; by PrOH and Mg(OH)₂, by isobutyl, *n*-hexyl, and allyl alcohols, menthol, PhOH, *o*- and *p*-cresol in presence of KOAc, the yields of ester varying between 93% and 58%. Particular care in the desiccation of alcohols or phenols is unnecessary. KHCO₃, Na₂CO₃, NaSO₃, and NH₄OAc are active, whereas KNO₃, NH₄Cl, KHC₂O₄, HCl, H₂O, H₂SO₄, H₂O, and HCl are ineffective. Production of MeOBz from ω -trichloroacetophenone and aq. MeOH is observed in presence of KOAc or Mg(OH)₂. Hydrolysis of ω -trichloroacetophenone is effected in boiling H₂O or aq. COMe₂ in presence of a little KOAc, whereas H₂O at 170° is almost without action. ω -Dichloroacetophenone is readily converted by 2*N*-NaOH into mandelic acid, indications being observed of the intermediate production of phenylglyoxal; CaCO₃ or Mg(OH)₂ are almost inactive in H₂O or aq. COMe₂, whereas NH₃ in H₂O affords benzoylphenylglyoxaline and 3-hydroxy-1:4-diphenylpyrazine. NaOMe and MeOH transform ω -dichloroacetophenone into *phenylglyoxal dimethylacetal*, b. p. 110—114°/13 mm.; KOAc in cold MeOH is without action, whereas in hot solution the Cl is ultimately removed. H. WREN.

Nuclear synthesis of ketimines and ketones by condensation of nitriles with aromatic and heterocyclic compounds. III. Syntheses with diphenyl ether, benzene, chlorinated benzenes, and 2-methylindole. Nitro- and amino-aryl ketones. J. HOUBEN and W. FISCHER (Ber., 1931, 64, [B], 2645—2653; cf. A., 1930, 1583).—Condensation of Ph₂O with trichloroacetoneitrile in presence of AlCl₃, PhCl, and HCl followed by treatment of the product with boiling H₂O affords ω -trichloro-*p*-phenoxyacetophenone, b. p. 172—174°/0.3 mm. (yield 70%), converted by NaOH into *p*-phenoxybenzoic acid, m. p. 156—159°. $\omega\omega$ -Dichloroacetophenone is prepared by condensation of C₆H₆ with CHCl₂·CN in presence of AlCl₃ and HCl or, preferably, by chlorination of CPhMe; the corresponding imine (*hydrochloride*) is smoothly converted into mandelic acid by successive treatment with boiling dil. HCl and dil. NaOH. Condensation between PhCl or the chlorotoluenes and CCl₃·CN necessitates the use of larger amounts of AlCl₃ and higher temp.; the yields are poor and, except in the case of 6-chloro-*m*-tolyl CCl₃ ketone, b. p. 155—160°/11 mm., the products are identified by conversion into the corresponding acids. 2-Methylindole and CCl₃·CN yield 3-trichloroacetimino-2-methylindole, m. p. 133—134° [*hydrochloride*, decomp. about 210° (also +CHCl₃)], converted by boiling H₂O or HCl into 3-trichloroacetyl-2-methylindole, m. p. 166.5°, which gives 2-methylindole-3-carboxylic acid, m. p. 174° (decomp.), when boiled with dil. NaOH. ω -Trichloroacetophenone and fuming HNO₃ at about 50° afford ω -trichloro-*m*-nitroacetophenone, m. p. 192—193°/18

mm., in 96% yield, quantitatively transformed by alkali into *m*-nitrobenzoic acid. It is reduced by SnCl₂ and HCl in EtOH to ω -trichloro-*m*-aminoacetophenone (*hydrochloride*), which gives *m*-aminobenzoic acid with 15% NaOH at room temp. 2-Nitro-4-trichloroacetotoluene, b. p. 205—206°/20 mm., similarly gives 2-nitro-*p*-toluic acid. Chlorination and bromination of ω -trichloroacetophenone proceeds less homogeneously than the nitration. H. WREN.

***p* - Dimethylaminobenzylidene - ketones.** I. Auxochrome groups. H. RUPE, A. COLLIN, and L. SCHMIDERER (Helv. Chim. Acta, 1931, 14, 1340—1354).—*p*-Dimethylaminostyryl Me ketone (I) (A., 1906, i, 858) [*semicarbazone*, m. p. 207—208°; *methiodide*, colourless, m. p. 177° (decomp.)] dyes mordanted (tannic acid) cotton a bright yellow; the hydrochloride and *perchlorate*, decomp. 152.5—156°, are obtained colourless only with difficulty. Oximation of (I) in neutral solution gives an *oxime*, m. p. 185.5—186.5° (cf. *loc. cit.*), whilst in dil. HCl an *oxime*, m. p. 96—97°, results; the latter, but not the former, is hydrolysed by 2*N*-HCl. 1:4-Addition of MgPhBr to (I) occurs, yielding β -phenyl- β -*p*-dimethylaminophenylethyl Me ketone (II), colourless, m. p. 99—100° (*semicarbazone*, m. p. 180—180.5°). Catalytic reduction (Ni) of (I) gives β -*p*-dimethylaminophenylethyl Me ketone (III), colourless, b. p. 168—169°/11 mm., m. p. 50.5—51.5° (*semicarbazone*, m. p. 190—191°), or δ -*p*-dimethylaminophenylbutan- β -ol, b. p. 173—174°/12 mm. (*acetate*, b. p. 176°/11 mm.), according to the amount of H₂ consumed. MgPhBr and (III) afford β -phenyl- δ -*p*-dimethylaminophenylbutan- β -ol, m. p. 56—57°, whilst Clemmensen reduction of (I) yields (II). The carbinol from *p*-NMe₂·C₆H₄·CHO and MgPhBr is dehydrated by repeated distillation in vac. to α -*p*-dimethylaminophenyl- Δ^2 -butene, colourless, m. p. 32.5° (lit. 25°), reduced catalytically (Ni) in aq. EtOH to α -*p*-dimethylaminophenylbutane, colourless (*perchlorate*, m. p. 37°).

Di-*p*-dimethylaminostyryl ketone (IV), orange-red, which also gives colourless salts, is reduced (Ni) to di- β -*p*-dimethylaminophenylethyl ketone, colourless, m. p. 86—87° (*semicarbazone*, m. p. 151—152°), converted by MgPhBr into γ -phenyl- $\alpha\alpha$ -di-*p*-dimethylaminophenylpentan- γ -ol, m. p. 110—111°. *p*-NMe₂·C₆H₄·CHO and (III) in EtOH-NaOH give β -*p*-dimethylaminophenylethyl *p*-dimethylaminostyryl ketone, bright orange, m. p. 126—126.5° (*semicarbazone*, m. p. 211—212°), forming a colourless solution in dil. HCl. 1:4-Addition of MgPhBr to (IV) also occurs, yielding β -phenyl- β -*p*-dimethylaminophenylethyl *p*-dimethylaminostyryl ketone, yellow, m. p. 159—160° (*semicarbazone*, m. p. 211—212°), also formed from *p*-NMe₂·C₆H₄·CHO and (II) in EtOH-NaOH; this also gives a colourless solution in dil. HCl. Ph *p*-dimethylaminostyryl ketone, m. p. 107.5° (lit. 114°), also gives a colourless hydrochloride.

These results show that coloured *p*-dimethylaminostyryl ketones are converted into colourless compounds by salt formation on the *tert*-N atom (abolition of the auxochrome group), by reduction of the double linking or replacement of CO by CH₂ in the chromophoric grouping ·CO·CH·CH(Ar).

H. BURTON.

into (A) ketonic and (B) alcoholic constituents. (A) consists essentially of 1-2-methyl-5-isopropenyl- Δ^2 -cyclohexenone (I), b. p. 101°/14 mm., $[\alpha]_{5461} -35.14^\circ$ (semicarbazone, m. p. 185—186°; 2:4-dinitrophenylhydrazones, m. p. 173°), which with piperonal and EtOH-NaOEt gives a compound, $C_{36}H_{38}(or\ 38)O_7$, m. p. 141—143° (sinters at 130°). (I) is oxidised by alkaline H_2O_2 in MeOH to its 2:3-oxide, b. p. 113—115°/18 mm., $[\alpha]_{5461} -11.2^\circ$ [semicarbazone, decomp. 209—210° (sinters at 197°)], by aq. $KMnO_4$ to liquid acids and some *as*-dimethylsuccinic acid [probably formed from eucarvone, occurring in small amount in (I)], and by CrO_3 in dil. H_2SO_4 to (probably) *o*-hydroxy-3-methylacetophenone, m. p. 88—90° (semicarbazone, decomp. 218—220°; oxime, m. p. 138—140°). (I) is converted by boiling 10% H_2SO_4 into 5-isopropyl-*m*-cresol (tetrabromide, m. p. 138—140°), and reduced catalytically (Pd—"norite") in AcOH to 1-3-methyl-5-isopropylcyclohexanone (II), b. p. 141°/100 mm., 217°/754 mm., $[\alpha]_{5461} -21.68^\circ$ (oxime, m. p. 74—75°; *p*-nitrophenylhydrazones, m. p. 183—185°; 2:4-dinitrophenylhydrazones, m. p. 110—111°; NO-derivative, decomp. 141—142°), when regenerated from its semicarbazone, decomp. 203°, $[\alpha]_{5461} +28.75^\circ$ in AcOH, together with a small amount of an optically inactive isomeride, b. p. 138—139°/100 mm. (semicarbazone, m. p. 197—198°; NO-derivative, decomp. 138°); the semicarbazones are separated by fractional crystallisation from AcOEt.

(B) is separated by distillation into a mixture (C), b. p. 100°/16 mm., of doubly unsaturated alcohols containing a little of the dicyclic ketone (2:4-dinitrophenylhydrazones, m. p. 212—213°) obtained by Semmler and Schiller (B., 1927, 713) from Δ^3 -carene and $KMnO_4$ in $COMe_3$. (C) is oxidised by $KMnO_4$ in $COMe_3$ to small amounts of 3- and 4- (semicarbazones, decomp. 205—206°)-methylacetophenones. Catalytic reduction (Pd—"norite") of (C) proceeds only slowly and incompletely, yielding a product consisting (probably) of mainly *m*- and *p*-cymenes. Reduction (incomplete) of (C) with Na and EtOH and oxidation of the product formed with CrO_3 in AcOH gives some 5-hydroxy-3-methylacetophenone and a neutral oil. Partial catalytic reduction of the oil affords a product containing (II), a ketone, $C_{10}H_{16}O$ [semicarbazone, m. p. 228—229° (decomp.)], probably identical with that of m. p. 223—224°, described by Semmler and Schiller (*loc. cit.*), and an alcohol, $C_{10}H_{18}O$, b. p. 110—112°/25 mm., $[\alpha]_{5461} +3.79^\circ$, resembling dihydroisocarvestrenol (Fisher and Perkin, J.C.S., 1908, 93, 1889).

H. BURTON.

Neutral products of oxidation of pinene. K. SŁAWINSKI, J. PIŁCZEWSKI, and W. ZACHAREWICZ (Rocz. Chem., 1931, 11, 763—773).—Pinene on oxidation with $KMnO_4$ in $COMe_3$ solution yielded, amongst other products, a fraction, b. p. 37—102°/3 mm., which deposited a small quantity of crystals, $C_{10}H_{16}O_2$, m. p. 124—125°, on keeping, and a fraction, b. p. 101—102°/1 mm., which deposited pinene glycol, $C_{10}H_{18}O_2$, m. p. 56—57° (monourethane, decomp. 78°). The lower fraction gave a semicarbazone, $C_{11}H_{19}ON_3$, decomp. 204°, but did not form a urethane; on further oxidation α -pinonic acid was obtained. The glycol on treatment with P_2O_5 yielded, amongst other products, pinol, whilst oxidation with $KMnO_4$

gave α -pinonic acid. With Ac_2O a mixture of mono- and di-acetates, b. p. 118—119°/1 mm., was obtained, and this, on hydrolysis, yielded the original glycol, together with an alcohol (I), b. p. 70—72°/1 mm., which gives an unidentified polyhydric alcohol on oxidation with $KMnO_4$.

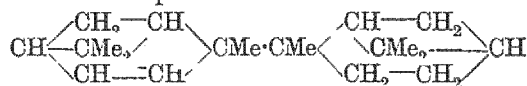
R. TRUSZKOWSKI.

Camphor and terpenes. VIII. Conversion of *d*-camphor into *l*-camphor. J. HOUBEN and E. PFANKUCH (Ber., 1931, 64, [B], 2719—2720; cf. A., 1931, 1300).—*d*-Camphor, $[\alpha]_D^{20} +45^\circ$, is transformed into 1-4-chlorocamphor, m. p. 198—199°, $[\alpha]_D^{20} -30^\circ$ in EtOH, the semicarbazone, m. p. 260—265° (decomp.), of which is reduced by Na and EtOH to *l*-camphorsemicarbazone. The *l*-camphor, *l*-camphoroxime, and *l*-camphor-1-carboxylamide derived from the last-named compound have $[\alpha]_D^{20} -29^\circ$ in EtOH, $[\alpha]_D^{20} +25.5^\circ$ in EtOH, and $[\alpha]_D^{20} -49^\circ$ in AcOH, respectively.

H. WREN.

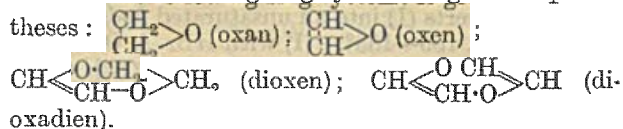
Determination of configuration in the terpene series. V. J. VON BRAUN and W. KELLER.—See this vol., 43.

Dipinenes. R. DULOV (Bull. Inst. Pin, 1931, 123—124, 159—160, 173—176, 199—200, 219—221).—The history and methods of prep. of dipinene from α - and β -pinene are reviewed. The mechanisms suggested by Bischoff and Nastvogel, by Bruhn, and by Kondakov and Saprikin are discussed and rejected in favour of simple 1:4-addition between 2 mols. of α - and/or β -pinene, the double linking being in conjugated relationship with the bridge linking. Dipinene is probably a difficultly separable mixture of at least 2 compounds, having 1 and 2 double linkings, respectively. No evidence of a phenanthrene structure has been found. α -Dipinene, b. p. 194°/27 mm., $d_{20}^{25} 0.930$, $n_D^{20} 1.5107$, and β -dipinene, b. p. 175°/15 mm., $d_{20}^{25} 0.938$, $n_D^{20} 1.5177$, obtained best by the action of H_2SO_4 in EtOH on pinene or nopinene, are both mixtures; the α -isomeride contains mono- and some di-ethylenic compounds, and the complexity of the β -isomeride is shown by its Raman spectrum. No cryst. hydrochloride, hydrobromide, halide, nitrosochloride, nitrosite, or nitrosate is obtained; only about 1% of H_2 is absorbed in presence of Pt-black. Dehydrogenation of α -dipinene with S at 170—250° gives a product, m. p. 64—65° (picrate, m. p. 132°), which is probably diisopropylidiphenyl, and a fraction which is oxidised to hydroxyisopropylbenzoic acid, m. p. 116.5°. This confirms the presence in α -dipinene of a compound of the structure:

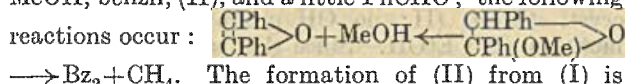


C. HOLLINS.

Three- and six-membered cyclic oxido-compounds. W. MADELUNG and M. E. OBERWEGNER (Annalen, 1931, 490, 201—235).—The nomenclature used for the following ring systems is given in parentheses:

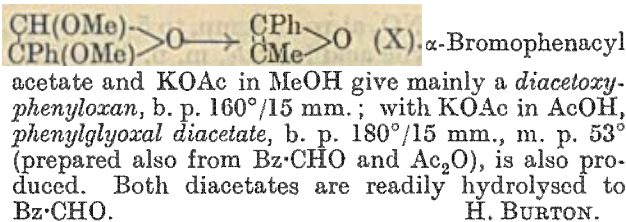
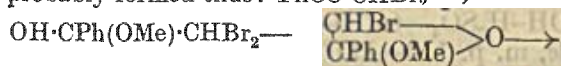


Treatment of desyl chloride (I) with powdered KOH in boiling PhMe gives K benzilate and *diphenyloxan* (*tolane oxide*) (II), m. p. 52° (contaminated with deoxybenzoin); (II) is obtained pure by methods described below. (II) does not polymerise readily, undergoes ready autoxidation, can be distilled, is stable to cold but is resinified by hot H₂O (or acids), and is converted by conc. HCl at 120° into (I). Similarly, phenacyl bromide and CaO in PhMe give about 8% of *phenyloxan* (*phenylacetylene oxide*) (III) (contaminated with CPhMe), converted by conc. HCl into phenacyl chloride; when Ag₂O is used, a small amount of a *dimeride*, m. p. 136°, of (III) is produced also. (I) and MeOH-NaOMe afford mainly *α-methoxy-αβ-diphenyloxan* (IV), b. p. 194–196°/16 mm., which also undergoes ready autoxidation forming benzoin and BzOH. Treatment of (IV) with Ac₂O and a trace of conc. H₂SO₄ yields *α-acetoxy-αβ-diphenyloxan*, b. p. 192°/15 mm., m. p. 109°, whilst with MeOH-HCl β-2 : 5-dimethoxy-2 : 3 : 5 : 6-tetraphenyldioxan (V), m. p. 285°, results; the compound, C₃₀H₂₈O₄, described by Irvine and Weir (J.C.S., 1907, 94, 1391) is (V) (cf. Bergmann and Weil, A., 1930, 1438). Thermal decomp. of (IV) affords CH₄, MeOH, benzil, (II), and a little PhCHO; the following reactions occur :



→ Bz₂ + CH₄. The formation of (II) from (I) is considered to involve similar decomp. of an intermediate hydroxyoxan. *α-Ethoxy-αβ-diphenyloxan*, b. p. 188°/12 mm., unlike (IV), is converted by Ac₂O + H₂SO₄ and EtOH-HCl into benzoin Et ether. When (IV) is kept in absence of air, α-2 : 5-dimethoxy-2 : 3 : 5 : 6-tetraphenyldioxan (VI), m. p. 223°, is produced; (VI) is converted by MeOH-HCl into (V). The α-, m. p. 232°, and β-, m. p. above 290°, -2 : 5-dimethoxy-2 : 3 : 5 : 6-tetraphenyldioxans are obtained similarly. Addition of a drop of conc. H₂SO₄ to a solution of (V), (VI), or methoxytetraphenyldioxan (VII) (Bergmann and Weil, *loc. cit.*) in Ac₂O at room temp. produces a violet coloration which immediately becomes rose-carmine; 2 : 5-diacetoxy-2 : 3 : 5 : 6-tetraphenyldioxan (VIII), m. p. 297°, separates from the solution. When the reaction mixture is heated the solution becomes yellow (immediate addition of NaOAc at this point leads to the isolation of a little 2-acetoxy-2 : 3 : 5 : 6-tetraphenyl-Δ⁵-dioxen, m. p. 174°) and tetraphenyldioxadien (*tetraphenyldioxin*) (IX), m. p. 214°, is formed. The compounds described by Irvine and McNicoll (J.C.S., 1908, 93, 951, 1601) as triacetoxyhydrofuran and *cis*-dibenzoylstilbene are (VIII) and (IX), respectively. *cis*-Dibenzoylstilbene, formed together with the *trans*-form from (I) and dry Na₂CO₃ at 200°, is converted by MeOH-HCl into 2 : 5-dimethoxy-2 : 3 : 4 : 5-tetraphenyl-2 : 5-dihydrofuran, m. p. 164°. Thermal decomp. of (VII) gives CH₄, benzil, and (II).

Treatment of ωω-dibromoacetophenone with MeOH-NaOMe below 0° gives (cf. Evans and Parkinson, A., 1913, i, 1355) CHBr₃, BzOMe, phenylglyoxal Me acetal, and *α-methoxy-β-phenyloxan* (X), b. p. 118°/14 mm. (converted by MgPhBr into benzoin); (X) is probably formed thus: PhCO·CHBr₂ →



Esters of furfurylacrylic [β-furylacrylic] acid. A. BLUMANN and F. HESSE (Perf. and Essen. Oil Rec., 1931, 22, 382).—Me β-furylacrylate has m. p. 27·5°, b. p. 114–115°/16 mm. The Et ester has m. p. 24·5°, b. p. 120–121°/17 mm. E. H. SHARPLES.

5-Bromofurylacetylene. H. GILMAN, A. P. HEWLETT, and G. F. WRIGHT (J. Amer. Chem. Soc., 1931, 53, 4192–4196).—β-Furylacryloyl chloride (1 mol.) and Br (1 mol.) in cold CS₂ give 56% of β-5-bromofurylacryloyl chloride, b. p. 182–188°/6 mm., m. p. 54°; with 3 mols. of Br in the hot, α-bromo-β-5-bromofurylacryloyl chloride (I), b. p. 182–183°/21 mm., m. p. 72°, results. (I) is converted by dil. NaOH at 70–80° into 5-bromofurylpropionic acid, m. p. 143° (reduced by Zn and aq. NH₃ to furylpropionic acid), which when distilled in steam gives 32% of 5-bromofurylacetylene (II), b. p. 63–64°/24 mm., and varying amounts of 5-bromofuryl Me ketone, m. p. 96° (oxime, m. p. 79·5°). The ketone is also formed by the action of aq. NaOH on (I) or, better, Et αβ-dibromo-β-5-bromofurylpropionate, and from 5-bromofurfuraldehyde and diazomethane. The Grignard reagent from (II) with CO₂ and α-naphthylcarbimide gives 5-bromofurylpropionic acid and its α-naphthalide, m. p. 150°, respectively. C. J. WEST (b).

Dihydro-1 : 4-pyrans. I. Action of sodium cyanide on αδ-dibromo-αδ-diaroylbutanes. R. C. FUSON, S. B. KUYKENDALL, and G. W. WILHELM (J. Amer. Chem. Soc., 1931, 53, 4187–4192).—αδ-Dibenzoylbutane and Br in CCl₄ give αδ-dibromo-αδ-dibenzoylbutane, m. p. 176–177°, converted by NaCN in EtOH-AcOEt into 3-cyano-6-benzoyl-2-phenyl-5 : 6-dihydro-1 : 4-pyran, $\begin{array}{c} \text{O} < \text{CPh} \cdot \text{C(CN)} \\ \text{CHBz} \cdot \text{CH}_2 \end{array}$,

m. p. 105·5–106° (corr.). Bromination of αδ-dip-toluoylbutane gives a mixture, m. p. 154–170°, of the αδ-Br₂-derivatives, one of which is obtained pure, m. p. 174–174·5° (corr.); the pure form (or the mixture) is converted as above into 3-cyano-6-p-toluoyl-2-p-tolyl-5 : 6-dihydro-1 : 4-pyran, m. p. 141–141·5° (corr.). Adipyl chloride, PhOMe, and AlCl₃ afford αδ-dianisoylbutane, m. p. 141·5–142·5° (corr.) (dioxime, m. p. 201–201·5°), and δ-anisoylvaleric acid, m. p. 126° (corr.). 3-Cyano-6-anisoyl-2-anisyl-5 : 6-dihydro-1 : 4-pyran, m. p. 141–141·5°, is prepared from a mixture of isomeric αδ-dibromo-αδ-dianisoylbutanes. C. J. WEST (b).

Derivatives of kojic acid. J. W. ARMIT and T. J. NOLAN (J.C.S., 1931, 3023–3031).—Kojic acid and diazomethane in Et₂O give 5-methoxy-2-hydroxymethyl-γ-pyrone (I), m. p. 165°, methylated (MeI and Ag₂O in MeOH) to 5-methoxy-2-methoxymethyl-γ-pyrone (II), m. p. 89–90°. 5-Methoxy-2-hydroxymethyl-4-pyridone (+H₂O), m. p. 173–175° after loss of H₂O at 120°, prepared from (I) and aq. NH₃ at

90°, is oxidised by HNO_3 at room temp. to 5-methoxy-4-pyridone-2-carboxylic acid [*nitrate*, m. p. 236—237° (decomp.)], converted by diazomethane into an ester, $\text{C}_9\text{H}_{11}\text{O}_4\text{N}$, m. p. 134°, becoming crimson (softens at 94°). Reduction of 5-methoxy-1-methyl-2-hydroxy-methyl-, m. p. 203—204°, and 5-methoxy-1-methyl-2-methoxymethyl-4-pyridone ($+3\text{H}_2\text{O}$), m. p. 57°, m. p. (anhyd.) 113°, prepared from NH_2Me and (I) and (II), respectively, with Na—Hg in slightly acid solution gives 5-methoxy-1:2-dimethyl-4-pyridone, partly demethylated by Na and boiling amyl alcohol to the 5-hydroxy-derivative, m. p. 273—274° (darkens at 250° and sinters at 263°). Hydroxypiperidines could not be obtained from these pyridones by any method of reduction tried. Catalytic reduction (colloidal Pd) of kojic acid and (II) results in the absorption of 6H per mol. of each, but the products isolated could not be characterised definitely. The Ac_2 derivative (III) of kojic acid absorbs 10H on reduction (colloidal Pt+Pd) giving a mixture, the high-boiling (138—180°/10—12 mm.) fractions of which with $\text{NH}_3\cdot\text{NHPh}$ afford (probably) the 3:4-bisphenyl-hydrazone, m. p. 207°, of 3:4-diketo-6-acetoxymethyl-tetrahydropyran. The Bz and Bz_2 derivatives of kojic acid could not be reduced catalytically. (III) and NH_2Me in MeOH give the NH_2Me salt, m. p. 130° (sinters at 125°), of kojic acid. H. BURTON.

Application of the Simonis reaction to mono-hydric phenols. A. ROBERTSON (Nature, 1931, 128, 908; cf. A., 1931, 1303).—*o*-Cresol, *o*- and *p*-chloro- and -bromo-phenols, and β -naphthol give rise to 1:4-pyrones. Condensation of *m*-cresol with Et acetoacetate in presence of P_2O_5 yields 4:7-dimethyl-coumarin, but with esters mono-substituted in α -position 1:4-pyrones are obtained, e.g., Et α -methyl-acetoacetate yields 2:3:5-trimethyl-1:4-benzo-pyrene. L. S. THEOBALD.

Constitution of wogonin. Absorption spectra of flavones. IV. S. HATTORI (Acta Phytochim., 1931, 5, 219—237).—Diethylantiarol, AcCl , and AlCl_3 give 2-hydroxy-3:4-dimethoxy-6-ethoxyacetophenone, m. p. 97—98°, which reacts with Bz_2O and NaOBz to form 5-ethoxy-7:8-dimethoxy-, m. p. 182—183°, reduced by HI to 5:7:8-trihydroxy-flavone (I), identical with that obtained from wogonin, which must be 5:7-dihydroxy-8-methoxyflavone. Reduction of 2:3:4:6-tetramethoxybenzoylacetophenone gives chiefly (I) and some 5:6:7-trihydroxy-flavone (cf. Bargellini, A., 1919, i, 545), identical with baicalein. 2-Hydroxy-3:4:6-trimethoxyacetophenone is converted by anisic anhydride and Na anisate into 5:7:8:4'-tetramethoxyflavone, demethylated by HI to 5:7:8:4'-tetrahydroxyflavone, m. p. 247—249° (*Ac* derivative, m. p. 252—253°), also prepared from 2:3:4:6:4'-pentamethoxybenzoylacetophenone and HI, a reaction which in one case only gave 5:6:7:4'-tetrahydroxyflavone (scutellarein; cf. A., 1915, i, 84). Baicalein Me_3 ether and KOH afford antiarol. The preparation of dimethyl-wogonin from wogonin by heating with diazomethane is described. The absorption spectra of 5-ethoxy-7:8-dimethoxy-, 5:7:8-trihydroxy- (obtained by different methods), 5:7:8:4'-tetramethoxy-, and

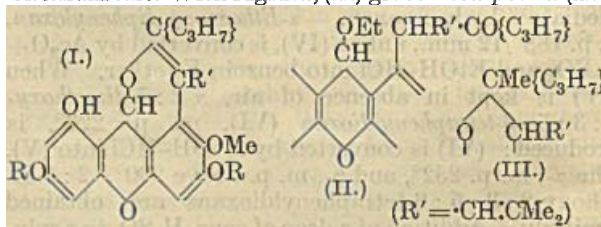
5:7:8:4'-tetrahydroxy-flavone (prepared in 2 ways) and their *Ac* derivatives are all identical.

F. R. SHAW.

Partly hydrogenated naphthalene lactones. G. HUPPMANN (Süddeut. Apoth.-Ztg., 1931, 71, 137—139; Chem. Zentr., 1931, i, 2756).—Condensation of malic acid with *ar*- β -tetralol affords tetrahydronaphtho- α -pyrone, m. p. 131°; Et acetoacetate and *ar*- β -tetralol afford γ -methyltetrahydronaphtho- α -pyrone, m. p. 154°. Hydrolysis with KOH gives the K salt of the corresponding acid, but the acid cannot be isolated. Reduction (Na—Hg) affords dihydro- γ -methyltetrahydronaphtho- α -pyrone, m. p. 96°, by way of the free acid, m. p. 107°, and treatment of this with H_2SO_4 . Citric acid and *ar*- β -tetralol yield tetrahydronaphtho- α -pyrone- γ -acetic acid, $\text{C}_{15}\text{H}_{14}\text{O}_4$, m. p. 189°, with loss of CO_2 and formation of γ -methyltetrahydro- α -pyrone.

A. A. ELDRIDGE.

Constitution of mangostin. II. M. MARAKAMI (Proc. Imp. Acad. Tokyo, 1931, 7, 311—314; cf. A., 1931, 1158).—When heated with conc. HCl and AcOH dimethylmangostin (I; $\text{R}=\text{Me}$) gives a compound, $\text{C}_{25}\text{H}_{29}\text{O}_5\text{Cl}+2\text{H}_2\text{O}$, decomp. 159°, and $+0.5\text{HCl}, 1.5\text{H}_2\text{O}$, which with KOH affords a Cl-free product which could not be crystallised, but gives a cryst. ethoxide (II; no OH group by Zerevitinov's method) with EtOH. Since this is reconverted into a hydrochloride by conc. HCl , the latter must be an oxonium salt. With MgMeI , (II) gives a compound (III),



m. p. 141°, which cannot be reconverted into an oxonium salt. On the basis of this and other evidence the structure (I) ($\text{R}=\text{H}$) is assigned to mangostin, which may be partly converted into the quinonoid form. Structures for the compounds obtained with SOCl_2 and Et boroacetate are also suggested.

J. W. BAKER.

Formation of thionaphthindoles. II. E. W. McCLELLAND and J. L. D'SILVA (J.C.S., 1931, 2972—2975).—The oil previously obtained (A., 1929, 1084) from 2-keto-1:2-dihydrobenzothiazole, Ac_2O , and KOAc, and described as *o*-thiolacetophenone, is 3-acetoxy-1-thionaphthen (I), converted by NH_2Ph , NH_2Me , or 2*N*-NaOH into 3-oxy-1-thionaphthen (II) [semicarbazone, also obtained from (I) (cf. loc. cit.)]. (I) is oxidised by H_2O_2 in AcOH to 3-oxy-1-thionaphthen 1-dioxide. The formation of thionaphthindole from (I) (cf. loc. cit.) proceeds by way of the phenylhydrazone of (II). The isothiazole, $(\text{Et}\cdot\text{CO})_2\text{O}$, and $\text{Et}\cdot\text{CO}_2\text{Na}$ at 145—150° give a small amount of a substance, $\text{C}_{12}\text{H}_{13}\text{ONS}$, m. p. 152—153°, and mainly 3-propionyloxy-2-methyl-1-thionaphthen (III), m. p. 75°, also prepared from α -*o*-carboxyphenylthiolpropionic acid and $(\text{Et}\cdot\text{CO})_2\text{O}$. (III) is oxidised by H_2O_2 in AcOH to its 1-dioxide, m. p. 109—110°, hydrolysed by $\text{EtOH}-\text{H}_2\text{SO}_4$ to 3-oxy-2-methyl-1-thionaphthen 1-dioxide, m. p. 110—111°. Hydrolysis of (III) with

EtOH-NaOH and subsequent oxidation with $K_3Fe(CN)_6$ gives 2:2'-bis-(3-oxy-2-methyl-1-thionaphthen), m. p. 151—153°, oxidised by H_2O_2 in AcOH to 2:2'-bis-(3-oxy-2-methyl-1-thionaphthen)-1-dioxide, m. p. above 300°. H. BURTON.

Thermal conversion of ethyl 1-pyrrylacetate into pyridine. W. E. SOHL and R. L. SHRINER (J. Amer. Chem. Soc., 1931, 53, 4168—4170).—Pyridine, CO_2 , C_2H_4 , and H_2 are formed when Et 1-pyrrylacetate is heated. Et nicotinate is the probable intermediate, since, under the same conditions, it gives pyridine, CO_2 , and C_2H_4 . C. J. WEST (b).

Salts of the ammono-enolic modification of pyridines and quinolines alkylated in the 2- and 4-positions. F. W. BERGSTROM (J. Amer. Chem. Soc., 1931, 53, 4065—4077).—2-Alkylquinolines can be regarded as cyclic ammono-ketone acetals. All the substituted quinolines (and pyridines) examined react with $NaNH_2$ or KNH_2 in liquid NH_3 , to give coloured (red or reddish-brown) salts of the ammono-enolic modifications. The salts from 2-alkylquinolines react with alkyl halides, thereby lengthening the 2-alkyl group. The K salts from 2-ethyl- and 2-propyl-quinolines with EtBr and MeI, respectively, give the same 2-sec.-butylquinoline, b. p. 118—121°/3—5 mm. (picrate, m. p. 163.5—164.5°); the change $(CH_2R') \cdot CR:N^+ + KNH_2 \rightarrow (CHR') \cdot CR:NK^+$ occurs. The K salt of 2:6-dimethylquinoline and EtBr afford 86% of 6-methyl-2-propylquinoline, b. p. 131—134.5°/3—4 mm. (picrate appears to decompose when recrystallised; 2:4:6-trinitro-m-tolylloxide, m. p. 172.5—173.5°). The K salt of 2:4-dimethylquinoline and MeI give 4-methyl-2-ethylquinoline (?) [picrate, m. p. 167—168° (corr.)]; with EtBr, 4-methyl-2-propylquinoline (?) [picrate, m. p. 196—198° (corr.)]; chloroaurate, m. p. 130° (decomp.) results. An attempt to establish the structure of these compounds by treating 2-chloro-4-methylquinoline with $MgPrBr$ gave 4-methylquinoline (which also affords metallic salts). 2-isoPropylquinoline, b. p. 124—125.5°/7 mm., is obtained in 70% yield from MeBr and the K salt of 2-ethylquinoline, whilst 4-ethyl- and 4-propyl-quinolines are prepared from the K salt of 4-methylquinoline and MeI and EtBr, respectively. Na, K, and Ba salts of numerous 2- and 4-alkylated quinolines and pyridines are also prepared. C. J. WEST (b).

Copper salts of quinolinic acid. J. V. DUBSKÝ and A. OKAČ (Coll. Czech. Chem. Comm., 1931, 3, 465—479).—Contrary to Boeseken (A., 1894, i, 259), addition of $Cu(OAc)_2$ to aq. Na H pyridine-2:3-dicarboxylate affords only a blue $Cu + H_2O$ salt, (I), decomp. 300° (various constitutions suggested), which does not lose H_2O at 130°. The same salt is obtained by adding $Cu(OAc)_2$ to the free acid or its Na_2 salt. Only in presence of excess of alkali is an intermediate green product (*loc. cit.*) obtained, but this is a mixture of basic salts. With aq. NH_3 , (I) gives the $Cu NH_4 + 2H_2O$ salt, and with cold alkali affords $Cu Na_2 + 8H_2O$ and $Cu K_2 + 2H_2O$ salts. With warm HNO_3 (d 1.2) or with the original acid (I) gives the salt $[C_5H_3(CO_2H) \cdot CO^-]_2 Cu$ (II), decomp. 297—304°, also obtained from $Cu(OH)_2$ and

the original acid or by HNO_3 on the $CuNa_2 + 8H_2O$ salt [which results from the action of NaOH on (II)]. The $Cu (NH_4)_2$ salt, decomp. 260—300°, is similarly obtained. These alkali salts give no ionic reactions for Cu. The Na H, decomp. 260—320°; Ag H + H_2O , decomp. 210°; and Ag_2 salts are described.

J. W. BAKER.

Derivatives of 3:3-dimethylindolinone. I. K. BRUNNER [with E. WIEDNER and W. KLING] (Monatsh., 1931, 58, 369—398).—The products of direct substitution of 3:3-dimethyl-2-indolinone are identified in general by synthesis, the method being to apply a slightly modified Fischer indole synthesis ($ZnCl_2$ in EtOH) to nuclear-substituted isobutaldehydephenylhydrazones, and to oxidise the resulting crude indolenine, either as base or as zincchloride, with alkaline $KMnO_4$. 4:7(?) - Dichloro-3:3-dimethylindolinone, m. p. 185.6° (Na salt), is the product of chlorination in AcOH at 6—10°. 5:7-Dibromo-3:3-dimethylindolinone, m. p. 185.5°, prepared synthetically, is identical with the product of direct bromination (m. p. 187.6°; cf. A., 1897, i, 438; 1907, i, 240); the 4:7- Br_2 -compound has m. p. 168°. Iodination in AcOH gives 5-iodo-3:3-dimethylindolinone, m. p. 173.7° (Na salt), identified by synthesis from the 5- NH_2 -compound (below); but I and HgO in CCl_4 give in addition an isomeride, m. p. 202°. The 5- NO_2 , m. p. 262° (Ag salt), and 7- NO_2 , m. p. 194°, -compounds, prepared by means of *p*- and *o*-nitrophenylhydrazines, respectively, were previously obtained by direct nitration (*loc. cit.*); both on further nitration give 5:7-dinitro-3:3-dimethylindolinone, m. p. 204°, and the 5- NO_2 -compound also gives the $(NO_2)_2$ -compound and nitrous fumes when treated with $K_2Cr_2O_7$ in conc. H_2SO_4 . Cyclisation of isobutaldehyde-m-nitrophenylhydrazone, m. p. 96—97°, and subsequent oxidation gives 4(or 6)-nitro-, m. p. 167°, and 6(or 4)-nitro-3:3-dimethylindolinone, m. p. 174—175°. 5-Nitro-3:3:7-trimethyl-, m. p. 265—266°, 7-nitro-3:3:5-trimethyl-, m. p. 212—213°, and nitro-3:3:6(or 4)-trimethyl-indolinone, m. p. 252—253°, are obtained by direct nitration in AcOH, and also in the first case in absence of a solvent. 5-Amino-3:3-dimethylindolinone ($Zn-HCl$ reduction), m. p. 184° [hydrochloride; sulphate, m. p. about 268° (decomp.)]; $HgCl_2$ salt; chloroplatinate; picrate, m. p. 194—195° (decomp.); Ac , m. p. 261°, Ac_2 , m. p. 164°, Ac_3 , m. p. 161°, and Bz , m. p. 219°, derivatives; azo-dyes with β -naphthol and R-salt (both red)], gives a quinaldine, m. p. above 300° (dichromate; chloroplatinate; picrate, m. p. 239—240°), by the Dobner-Miller synthesis, and the 5-I-compound by the Gattermann reaction, but was not successfully converted into the 5-OH-compound. isoButaldehyde-p-, m. p. 132—133°, and -o-nitrophenylhydrazone, m. p. 61—62°, and 3:3:6(or 4)-trimethylindolinone, m. p. 177—178° (W. Brunner, Diss., Freiburg, 1914), are also described. H. A. FRIGGOTT.

3-Benzoylcarbazole. W. H. HUNTER and S. F. DARLING (J. Amer. Chem. Soc., 1931, 53, 4183—4186).—3-Amino-4-anilinobenzophenone, m. p. 163—165°, prepared by reducing the 3- NO_2 -derivative, is converted by $NaNO_2$ and AcOH into 5-benzoyl-1-

phenylbenztriazole, m. p. 128° [α -oxime (I), m. p. 163—165°; β -oxime (II), m. p. 200—201°], which when heated at 328—375° gives 3-benzoylcarbazole, m. p. 203—205° (oxime, m. p. 238°). (I) is converted by PCl_5 into 1-phenylbenztriazole-3-carboxyanilide, m. p. 227—228° (also prepared from the free acid, NH_2Ph , and POCl_3), whilst (II) similarly gives 5-benzamido-1-phenylbenztriazole, m. p. 230—231° (also prepared from the free amine or its Sn salt and BzCl). (I) is, therefore, the *syn*- and (II) the *anti*-form. C. J. WEST (b).

Berginisation of heterocyclic compounds. N. A. ORLOV [with E. I. PROKOPEZ, I. I. JERU, G. M. MAX, W. N. CHADSHINOV, N. I. BURD, and V. D. SUKATSHEVA] (Ber., 1931, 64, [B], 2631—2636).—Carbazole is converted by compressed H_2 in presence of freshly-pptd. MoS_3 at 430—440° into NH_3 , aromatic hydrocarbons, dimethyldicyclopentyl, and dicyclohexyl. Replacement of MoS_3 by $(\text{NH}_4)_2\text{MoO}_4$ deposited on pumice and treated superficially with H_2S leads to the production of NH_3 , probably *o*-toluidine and *o*-ethylaniline, dimethyldicyclopentyl (oxidised by HNO_3 to butyric acid), and indole. Diphenylene oxide in presence of MoO_3 at 450—470° or 400—410°, less completely in presence of MoS_3 , yields H_2O , little PhOH , C_6H_6 , methylcyclopentane, cyclohexane, dicyclic naphthenes, and more complex aromatic hydrocarbon sol. in H_2SO_4 and probably containing phenylcyclohexane. Thiodiphenylamine in presence of MoO_3 yields NH_3 and H_2S [which unite to $(\text{NH}_4)_2\text{S}$] and gives C_6H_6 and apparently cyclohexane, NH_2Ph , possibly dicyclohexyl, and NHPh . H. WREN.

Mercury compounds of 5-phenyl-5-ethylbarbituric acid. E. RUPP and A. POGGENDORF (Arch. Pharm., 1931, 269, 607—609).—Na 5-phenyl-5-ethylbarbiturate and $\text{Hg}(\text{OAc})_2$, in very dil. AcOH give 1-acetoxymercuri-5-phenyl-5-ethylbarbituric acid; the 1-bromo- and 1-hydroxy-mercuri-derivatives are also described. H. BURTON.

Alkyl derivatives of orotic acid. M. BACHSTEEZ (Ber., 1931, 64, [B], 2683—2688; cf. A., 1930, 781; 1931, 495).—Condensation of Et oxalacetate with the requisite substituted carbamide gives the following Et -uracil-4(6)-carboxylates, $\text{NR} \begin{smallmatrix} \text{CO}\cdot\text{CH} \\ \text{CO NH} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{Et}$: methyl- [free acid, m. p. 310° (corr.)]; ethyl-, m. p. 86° (corr.) [acid, m. p. 235° (corr.)]; allyl-, m. p. 97° (corr.) [acid, m. p. 204—205° (corr.)]; benzyl-, m. p. 137° (corr.) [acid, m. p. 247° (corr.)]. Methylcarbamide and Et acetoacetate afford 1 : 4-dimethyluracil, m. p. 269° (corr.). Ag uracil-4(6)-carboxylate and the alkyl halide yield the following isomeric -uracil-4(6)-carboxylic acids, $\text{NH} \begin{smallmatrix} \text{CO}\cdot\text{CH} \\ \text{CO NR} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{H}$: methyl-, m. p., 250° (corr.); ethyl-, m. p. 211—212°; allyl-, m. p. 206—207°; benzyl-, m. p. 208—209°. Orotic acid is unchanged by diazomethane, whereas the Et ester yields Me methyluracil-4(6)-carboxylate, m. p. 140—141° (corr.), hydrolysed to β -methylorotic acid identical with that prepared from methylcarbamide. Et orotate and Me_2SO_4 give a difficultly separable mixture of Me and Et methylorotates. H. WREN.

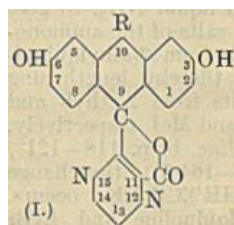
Pyrimidines. Formation of diazouracil anhydride from aminouracil. T. B. JOHNSON, O.

BAUDISCH, and A. HOFFMANN (Ber., 1931, 64, [B], 2629—2631).—Aminouracil in $N\text{-HCl}$ with aq. NaNO_2 at -5° gives diazouracil anhydride, $\text{CO}\cdot\text{N}=\text{C}\cdot\text{O} \begin{smallmatrix} \text{NH}\cdot\text{CH}\cdot\text{C}\cdot\text{N} \end{smallmatrix} \text{N}$ or



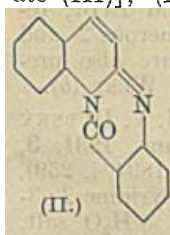
decomp. 198° after darkening, which slowly couples with amines and phenols in alkaline solution and decomposes in light. With α -naphthol it yields a product, m. p. (indef.) 270° (decomp.). The production of the diazo-anhydride or of the red diazonium hydrate appears to depend on the acidity of the medium employed in the diazotisation of aminouracil. H. WREN.

Dyes derived from pyrazine-2 : 3-dicarboxylic acid. S. C. DE and P. C. DUTTA (Ber., 1931, 64, [B], 2606—2609).—The phthaleins derived from pyrazine-2 : 3-dicarboxylic acid are more intensely coloured but less fluorescent than those obtained from



phthalic acid. The following compounds are described : resorcinolpyrazinedicarboxylein (12 : 15-diazo fluorescein) (I; $\text{R}=\text{O}$), m. p. above 295°, from pyrazine-2 : 3-dicarboxylic acid, resorcinol, and ZnCl_2 , at 200°, and its 2 : 4 : 5 : 7- Br_4 -derivative, m. p. above 280°; 2 : 7-dimethyl-, m. p. 190°, and 1 : 8-dihydroxy-12 : 15-diazo fluorescein, m. p. 235°; m-aminophenolpyrazinedicarboxylein (I; $\text{R}=\text{NH}$), m. p. above 295°; 12 : 15-diazo- NN' -tetramethylrhodamine, m. p. 178—180°, and the corresponding Et_4 derivative, m. p. 270°; m-phenylenediaminepyrazinedicarboxylein, m. p. above 295°. H. WREN.

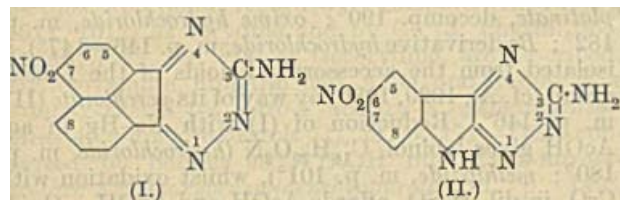
Benzquinazocolines. P. K. BOSE and D. C. SEN (J.C.S., 1931, 2840—2846).—2-Chloropyridine heated with anthranilic acid (I) gives 2-anilinopyridine and the quinoquinolone described by Reissert (A., 1895, i, 244). Similarly, 2-chloroquinoline and (I) afford 2-quinolone, 2-anilinoquinoline, and ketobenzquinazocoline (II), m. p. 170° [also formed using Me anthranilate (III)]; (II) is hydrolysed by EtOH-KOH (not by acid) to a carboxylic acid [N -2'-quinolylanthranilic acid or its isomeric (anil) modification], m. p. 198°. The compound, m. p. 213°, obtained by Ephraim (A., 1892, 1488) from 2-chloro-4-methylquinoline and (I) should be assigned a structure similar to (II), since it is hydrolysed to an acid (IV), $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$, m. p. 210°, and converted by MeI in MeOH-KOH into a substance, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$, m. p. 140°, probably the Me ester of (IV). 2-Chloro- and 2-chloro-4-methylquinolines with N -methylanthranilic acid give N -2'-quinolyl- N -methyl-, m. p. 190°, and N -2'-quinolyl- N -4'-dimethyl-, m. p. 220°, -anthranilic acids, respectively, indicating that one of the N -H atoms of (I) is responsible for ring closure (as above). 4-Chloro-2-methylquinoline and (I) afford N -2'-methyl-4'-quinolylanthranilic acid, m. p. 307°, whilst 2-chloro-4 : 7-dimethylquinoline and (I) give a compound, $\text{C}_{18}\text{H}_{14}\text{ON}_2$, m. p. 150°, hydrolysed to an acid, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$, m. p. 226°. Condensation of



2-quinolone with (III) in presence of PCl_3 gave, in one case only, a small amount of a substance, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$, m. p. 226—227°. 2-Pyridone, 2-quinolone, and 4-methyl-2-quinolone do not react with (I) in presence of PCl_3 . H. BURTON.

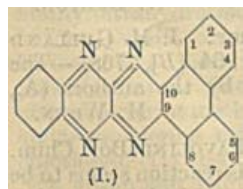
Autoxidation of uric acid in presence of amines. M. FREREJACQUE (Compt. rend., 1931, 193, 860—863).—Oxidation of uric acid (cf. A., 1931, 101) with KMnO_4 in an atm. of O_2 in presence of KOH and NH_2Ph affords a ureide, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_5$, decomp. 290° (block), which is hydrolysed to allantoin and NH_2Ph . Similar compounds (decomp. 290°) are obtained using *m*- and *p*- but not *o*-toluidine (steric effect?). Piperidine gives a tert. amine (chloroplatinate, decomp. 280°; a picrate, decomp. 240°; perchlorate, decomp. 270°). These compounds are analogous to iminoallantoin (cf. Denicke, A., 1906, i, 938), but are derivatives of isoallantoin, $\text{CO} < \text{NH} \cdot \text{CR} \cdot \text{NH} > \text{CO}$, which precedes the formation of allantoin. F. R. SHAW.

Synthesis of triazines. Action of aminoguanidines on α -diketones. S. C. DE and P. C. DUTTA (Ber., 1931, 64, [B], 2604—2606).—5-Nitroacenaphthenequinone and aminoguanidine hydrochloride in boiling AcOH afford 7-nitro-1-aminoacenaphthatri-



azine (I), m. p. not below 290°; the corresponding 7:8-(NO_2)₂ compound, m. p. above 300°, is obtained similarly from 5:6-dinitroacenaphthenequinone. The following 3-aminoindotriazines (cf. II) are prepared from the requisite isatins: 6-nitro-, m. p. not below 300°; 6-bromo-, m. p. above 295°; 6:8-dibromo-, m. p. above 295°; 6-bromo-8-nitro-, m. p. 268° (decomp.); 6-chloro-, m. p. 184°. H. WREN.

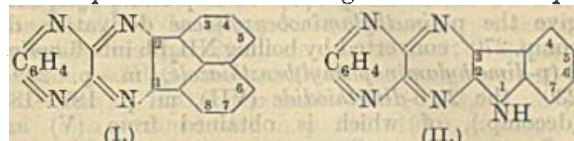
Dyes derived from phenanthraquinone; quinoxalinophenanthrazines. S. C. DE and P. C. DUTTA (Ber., 1931, 64, [B], 2598—2602).—The dyes formed from 2:3-diaminoquinoxaline and substituted phenanthraquinones are generally darker in shade than the corresponding phenanthra-phenazines and -naphthazines, but lighter than the -phenazinazines. The following quinoxalino-phenanthrazines (cf. I) are described:



-2-nitro-, not molten below 290°; -4-nitro-, m. p. above 295°; -2:7-dinitro-, m. p. above 295°; -4:5-dinitro-, m. p. above 300°; -2:7-diamino-, m. p. not below 295°; -4:5-diamino-, m. p. above 295°; -2-amino-, m. p. above 295°; -4-amino-, m. p. above 290°; -2:7-dihydroxy-, m. p. above 290°; -4:5-dihydroxy-, m. p. above 300°; -2-hydroxy-, m. p. above 300°; -4-hydroxy-, m. p. above 290°; -2-bromo-, m. p. above 295°; 2:7-dibromo-, m. p. above 300°; quinoxalino-di-

bromophenanthrazine, m. p. above 300°, and -bromodinitrophenanthrazine, m. p. above 300°. H. WREN.

Dyes derived from acenaphthenequinone and isatin; quinoxalino-acenaphthazines and -indazines. P. C. DUTTA and S. C. DE (Ber., 1931, 64, [B], 2602—2604).—Acenaphthenequinone and 2:3-diaminoquinoxaline in boiling AcOH afford quin-



oxalinoacenaphthazine (I), m. p. above 300°; the 5-nitro-, m. p. above 300°, and 5:6-dinitro-, m. p. above 300°, derivatives are prepared similarly. Isatin and 2:3-diaminoquinoxaline in AcOH give quinoxalinoindazine (II), m. p. not below 295°. The 5-bromo-, m. p. not below 295°; 5:7-dibromo-, 5-bromo-7-nitro-, m. p. above 290°; 5-chloro-, m. p. above 295°, and 5-nitro-, m. p. above 290°, derivatives are described. H. WREN.

Berginisation of thiodiphenylamine. N. N. BURDA (Ukrain. Chem. J., 1931, 6, [Sci.], 161—167).—Thiodiphenylamine and H_2 at 400—425° and 100 atm. pressure yield successively NHPh_2 , NH_2Ph , and C_6H_6 . R. TRUSZKOWSKI.

Thiazoles. XVII. Connexion between constitution and colour in the thioflavine group. M. T. BOGERT and W. S. TAYLOR (Coll. Czech. Chem. Comm., 1931, 3, 480—497).—Synthesis of thioflavine derivatives has been effected (a) with substituents in the 2-Ph group, from α -aminothiophenol or α -aminophenyl disulphide; (b) with a 6-NMe₂ group and substituents in the 2-Ph group, from 2-amino-5-dimethylaminobenzenethiosulphuric acid (I) (A., 1902, i, 145); and (c) from *p*-phenylenediamine-mono- and -di-thiosulphuric acids. (a) α -Aminophenyl disulphide heated with *p*-NMe₂· C_6H_4 ·CHO at 150° gives 2-(*p*-dimethylaminophenyl)benzthiazole, m. p. 174—175°, the

3-methiodide (II), $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ | \\ \text{NMe} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 223—224° (decomp.), of which is not identical with the 2-methiodide, m. p. 202—203° (decomp.), obtained by similar condensation of $\alpha\text{-NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SH}$ with the methiodide of *p*-NMe₂· C_6H_4 ·CHO, thus confirming Green's structure (J.C.S., 1889, 55, 227) for the thioflavine dyes. (b) Contrary to Heller (A., 1925, i, 313) *p*-nitrobenzoyl chloride reacts with (I) in boiling AcOH to give 6-dimethylamino-2-(*p*-nitrophenyl)benzthiazole, reduced to the corresponding 2-*p*-aminophenyl derivative (A., 1927, 680). 6-Dimethylamino-2-(*p*-dimethylaminophenyl)benzthiazole (*loc. cit.*, intermediate anil isolated) with MeI at 100—110° gives a 3-mono- (III), m. p. 224—225° (decomp., in bath at 220°), and a di-, m. p. 203—204° (decomp.), -methiodide, the isomeric 2-methiodide (IV), m. p. 210—211° (decomp.), being obtained from (I) and *p*-NMe₂· C_6H_4 ·CHO. (c) *p*-Phenylenediamine-3-thiosulphuric acid, + H_2O and anhyd. (V), m. p. 204—206° (decomp.), and PhCHO give 6-amino-2-phenylbenzthiazole (together with a substance, m. p. 168—169°), methylated by MeOH and HCl to the

6-dimethylamino-compound, which with MeI at 100—110° gives a *methiodide*, m. p. 202—203° (decomp.). (IV) with *p*-nitrobenzoyl chloride gives 6-*p*-nitrobenzamido-2-(*p*-nitrophenyl)benzthiazole, unchanged at 300°, hydrolysed to the 6-amino-compound, m. p. 266—270°, which is reduced by Sn and HCl to 6-amino-2-(*p*-aminophenyl)benzthiazole, (IV), m. p. 258—259°. Similarly (V) and *p*-NMe₂·C₆H₄·CHO give the *p*-dimethylaminobenzylidene derivative, decomp. 270°, converted by boiling NH₂Ph into 6-amino-2-(*p*-dimethylaminophenyl)benzthiazole, m. p. 229—230°, the 2:6-dimethiodide (VII), m. p. 187—188° (decomp.), of which is obtained from (V) and *p*-NMe₂·C₆H₄·CHO: (V) and *p*-NO₂·C₆H₄·CHO give 6-(*p*-nitrobenzylideneamino)-2-(*p*-nitrophenyl)benzthiazole, m. p. 240—246°, reduced by Sn and HCl to (VI). By similar methods from *p*-phenylenediamine-3:6-dithiosulphuric acid, m. p. 237—238° (J.C.S., 1903, 83, 1201, m. p. 233—235°), are obtained 6-(*p*-dimethylaminobenzylideneamino)-2-(*p*-dimethylaminophenyl)benzthiazole-5-thiosulphuric acid, softens above 200°, cyclised to 2:2'-di-(*p*-dimethylaminophenyl)benzthiazole, m. p. 297°. Of the above methiodides only (II), (III), (IV), and (VII) dye silk and, in general, the tinctorial value of the NR₂ group is reduced or destroyed by conversion into NR₃:I. All m. p. are corr. J. W. BAKER.

Tetramethyleneammonium trithiocarbonate and 2-thion-4:6-dialkyl-1:3:5-dithioazines. T. G. LEVI (Gazzetta, 1931, 61, 673—680).—CH₂O condenses with NH₄ trithiocarbonate (improved prep.) giving *tetramethylenediammonium trithiocarbonate*, [(CH₂)₂NS]₂·CS₃. Higher aliphatic aldehydes give, instead of the carbethialdine (A., 1873, 47), a 2-thion-4:6-dialkyl-1:3:5-dithioazine,

NH<CH₂R·S>CS. The *Me* [m. p. 74° (decomp.)] and *Et* (m. p. 73°) compounds are described. PhCHO gives, not the carbobenzthialdine (A., 1930, 227), but benzthialdine. Furfuraldehyde gives a *thialdine*, NH<C₅H₄O·S>C₅H₄O, m. p. 112°.

E. E. J. MARLER.

Synthesis of mercaptothiazoles and some new S-substituted dithiourethanes. T. G. LEVI (Gazzetta, 1931, 61, 719—728).—An improvement on the method of Miolati (A., 1893, i, 634) for the prep. of thiolthiazoles from NH₄ dithiocarbamate and halogenoketones leads to the isolation of the following intermediates: *S*-acetonyl (m. p. 80—82°), *S*-phenacyl (m. p. 100—103°), and *S*-carbethoxyacetonyl (m. p. 121°) dithiocarbamates. 2-Thiol-4-phenylthiazole is oxidised to a *disulphide*, (CH₂N<CPh·S>C·S)₂, m. p. 154°, gives with

S₂Cl₂ a *tetrasulphide* (CH₂N<CPh·S>C·S)₂·S₂, m. p. 117°, and with MeI the *Me ether (hyaroidide)*, also obtained from the disulphide with KCN and MeOH. 2-Thiol-4-methylthiazole with S₂Cl₂ gives a *tetrasulphide* [unstable *hydrochloride*, m. p. 96—98° (decomp.)]. *S*-Benzoyl [m. p. 124° (decomp.)] and *N*-piperidyl-*S*-benzoyl (m. p. 99°) dithiocarbamates have higher m. p. than those recorded by von Braun (A., 1903, i,

13). *S*-Acetyl (m. p. 106°), *S*-propionyl (m. p. 99°), and *N*-piperidyl-*S*-acetyl (m. p. 60—61°) dithiocarbamates are obtained from NH₄ dithiocarbamate and acyl chlorides. NH₄ trithiocarbamate with halogenoketones gives compounds of the type S:C(SR)₂.

E. E. J. MARLER.

4-Nitro-5-(3-pyridyl)pyrazole, a new oxidation product of nicotine. I. G. A. C. GOUGH and H. KING (J.C.S., 1931, 2968—2971).—During the prep. of nicotinic acid (I) by HNO₃-oxidation of nicotine (Org. Synth., 1925, 4, 49), about 5% of a base (II), C₈H₆O₂N₄ [probably 4-nitro-5-(3-pyridyl)pyrazole], m. p. 272—274° (*Ag* salt; *hydrochloride*, m. p. 300°), is produced; (II) is weakly acidic and sparingly sol. in H₂O. Reduction of (II) with Sn and 16% HCl gives a base, C₈H₈N₄, oily (*dihydrochloride*, m. p. 300—302°; *dipicrate*, m. p. 219—220°), containing an aromatic NH₂ group and oxidised by aq. KMnO₄ to (I). A mechanism is suggested for the production of (II). H. BURTON.

Lobinine, a new alkaloid from the Lobelia plant. H. WIELAND and M. ISHIMASA [with W. KOSCHARA] (Annalen, 1931, 491, 14—29).—*Lobinine* (I), C₁₈H₂₇O₂N, probably 2-phenacyl-1-methyl-7-β-hydroxypropylhexamethyleneimine, not obtained cryst. (*hydrochloride*, m. p. 144° becoming red, [α]_D —106.1° in H₂O; *hydriodide*, m. p. 130°; *chloroplatinate*, decomp. 190°; *oxime hydrochloride*, m. p. 182°; *Bz* derivative *hydrochloride*, m. p. 146—147°), is isolated from the accessory alkaloids of the *Lobelia* group (cf. A., 1929, 1086) by way of its *perchlorate* (II), m. p. 146°. Reduction of (I) with Na-Hg in aq. AcOH gives lobinol, C₁₈H₂₅O₂N (*hydrochloride*, m. p. 180°; *methiodide*, m. p. 101°), whilst oxidation with CrO₃ in dil. H₂SO₄ affords AcOH and BzOH. Oxidation of (II) with CrO₃ in aq. AcOH gives the *perchlorate*, m. p. 133°, of lobinone (III), C₁₈H₂₅O₂N (*hydrochloride*, m. p. 94°, becoming red, [α]_D —18.6° in H₂O). Treatment of (III) with EtOH-KOH affords NH₂Me, whilst lobinone *methiodide*, m. p. 141°, is converted by cold aq. NaHCO₃ into NHMe₂ and a doubly-unsaturated *diketone* (IV), C₁₇H₂₀O₂ (probably α-benzoyl-θ-acetyl-Δ^{8,9}-octadiene), m. p. 83° becoming red, which dissolves in alkalis with an intense violet colour. Catalytic reduction (Pt-black) of (IV) in AcOH gives a saturated glycol (not characterised) oxidised by CrO₃ in AcOH at room temp. to a *diketone*, C₁₅H₂₄O₂ (probably α-benzoyl-θ-acetyloctane), m. p. 53°. This with CrO₃ in AcOH at 100° gives BzOH and suberic acid. H. BURTON.

Corytuberine dimethyl ether. J. M. GULLAND and R. D. HAWORTH (Ber., 1931, 64, [B], 2768).—The compound has been described by the authors (A., 1928, 1030; cf. A., 1931, 1311). H. WREN.

Thalleioquin reaction. T. PAVOLINI (Boll. Chim. farm., 1931, 70, 795—799).—This reaction seems to be given only by *p*-OH-derivatives of cinchonine and is due to the formation of colouring matters of the indamine type. The probable mechanism of the reaction is given. T. H. POPE.

Synthesis of phenolic aporphines. II. Protection of hydroxyls by the carbethoxyl group, and the action of benzyl chloride on nitrophenyl-

acetic acids. J. M. GULLAND, K. I. ROSS, and C. J. VIRDEN (J.C.S., 1931, 2881—2885).—The CO_2Et -group, although efficient as a protective radical during the Bischler-Napieralski reaction, is unsuitable for standard use during aporphine syntheses. 2-Nitro-3-methoxy-4-ethylcarbonatophenylacetyl chloride and β -3:4-dimethoxyphenylethylamine give the corresponding amide, which is converted by PCl_5 in CHCl_3 into 2'-nitro-3':6:7-trimethoxy-4'-ethylcarbonato-1-benzyl-3:4-dihydroisoquinoline, m. p. 137° [methiodide, m. p. 160° (decomp.)]; 2'-nitro-6:7-dimethoxy-3':4'-diethylcarbonato- [picrate, m. p. 178—179°; methiodide, m. p. 166.5° (decomp.)], is similarly prepared. CH_2PhCl gives with a Na_2CO_3 solution of $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ only the acid, but with the nitrated acids varying proportion of the CH_2Ph esters are obtained; CH_2Ph p-nitrophenylacetate, m. p. 92° (also prepared from the acid chloride and $\text{CH}_2\text{Ph}\cdot\text{OH}$), and CH_2Ph 6-nitro-3:4-dimethoxyphenylacetate, m. p. 117°, are described. F. R. SHAW.

Synthesis of phenolic aporphines. III. 3-Hydroxy-4:5:6-trimethoxyaporphine. J. M. GULLAND, K. I. ROSS, and N. B. SMELLIE. IV. Laurotetanine. R. L. DOUGLAS and J. M. GULLAND (J.C.S., 1931, 2885—2893, 2893—2903).—III. Stages leading to the synthesis of 3-hydroxy-4:5:6-trimethoxyaporphine, regarded by Gadamer (A., 1911, i, 1011, 1012) as corydine and by Go (J. Pharm. Soc. Japan, 1929, 49, 128) as isocorydine, are described. 2-Nitrovanillin, hippuric acid, Ac_2O , and NaOAc give 5-keto-2-phenyl-4-2'-nitro-4'-acetoxy-3'-methoxybenzylidene-4:5-dihydro-oxazole (I), m. p. 171—172°, converted by boiling 96% EtOH into *Et* 2-nitro-4-acetoxy-3-methoxybenzylidenhippurate, m. p. 149°, hydrolysed by 2*N*- NaOH to 2-nitro-4-hydroxy-methoxybenzylidenhippuric acid, m. p. 197—198°, also formed by hydrolysis of (I) with 50% H_2SO_4 . Hydrolysis of (I) with aq. $\text{EtOH}\cdot\text{HCl}$ under pressure gives 2-nitro-4-hydroxy-3-methoxyphenylpyruvic acid, m. p. 182°, oxidised by alkaline H_2O_2 to 2-nitro-4-hydroxy-3-methoxyphenylacetic acid. 2'-Nitro-benzyl-3'-methoxyphenylacetate- β -3:4-dimethoxyphenylethylamide, m. p. 112—113°, is converted by PCl_5 in CHCl_3 into the hydrochloride, m. p. 232—233° (decomp.), of 2'-nitro-4'-benzyloxy-6:7:3'-trimethoxy-1-benzyl-3:4-dihydroisoquinoline (II), m. p. 119°, the methiodide, m. p. 108°, decomp. 200°, or the methosulphate of which is reduced by Zn dust and conc. HCl to 2'-amino-4'-benzyloxy-6:7:3'-trimethoxy-1-benzyl-2-methyltetrahydroisoquinoline, oily (dipicrolonate, m. p. 207°). Details of the conversion of this into 3-hydroxy-4:5:6-trimethoxyaporphine are to be published later. Catalytic reduction ($\text{Pd}\cdot\text{charcoal}$) of nitropapaverine methochloride in H_2O gives (probably) aminopapaverine methochloride, whilst the methochloride of (II) absorbs the calc. amount of H for the NO_2 group and 1 double linking, but does not afford the aminotetrahydroisoquinoline derivative.

IV. 3-Hydroxy-2:5:6-trimethoxyaporphine has been synthesised for comparison with laurotetanine. Benzylvanillin, hippuric acid, Ac_2O , and NaOAc give 5-keto-2-phenyl-4-4'-benzyloxy-3'-methoxybenzylidene-4:5-dihydro-oxazole, m. p. 195—196°, hydrolysed by aq. $\text{Ba}(\text{OH})_2$ and aq. NaOH to 4-benzyloxy-3-methoxyphenylpyruvic acid, m. p. 179°, and 4-benzyloxy-3-methoxybenzylidenhippuric acid, m. p. 210°, respectively. The 6- NO_2 -derivative, m. p. 222°, of 4-benzyloxy-3-methoxyphenylacetic acid, m. p. 116°, is hydrolysed by conc. HCl in AcOH to 6-nitro-4-hydroxy-3-methoxyphenylacetic acid, m. p. 184°. 6'-Nitro-4'-benzyloxy-3'-methoxyphenylacetate- β -3:4-dimethoxyphenylethylamide, m. p. 168°, is converted by PCl_5 into 6'-nitro-4'-benzyloxy-6:7:3'-trimethoxy-1-benzyl-3:4-dihydroisoquinoline, m. p. 155—156° [hydrochloride (+3 H_2O), m. p. 210° after softening at 95—105° (loss of H_2O)], the methiodide (+2 H_2O), m. p. 202° (also obtained with m. p. 196—197°), of which is reduced by Zn dust and conc. HCl at 0° to 6'-amino-4'-benzyloxy-6:7:3'-trimethoxy-2-methyltetrahydroisoquinoline (III) [dipicrolonate (IV), m. p. 193—194°]. Diazotisation of the solution obtained during the above reduction and subsequent treatment with Cu powder gives a little unidentified substance (picrolonate, m. p. 245°). Decomp. of (IV) with $\text{MeOH}\cdot\text{H}_2\text{SO}_4$, separation of the picrolonic acid, treatment of the resultant solution with conc. aq. $\text{Ba}(\text{NO}_3)_2$, removal of BaSO_4 , and boiling the diazo-solution give 3-benzyloxy-2:5:6-trimethoxyaporphine, debenzylated by conc. HCl to the 3-hydroxy-derivative (description to be published later).

The dipicrolonates of 6'- and 2'-amino-5:6:3':4'-tetramethoxy- and 2'-amino-6:3':4'-trimethoxy-1-benzyl-2-methyltetrahydroisoquinolines have m. p. 150° (decomp.), 201° (decomp.), and 207° (decomp.), respectively; these salts are recommended for the purification of the above bases. The yields of arylpyruvic acids obtained by hydrolysis of the azlactones from hippuric acid and the following araldehydes by aq. $\text{Ba}(\text{OH})_2$ (cf. above) are quoted in parentheses: piperonal (85%), PhCHO (25%), anisaldehyde (23%), vanillin (0), and *m*- and *p*-hydroxybenzaldehydes (0). 5-Keto-2-phenyl-4-*m*- and -*p*-nitrobenzylidene-4:5-dihydro-oxazoles have m. p. 174° and 233°, respectively; the former is hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to *m*-nitro- α -benzamido-cinnamic (*m*-nitrobenzylidenhippuric) acid, m. p. 223—224°.

H. BURTON.

Trypanocidal activity and chemical constitution. III. Sulphur derivatives of aromatic organic arsenicals (cont.). Gold derivatives of 2-thiolbenziminazole-5-arsinic acid. J. G. EVERETT (J.C.S., 1931, 3032—3043; cf. A., 1931, 106).—Equimol. amounts of 2-thiolbenziminazole-5-arsinic acid (I) and aq. AuCl_3 give 2-aurothiolbenziminazole-5-arsinic acid (II) and the sulphate (III), m. p. 210° (softens at 190°), of benziminazole-5-arsinic acid. 3 Mols. of (I) and 1 mol. of aq. AuCl_3 afford *o*-arsino-2-aurothiolbenziminazole-5-arsino-2-thiolbenziminazole (IV) and a little (III); (IV) is also prepared from (I) and (II). Treatment of (IV) with aq. $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ gives (II) and 2-carboxymethylthiolbenziminazole-5-arsinic acid, whilst with I in aq. NaHCO_3 , (II) and benziminazole-5-arsinic acid result. Treatment of (II) with dil. HCl or 25% NaOH affords Au and (IV), whilst oxidation with I in aq. NaHCO_3 furnishes Au and benziminazole-5-arsinic acid. 2-Thiolbenziminazole similarly affords 2-aurothiolbenziminazole, decomp. 235°, or 2-auro-

thiolbenziminazole-2-thiolbenziminazole (V), softens and shrinks at 193°, which undergo similar reactions to (II) and (IV). (IV) and (V) are co-ordination compounds of the type $\text{R}\cdot\text{S}\cdot\text{Au}\cdots\text{RSH}$. (II) and H_2S in dil. HCl give 2-aurothiolbenziminazole-5-arsenic disulphide, whilst (IV) similarly affords the hydrochloride of 2-aurothiolbenziminazole-5-arsenic disulphide (VI); (VI) is oxidised by I in aq. suspension to (IV). The above compounds have been tested against *T. equiperdum* in mice; (VI) is the only substance with marked therapeutic activity. H. BURTON.

Trypanocidal action and chemical constitution. X. Arylthioarsinites. A. COHEN, H. KING, and W. I. STRANGEWAYS (J.C.S., 1931, 3043—3057).—Aryldithioarsinites, $\text{Ar}\cdot\text{As}(\text{SR})_2$, are prepared from $\text{Ar}\cdot\text{AsO}$ and 2 mols. of SHR in aq. or NaHCO_3 solution. The following are described: (a) from acetanilide-*p*-arsenoxide: *di*(carboxymethyl), m. p. 108—110°; *di*(β -carboxyethyl), m. p. 147°; *di*(β -amino- β -carboxyethyl), m. p. 187° (decomp.) (using cysteine); *di*(*o*-carboxyphenyl), m. p. 225°; *di*(*m*-carboxyphenyl), m. p. 219°; *di*(glutathionyl), decomp. 115°, and *di*(carbamylnethyl), m. p. 120° (using $\text{HS}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$), acetanilide-*p*-thioarsinites; (b) from benzamide-*p*-arsenoxide; *di*(β -carboxyethyl), m. p. 160°; *di*(β -amino- β -carboxyethyl) (I), decomp. 240°; *di*(*o*-carboxyphenyl), m. p. 247° (decomp.); *di*(*m*-carboxyphenyl), m. p. 285° (softens at 270°); *di*(glutathionyl), m. p. 130° (decomp.), and *di*(carbamylnethyl) (II), m. p. 193°, benzamide-*p*-thioarsinites. These thioarsinites are not hydrolysed to any appreciable extent by aq. NaHCO_3 (cf. A., 1930, 796), but considerably by aq. NaOH (cf. Barber, A., 1929, 833); this view is supported by polarimetric observations on (I) in these alkalis. (II) dissolves readily in aq. NaOH , but neutralisation of the solution with CO_2 causes its re-synthesis; the reactions $\text{R}\cdot\text{As}(\text{SR}')_2 + 2\text{H}_2\text{O} \xrightarrow[\text{II}]{\text{OH}'} \text{R}\cdot\text{As}(\text{OH})_2 + 2\text{HSR}'$ undoubtedly occur.

The NaOH solutions give an intense coloration with Na nitroprusside (test for HSR'), whilst the original thioarsinites in aq. NaHCO_3 do not (or only slightly). Cystine (and other disulphides) with benzamide-*p*-arsenoxide in *N*- NaOH immediately develops the nitroprusside reaction; the change $\text{R}\cdot\text{AsO} + (\text{SR}')_2 + 2\text{H}_2\text{O} \xrightarrow{\text{OH}'} \text{R}\cdot\text{AsO}_3\text{H}_2 + 2\text{HSR}'$ is confirmed polarimetrically. Thiols do not reduce arsenic acids in alkaline solution, and the mechanism suggested by Barber (*loc. cit.*) for the reaction between such substances, is, therefore, invalidated. In almost neutral solution, the changes occurring are probably: $\text{R}\cdot\text{AsO}(\text{OH})_2 + 4\text{HSR}' \longrightarrow \text{R}\cdot\text{As}(\text{SR}')_4 \longrightarrow \text{R}\cdot\text{As}(\text{SR}')_2 + (\text{SR}')_2$. The tetrathioarsenates described in B.P. 331,195 (B., 1930, 967) are equimol. mixtures of thioarsinites and disulphides.

4:4'-Arsenobenzoic acid and 2 mols. of cystine in aq. NaOH give (after neutralisation) *di*(β -amino- β -carboxyethyl) benz-*p*-thioarsinite, decomp. 245°, prepared also from *p*-benzarsenoxide and cysteine. 2-Carboxymethylthiol-4 (or 5)-methylglyoxaline-5 (or 4)-carboxylic acid (+ H_2O), decomp. 188°, is obtained from the 2-thiol derivative and $\text{CH}_3\text{Cl}\cdot\text{CO}_2\text{H}$. Dithiol-ethane condenses with acetanilide-*p*-arsenoxide and

p-benzarsenoxide in EtOH to give cycloethylene acetanilide-*p*-thioarsinite, $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{As} \begin{smallmatrix} \text{S}\cdot\text{CH}_2 \\ \text{S}\cdot\text{CH}_2 \end{smallmatrix}$, m. p. 155°, and cycloethylene benz-*p*-thioarsinite, m. p. 223—224°, respectively. Oxidation of di(carboxymethyl) benzamide-*p*-thioarsinite with H_2O_2 gives benzamide-*p*-arsinic acid and disulphidoacetic acid (cf. A., 1930, 796).

The thioarsinites have been tested against *T. equiperdum* in mice. As the mol. wt. of the thiol constituent increases the toxicity decreases, and they possess greater therapeutic activity than the parent arsenoxides. H. BURTON.

Organo-mercuric derivatives of benzoic acid. A. N. NESMEJANOV and L. G. MAKAROVA (J. Gen. Chem. Russ., 1931, 1, 598—615).—The complete series of *o*-, *m*-, and *p*-isomerides of Me and Et esters of chloro-, bromo-, iodo-, cyano-, and thiocyanomercuribenzoic acids, $\text{CO}_2\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{HgX}$, was prepared from the corresponding aminobenzoic esters, which were transformed into esters of chloromercuribenzoic acids through the diazo-compounds. New compounds of this series are: *o*-derivatives, $\text{R}=\text{Me}$; $\text{X}=\text{Br}$, m. p. 175°, $\text{X}=\text{I}$, m. p. 172°, $\text{X}=\text{CN}$, m. p. 175°, $\text{X}=\text{CNS}$, m. p. 155°. $\text{R}=\text{Et}$; $\text{X}=\text{Cl}$, m. p. 256° [diazonium salt, m. p. 77° (decomp.)], $\text{X}=\text{Br}$, m. p. 280°, $\text{X}=\text{I}$, decomp. 267°, $\text{X}=\text{CN}$, m. p. 132—144°, $\text{X}=\text{CNS}$, m. p. 226°. *m*-Derivatives, $\text{R}=\text{Me}$; $\text{X}=\text{Cl}$, m. p. 208° [diazonium salt, m. p. 100° (decomp.)], $\text{X}=\text{Br}$, m. p. 204°, $\text{X}=\text{I}$, m. p. 164·5°, $\text{X}=\text{CN}$, m. p. 186°, $\text{X}=\text{CNS}$, m. p. 189—190°. $\text{R}=\text{Et}$; $\text{X}=\text{Cl}$, m. p. 172° [diazonium salt, m. p. 61° (decomp.)], $\text{X}=\text{Br}$, m. p. 172—173°, $\text{X}=\text{I}$, m. p. 142°, $\text{X}=\text{CN}$, m. p. 162°, $\text{X}=\text{CNS}$, m. p. 158°. *p*-Derivatives, $\text{R}=\text{Me}$, $\text{X}=\text{Cl}$, m. p. 259° [diazonium salt, m. p. 103—104° (decomp.)], $\text{X}=\text{Br}$, m. p. 246°, $\text{X}=\text{I}$, m. p. 224°, $\text{X}=\text{CN}$, m. p. 250°, $\text{X}=\text{CNS}$, m. p. 228—229°; $\text{R}=\text{Et}$, $\text{X}=\text{Cl}$, m. p. 222—223° [diazonium salt, m. p. 107·5° (decomp.)], $\text{X}=\text{Br}$, m. p. 211°, $\text{X}=\text{I}$, m. p. 204°, $\text{X}=\text{CN}$, m. p. 210—211°, $\text{X}=\text{CNS}$, m. p. 222°. The following esters of the general formula $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{R})_2$ were obtained: *o*-ester, $\text{R}=\text{Et}$, m. p. 117°; *m*-esters, $\text{R}=\text{Me}$, m. p. 129°, $\text{R}=\text{Et}$, m. p. 103—104°, *p*-esters, $\text{R}=\text{Me}$, m. p. 264—265°, $\text{R}=\text{Et}$, m. p. 194°. The following *m*-acids of the general formula $\text{HgX}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ were prepared: $\text{X}=\text{Cl}$, Br, and I. The anhydrides of *m*- and *p*-mercuribenzoic acid, and mercuridi-*m*- and -*p*-benzoic acids were also prepared. E. B. UVAROV.

Organic compounds of selenium. II. Action of selenium oxychloride on ethers. F. N. ALQUIST and R. E. NELSON (J. Amer. Chem. Soc., 1931, 53, 4033—4037; cf. A., 1930, 798).— SeOCl_2 reacts with ethers ($\text{Ph}\cdot\text{OR}$) in Et_2O at room temp. for 5 days to give 40—87% of $(p\text{-RO}\cdot\text{C}_6\text{H}_4)_2\text{SeCl}_2$; the following are described: *dianisyl*-, m. p. 163°, *di*-*p*-ethoxyphenyl-, m. p. 139°, *di*-*p*-propoxyphenyl-, m. p. 91°, *di*-*p*-butoxyphenyl-, m. p. 93°, *di*-*p*-phenoxyphenyl-, m. p. 135—140°, *di*-3-bromo-4-methoxyphenyl-, m. p. 180°, and *di*-4-methoxy-3-methylphenyl-, m. p. 155—158°, -selenium dichlorides. $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OMe}$, and *o*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ do not react under the above conditions. These dichlorides are converted by aq. NaHCO_3 or NaOH into the corresponding

dihydroxides, m. p. 134°, 146—148°, 51—54°, 58—60°, 122—125°, 150°, and 91°, respectively, and reduced by Zn in CHCl_3 to the corresponding *selenides*, $(p\text{-RO}\cdot\text{C}_6\text{H}_4)_2\text{Se}$, m. p. 54°, 60—62°, 46—48°, oily, 93—85°, 95°, and 36°, respectively. These selenides and Br in CHCl_3 give the corresponding *dibromides*, m. p. 125°, 117°, 69°, 65°, 113°, 87°, and 136°, respectively.

It is assumed that SeOCl_2 condenses with the *p*-position of the C_6H_5 ring; if this is blocked by NO_2 or Br, reaction does not occur at room temp. An *o*- NO_2 group also prevents reaction. C. J. WEST (*b*).

Peptides of tervalent amino-acids. I. Titration constants of histidylhistidine and of aspartylaspartic acid. J. P. GREENSTEIN (J. Biol. Chem., 1931, 93, 479—494).—Determination of the titration consts. of the acidic and basic groups of histidylhistidine and aspartylaspartic acid reveals a weakening of these groups as compared with the parent NH_2 -acids. The isoelectric points of these peptides are respectively more acid and more alkaline than those of the NH_2 -acids. The resemblance of their titration curves to that of a protein is marked, and is attributed to the accumulation of free acidic and basic groups.

A. COHEN.

Comparative rates of hydrolysis of adenylic, guanylic, and xanthylic acids. P. A. LEVENE and A. DMOCHOWSKI (J. Biol. Chem., 1931, 93, 563—570).—Xanthylic acid, $[\alpha]_D^{25} = -41.66^\circ$ in 5% NaOH solution, is prepared by treating an aq. solution of Na guanylate with AcOH and then aq. KNO_3 solution, pptg. the acid from the filtrate by $\text{Pb}(\text{OAc})_2$, and converting the Pb salt into the acid. Nucleosidase from pig-intestinal wall does not remove the base from the three nucleotides. A purified enzyme from pig-kidney, active in splitting nucleosides, also has no action on the acids. Guanylic and xanthylic acids are hydrolysed at the same rate by *N*-HCl at 50° and 70°, whilst with H_2O , whereas adenylic and guanylic acids are not hydrolysed, xanthylic acid suffers 40% decomp. to *d*-ribosephosphoric acid. F. O. HOWITT.

Preparation of glutenin in carbamide solutions. W. H. COOK and C. L. ALSBERG (Canad. J. Res., 1931, 5, 355—374).—Flour is extracted with 30% carbamide solution, starch is removed by a Sharples centrifuge, and the gliadin pptd. either by the addition of MgSO_4 or by dilution to give 10% carbamide solution. The use of EtOH to ppt. glutenin reduces the original solubility of the protein. Drying, even at room temp., renders glutenin insol. in 30% carbamide solution. The amide- and arginine-N contents of glutenin prepared by the carbamide method are intermediate between those of samples isolated from alkali and those isolated from acid. The denaturation of glutenin by carbamide solutions is less than that by dil. alkalis and not greater than that by dil. acids.

A. G. POLLARD.

Preparation and heat-denaturation of gluten proteins. W. H. COOK (Canad. J. Res., 1931, 5, 389—406).—Owing to fractionation during isolation, gliadin prepared by different methods has a varying crit. peptisation temp. (C.P.T.) and viscosity in 30% carbamide buffer solutions, but const. N content. Gluten can be fractionated by addition of LiCl to its

solution in 30% carbamide solution. The viscosity of gluten in buffered 30% carbamide solution does not change with time or alteration of p_H , but is decreased by heating to 70°. Gliadin, when dispersed, but not when solid, decreases in C.P.T. and viscosity when heated to 70°, the glutenin being first affected.

R. S. CAHN.

Products of hydrolysis of tussah-silk fibroin (Liao Ning Sing Shen-Tung yarn). E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1931, 202, 37—48).—Tussah-silk fibroin was hydrolysed in stages with increasing concn. of acid. At stage I (25% H_2SO_4) the majority was hydrolysed, giving all the NH_2 -acids present including norvaline, chitosamine, and *L*-alanyl-*L*-tyrosine. At stage II (40% H_2SO_4) all the previously obtained NH_2 -acids except tryptophan and aspartic acid were observed. Stage III (boiling 70% H_2SO_4) gave a little glycine, much alanine and *di*-*L*-alanyl-*L*-alanyl-*L*-glycine (I), decomp. about 256°. Benzoylation of (I) and hydrolysis gave benzoylalanine; (I) and trypsin-kinase afforded glycine. (I) after esterification, interaction with $\text{CH}_2\text{Ph}\cdot\text{NH}_2$, and hydrolysis gave glycylbenzylamine (*phenylcarbimido*-derivative, m. p. 202°), indicating that glycine carries the CO_2H group. *L*-Alanylbenzylamine (*phenylcarbimido*-derivative, m. p. 223°) was prepared.

J. H. BIRKINSHAW.

Electrometric analysis of animal and vegetable proteins. J. ERRERA, H. VOGELS, and L. HAUSS (Compt. rend., 1931, 193, 959—961).—The electrometric titration curves of maize proteins and gelatin are analysed. Such curves permit the analysis of a complex mixture of proteins.

C. C. N. VASS.

Combination of standard gelatin with hydrochloric acid and sodium hydroxide. D. I. HITCHCOCK (J. Gen. Physiol., 1931, 15, 125—138).—Gelatin dries to const. wt. in vac. only below 100°; its ash and N content, κ , and isoelectric point were determined. Further methods of characterisation were obtained by e.m.f. measurements of the combination of gelatin with H ions and Cl ions in HCl, and by plotting a combination curve of gelatin with H ions and OH ions in varying p_H .

H. DAVSON.

Destruction of large quantities of organic matter with perchloric acid. E. KAHANE (Compt. rend., 1931, 193, 1018—1020).—The matter to be prepared for analysis (*e.g.*, viscera etc.), preferably dried, is heated with H_2SO_4 and excess of HNO_3 , the H_2O formed and excess of HNO_3 are removed by heating to 180—190°, and 60% aq. HClO_4 is then added dropwise. Oxidation readily proceeds to completion, and there is no danger of accumulation in solution of dangerous amounts of HClO_4 .

H. A. PIGGOTT.

Micro-determination of carbon and hydrogen. A. FRIEDRICH (Mikrochem., 1931, 10, 329—354).—Apparatus is described in which the absorption tubes are closed so that the whole combustion may be carried out in O_2 , and in which a special regulator is employed to provide a steady stream of O_2 . The period of contact of the gases with the hot Pt is 60—75 sec. A 1.5-mg. sample is sufficient, and 2 analyses may be carried out within 1 hr. The errors which arise in the analysis of compounds containing

S, N, or halogen have been investigated, and full details are given for the pre-treatment of the PbO_2 in a manner which removes all CO_2 but does not cause the formation of PbO . H. F. GILLBE.

Micro-determination of carbon by wet oxidation. II. Oxidation of liquids. E. SCHADEN-DORFF and M. K. ZACHERL (Mikrochem., 1931, 10, 99—108).—Details are given of an apparatus suitable for the oxidation of liquids by Ag_2CrO_4 - $\text{K}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 mixtures, and of the analytical procedure for simple compounds and biological materials. The influence of H_2O on the oxidation has been examined. With dil. carbamide solutions it is necessary to concentrate the solution by addition of Na_2SO_4 and keeping the mixture over H_2SO_4 , but accurate results are obtained for urine if O_2 is passed through the solution before the oxidation. The results obtained with blood-serum are consistent, although slightly higher than those obtained by other methods.

H. F. GILLBE.

Advances in the determination of carbon and hydrogen in organic elementary analysis. J. LINDNER [with N. FIGALA] (Mikrochem., 1931, 10, 321—328).—After titration with phenolphthalein of a solution containing BaCO_3 as a ppt., the colour always becomes pink again on keeping the mixture; if the solution is warmed this change is completed within 10—20 min., and a final end-point may then be obtained. The effect is concerned with the form of the ppt. and is influenced by Ca salts. Quantities of CO_2 down to 1 mg. may be determined with a max. error of 0.2% under suitable conditions, which include the use of a satisfactory absorption vessel and a small vol. (1.5—2 c.c.) of 0.05*N*-solution. Only slight modifications have been made recently in the PH_3 method for the determination of H; with a 3—4-mg. sample an error of the order of 0.05% may be anticipated.

H. F. GILLBE.

Microanalytical methods for the industrial laboratory. II. Modification of Pregl's method for the micro-determination of carbon and hydrogen, using only oxygen. (Fr.) VETTER (Mikrochem., 1931, 10, 109—113).—To overcome difficulties arising from the impurities present in air, the combustion and washing through of the CO_2 are effected with pure O_2 . The determination is accurate and may be completed within 40 min. The sample should not exceed 5 mg., and the roll of Cu gauze should not be omitted.

H. F. GILLBE.

Detection of organic compounds. VII. L. ROSENTHALER (Pharm. Ztg., 1931, 76, 1301—1302).—The behaviour of $\text{Hg}(\text{OAc})_2$ towards alcohols, aldehydes, carbohydrates, and hydroxy-acids, reactions of various aromatic amines and phenols with $\text{Cu}(\text{CN})_2$,

$\text{Cu}(\text{CNS})_2$, and CuSO_4 , and a colour reaction between *m*-cresol and vanillin- H_2SO_4 mixture are described. The raspberry-red colour (persisting on dilution with H_2O) produced in the last-named reaction is probably responsible for the colour obtained in the Lind reaction for myrrh. Many strong, H_2O -sol. org. bases produce a red colour with Schiff's reagent and it is not sp. for pyramidone. NH_4 lactate, oxalate, tartrate, and citrate yield HCN on distillation with P_2O_5 .

E. H. SHARPLES.

Determination of pentaerythritol. M. Y. KRAFT (J. Chem. Ind., Russia, 1931, 8, 507).—Pentaerythritol in admixture in solution is determined ($\pm 0.25\%$) by shaking with PhCHO , HCl , and EtOH , filtering after 12 hr., and drying and weighing the acetal, $\text{CHPh}(\text{OCH}_2)_2\text{C}(\text{CH}_2\text{O})_2\text{CHPh}$, m. p. 157° .

CHEMICAL ABSTRACTS.

Volumetric determination of novocaine. J. RAE (Pharm. J., 1931, 127, 394).—An iodometric method of determining novocaine (not affected by the presence of adrenaline) is described.

R. S. CAHN.

Use of bromine as a reagent in the determination of alkaloids. S. G. WALTON and R. G. O'BRIEN (Analyst, 1931, 56, 714—735).—The thalleioquin reaction is quant. under certain defined conditions. 0.0001 g. of alkaloid in 10 c.c. may be determined. Cl_2 cannot satisfactorily replace Br. EtOH interferes and free acid prevents the formation of the colour; neutral salts are without action. In presence of strychnine, caffeine, atropine, cinchonine, cinchonidine, and cocaine the test is untrustworthy, but if an excess of Br is used before aeration, and KI added to form the quinine-I compound, this may be determined by the addition of excess 0.01*N*- $\text{Na}_2\text{S}_2\text{O}_3$ and back titration with I solution. Cupreine gives satisfactory results by the I method. Morphine interferes with the thalleioquin reaction owing to the formation of a Br-compound, which may be determined by the above I method. Some of the opium alkaloids form Br_2 - and others Br_3 -derivatives. Many alkaloids, after oxidation with Br, give a red colour on adding H_2O_2 followed by very dil. alkali. Codeine and ethylmorphine treated with Br and H_2O_2 give a red colour at 60 — 70° . Emetine and cephaeline give with Br a yellow colour sensitive to 1 part of alkaloid in 25,000 parts of solution. These alkaloids cannot be determined by the I method. Phenolic compounds add 4Br readily and, on treatment with KI, revert to the Br_3 -derivative, liberating I, which may be titrated with $\text{Na}_2\text{S}_2\text{O}_3$. Although quinine does not contain a phenolic group, it probably forms an active grouping $\text{CO}\cdot\text{CBr}_2$; by conversion into $\text{C}(\text{OH})\cdot\text{CBr}$ this liberates I on adding KI.

T. McLACHLAN.

Biochemistry.

Animal life in synthetic mixtures of nitrogen and oxygen. J. W. HERSHEY (Trans. Kansas Acad. Sci., 1930, 33, 133—136).—Small animals died in gas containing 21% O_2 and 69% N_2 but lived normally when the O_2 content was 25—60%.

CHEMICAL ABSTRACTS.

Micro-determination of oxygen and carbon dioxide in blood. H. W. MOOK (Biochem. Z., 1931, 242, 338—347).—A solution of 0.5 g. of $\text{K}_3\text{Fe}(\text{CN})_6$ in 100 c.c. of H_2O made alkaline with 1 c.c. of 25% NH_3 absorbs all the CO_2 from the gas liberated from blood on evacuation and leaves all the O_2 free. The

application of the apparatus previously described (A., 1930, 1201) to the determination of O_2 and CO_2 in 50—70 c.c. of blood is described. A procedure for withdrawing the blood from the finger without permitting gaseous exchanges to occur is also described.

W. MCCARTNEY.

Copper and blood formation. VON LINDEN (Med. Welt, 1931, 5, 629; Chem. Zentr., 1931, i, 3254).—Cu plays an important part in the living organism and, in certain conditions, has therapeutic val.

A. A. ELDRIDGE.

Action of phenylhydrazine and phenylhydroxylamine on the metabolism of red blood-cells. Determination of metabolism of red blood-cells. O. WARBURG, F. KUBOWITZ, and W. CHRISTIAN (Biochem. Z., 1931, 242, 170—205).—Methæmoglobin, produced in erythrocytes by amyl nitrite, oxidises carbohydrate, becomes reduced to hæmoglobin, and on shaking with O_2 gives oxyhæmoglobin. The action is not catalytic but stoicheiometric. The methæmoglobin obtained by treatment of erythrocytes with $NHPh\cdot OH$ is reduced anaerobically to hæmoglobin and the solution on oxygenating gives only hæmoglobin. If, however, the methæmoglobin reacts in the cell aerobically with carbohydrate, reoxidation gives back methæmoglobin, the reaction being catalytic. The respiration of rabbit's erythrocytes with $NHPh\cdot OH$ is 20 times normal. $NHPh\cdot NH_2$ added to the red cells *in vitro* colours them brown and respiration is greatly increased. $NHPh\cdot NH_2$ destroys hæmoglobin, liberating hæmin and denaturing globin. The liberated hæmin oxidises oxy- to met-hæmoglobin and the latter oxidises carbohydrate. Hæm, so formed, is then reoxidised by O_2 to hæmin and hæmoglobin to oxyhæmoglobin, thus regenerating the original system. When $NHPh\cdot NH_2$ is injected into rabbits, the respiration of red cells increases by 20 to 40 times. These cells are not brown as in experiments *in vitro* and they contain denatured globin but no free hæmin, this having been excreted or destroyed.

P. W. CLUTTERBUCK.

Physical chemistry of proteins. VIII. Solubility of hæmoglobin in concentrated salt solutions. Salting out of proteins. IX. Effect of electrolytes on solubility of hæmoglobin in solutions of varying hydrogen-ion activity. Comparable behaviour of caseinogen. A. A. GREEN (J. Biol. Chem., 1931, 93, 495—516, 517—542).—VIII. The solubilities of carboxy- and oxy-hæmoglobin in conc. K_2HPO_4 buffers, and of the former in Na_2SO_4 , $(NH_4)_2SO_4$, $MgSO_4$, and Na citrate, have been determined by equilibration and conform, at const. temp. and p_H , to the equation $\log S - \beta - K'\mu$, where μ is the ionic strength. β depends on the protein and p_H . Increase of temp. from 0° to 25° decreases the solubility of carboxyhæmoglobin in phosphate solutions tenfold. K' , which is independent of temp. and p_H , varies with the electrolyte, decreasing in the order $KH_2PO_4 + K_2HPO_4$, Na_2SO_4 , Na citrate, $(NH_4)_2SO_4$, $MgSO_4$.

IX. Further solubility measurements at 25° are recorded. Hæmoglobin behaves as a bivalent acid or base on either side of the p_H of min. solubility (6.6). An equation is deduced relating the total solubility to

that of the neutral mol. in terms of the apparent dissociation const. The latter and also the isoelectric point vary with electrolyte concn. The solubility of caseinogen in $NaCl + NaOH$ or HCl also indicates behaviour as a bivalent acid or base.

A. COHEN.

Oxidation of hæmoglobin by methylene-blue. O. WARBURG and A. REID (Biochem. Z., 1931, 242, 149—158).—The reversible reaction between methylene-blue (1 mol.) and hæmoglobin (2 mol.) is followed manometrically, the substances being mixed in an atm. of CO . When hæmoglobin and CO are in equilibrium, very little free hæmoglobin exists. If methylene-blue is then added, methæmoglobin is formed, the reaction again coming to an equilibrium. If, however, the free methæmoglobin is removed from solution by addition of HCN , the process goes much further. $M + 2HbCO + 2HCN \rightleftharpoons MH_2 + 2HbCN + 2CO$. Oxidation of hæmoglobin is therefore measured by elimination of CO (positive pressure) and reduction of methæmoglobin by absorption of CO (negative pressure).

P. W. CLUTTERBUCK.

Methæmoglobin and oxygen. W. HEUBNER (Biochem. Z., 1931, 241, 493; cf. Michaelis, A., 1931, 1319).—In some of the experiments of the author and Rhode (A., 1924, i, 229) light and bacteria were not excluded and hence the explanations of Michaelis can be applied.

W. MCCARTNEY.

Determination of plasma volume. I. Dye method. S. GRAFF and H. T. CLARKE. **II. Rate of dye mixing.** S. GRAFF, D. A. D'ESOP, and A. J. B. TILLMAN (Arch. Int. Med., 1931, 48, [i], 808—820, 821—827).—I. The concn. of $K_2C_2O_4$ producing min. crenation and hæmolysis in blood is 1%. The optical absorption of brilliant-vital-red solutions is increased by colloids and decreased by electrolytes, the region of max. absorption being also changed. The spectrophotometric evaluation of the dye content in plasma in presence of oxyhæmoglobin is described. II. Following intravenous injection of the dye, the concn. attains a max. and then falls to an equilibrium val. within 6 min. due to varying rates of circulation in different parts of the system. The concn. then decreases at the rate of 10—20% per hr. Divergences may occur in pregnancy and pathological cases.

F. O. HOWITT.

Determination of albumin-globulin ratios in human serum. W. R. CAMPBELL and M. I. HANNA (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 29—31).—The method depending on the determination of total serum-protein by Kjeldahl determination of N and of albumin in a similar fashion after removal of globulins by Na_2SO_4 is applied to a rapid modification suitable for clinical purposes.

F. O. HOWITT.

Conversion of serum-albumin into serum-globulin. A. FISCHER (Naturwiss., 1931, 19, 965—966).—Proteins form a complex with heparin, the composition of which varies with the concn. of heparin; the solubility of the proteins is thereby increased and the isoelectric point is shifted to the acid side. Addition of heparin to a solution of albumin at p_H 5 gives a ppt. which has all the properties of a euglobulin, provided that the protein is in excess; further

addition of heparin causes the globulin to dissolve. The facts support Sørensen's theory of the reversibility of a dissociable protein system.

P. G. MARSHALL.

Mol. wts. of the proteins in their native state. T. SVEDBERG (Nature, 1931, 128, 999—1000).—Redeterminations of sedimentation consts. [by B. SJÖGREN and Miss I. B. ERIKSSON] show that serum-albumin and -globulin, amandin, phycoeyan, phycoerythrin, and hæmocyannin possess the same mol. wts. whether native or purified. In other cases, the action of $(\text{NH}_4)_2\text{SO}_4$, used in the purification process, results in aggregation. Hæmoglobin is not affected by $(\text{NH}_4)_2\text{SO}_4$.

L. S. THEOBALD.

Determination of oxidised glutathione [in blood]. Relation between oxidised and reduced glutathione. H. L. MASON (Proc. Staff Meetings Mayo Clinic, 1931, 6, 168—169).—The H_2WO_4 extract (25—50 c.c.) is evaporated under reduced pressure to 1 c.c. or less; the residue is extracted with HCl in EtOH, and the EtOH extract (after centrifuging), or an aliquot portion, is added to Na-Hg and Hg at 0°, 5N-HCl being added dropwise. The solution is diluted, treated with KI and starch, titrated with 0.01N-I to a blue colour, and titrated back to colourless with 0.002N- $\text{Na}_2\text{S}_2\text{O}_3$. A colorimetric procedure is described. The blood filtrates are prepared by a slight modification of Folin and Wu's method. The amount of oxidised glutathione in oxygenated blood is 20—50% of the total.

CHEMICAL ABSTRACTS.

Antitryptic factor in human blood-serum. W. CORNELI (Biochem. Z., 1931, 242, 61—66).—The hydrolysis of varying amounts of the serum by varying amounts of purified trypsin is investigated.

P. W. CLUTTERBUCK.

Activation of Robison's hexosemonophosphoric acid in red cells and the preparation of activating enzyme solutions. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1931, 242, 206—227).—Methæmoglobin in red cells oxidises glucose, but mixed with glucose *in vitro* does not react. If red cells are hæmolyzed with H_2O , the stromata removed by centrifuging, and glucose added to the clear centrifugate, neither O_2 utilisation nor glycolysis results nor are the cell reactions with methylene-blue and methæmoglobin obtained. If, however, glucose is replaced by Robison's hexosemonophosphoric acid, then the clear centrifugate behaves towards methylene-blue and methæmoglobin like the intact cell, the respiration being as great or greater. If the centrifugate is treated with $\text{Al}(\text{OH})_3$ and centrifuged, it is inactivated in respect to hexosephosphate. Activation requires the presence of at least two substances, the isolation of dry preps. of each of which is described, and in virtue of their properties they are regarded as enzyme and co-enzyme. In enzyme-co-enzyme solutions, hexosemonophosphate is attacked not only by methæmoglobin and methylene-blue, but also by O_2 , activation then carrying the reaction further than it goes under physiological conditions. This over-activation explains why an oxidation may be sensitive to CO and HCN in the cell, but may not be so sensitive in the enzyme solution.

P. W. CLUTTERBUCK.

Effect of sodium chloride on the activity of blood-catalase *in vivo*. G. M. SAVOSTJANOV (Biochem. Z., 1931, 241, 409—412).—The catalase content of the blood of rabbits is not appreciably affected by intravenous administration of 0.85% aq. NaCl or by oral administration of 20% solution, although 10% solution caused rapid, and the 20% slow, increase in the Cl content. Since, *in vitro*, the catalase content is appreciably reduced even by 0.1% NaCl there must be protective influence in the blood *in vivo*.

W. MCCARTNEY.

Chemical composition of the blood of *Camelus Bactriens*. C. T. LOO (Chinese J. Physiol., 1931, 5, 377—380).—The results of the determination of the various constituents of heparinised or oxalated camel's blood are recorded, and compared with vals. for horse, ox, sheep, and man. Non-protein-N, urea-N, Cl' , and inorg. and total P are high, whilst uric acid and lipid P are low.

A. COHEN.

Blood-sugar. E. J. BIGWOOD and A. WUILLOT (Compt. rend. Soc. Biol., 1930, 104, 329—331; Chem. Zentr., 1931, i, 3697).—Hagedorn's reagent oxidises a substance, probably of the glutathione series, which is not oxidised in Fontes and Thivolle's method. The substance is present only in the erythrocytes.

A. A. ELDRIDGE.

(a) State of the blood-sugar as shown by compensation dialysis *in vivo*. (b) Nature of the blood-sugar as shown by a comparison of the optical rotation and the reducing power of the *in vivo* dialysate. M. H. POWER and C. H. GREENE (J. Biol. Chem., 1931, 94, 281—293, 295—305).—(a) A modified type of the apparatus of Abel (A., 1914, i, 217) was inserted between the femoral vein and artery on each side of dogs, the dialysate liquids being without glucose on one side (dialysate A) and containing 0.20% on the other (dialysate B). After 4 hr. vividiffusion the glucose contents of A and B attained a common level of 0.12—0.13%, the val. of the plasma-sugar. The use of Et_2O for anaesthesia produced irregular results owing to its effect on the blood-sugar. The reducing substances in the dialysates were almost totally fermentable. Hence the plasma-glucose is freely diffusible (cf. A., 1921, i, 286; 1922, i, 291, 295; 1931, 754). The plasma-sugar is always higher than the corpuscular sugar, which is fairly const. over a considerable range of concn. of plasma-glucose. No redistribution of glucose between the cells and plasma occurs in blood on withdrawal.

(b) Dialysates A and B (see above) remained const. in rotatory power for periods up to 312 hr. The average vals. obtained, expressed as glucose, were 0.01—0.04% lower than those given by the reducing power. Hence substances undergoing spontaneous mutarotation were not present. Acidification to p_H 2 of the dialysates produced a marked and immediate increase in the rotation which then agreed with the vals. based on reducing power (cf. A., 1926, 861). This change in rotation was partly reversible. Hence in blood only α -D-glucose is present, other substances such as lactic acid playing a part in the optical phenomena, especially at certain ranges of $[\text{H}']$.

F. O. HOWITT.

Determination of true blood-sugar without yeast. A. FUJITA and D. IWATAKE (*Biochem. Z.*, 1931, 242, 43—60).—A new deproteinising method by means of $\text{Cd}(\text{OH})_2$ gives filtrates which, since they are free from glutathione, ergothioneine, and uric acid, give true blood-sugar vals. by any of the usual methods. An iodometric determination using $\text{K}_3\text{Fe}(\text{CN})_6$ is described. The reducing power of glutathione varies with its concn. and the presence or absence of sugar. In presence of considerable amounts of glutathione, the yeast method does not give correct sugar vals. The Hagedorn-Jensen method always gives too high results. P. W. CLUTTERBUCK.

Combined sugar of tungstic acid filtrates of blood. F. H. SCHARLES and E. S. WEST (*J. Biol. Chem.*, 1931, 93, 359—364).—The presence of a hydrolysable sugar complex in tungstic acid filtrates of blood (Tompsett, A., 1930, 1306) is not confirmed. On acid hydrolysis of such filtrates, the fermentable sugar remains unchanged, whilst the non-fermentable reducing substances increase to a max. in 5 hr. and finally fall below the original val. in 20 hr. This is not due to glutathione, but to unstable reducing material formed during hydrolysis. Since pptn. by $\text{HgSO}_4\text{--BaCO}_3$ completely removes the non-fermentable reducing substance at any point in the hydrolysis, there is no sugar in any form in tungstic acid filtrates. A. COHEN.

Picric acid blood-sugar method after zinc precipitation. V. C. MYERS and C. W. R. ROOT (*J. Lab. Clin. Med.*, 1931, 16, 890—897).—The filtrate after pptn. of blood-proteins with ZnSO_4 and NaOH is saturated with picric acid and analysed by Myers and Bailey's method (A., 1916, i, 300). Non-glucose reducing substances are pptd. by the ZnSO_4 .
CHEMICAL ABSTRACTS.

Determination of free, protein-, and combined non-protein-sugar in normal and pathological serum, urine, and body-fluids. B. LUSTIG and A. LANGER (*Biochem. Z.*, 1931, 242, 320—337).—By modifications of the method of Tillmans and Philippi (A., 1930, 108) the various sugar fractions can be determined in small amounts (0.05—0.4 c.c.) of the fluids mentioned. Hydrolysis is unnecessary and the errors of other methods are avoided. The procedure has been applied to determinations in the fluids from persons suffering from various diseases. W. MCCARTNEY.

Alterations in the rotation and mutarotation of glucose. II. Effect of salts and organic substances. H. N. NAUMANN (*Biochem. Z.*, 1931, 242, 259—265; cf. A., 1931, 1275).—Under usual experimental conditions the salts used for deproteinisation, prevention of coagulation of blood, and clarification have no effect on the rotation of glucose solutions. The rotation is affected by EtOH and AcOH , but not by substances usually present in body-fluids (urea, creatine, creatinine, uric acid). W. MCCARTNEY.

Gasometric determination of lactic acid in the blood. B. F. AVERY and A. B. HASTINGS (*J. Biol. Chem.*, 1931, 94, 273—280).—Blood or serum (1 c.c.) is deproteinised by H_2WO_4 , the filtrate freed from carbohydrates by treatment with CuSO_4 and $\text{Ca}(\text{OH})_2$ (A., 1918, ii, 86), and the lactic acid in the solution

determined by oxidation to CO_2 by KMnO_4 , using the manometric gas apparatus of Van Slyke (A., 1927, 800). A correction for CO_2 evolved from some unknown substance is applied. F. O. HOWITT.

Influence of fat deprivation and feeding on the distribution of blood-lipins. S. M. LING (*Chinese J. Physiol.*, 1931, 5, 381—397).—The lipin contents of whole blood and plasma have been determined for two dogs on diets varied in fat content. Corpuscle vals. were determined indirectly. Removal of fat from a mixed diet causes a decrease in blood-lipins other than lecithin and cholesterol. During fasting a bigger reduction in blood-fat occurs, in which lecithin and cholesterol are mainly affected. 6—7 hr. after ingestion of olive oil all lipid constituents are increased, to a greater extent, generally, in the plasma. In the transport of absorbed fat, lecithin and cholesterol appear to be employed. A. COHEN.

Determination of cholesterol in whole blood. J. C. FORBES and H. IRVING (*J. Lab. Clin. Med.*, 1931, 16, 909—912).—A modification of the method employed for plasma and serum (A., 1931, 1080).

CHEMICAL ABSTRACTS.

Micro-determination of lecithin in blood and plasma. W. LINTZEL and G. MONASTERIO (*Biochem. Z.*, 1931, 241, 273—279; cf. A., 1931, 1178).—The method previously described has been modified and applied to the determination of lecithin in 10 c.c. of blood or plasma. The NMe_3 liberated from choline derived from the lecithin is determined by titration. Results for horse, sheep, and human blood and plasma show that the lecithin content of the plasma is slightly lower than that of the whole blood. W. MCCARTNEY.

Sensitivity of methods for determination of cholesterol, phosphorus, and calcium in the same sample of blood-serum. G. H. BARIL and J. LABARRE (*Trans. Roy. Soc. Canada*, 1931, [iii], 25, V, 43—44).—The method of the authors for the determination of Ca (A., 1931, 377) is applicable to a concn. of not less than 0.005%, the standard colorimetric method for cholesterol to one of not less than 0.004%, and the method of Benedict and Theis (A., 1924, ii, 700) for P to not less than 0.5 c.c. of serum. F. O. HOWITT.

Normal variations in the inorganic phosphorus of the blood of dairy cattle. L. S. PALMER, W. S. CUNNINGHAM, and C. H. ECKLES (*J. Dairy Sci.*, 1930, 13, 174—195).—Daily, and probably hourly, variations occur in the inorg. P content of the blood of dairy cattle. Vals. are affected slightly by feeding, but not appreciably by drinking. Exercise produces a slight increase in blood- PO_4''' , followed by a marked decline lasting for several hr. Parturition causes a considerable decline in blood- PO_4''' . Calf blood, at birth, shows higher vals. than that of the dam, and later increases with age up to 6 months, subsequently declining steadily to the normal val. of adults. A. G. POLLARD.

Normal variations in the calcium content of the blood of dairy cattle. L. S. PALMER and E. C. ECKLES (*J. Dairy Sci.*, 1930, 13, 351—359).—Daily variations occur in the Ca content of the blood-plasma of dairy cattle, although a high coeff. of

correlation exists in vals. on successive days. In samples taken on 3 successive days deviations in Ca contents from the theoretical are negative when the plasma-Ca is low and positive when it is high.

A. G. POLLARD.

Biometry of calcium and inorganic phosphorus in the blood-plasma of dairy cattle. L. S. PALMER, R. A. GORTNER, and R. RUDE (J. Dairy Sci., 1931, 13, 360—367).—There is no correlation between the Ca and inorg. P contents of the blood-plasma of dairy cattle, and no significant amount of Ca phosphate exists in the blood. The theory that the mineralisation of bone is a simple pptn. of salts from body-fluid is untenable.

A. G. POLLARD.

Acid-base equilibrium of new-born infants. I. Normal standards. L. A. HOAG and W. H. KISER, jun. (Amer. J. Dis. Children, 1931, 41, 1045—1065).—The p_H val. of the blood of normal infants 8 hr. to 13 days old is 7.528 ± 0.0538 , the CO_2 content 54.4 vol.-%, and the NaCl content 621 ± 18 millimols. per litre of serum. The base bound as HCO_3' is 23.4 ± 1.88 and that bound as chloride 106.2 ± 2.93 millimol. per litre of serum. CHEMICAL ABSTRACTS.

Micro-apparatus for determination of alkali reserve. H. W. MOOK (Biochem. Z., 1931, 242, 348; cf. A., 1930, 1201).—Errors in the method previously described are corrected. W. MCCARTNEY.

Origin of autohaemagglutinin. I. NAKAMURA (Keijo J. Med., 1931, 2, 425—451).—The autohaemagglutinin is determined by centrifuging the blood with Na citrate, and adding to several tubes, each containing a drop of progressively diluted serum, a drop of 10% suspension of blood corpuscles in aq. NaCl. After cooling for 30 min. at 0°, the tubes are examined for haemagglutination. Autohaemagglutinin is not produced in rabbits by auto- or hetero-immunisation, and there is no direct relation between autohaemagglutinin and artificially produced anaemia. Autohaemagglutinin increases after the injection of unboiled milk. Removal of the spleen and injuries to the liver inhibit the production of autohaemagglutinin, and in the dysfunction of the reticuloendothelial system brought about by injection of "electrolog clin," it is either inhibited or accelerated. The active principle of the milk is a lipin, since it is contained in the Et_2O and C_6H_6 , and not in the $COMe_2$ extract. Lecithin and choline show, however, no increase in haemagglutinin production.

A. LAWSON.

Haemolytic action of glycyrrhizin. A. BUSACCA (Arch. Farm. sperim., 1931, 53, 66—71).—Glycyrrhizin exerts haemolytic action, 0.8 g. per c.c. of fresh washed red corpuscles of sheep's blood being required to act in 30 min. at 37°. The action is prevented by the serum of fresh guinea-pig's blood or by that of normal or syphilitic human blood, or by cholesterol suspended in normal saline.

T. H. POPE.

Effect of haemolytics on the rate of sinking of blood-corpuscles. F. HINTEREGGER (Biochem. Z., 1931, 241, 469—475).—No decisive relation can be traced between the action of haemolytics (hypotonic NaCl solution, $EtOH$, Et_2O , Na salts of bile acids, saponins, viper venom, and immune haemolysin) and the rate of sinking of blood-corpuscles. Neither the

formation of compounds of haemolytics with plasma nor their effect on the adsorptive powers of proteins explains the effects on the rate. Also, there is no relation between the rate and the charge on the corpuscles.

W. MCCARTNEY.

Osmotic equilibrium between yolk and white in hen's eggs. O. MEYERHOF (Biochem. Z., 1931, 242, 243—248).—Grollman's result (A., 1931, 1177) according to which the accepted f.p. depression of hen's egg-yolk of 0.6° is unreal, and due to delayed freezing, the true val. being almost as low (0.48°) as for egg-white (0.45), is incorrect and due to an error in calculation. No account was taken of the H_2O of swelling of the collodion dialysis sacs. Recalculation shows that the Δ -vals. of egg-yolk lie between 0.55 and 0.60.

P. W. CLUTTERBUCK.

Manoiloff and other colour sex-reactions in man, animals, and plants. A. WOLANSKI (Acta Biol. Exp. Warsaw, 1931, 6, 173—207).—The Manoiloff reaction is given correctly by extracts of the sexual organs of salt and fresh fish in all cases examined. In frogs and cattle the reaction is most distinct for liver extracts. Human blood-clots and serum give correct results in 92% of 595 cases examined, if the haemoglobin content of the extracts is the same for all tests; saliva can also be used for sex determination. The presence of papayotin is necessary only for weak extracts, when greater intensity of coloration is obtained. The reaction is due to differences in the conens. of two distinct substances, probably not proteins, of which one is comparatively thermostable, whilst both are relatively resistant to freezing and putrefaction, but are very susceptible to ageing. In the case of plants, the substances responsible are formed in the leaves, from which they are conveyed to and conc. in the carpels of the blossoms. More definite reactions are given if the blossoms are dried before extraction. Satisfactory results are also often given by Biernacki's reagent, or by the addition of 1% Me-green to an isotonic NaOH-KOH extract of the material.

R. TRUSZKOWSKI.

Cleavage products of capsule proteins of *Hemifusus tuba*, Gmel. J. SO and J. SAGARA (J. Biochem., Japan, 1930, 12, 473—474).—The capsule protein of the gastropod *H. tuba* is of the nature of keratin or elastin.

CHEMICAL ABSTRACTS.

Isolation of carotene from adrenal glands. O. BAILLY and R. NETTER (Compt. rend., 1931, 193, 961—963).—The adrenals of the ox were extracted with $EtOH$ acidified with 0.2% $AcOH$ and then with $COMe_2$. After removal of the solvent, the residue was treated with KOH in $EtOH$, finally extracted with Et_2O , and recrystallised from $MeOH$ in 0.03% yield. The carotene so obtained is identical with that from vegetable sources.

C. C. N. VASS.

Preparation of cephalin. F. MALTANER (J. Amer. Chem. Soc., 1931, 53, 4019—4020).—A modification of the method previously described (Amer. J. Physiol., 1931, 97, 74). 1 lb. of fresh ox brain gives about 1 g. of cephalin.

C. J. WEST (b).

Buffering power of phosphatides. W. FABISCH (Biochem. Z., 1931, 242, 121—129).—Lecithin is not able to form salts with acids or bases nor is it able to combine with Cl' . Aq. solutions of it are able to act only very feebly as a buffer, probably in virtue of traces of impurity. P. W. CLUTTERBUCK.

Determination of glycogen in tissues. M. SAHYUN (J. Biol. Chem., 1931, 93, 227—234).—Modifications of Pflüger's method are presented in the following procedure. The tissue is hydrolysed by conc. KOH at 100° for 30—40 min. instead of 2 hr. Glycogen is then pptd. by EtOH in the presence of charcoal to complete its deposition, and separated at the centrifuge. Hydrolysis of the glycogen is effected by $2N\text{-H}_2\text{SO}_4$ at 100° for 2 hr. instead of HCl , since Cl' interferes with the subsequent determination of reducing sugar by the Folin-Wu method. A. COHEN.

Glycogen. Hydrolysis of glycogen in various concentrations of acids, and hydrolysis with takadiastase. M. SAHYUN and C. L. ALSBERG (J. Biol. Chem., 1931, 93, 235—254).—The hydrolysis of glycogen by H_2SO_4 or HCl is a pseudo-unimol. reaction. In the course of the reaction glycogen is first partly hydrolysed to a type of glycogen giving non-opalescent solutions. The latter is converted into polysaccharides which yield the reducing sugar, the sp. rotation of which is that of glucose.

Takadiastase, which may be purified by ultrafiltration, hydrolyses 52% of glycogen when equilibrium is reached. Fructose hastens the disappearance of opalescence. The rate of enzymic hydrolysis is not influenced by fructose, but is decreased by glucose and galactose. In the latter case the decrease may be due to polysaccharide synthesis, since a decrease in reducing sugars is observed when takadiastase acts on a mixture of glucose and galactose. A. COHEN.

Copper compound of oxidised glutathione. A. KOZŁOWSKI (Biochem. Z., 1931, 241, 403—406).—It is advantageous to use COMe_2 for extraction when preparing glutathione from yeast. A method of obtaining an amorphous Cu compound of oxidised glutathione is described. W. MCCARTNEY.

Crystalline copper derivative of oxidised glutathione. A. KOZŁOWSKI (Biochem. Z., 1931, 242, 249—250).—Oxidised glutathione in 1% aq. solution yields a cryst. Cu compound when treated with 3% CuSO_4 solution in presence of NaOAc . The compound differs in solubility and Cu content from the amorphous prep. previously described (see above). W. MCCARTNEY.

Oxidation catalysis of crystalline glutathione with particular reference to copper. C. VOEGTLIN, J. M. JOHNSON, and S. M. ROSENTHAL (J. Biol. Chem., 1931, 93, 435—453).—The oxidation of glutathione in phosphate buffer at p_H 7.27 is greatly accelerated by small amounts of Cu and also by Pd , Au , Co , Se , and Te salts. The formation of H_2O_2 is not observed. Fe , Mn , Ni , Sn , Pb , Cr , Ce , Hg , Pt , Os , and As have no action and Ag , Zn , Cd , Bi , and Sb inhibit the oxidation. The alleged autoxidation of glutathione is accounted for by the presence of traces of Cu arising from the method of prep., and methods are described whereby glutathione

of greatly reduced Cu content may be obtained. These employ pptn. of the Cd or Ag compound of glutathione (Hg and As compounds are also described). The greatly decreased O_2 consumption of such glutathione is not influenced by Fe and cysteine or glycylcysteine. Prolonged incubation at 37° renders the glutathione sensitive to Fe catalysis, which is not due to glycylcysteine anhydride. The physiological significance of the results is discussed. A. COHEN.

Uteroverdin. R. LEMBERG, J. BARCROFT, and D. KEILIN (Nature, 1931, 128, 967—968).—"Uteroverdin," $\text{C}_{35}\text{H}_{38-42}\text{O}_6\text{N}_4$, an Et_2O -sol. pigment from the dog's placenta, contains 4 pyrrole nuclei, and is probably the Me_2 ester of a dehydro- or dehydro-mesobilirubin. L. S. THEOBALD.

Constituents of the aqueous and vitreous humours and the lens. Animal eyes. C. S. O'BRIEN and P. W. SALIT (Amer. J. Ophthalmol., 1931, 14, 582—589).—The vitreous humour (15 c.c.) of the ox eye contains 1.16% of solids; "total N 22.4 mg., non-protein-N 15.2 mg., protein-N 4.50 mg.," chloride 681.6 mg., sugar 55.5 mg. (adult), 56.6 mg. (calves 6 weeks), Ca 7.2 mg., urea 14.23 mg., creatinine 1.1 mg. per 100 cc. Aq. humour (1.66 c.c.) contains "total N 24.9 mg., non-protein-N 21.1 mg., protein-N 23.75 mg.," chloride 709 mg., sugar 87.1 mg. (adult), 108 mg. (calves 6 weeks), Ca 5.7 mg., urea 16.71 mg., creatinine 1.19 mg., per 100 c.c. The lens (1.9 g.) contained chlorides 187—340 mg., sugar 134.7, 144.8 mg., urea 20.8 mg. Data are also given for stale and for preserved vitreous and aq. humour. CHEMICAL ABSTRACTS.

Carbohydrates of the muscles of the frog (*Rana pipiens*). M. SAHYUN (J. Biol. Chem., 1931, 94, 29—38).—The winter frog (*R. pipiens*) used in this work stores more muscle-glycogen than the spring frog. The individual muscles on the same side of the frog do not necessarily contain the same amount of glycogen, but the content of homologous muscles on opposite sides is equal (cf. Anderson and Macleod, A., 1930, 1464). Parallel results are obtained for the reducing substance content of muscle. The female stores more glycogen than the male. Glycogenolysis does not take place in intact frog muscle at room temp. for at least 2 hr. The method of Somogyi (A., 1931, 755) for obtaining protein-free filtrate for carbohydrate determination is modified by increase of CuSO_4 concn. to 10%. Acid hydrolysis of the muscle filtrate increases its reducing power by 90%, and a comparison of solutions by ultrafiltration before and after hydrolysis shows that no carbohydrate with a mol. greater than raffinose is present. That glycogen is a considerable source of muscle-sugar is shown by the fact that after exercise muscle-glycogen decreases 80%, reducing carbohydrate increases 60% before hydrolysis, and hydrolysable carbohydrate decreases considerably. A. LAWSON.

Carbohydrates of muscle. M. SAHYUN (J. Biol. Chem., 1931, 94, 253—262).—Dog- or frog-muscle, the former being frozen by liquid air, is deproteinised, giving filtrate A, which is treated with CuSO_4 and Ca(OH)_2 (A., 1918, ii, 86) in order to remove reducing non-carbohydrate substances from true carbohy-

drates, which are recovered from the ppt. by addition of H_2SO_4 , giving filtrate *B*. The kinetics of the acid hydrolysis of *B* indicate the presence only of a hexosemonophosphoric ester. Extraction of dog-muscle without the use of liquid air results in formation of hexosediphosphoric acid (cf. A., 1928, 665). *A* contains a saccharide or glucoside which is ultrafiltrable, EtOH-sol., and reduces only after hydrolysis.

F. O. HOWITT.

Micro-determination of ammonia in frog muscle. G. EMBDEN (J. Biol. Chem., 1931, 94, 315).—A reply to criticisms of Benedict and Nash (A., 1929, 953).

Uric acid and purine-nitrogen in human muscle. A. VALENTI (Ar. Int. Pharmacodyn. Ther., 1930, 38, 458—462; Chem. Zentr., 1931, i, 3257).—Average vals. were: uric acid 0.0379, purine-N 0.0158%.

A. A. ELDRIDGE.

Chemical composition of the human skeleton.

I. Calcification of the tibia of the normal newborn infant. L. E. BOOHER and G. H. HANSMANN (J. Biol. Chem., 94, 195—205).—The percentages of ash and Ca in the fat-free tibia are approx. const., and independent of the Ca, P, and vitamin-*D* intake of the mother, and also of active calcification occurring in the latter.

H. DAVSON.

Comparative ash content of the metaphyses and shafts of bones. A. F. HESS, F. S. BERLINER, and M. WEINSTOCK (J. Biol. Chem., 1931, 94, 9—19).—Determinations of ash in the shafts and metaphyses of bones of rachitic rats show parallel decreases from normal in both cases, but on recovery, induced by normal feeding, the rate of calcification is greater in the metaphyses. It is possible to note by Röntgenogram the deposition in the rachitic epiphyses of the small amount of bone corresponding with 1 mg. of ash. In older rats, bone ash is higher and serum-P lower than in younger rats.

A. LAWSON.

Solubility of bone in solutions of magnesium salts. J. C. FORBES (J. Biol. Chem., 1931, 93, 255—268).—Mg salts increase the solubility of bone-Ca in aq. solution, the effect increasing with the concn. of Mg. In distilled H_2O , Ca appears to be dissolved as a phosphate and a basic Ca compound, since the Ca : P ratio is greater than the val. calc. for $\text{Ca}_3(\text{PO}_4)_2$, and the p_{H} is increased. The solubilising effect of Mg is inhibited by increasing the concn. of Ca or $\text{PO}_4^{'''}$ in the original solution. In cases where $[\text{Mg}^{''}]$ is low, deposition of Ca from solution is observed.

A. COHEN.

Chemical composition of bone ash. S. MORGULIS (J. Biol. Chem., 1931, 93, 455—466).—Data are given for the composition of the bone ash from a variety of fishes and mammals. The proportion of CaCO_3 in the former is about half that in the latter. The presence of CaHPO_4 is not confirmed, but, in addition to CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$, a basic compound, probably $\text{Ca}(\text{OH})_2$, is present. The calc. mol. relationships favour the view that the complex $\text{Ca}[(\text{Ca}_3(\text{PO}_4)_2)_3](\text{OH})_2$ is the main constituent of bone ash.

A. COHEN.

Physiological significance of manganese and other elements occurring in small amounts in

organisms. G. BERTRAND (Z. angew. Chem., 1931, 44, 917—921).—A review. The naturally occurring elements are divided into two groups, the formative elements from which fats, carbohydrates, proteins, and other fundamentally inert substances are constructed, and the catalysing elements which occur only in traces and initiate the heterogeneous chemical reactions of the living organism.

F. O. HOWITT.

Significance of alcohol-soluble constituents in the serological activity of milk. M. DEHIO (Z. Immunität., 1931, 70, 58—76; Chem. Zentr., 1931, i, 3188).

State of calcium phosphate in milk. M. PIETTRE (Compt. rend., 1931, 193, 1041—1044).—The separation of $\text{Ca}_3(\text{PO}_4)_2$ from milk by centrifuging, coagulation, and dialysis against H_2O , glycerol, or aq. sucrose solutions was investigated. Milk to which Na_2 or Na_3 citrate was added furnished on dialysis a caseinogen practically free from Ca. Hence all the colloidal Ca in milk appears to be in the form of $\text{Ca}_3(\text{PO}_4)_2$.

F. O. HOWITT.

Effect of diet on the manganese content of milk. A. R. KEMMERER and W. R. TODD (J. Biol. Chem., 1931, 94, 317—321).—The Mn content of cow's milk as determined by the method of Skinner and Peterson (A., 1930, 1326) averages 0.000003% and that of goat's milk 0.0000082%. These vals. are not appreciably increased by a 5-fold increase in Mn intake.

F. O. HOWITT.

Changes in the composition of the gastric juice under different stimuli. D. R. WEBSTER (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 213—223).—The composition of the gastric juice of dogs varies according to the type of stimulus activating the secretion. Humoral stimuli favour the production of HCl and other inorg. constituents, whilst the secretion of org. substances including enzymes is less marked. Nervous stimuli, whilst also favouring the production of HCl, are accompanied by a well-marked discharge of pepsin, mucin, and other org. matter.

F. O. HOWITT.

Gastric secretion after histamine. Sodium and potassium content and pepsin determination. J. H. AUSTIN and G. D. GAMMON (J. Clin. Invest., 1931, 10, 287—307).—The rate of secretion of Na and K in the stomach has been measured in patients following histamine injection and in fundic pouches in dogs stimulated by feeding and histamine.

CHEMICAL ABSTRACTS.

Micro-determination of bile-acids in bile. I. SAKAMOTO and H. FUJIKAWA (J. Biochem., Japan, 1931, 13, 309—319).—Nakagawa and Fujikawa's colorimetric method is applicable to human or dog's bile, but not to rabbit's bile.

CHEMICAL ABSTRACTS.

Extraction of bile acids from bile. S. NAKAGAWA and K. YOSHIKAWA (J. Biochem., Japan, 1931, 13, 321—341).—The bile acids are completely extracted in presence of animal charcoal if the medium contains 85% EtOH and has p_{H} 10.2—10.6.

CHEMICAL ABSTRACTS.

Fate of bilirubin introduced into blood vessels. III. Excretion of bilirubin from the liver. (2) Influence of poisons on vegetative nerve.

Formation of gallstones. IV. Influence of intravenous injection of glucose. S. SAIKI (Japan. J. Gastroenterol., 1931, 3, 119—122, 123—126).—Paralysis of the sympathetics inhibits, and increased tension stimulates, bilirubin excretion in rabbits. Injection of 25% glucose solution (5 c.c.) accelerates, or (10 c.c.) obstructs, the excretion.

CHEMICAL ABSTRACTS.

Absorption spectrum of bilirubin in various solvents. III. P. MULLER and L. ENGEL (Z. physiol. Chem., 1931, 202, 56—66; cf. A., 1931, 1322).—The absorption spectrum of bilirubin in human serum is similar to, but not identical with, that in CHCl_3 . The absorption curves of various diazotised sera deviate somewhat in the short-wave region, due to a varying content of uncoupled bilirubin. Bilirubin from directly and indirectly coupled sera shows no difference in spectrum or cryst. form.

J. H. BIRKINSHAW.

Effect of *l*-proline and *l*-oxyproline on urobilin and urobilinogen. C. GIORDANO and L. GRIVA (Arch. Sci. med., 1929, 53, No. 12, 7 pp.; Chem. Zentr., 1931, i, 3584).—Oral administration of gelatin, *l*-proline, and *l*-oxyproline does not cause an increase in urinary urobilin and urobilinogen in dogs and in obstructive icterus, but intramuscular injection of proline or oxyproline intensifies Ehrlich's aldehyde reaction and the Zn salt fluorescence of urine.

A. A. ELDRIDGE.

Determination of sugar in urine by Benedict's method. F. GRAF (Pharm. Ztg., 1931, 76, 1304).—A detailed description of Benedict's method is given. If chemically pure Na_2CO_3 is used, instead of the white ppt. of $\text{Cu}_2(\text{CNS})_2$ a red ppt. of Cu_2O is obtained. For the desired reaction it is necessary for a trace of NH_3 to be present. This is usually the case with commercially pure Na_2CO_3 . E. H. SHARPLES.

Detection of diastase in urine. E. HERZFELD (Biochem. Z., 1931, 242, 251—258).—Since "starch iodide" is decolorised by proteins and their decomp. products the procedure of Wohlgemuth (A., 1930, 1207) does not alone suffice for measuring the diastase content of urine or of other body-fluids. A method is described by which the glucose can be determined as osazone. This method may be used together with that of Wohlgemuth for determining the approx. diastase content of biological fluids.

W. MCCARTNEY.

Nutritional anaemia of the rat. I. Influence of iron on blood regeneration. II. Influence of iron + supplements of other inorganic elements on blood regeneration. H. H. BEARD and V. C. MYERS. **III. Prevention of anaemia by means of inorganic elements.** H. H. BEARD, C. RAFFERTY, and V. C. MYERS. **IV. Production of haemoglobinemia and polycythemia in normal animals by means of inorganic elements.** V. C. MYERS, H. H. BEARD, and B. O. BARNES. **V. Action of iron and iron supplemented with other elements on the daily reticulocyte, erythrocyte, and haemoglobin response.** H. H. BEARD, R. W. BAKER, and V. C. MYERS. **VI. Effect of inorganic elements on the rate of blood regeneration and growth.** H. H. BEARD (J. Biol. Chem., 1931, 94,

71—88, 89—110, 111—115, 117—122, 123—134, 135—146).—I. Young rats rendered anaemic by feeding with whole milk for 6 weeks after weaning are given doses of Fe, electrolytic Fe, and the H_2S filtrates from the latter ranging from 0.08 to 2.5 mg. daily in the form of the chloride. 0.25 mg. Fe is the smallest unsupplemented daily dose required to give average haemoglobin and erythrocyte recovery in 6 and 4 weeks respectively when this is added to the whole-milk diet. 2.0 mg. Fe daily is the most effective dose, average recovery in both cells and haemoglobin occurring in 18 weeks. Results obtained after special precautions to ensure that no metallic impurities from the cages and the milk supply were introduced confirmed the normal results. Nutritional anaemia in young rats fed on whole milk is an inorg. Fe-deficiency disease from the time of weaning until 100 g. body-wt. is reached. In view of the above results, no other factors in addition to Fe are necessary for haemoglobin formation in anaemia of this kind.

II. Young rats, rendered anaemic by feeding on whole milk, fed daily with 0.5 mg. Fe, and in addition with proper doses of Cu, Ni, Ge, Mn, As, Ti, Zn, Rb, Cr, V, Se, Hg separately, experience haemoglobin and erythrocyte recovery in 2—3 and 2—2.5 weeks, respectively, as compared with 6 and 3.8 weeks, respectively, with the Fe alone. The min. effective dose (taking haemoglobin recovery on 0.5 mg. Fe alone as being 6 weeks) of these elements with 0.5 mg. Fe is as follows: Cu, 0.025; Ni and Ge, 0.05; As, 0.01; Mn, Ti, and Zn, 0.1; Rb, Cr, V, and Se, 0.05; Hg, 0.04 mg. Haemoglobin and red blood-cell regeneration can be prolonged, hastened, and attained in 6 weeks, depending on the dosage of the supplementary element with the 0.5 mg. Fe.

III. Inorg. Fe (as the H_2S filtrate from electrolytic Fe) prevents the development of anaemia in rats fed on a whole-milk diet, but with supplements of Cu, Ni, Mn, or As, the effect is not better than with Fe alone.

IV. Polycythemia and haemoglobinemia are produced in rats to a marked extent with daily addition to the normal diet of 1.0% V and Co separately, and to a smaller extent with 0.5 mg. Fe, alone and supplemented separately with 0.1 mg. Ge, Zn, and Mn, 0.05 mg. Cu and Ni, and 0.01 mg. As. Addition of 1% Fe, Cu, Mg, Mn, Zn, Ni, Cr, Se, or Al to the normal diet in most cases causes small decreases in erythrocyte and haemoglobin concentration.

V. Rats at weaning (40—50 g. body-wt.) have about 10 g. of haemoglobin per 100 c.c. with an average concn. of about 3% reticulocytes. 4 weeks later the haemoglobin is 13—14 g. per 100 c.c., and the red blood-cell count 7—8 million per c.mm. with no change in reticulocyte level. Young rats developing anaemia on a whole-milk diet experience a gradual fall in red blood-cells and haemoglobin with a progressive increase in the reticulocytes. The ability to form red blood-cells is lacking. Administration of 0.25 mg. Fe daily gives a reticulocyte peak from 15% to 45% of erythrocytes in 4 days, and, after 6 days, a gradual fall in reticulocyte val. accompanied by a gradual erythrocyte and haemoglobin increase. Fe is believed to stimulate the haematopoietic organs in the bone marrow to produce reticulocyte amounts above that already present. Supplement of the 0.25 mg. Fe with

optimum doses of Cu, Mn, As, Ge, V, or Zn, in each case, causes at first no change in the rate and degree of reticulocyte response from that with Fe alone, but a larger fall in reticulocytes occurs in the 5th or 6th day than takes place with Fe alone. The supplementary elements increase the rate of maturation of red blood-cells.

VI. In anæmic rats recovering under daily dosage of 0.5 mg. Fe, a linear relationship exists between the average hæmoglobin content and the duration of the recovery period in weeks, parallel results being obtained for the erythrocyte recovery. Individual weekly determinations of hæmoglobin and erythrocytes vary, however, from the average weekly results for these constituents. A close relationship exists between the increase of hæmoglobin and body-wt., the two processes taking place simultaneously under Fe therapy during the first 3 weeks. Supplements of optimum doses of Cu, Ti, Ni, Se, As, Ge, Zn, Mn, Cr, V, Pb, Hg, Mg, or Al cause better growth than Fe alone, the reason being either that these play a role in the growth process or exert an indirect influence due to increased metabolism caused by hæmoglobin increase. With three or four exceptions unfavourable or ineffective doses of the other elements supplementing Fe give less growth than Fe alone. Doses of Fe varying from 0.05 to 0.25 mg. supplemented with optimum doses of the other elements cause effects on the growth similar to those in blood regeneration (Part II), thus showing the correlation between the two processes.

A. LAWSON.

Natural copper deficiency in cattle rations. W. M. NEAL, R. B. BECKER, and A. L. SHEALY (Science, 1931, 74, 418—419).—Details of a naturally-occurring nutritional anæmia of cattle due to a deficiency of Fe, or of Fe and Cu, are described.

L. S. THEOBALD.

Lack of tryptophan and histidine as a cause of anæmia. G. FONTES and L. THIVOLLE (Compt. rend. Soc. Biol., 1931, 106, 217—219; Chem. Zentr., 1931, i, 3581).

Glucose level of arterial and venous blood in arthritis. R. M. STECHER and H. J. JEGHERS (Arch. Int. Med., 1931, 48, [i], 801—807).—Examination of venous and finger-blood (identical with arterial blood; A., 1923, i, 503) of normal and arthritic persons indicates a decreased and delayed removal of sugar from the blood of the latter.

F. O. HOWITT.

Artificial Banti's disease. SEITZ (Arch. exp. Path. Pharm., 1931, 163, 438—455).—Extensive chemical, histological, and hæmatological examination has been made of dogs poisoned by "pyrocin." The symptoms resemble those of the naturally-occurring Banti's disease together with certain blood changes, such as are present in pernicious anæmia.

W. O. KERMAK.

Beriberi. N. BERNARD (Ann. Inst. Pasteur, 1931, 47, 508—578).—Beriberi results from the action of a toxin which is produced by a bacillus (*B. asthenogenes*) growing on gastro-intestinal contents rich in carbohydrates and is harmful to an organism only when the resistance of the latter has become impaired by defective nutrition. This view is confirmed by

extensive observations on experimental beriberi in pigs.

W. O. KERMAK.

Nitrogen and sulphur metabolism in Bright's disease. II. G. P. GRABFIELD (J. Clin. Invest., 1931, 10, 309—318).—Excretion of N and S in patients without renal oedema was studied. There was a tendency to go into negative S balance while in positive N balance. The urinary N : S ratio was low even with positive S balance. Defect in S metabolism is suggested.

CHEMICAL ABSTRACTS.

Feeding of iron in bush sickness. B. C. ASTON (New Zealand J. Agric., 1931, 42, 369—376; 43, 11—13).—The successful use of FeCO_3 (finely powdered spathic Fe ore) in salt licks or mixed with silage and of Fe NH_4 citrate in food pellets is recorded.

A. G. POLLARD.

Urinary calculi in sheep. B. E. PONTIUS, R. H. CARR, and L. P. DOYLE (Proc. Amer. Soc. Animal Produc., 1930, 185—190).—The calculi consisted principally of Ca phosphate or Al silicate and were associated with alkaline urine. The effect of various diets on the p_H and mineral composition of the urine was studied.

CHEMICAL ABSTRACTS.

Action of cancerous and embryonic extracts on cell metabolism. F. PENTIMALLI (Biochem. Z., 1931, 242, 233—243).—Cancerous and embryonic extracts considerably inhibit anaerobic glycolysis of muscle, the action being greater with normal than with regenerating tissue. The action on respiration is less clearly defined.

P. W. CLUTTERBUCK.

Deposition of calcium compounds in multiple inoculation sarcoma. L. KLUGE (Biochem. Z., 1931, 242, 228—232).—The blood-Ca vals. after injection of org. Ca compounds (gluconate, pyrocatecholdisulphonate) are different from those after the injection of inorg. salts, the Ca of the complex org. substances being retained in the blood in an active form for a much longer time. By narcosis, a disturbance of tissue-Ca exchange is obtained. The glycolytically active pyrocatecholdisulphonate does not penetrate a tumour *in vivo*.

P. W. CLUTTERBUCK.

Oral administration of invert sugar, with injection of insulin, in diabetes mellitus. O. PUCSKO (Deut. Arch. klin. Med., 1931, 170, 274—293; Chem. Zentr., 1931, i, 3254).—In the case of glucose, decrease in the ketonic substances occurs shortly after the administration; in that of fructose it takes place several hours afterwards. Simultaneous administration as invert sugar utilises the advantages of both. Sucrose lacks the favourable effect of invert sugar.

A. A. ELDRIDGE.

Effect of insulin, synthalin, and sodium sulphate waters on diabetes mellitus. O. KAUFFMANN-COSLA and R. ZORKENDORFER (Deut. Arch. klin. Med., 1931, 170, 302—309; Chem. Zentr., 1931, i, 3254).—After administration of insulin, but not of synthalin, and to some extent after that of Karlsbad H_2O , the diminished oxidising power of the organism is increased.

A. A. ELDRIDGE.

Effect of various organs on the acetone content of the blood in phloridzin and pancreatic diabetes. H. E. HIMWICH, W. GOLDFARB, and A.

WELLER (J. Biol. Chem., 1931, 93, 337—342).—The COMe_2 metabolism of phloridzinised and pancreat-ectomised dogs has been determined. COMe_2 is, in nearly all cases, liberated by the liver into the blood. Muscle and the organs drained by the portal vein act similarly, adding COMe_2 to the blood in some cases, removing it in others. A. COHEN.

Distribution of sugar in normal and diabetic blood, and comparison of the direct and indirect methods of measuring corpuscle-sugar. J. R. SPANNUTH and M. H. POWER (J. Biol. Chem., 1931, 93, 343—358).—Glycolysis leads to low results in the direct determination of reducing sugar in blood-corpuscles. The vals. calc. from the sugar content of whole blood and plasma are more trustworthy. The average ratio of fermentable reducing sugars in corpuscles and plasma is 0.84 in normal subjects and about the same in diabetics. Ingestion of 100 g. of glucose by a normal subject does not appreciably affect this ratio; diabetics show a temporary decrease under the same conditions. Intravenous injection of insulin increases the ratio to about 1.0 in normal persons. The permeability of corpuscles to glucose, and the distribution of glucose between corpuscles and plasma, are the same in normal and diabetic blood. A. COHEN.

Hyperglycæmic activity of the blood of depancreatized dogs unchanged by previous injection of insulin. L. KÉPINOV and S. PETIT-DUTAILLIS (Compt. rend. Soc. Biol., 1930, 103, 1190—1192; Chem. Zentr., 1931, i, 3581).—The hyperglycæmic action on dogs of the blood of depancreatized dogs is independent of the amount of sugar present in the diabetic blood, and is unaffected by previous administration of insulin to the donor. A. A. ELDRIDGE.

Utilisation of ingested protein by depancreatized and normal dogs. E. J. MALTBY (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 201—204).—Ingestion of lean meat by depancreatized dogs is followed by absorption of 60%, whilst 40% is excreted almost entirely as protein. The absorbed fraction represents that part which experienced preliminary gastric digestion, thus preparing it for the action of trypsin-like enzymes in the intestine.

F. O. HOWITT.

Blood-amylase in relation to disease of the pancreas. R. ELMAN (Arch. Int. Med., 1931, 48, [i], 828—835).—Disease of the pancreatic acini is associated with a decreased or an increased level of blood-amylase.

F. O. HOWITT.

Blood-fat and -lipins in hepatic disturbance. I, II. M. NAKATSUKA (Japan. J. Gastroenterol., 1931, 3, 153—159, 160—165).—In hepatic injury by CCl_4 , CHCl_3 , and small doses of P, the blood-lipins are increased; large doses of P produce a decrease. Laparotomy has no effect. Ligation of the common bile duct, but not of the hepatic artery, produces lipæmia. X-Rays cause a temporary increase in blood-lipins. CHEMICAL ABSTRACTS.

Variations in the condition of calcium in the organism: relation to the problem of inflammation. S. HERMANN and M. ZENTER (Arch. exp. Path. Pharm., 1931, 163, 219—242).—The serum-Ca

not combined with protein was determined in the centrifugate after heating 2 c.c. of serum with 4 c.c. of 22% phosphotungstic acid. The ratio of total to free Ca in the serum (Ca quotient) is const. for the same rabbit under normal conditions and for different rabbits varies from 2.3 to 3.5. The Ca quotient is lowered by large withdrawals of blood, oral or parenteral administration of various acids, e.g., gluconic, salicylic, or atophan, parenteral administration of alkali and various other substances including certain proteins, oral administration of quinine and pyramidone, and by hot baths. It is increased by oral administration of alkali. Inhibition of inflammation of the rabbit's eye runs parallel with the decrease of the Ca quotient, except in the case of cold baths, which inhibit inflammation without alteration of the Ca quotient. The decrease in Ca quotient also runs parallel with a decrease in the percentage dry wt. of the serum. W. O. KERMACK.

Inflammation. H. GESSLER (Arch. exp. Path. Pharm., 1931, 163, 456—476, 477—486).—A rabbit's ear in which inflammation has been produced by the application of xylene or of heat or by mechanical irritation has a greater blood circulation than the normal ear, a higher temp. and also a marked rise in the metabolism of the tissue as measured by the increased O_2 consumption. The latter effect is probably not directly due to the hyperæmia or higher temp. W. O. KERMACK.

Bromine in the blood in maniacal-depressive insanity. H. ZONDEK and A. BIER (Biochem. Z., 1931, 241, 491—492).—The blood of persons suffering from maniacal-depressive insanity has 40—60% less Br than has the blood of healthy persons and (in some cases, at least) the cerebrospinal fluid of the former contains no Br. In other conditions of depression (but not in psychoses of other types or in somatic diseases) the Br content of the blood is also below normal. W. MCCARTNEY.

Diffusibility of proteins of normal and pathological plasma. O. H. GAEBLER (J. Biol. Chem., 1931, 93, 467—477).—The permeability of plane collodion membranes to protein differs with the direction of dialysis, the surface first evaporated and washed in H_2O being less permeable. Membranes washed with increasingly dil. EtOH are more uniformly permeable. Normal plasma-protein is more diffusible than that from patients with slight or marked albuminuria. The diffusibility is greatly decreased in nephrosis. The presence of excessive protein in urine cannot, therefore, be due to increased diffusibility of the plasma-protein. A. COHEN.

Ochronosis of cattle. II. Isolation of crystalline uroporphyrin from the bones. Identification by the p_H -fluorescence curves and by analysis. H. FINK and W. HOERBURGER (Z. physiol. Chem., 1931, 202, 8—22; cf. A., 1931, 978).—From the bones of an ox with ochronosis uroporphyrin was isolated as the Me_8 ester and identified by analysis, m. p., and p_H -fluorescence curve. Most of the uroporphyrin was present in the long tubular bones; the marrow contained none. J. H. BIRKINSHAW.

Influence of solar rays on metabolism, with reference to sulphur and pellagra in southern U.S.A. J. H. SMITH (Arch. Int. Med., 1931, 48, 907—1063).—Geographical position, and therefore climatic conditions, especially the intensity of solar radiation, influence the incidence of pellagra; their effect, however, depends on the nutritional state of the individual. Neither temp. nor humidity has a determining influence on the peak of pellagra, although its general incidence with the peak of solar radiation is shown by statistics. The abnormal metabolism of S is a feature of pellagra, and the adequate supply of S in the form of cystine has a protective influence, probably through its preventing the effect of solar radiation, or its maintenance of the cyanide-detoxifying power. Pigmentation has no such protective effect. There is a tendency for the seasonal influence of pellagra to rise and fall in the direction opposite to the rise and fall in the basic metabolic rate. A. LAWSON.

Hepatic function in pregnancy. I. Metabolism of carbohydrates. Y. YOKOTA (Japan. J. Obstet. Gynecol., 1931, 14, 66—90).—The blood-sugar of pregnant rabbits was 0.084—0.126 (average 0.1017) %, and of non-pregnant rabbits 0.082—0.124 (average 0.106) %. The change in blood-sugar due to various hepatic toxins followed almost the same course in both conditions. CHEMICAL ABSTRACTS.

Chlorides of sweat and water-chloride metabolism during pregnancy. B. TARLO and N. OLSKAYA (Kazan. Med. J., 1930, 26, 1123).—The Cl (mg. per 100 c.c.) in sweat, blood, and urine, respectively, was: non-pregnant women 461, 455, 1530; during first half of pregnancy 485, 499, 1407; during second half of pregnancy 367, 515, 926; during pregnancy with toxicosis 261, 500, 626.

CHEMICAL ABSTRACTS.

Purulent urine and the protein of pus. JUSTIN-MUELLER (J. Pharm. Chim., 1931, [viii], 14, 478—482).

Blood chemical changes in experimental streptococcus septicæmia. R. W. LINTON (J. Exp. Med., 1931, 54, 223—231).—In rabbits the blood-sugar falls at a const. rate, but hypoglycæmia does not occur. Glycogen is present in the liver at death. The CO₂ capacity is markedly lowered at first. Inorg. P is markedly increased and Ca decreased in the terminal phase. Non-protein-N and creatinine are greatly increased in the terminal stage.

CHEMICAL ABSTRACTS.

Iodine and bromine content of the thyroid gland. F. TANINO (Biochem. Z., 1931, 241, 392—397).—In the thyroid glands of diseased persons the ratio of the content of Br to that of I varies greatly, but increases with increasing content of colloidal material. In the glands of patients receiving I (and also Br) the ratio is very low. W. MCCARTNEY.

Iodine question and so-called "complete salt" [prophylaxy]. B. BLEYER and F. FISCHLER (Münch. med. Woch., 1931, 78, 742—744; Chem. Zentr., 1931, i, 3580).—A discussion. A. A. ELDRIDGE.

Iodine injury and "complete salt" prophylaxy. D. JAHN (Münch. med. Woch., 1931, 78, 744—

747; Chem. Zentr., 1931, i, 3580—3581).—A discussion. A. A. ELDRIDGE.

Disorders of the carbohydrate metabolism of rabbits in trypanosomiasis. T. VON BRAND and P. REGENDANZ (Biochem. Z., 1931, 242, 451—468).—In rabbits trypanosomiasis results in hypoglycæmia, and during the course of the disease the production of glycogen in the liver is so greatly reduced that no storage takes place even when large amounts of sucrose are administered. At the same time the accumulation of glycogen in the muscles is reduced. In spite of the administration, the sugar content of the blood of the infected rabbits may fall in the later stages of the disease, but there is no relation between this content before administration of sucrose and the power of the organism to produce glycogen. The hypoglycæmia is due, not to consumption of sugar by trypanosomes, but to disturbances in the organs concerned in carbohydrate metabolism. These disturbances are caused by toxins from the trypanosomes. W. MCCARTNEY.

Ferric iron content of normal and pathological sera. A. LANGER (Biochem. Z., 1931, 242, 316—319; cf. A., 1928, 192).—Normal serum contains, on the average, 0.11 mg. of Fe⁺⁺⁺ per 100 c.c. In diseases involving dyspnoea the average may be as high as 0.32 mg. per 100 c.c., but in other diseases the normal average val. is found. W. MCCARTNEY.

Effect of X-ray therapy on the partition of phosphorus compounds in the blood in disease. M. SOKOLOVITCH (Brit. J. Exp. Path., 1931, 12, 147—150).—The free P of the plasma and red corpuscles changes non-uniformly. The plasma-ester- and -lipin-P rise, and that of the red corpuscles falls.

CHEMICAL ABSTRACTS.

Influence of amino-acids on tissue respiration. II. Action of phenylalanine, tyrosine, leucine, aspartic acid, asparagine, and glutamic acid on kidney and liver. B. KISCH (Biochem. Z., 1931, 242, 26—42).—The respiration of kidney tissue of rat, guinea-pig, rabbit, cat, dog, and pig in Ringer's solution at p_H 7.4 is increased by addition of the above substances. Freshly-removed tissue gives a smaller effect than older tissue. The increase is particularly great with rat's tissue and with phenylalanine. P. W. CLUTTERBUCK.

Effect of amino-acids on tissue respiration. III. Effect of the hydrogen-ion concentration of the nutrient solution on the increased respiration in tissues caused by amino-acids. B. KISCH (Biochem. Z., 1931, 242, 436—440).—At p_H 6.9 the stimulating effect on the respiration of fresh and old tissue from the kidneys (or livers) of rats, guinea-pigs, rabbits, cats, and pigs caused by alanine, phenylalanine, leucine, and tyrosine is less pronounced than at p_H 7.4 or 8.0. Occasionally there is no effect at p_H 6.9 and sometimes, in the case of the old tissues, the effect is greater at p_H 8 than at 7.4. W. MCCARTNEY.

Rate of oxygen consumption by fertilised and unfertilised eggs. I. *Fucus vesiculosus*. II. *Cumingia tellinoides*. III. *Nereis limbata*. D. M. WHITAKER (J. Gen. Physiol., 1931, 15, 167—182, 183—190, 191—300).—I. Fertilisation of the

egg produces a 90% increase in O_2 consumption, whereas light, by causing photosynthesis, produces a liberation of O_2 . The O_2 consumption of the spermatozoa is high; their photosynthetic activity is doubtful.

II. Before fertilisation *Cumingia* eggs proceed to the metaphase of their first cleavage when their O_2 consumption becomes const. Fertilisation produces a decrease of 55% in O_2 consumption.

III. The secretion of a jelly by *Nereis* eggs tends to obscure the results by preventing gas equilibrium between the H_2O and air space above it. An increase of 35–45% in O_2 consumption is observed after fertilisation.

H. DAVSON.

Metabolism of Eskimos. P. HEINBECKER (J. Biol. Chem., 1931, 93, 327–336).—Further observations on the basal metabolism of Eskimos and the development of ketosis during fasting confirm the previous findings (cf. A., 1929, 210).

A. COHEN.

Clinical calorimetry. XLVII. Respiratory metabolism during prolonged meat diets. W. S. McCLELLAN, H. J. SPENCER, and E. A. FALK (J. Biol. Chem., 1931, 93, 419–434; cf. A., 1930, 1212).—The respiratory metabolism of three men living on a meat diet for 1 year has been investigated. The R.Q. was 0.72–0.78 at all times of the day on exclusive meat diets and the basal metabolic rate of two of them was 80–91% of normal. The basal urinary excretion of N varied from 0.5 to 0.8 g. per hr., higher vals. being recorded in a few tests following lean meat meals. Extra heat production is caused by lean meat. The discrepancies disclosed between the calc. vals. of food oxidised and actual composition of the diet may be due to errors in the R.Q. assumed for the diet constituents.

A. COHEN.

Feeding experiments with mixtures of highly-purified amino-acids. I. Diets containing 19 amino-acids. W. C. ROSE. II. Supplementing effect of proteins. R. H. ELLIS and W. C. ROSE. III. Supplementing effect of caseinogen fractions. W. WINDUS, F. L. CATHERWOOD, and W. C. ROSE (J. Biol. Chem., 94, 155–165, 167–171, 173–184).—I. Two diets containing different mixtures of 19 NH_2 -acids (roughly in the proportions in which they occur in caseinogen), glucosamine, dextrin, agar, lard, cod-liver oil, etc. were found inadequate for the growth of young rats. Vitamin-B was added in the form of yeast. Hence growth-promoting proteins contain a dietary component other than the 20 known NH_2 -acids.

II. Three diets similar to the above, except that the NH_2 -acid mixtures were supplemented successively with 5% of gelatin, gliadin, and caseinogen, produced improvements in growth, especially when caseinogen was the supplement.

III. Caseinogen was fractionated after hydrolysis with H_2SO_4 . After the removal of sparingly sol. dicarboxylic and diamino-acids, three other fractions were obtained by extraction with BuOH. The diets were similar to those in (I), with the addition of 5 g. of one of the caseinogen fractions. The BuOH-sol. portion contains a substance which stimulates growth in rats.

H. DAVSON.

Metabolism of cystine and methionine. R. W. JACKSON and R. J. BLOCK (Science, 1931, 74, 414).—The addition of cystine or methionine to a diet presumably deficient in the former produced a marked increase in wt. of albino rats; other NH_2 -acids or derivatives related to cystine had little or no effect.

L. S. THEOBALD.

Relation of creatinuria to muscle-glycogen. III. C. BRENTANO (Arch. exp. Path. Pharm., 1931, 163, 156–174).—In rabbits, agencies which bring about the decrease in muscle-glycogen cause creatine to appear in the urine, whilst the disappearance of urinary creatine is usually associated with an increase in muscle-glycogen. A similar relationship does not appear to exist between creatinuria and liver-glycogen. Creatinuria is therefore associated with glycogenolysis in the muscles, but not directly with the absolute content of glycogen in muscle.

W. O. KERMACK.

Relation between carbohydrate and creatine metabolism in muscle. T. MAYASAMA, C. BRENTANO, and O. RIESSER (Klin. Woch., 1931, 10, 840–841; Chem. Zentr., 1931, i, 3257).—The ratio phosphogen:glycogen for various muscles of the same rabbit is const., although the abs. val. may change, but differs for different animals. Adrenaline, tetrahydro- β -naphthylamine, caffeine, or hunger generally diminishes the phosphagen content, but not as much as the glycogen content. Simultaneously there is in most cases a large increase in creatine.

A. A. ELDRIDGE.

Influence of feeding proteins, amino-acids, and related substances on creatine-creatinine metabolism. H. H. BEARD and B. O. BARNES (J. Biol. Chem., 1931, 94, 49–69).—The average normal creatine content of the muscles of young rats of about 50 g. body-wt. is 4 mg. per g. The feeding of various NH_2 -acids in amounts up to 1 g. in every case increases the creatine content of the muscle as determined after periods ranging to 48 hr., the average per cent. increase over normal being as follows: alanine 12.5, glycine 15.4, aspartic acid 17.0, glutamic acid 20.5, phenylalanine 21.8, tyrosine 22.3, leucine 23.3, choline hydrochloride 23.3, creatine 23.6, histidine 24.0, arginine monohydrochloride 26.8, edestin 31.2, caseinogen 31.2, valine 34.3, cystine 37.0, glycoeyamine 48.5. With various NH_2 -acids not occurring in the protein mol., there is no increase in muscle-creatine. The feeding of the following NH_2 -acids in amounts up to 1.5 g. to adult rats causes increased daily elimination of creatine in the urine, the average per cent. increases being: aspartic acid 14.2, valine 14.8, histidine 19.5, glutamic acid 25.0, arginine monohydrochloride 26.8, cystine 28.1, tyrosine 30.7, glycine 35.9. Proteins or NH_2 -acids occurring in the protein mol. fed in comparatively large amounts at one time increase the daily creatine output in normal humans. Creatine formation and creatine excretion are either due to the feeding of large amounts of proteins and NH_2 -acids at one time, or these substances stimulate creatine-creatinine metabolism in some other way than by sp. dynamic action, with a resulting increase of creatine and elimination in the urine.

A. LAWSON.

Formation of urinary creatine and purines from protein. E. F. TERROINE, A. GIAJA, and L. BAYLE (Compt. rend., 1931, **193**, 956—959).—In the pig, the gradual transition from an adequate carbohydrate diet to a rich protein diet, of the same caloric val., causes together with an increased N excretion, a paralleled increased excretion of creatine, and an increased output of purines. C. C. N. VASS.

Purine metabolism. I. Determination of allantoin in dog urine. F. W. ALLEN and L. R. CERECEDO (J. Biol. Chem., 1931, **93**, 293—297).—The urea in the urine is destroyed by urease, protein is pptd., and the allantoin in solution converted by 0.2N-KOH into allantoic acid. The latter is hydrolysed by 0.1N-HCl to urea, which is determined volumetrically as dioxanthylcarbamide, using $K_2Cr_2O_7$. The allantoin-N : total N ratio increases from 2.5% on a synthetic diet to 9.5% on a protein-free diet.

A. COHEN.

Physiology of pyrimidines. IV. Intermediary metabolism of uracil. L. R. CERECEDO. **V. Effects of certain pyrimidines on the sulphur metabolism of the dog.** J. A. STEKOL and L. R. CERECEDO. **VI. Fate of parabanic acid, alloxan, and alloxantin in the organism of the dog.** L. R. CERECEDO (J. Biol. Chem., 1931, **93**, 269—274, 275—282, 283—291).—IV. The urea-N in the urine of dogs is increased by feeding oxaluric and formyloxaluric acids. Similar results are obtained by subcutaneous injection of the former, but the latter acid is toxic by this route. The results favour the view that, in the metabolism of uracil, oxaluric and formyloxaluric acids are the precursors of urea.

V. The increased excretion of urea following oral administration of isobarbituric, isodialuric, and formyloxaluric acids to dogs is accompanied by increased urinary ethereal sulphate and decreased neutral S. A compound isolated from such urine suggests that isobarbituric acid is partly excreted as a sulphate. For the breakdown of the above three acids a S compound, normally excreted as neutral S, appears to be necessary.

VI. Parabanic acid, fed to dogs, is mostly excreted unchanged, a small fraction being converted into $H_2C_2O_4$. Alloxan is excreted, partly as ethereal sulphate in the bile, and partly as murexide after conversion into alloxantin; a similar result is obtained by feeding alloxantin.

A. COHEN.

Origin of ammonia formation in the organism. A. FOLLING (Skand. Arch. Physiol., 1931, **61**, 23—26; Chem. Zentr., 1931, i, 3584).—Experiments do not support the view that diffusion of NH_3 takes place from the urine or renal filtrate into the blood.

A. A. ELDRIDGE.

Nitrogen distribution in urine during minimal endogenous nitrogen excretion and during protein feeding. Question of protein-reserve. E. F. TERROINE and G. BOY (Compt. rend., 1931, **193**, 1034—1037).—The N-distribution in the urine of a pig during heavy protein feeding followed by a non-protein diet indicates that a small amount of N is retained in the form of reserve protein when the diet is rich in protein.

F. O. HOWITT.

Feeding value of fresh skim-milk in comparison with fish meal. G. FROLICH and H. LUTHGE (Bied. Zentr., 1931, **3B**, 392—399).—Skim-milk and butter-milk have, for pigs, a supplemental protein val. similar to that of fish meal. They should be fed when either quite sweet or completely soured.

A. G. POLLARD.

Comparison of the dietary properties of soya-bean "milk" and cow's milk. S. WAN (Chinese J. Physiol., 1931, **5**, 353—362).—Rat-feeding experiments show that, contrary to the findings of Tso (A., 1930, 368), soya-bean "milk" is poorer in vitamin-A, although richer in vitamin-B, than cow's milk. Normal growth is supported by a diet of whole wheat (2 parts) and cow's milk powder (1 part) with a NaCl supplement, but not by a similar diet containing 1 part of soya-bean "milk" powder in place of that from cow's milk. This inadequate diet promotes better growth on addition of vitamins-A, -B, and -D, but remains inferior to the cow's milk diet because of the lower nutritive val. of soya-bean protein.

A. COHEN.

Nutrition : vegetable proteins. L. B. MENDEL and H. B. VICKERY (Carnegie Inst. Wash. Yearbook, 1929, **28**, 367—377; 1930, **29**, 380—389).—Dried leaves of watercress (*Nasturtium officinale*) are comparatively rich in vitamin-A and contain also -B, -F, and -G. Vitamin-E (also present in abundance) had no influence on the Fe assimilation or hæmoglobin content of rat's blood. A procedure for the prep. of histidine from erythrocytes, and its separation from arginine, is described. Horse hæmoglobin contains histidine 7.64, arginine 3.32, and lysine 8.10%. Thiol-histidine could not be isolated from zein. In the tobacco leaf nitrate-N forms 0—50% of the total H_2O -sol. N; the determination of NH_3 - and NH_2 -N is described. Tobacco seed (unsprouted) is free from nicotine; it contains vitamins-A, -B, and -G, and a high-grade protein. A solution of cystine in H_2SO_4 reacted with Ag_2SO_4 at p_H 6 to form NH_3 , cysteic acid, and $(C_3H_5NSO_2Ag)_2Ag_2SO_4$. Human hair contains arginine 8.0, lysine 2.5, and cystine 16.5% (wool : histidine 0.66, arginine 7.8, lysine 2.3%). Tobacco seed contained globulin, choline, betaine, adenine, guanine, and arginine. Tobacco leaf contained fumaric, succinic, malic, and citric acids.

CHEMICAL ABSTRACTS.

Endogenous metabolism of organic compounds in fasting angiostomic dogs. I. E. S. LONDON, N. P. KOTSCHNEV, A. K. ALEXANDRY, A. M. DUBINSKI, S. V. NEDSVEDSKI, and E. T. CHRUTZKI (Arch. exp. Path. Pharm., 1931, **163**, 401—437).—A detailed study has been made of the metabolism of carbohydrate, protein, and fat in angiostomic dogs during prolonged starvation. Carbohydrate flows from the liver to a number of organs, including the intestine, the kidneys, and muscles. The muscles, the liver, and the kidneys are chiefly concerned with the production of lactic acid from sugar and it is taken up by the intestine and the lungs. The breakdown of proteins occurs chiefly in the muscles and spleen, and the products are absorbed by the liver and the kidneys. Urea is produced in the liver and taken up by a number of organs, including intestines and spleen, whence it gradually passes into the blood.

stream and is finally excreted through the kidneys. Fats are mobilised from subcutaneous deposits and the muscles, and absorbed by the liver and pancreas. Cholesterol is produced by the adrenals and taken up by the spleen and kidneys. Lecithin migrates from the liver and collects in many of the other organs.

W. O. KERMACK.

Metabolism of bile acids. M. JENKE (Arch. exp. Path. Pharm., 1931, 163, 175—218).—Largely a crit. review. As the bile acids are not essentially altered by intestinal bacteria, the excretion in the faeces is a measure of the synthesis of bile acids which is taking place in the organism. In the intact dog this is only about 1/7 of that which takes place after a bile fistula has been established, so that results obtained from bile fistula animals must be interpreted with reserve. The diet of the animal influences the rate of production of bile acids.

W. O. KERMACK.

Action of the liver on copro- and uroporphyrin. H. T. SCHREUS and C. CARRIÉ (Strahlenther., 1931, 40, 340—350; Chem. Zentr., 1931, i, 3584).—Copro-, but not uro-, porphyrin is attacked by the liver; possibly copro- is converted into uroporphyrin. The effect may be due to a thermolabile substance which does not pass into liver extract but is resistant to digestive juices. A. A. ELDRIDGE.

Fate of orally administered cholesterol and coprosterol in the human intestine. M. BÜRGER and W. WINTERSEEL (Z. physiol. Chem., 1931, 202, 237—245).—Oral administration of coprosterol produces no increase in serum-sterol or in plasma-sterol inactive to Br. After cholesterol administration the faecal output of sterol increases to twice the normal val., but the proportion of saturated sterol decreases. Administered coprosterol is quantitatively recovered. Dihydrocholesterol feeding does not sensibly increase the serum-sterol; 95% of the dihydrosterol is recovered in the faeces.

J. H. BIRKINSHAW.

Fat metabolism. III. Isolation and "quantitation" of total fatty acids in small amounts of bile. C. W. McCLURE, M. E. HUNTSINGER, and E. BLOOMBERG. **IV. Organic phosphorus in bile.** C. W. McCLURE, E. L. BLOOMBERG, and M. E. HUNTSINGER (New England J. Med., 1931, 204, 764—770).—III. Bloor's method (A., 1928, 662) is employed.

IV. The org. P is present largely in the phospholipins which are extracted and oxidised to H_3PO_4 , the latter being determined colorimetrically by Fiske and Subbarrow's method. CHEMICAL ABSTRACTS.

Permeability. IV. Function of the liver and lipins. J. DAHMLOS (Biochem. Z., 1931, 242, 88—120).—Cholesterol and lecithin, when injected into the portal vein, are retained in the liver, but when injected into the jugular give rise to lipæmic turbidity in the carotid blood which lasts throughout the experiment. Only a small amount of the total lipin remains, however, in circulation, the chief portion being distributed through the body or accumulated in an organ. In the general circulation, cholesterol and lecithin after injection of H_2O act antagonistically on the Cl distribution between blood and tissues, whereas both lipins in the venous liver circulation cause increased retention of H_2O . After parenteral injection of

$H_2O + HCl$, cholesterol and lecithin have an opposite effect on the distribution of injected Cl between blood and tissues in both circulations, cholesterol increasing and lecithin decreasing the absorption of injected Cl by the tissues. After administration of $NaHCO_3$, both lipins increase its absorption by the liver, an exchange of HCO_3' and Cl' occurring. In the general circulation, however, the two lipins have opposite effects on the HCO_3' distribution.

P. W. CLUTTERBUCK.

Physical chemistry of resorption. II, III. P. J. JURIŠIĆ (Biochem. Z., 1931, 241, 476—484, 485—490; cf. A., 1928, 916).—II. There is no direct relation between the p.d. between the two sides of surviving frog skin which separates isotonic solutions and the transfer of liquid which takes place. The differences in the degree of swelling between the two surfaces of the skin must not be held responsible for the transfer of liquid which occurs in Reid's experiment (A., 1901, ii, 460).

III. Through the skin of the frog there passes a network of ultramicroscopic capillaries so constructed that in the surviving material H_2O under pressure passes from the inner to the outer side only. The H_2O colloiddally bound in the surviving skin cannot be expressed by a pressure of 700 mm. As regards their diffusion, under hydrostatic pressure, through the surviving skin acid and basic dyes are alike.

W. MCCARTNEY.

Oxidation-reduction potentials. I. Potentials in animal organs. L. PINCUSSEN and E. O. SEITZ (Biochem. Z., 1931, 241, 364—383).—A method by which the changes in oxidation-reduction potential occurring in fresh aq. extracts of animal organs (liver, lungs, muscle, spleen of rats and guinea-pigs) can be measured is described. The changes take place while the organs are kept in a vac. Curves plotted from the results have characteristic forms which vary from species to species and also according to the condition (normal, administration of KI, fasting) of the animal.

W. MCCARTNEY.

Glutathione in metabolism. E. WALDSCHMIDT-LEITZ, A. SCHÄFFNER, and W. KOCHOLATY (Naturwiss., 1931, 19, 964—965).—Liver-arginase is completely inactive in the absence of SH-compounds. Glutathione may be separated from arginase by extraction of the tissue with dil. EtOH or $COMe_2$. SH-compounds are also essential in deamination processes and are bound up with the oxidation-reduction potentials of the cells.

P. G. MARSHALL.

Metabolism of sugars injected intravenously at a constant rate. VI. Influence of hormones, of inanition, and of alimentary factors on the assimilation of galactose and glucose. M. WIERZUCHOWSKI (Acta Biol. Exp. Warsaw, 1931, 6, 251—321).—Aq. galactose or glucose was injected intravenously into dogs at a rate of 2 g. per kg. per hr., under various conditions. Urinary and blood-galactose at first rise, and then remain at a const. level. Adrenaline and thyroxine have no influence on assimilation or excretion of galactose, whilst insulin produces a feeble but distinct anti-galactæmic and -galactosuric effect. In the case of glucose, the urinary and blood-glucose curves exhibit an initial rise, a more

or less prolonged summit, and a final decline to a const. val.; the time required for the attainment of equilibrium is prolonged by previous inanition, but varies considerably with different individuals, from 7 to 30 hr. Insulin accelerates assimilation only during the period of rising glycosuria of the first phase, at the summit of which it is without action; the duration of max. glycosuria is, however, prolonged. Adrenaline intensifies glycosuria, which may attain a val. of 100% of glucose injected during the period of max. glycosuria. The inability of the organism to assimilate glucose during the first phase is less marked in the case of dogs on a fat diet than with fasting dogs, and is still less so in protein-fed animals; it is unaffected by previous muscular work. Insulin and adrenaline act similarly under these conditions as in the case of fasting dogs. Carbohydrate feeding (starch or sucrose) reduces the duration and intensity of the hyperglycaemia characteristic of the first phase; the initial rise is completely absent if glucose is injected at the height of digestion of a starch meal. It is concluded that the initial max. glycosuria may be due to augmented suprarenal secretion excited by injection of glucose.

R. TRUSZKOWSKI.

Production of glycogen from lactic acid in the liver *in vitro*. C. PI-SUNER BAYO and J. F. PI (Biochem. Z., 1931, 242, 306—315).—An apparatus for the investigation of the metabolism of tissues *in vitro* is described. Perfusion of the liver of white rats with Ringer solution containing γ -lactic acid through which O_2 is passed results in conversion of the acid into glycogen and, in some cases at least, the amount of the latter produced corresponds with the decrease in the lactic acid content of the solution. Results of other workers notwithstanding, it follows that the liver can synthesise glycogen from lactic acid. Possible reasons for the discrepancies are discussed.

W. MCCARTNEY.

Value of sugar and materials containing sugar as feeding stuffs. F. HONCAMP and W. WOHLBIER (Bied. Zentr., 1931, 3B, 450—462).—Sucrose, fed to pigs in conjunction with starchy foods (barley, potatoes), produced as great live wt. increases as the starchy foods themselves. 0.5—0.75 kg. of sugar per animal per day was used without digestive disturbances.

A. G. POLLARD.

Fate of *dl*- α -naphthylalanine in the animal body. E. FRIEDMANN (Biochem. Z., 1931, 242, 266—281).—*dl*- α -Naphthylalanine administered to dogs and rabbits can be recovered unchanged in their urine to the extent of about 40%. The compound isolated from dog's urine by Kikkoji (A., 1911, ii, 909) was the corresponding hydantoic acid which is produced from the unchanged material during concn. of the urine. The free NH_2 -acid has not been isolated from the urine nor have the 2-naphthylsulphonic or *p*-tolylsulphonic derivatives. *dl*- α -Naphthylalanine, m. p. 254—255°, is best prepared from α -naphthaldehyde by a modification of the method of Erlenmeyer. It has an intense sweet taste. The corresponding *hydantoic acid*, m. p. 202°, is prepared from the NH_2 -acid by the action of $KCNO$. It is converted into the *hydantoin*, m. p. 262—263°, by boiling with $AcOH$ and subliming in a high vac. The 2-naphthyl-

sulphonate, m. p. 181°, of *dl*- α -naphthylalanine and its *p*-tolylsulphonate, m. p. 193°, have also been prepared.

W. MCCARTNEY.

Fate of δ -phenyl- α -butadienecarboxylic acid and of cinnamaldehyde in the animal body. E. FRIEDMANN and H. MAI (Biochem. Z., 1931, 242, 282—287).—In the urine of rabbits to which the acid has been subcutaneously administered in doses of 0.2—0.55 g. per kg. no $COPhMe$, cinnamic acid, cinnamoylglycine, or *l*- β -hydroxy- β -phenylpropionic acid can be detected, but hippuric acid corresponding in amount with the wt. of material injected and also an unidentified acid are found. The result conflicts with Dakin's theory (A., 1909, ii, 684) and with his results. In the urine of a rabbit to which cinnamaldehyde had been administered $BzOH$, hippuric acid, cinnamoylglycine, and traces of an acid of m. p. 198° were found.

W. MCCARTNEY.

Administration of furylacrylic acid to rabbits. E. FRIEDMANN (Biochem. Z., 1931, 242, 288—291; cf. A., 1887, 1032).—Since the urine of rabbits to which furylacrylic acid has been administered contains 45—54% of it in the form of pyromucuric acid, but no furylacryluric acid, it seems that furylacrylic acid is more readily decomposed in the organism of herbivorous than in that of carnivorous animals. A second furan derivative is also always found in the urine after administration of the acid.

W. MCCARTNEY.

Feeding value of washed and chopped beet leaves compared with the original material in the feeding of milch cows. K. RICHTER, K. E. FERBER, and H. K. LOSE (Bied. Zentr., 1931, 3B, 408—418).—The feeding of unwashed beet leaves had a scouring effect on cows. Washing and chopping the material prevented this and also produced milk of increased fat content. The total yield of milk was not affected.

A. G. POLLARD.

Value for milk production of acid meadow grass used as hay, silage, and hay meal. W. LIEBSCHER (Bied. Zentr., 1931, 3B, 419—436).—Silage from sour meadow grass had no better feeding val. than when hayed. Grinding the hay improved its feeding val. to a small extent. Neither hay nor silage from sour land affected the live wt. or general health of milch cows.

A. G. POLLARD.

Wood and Capstick's method of calculating the maintenance requirement of the adult sheep. W. A. HENDRICKS and H. W. TITUS (J. Agric. Sci., 1931, 21, 726—738).—The advisability of assuming a proportionality between the maintenance requirement and the two-thirds power of the live wt. of the animal (Wood and Capstick, A., 1926, 637) is critically examined.

A. G. POLLARD.

Rate of growth and potassium-calcium ratio. L. KAUFMAN and M. LASKOWSKI (Biochem. Z., 1931, 242, 424—435).—The K content of pigeon's hearts and brains increases as the organs grow, while at the same time the Ca content decreases. When growth ceases the Ca content increases. Increase in the K : Ca ratio in these organs during development is to be attributed to increased activity which takes place as growth proceeds. In the growing eyes of

pigeons (before and after hatching) the K content increases and the Ca content decreases with age and, except when it is affected by decrease in certain constituents of the food or in its amount, the K : Ca ratio decreases. The alterations in the ratio which accompany change in activity and in rate of growth can be attributed to physico-chemical alterations in the protoplasm.

W MCCARTNEY.

Effects of high and prolonged magnesium lactate intake on metabolism of magnesium and calcium in man. H. E. CARSWELL and J. E. WINTER (J. Biol. Chem., 1931, 93, 411—418).—Two men were maintained for 20—24 days on a mixed diet containing adequate P to which was added 8 g. of Mg lactate daily. Definite Ca retention, slight Mg retention, and decreased faecal Ca resulted in one case, and slight Ca retention, marked Mg retention, and increased faecal Ca in the other. Both showed decreased urinary Ca and increased urinary and faecal Mg. Mg favours Ca deposition if sufficient P is present in the diet.

A. COHEN.

Phosphorus distribution in rat's striated muscle as influenced by age, diet, and irradiated ergosterol. V. V. COLE and F. C. KOCH (J. Biol. Chem., 1931, 94, 263—272).—The effect of a stock diet and that of a rachitic diet with and without irradiated ergosterol on the distribution of various forms of P in the rat's gastrocnemius were determined. Only the inorg. and labile P maintained a difference between the rats on stock diet and those on the rachitic diet, whilst large doses of irradiated ergosterol did not alter any of the vals. for rats on the rachitic diet.

F. O. HOWITT.

Relative nutritive efficiency of certain calcium compounds with growing swine. E. B. FRASER (Sci. Agric., 1931, 12, 57—80).—In pig-feeding trials CaSO_4 (from bones) was equal in val. to ground limestone as a source of Ca, but a 1 : 1 mixture of limestone and CaSO_4 produced a better daily live-wt. gain and greater food economy than either substance alone. Bone-meal was an efficient supplement for pig rations.

A. G. POLLARD.

Significance of the calcium and phosphorus content of food. K. WALTNER (Magyar Orvosi Arch., 1930, 31, 276—282; Chem. Zentr., 1931, i, 3254).—With quantities of Ca optimal for the growth of rats, equal quantities of Ca and P give optimal growth, 50% deficiency of P is inadequate, but double the quantity of P is harmless. Vitamin-D to a certain extent compensates for lack of Ca, but only to a small degree for that of P, in the food.

A. A. ELDRIDGE.

Changes in iron metabolism caused by functional changes in the organism. G. WALLBACH (Z. ges. exp. Med., 1931, 75, 378—400; Chem. Zentr., 1931, i, 3140).—Mice which had received injections of Witte's peptone or "nutrose" ingested Fe preps.; the distribution of Fe in the organism was then abnormal. The amount of Fe deposited is generally dependent on the functional condition of the cell and the structure of the compound ingested; the quantity of Fe administered is not decisive.

A. A. ELDRIDGE.

Nutritional requirements of trout. C. M. MCCAY, J. W. TITCOMB, E. W. CORB, M. F. CROWELL, and A. TUNISON (Trans. Amer. Fish Soc., 1930, 60, 127—139).—The min. protein requirement is approx. 10%. Trout depend for maintenance of life on a thermolabile substance, factor H.

CHEMICAL ABSTRACTS.

Nutrition of speckled trout. R. D. H. HEARD (Trans. Amer. Fish Soc., 1930, 60, 140—145).—Attempts to isolate the growth-promoting factor H are recorded.

CHEMICAL ABSTRACTS.

Influence of thiol and sulphoxide on gross regeneration in the hermit crab (*Pagurus longicarpus*). F. S. HAMMETT and D. W. SMITH (Protoplasma, 1931, 13, 261—267).—Regeneration in the foot of the hermit crab was stimulated by the SH group (in *p*-thiocresol) and retarded by the S:O group (in diphenyl sulphoxide).

A. G. POLLARD.

Proliferative reaction of the skin to the thiol group and its biological significance. F. S. HAMMETT (Protoplasma, 1931, 13, 331—347).—The stimulative action of $\text{CH}_2\text{Ph-SH}$ on skin proliferation in mice is established and discussed.

A. G. POLLARD.

Distribution of acetone in the organism of cold-blooded animals. E. RUSTUNG, F. KOREN, and A. FÖYEN (Biochem. Z., 1931, 242, 366—376).—In the muscle, liver, and blood of the cod there are respectively 0.001, 0.002, and 0.004% of volatile material (calc. as COMe_2) which gives the CHI_3 test. In sea-water at about 8° containing about 1.5% of COMe_2 , absorption of the ketone by the liver, blood, and muscle of the fish attains its max. in 2, 4, and 11 hr., respectively, and at equilibrium the concns. of COMe_2 in these parts of the fish are always lower than that in the surrounding H_2O , the difference being greatest in the case of the liver, perhaps because COMe_2 is particularly strongly attacked there. On the assumption that COMe_2 distributes itself between H_2O and lipin-fat in the same proportions *in vivo* as *in vitro* and that the rest of the dry material of the organism cannot bind the ketone, it is found that the concn. in the organism never exceeds (and in most cases does not reach) that in the surrounding H_2O , possibly because the ketone is decomposed in the organism. There is no evidence that the residual dry material can bind COMe_2 . The results are discussed in the light of those obtained with EtOH by K. Hansen ("Zur Theorie der Narkose," Oslo, 1925) and in relation to Meyer and Overton's theory of narcosis.

W. MCCARTNEY.

Effect of carbon dioxide on ether, ethylene, and nitrous oxide anaesthesia. G. B. KLEINDORFER (J. Pharm. Exp. Ther., 1931, 43, 445—448).—5—10% of CO_2 produces an additive effect on Et_2O , C_2H_4 , and N_2O anaesthesia.

P. G. MARSHALL.

Benzene and benzene content of the blood following their introduction into the organism in various ways. N. V. LAZAREV, A. I. BRUSILOVSKAYA, and I. N. LAVROV (Biochem. Z., 1931, 242, 377—384).—The benzene and C_6H_6 content of blood can be determined by expelling the hydrocarbons with air, burning them in an electric furnace, and automatically determining the CO_2 produced

by conductometric titration (Matveyev, Pronin, and Frost, Russ. J. Pr. Chem., 1931, 3, 1223). From results obtained with the arterial and venous blood of rabbits to which the substances had been administered by inhalation, by stomach tube, intraperitoneally, and subcutaneously conclusions are reached concerning the solubilities of the substances in blood, their toxicities, and their methods of action. When equal concns. of the substances are used, the C_6H_6 content of the blood is always much greater than its benzene content and, in the inhalation experiments, the rate at which arterial blood absorbs (and afterwards loses) the substances differs considerably from the corresponding rate for venous blood, whilst the amounts absorbed by the two types of blood also differ. W. McCARTNEY.

Detoxification of hydrogen cyanide with dihydroxyacetone and glucose in tissue. C. WIEGAND (Arch. exp. Path. Pharm., 1931, 163, 150—155).—The action of KCN on the respiration of liver tissue is inhibited by dihydroxyacetone and in smaller degree by glucose. The action is apparently dependent on CN' being taken up by these two compounds in such a way that it is unable to unite with Fe in the cell. W. O. KERMACK.

Joint action of quinine and ethyl urethane in relation to their use in treating malaria. I. Cause of death in subacute poisoning by ethyl urethane. A. SPANIO (Arch. Farm. sperim., 1931, 53, 53—65).—The min. fatal intravenous dose of Et urethane is 2 g. per kg. of body-wt. Death ensues mainly by paralysis of the respiratory centre. T. H. POPE.

Effect of atropine on blood-sugar concentration. S. LANG (Biochem. Z., 1931, 242, 469—471; A., 1928, 326).—Since, in rabbits, small doses of atropine reduce the sugar content of the blood whilst larger doses increase it, confirmation of previous results is provided. W. McCARTNEY.

Pharmacological action of physostigmine analogues. J. A. AESCHLIMANN and M. REINERT (J. Pharm. Exp. Ther., 1931, 1931, 43, 413—444).—Some carbamic esters of phenols containing an additional basic radical show a physostigmine-like activity. This activity is strong in Me, Me₂, CH₂, CH₃, and CH₂Ph carbamates and weak in Et and Ph esters. The compounds MeSO₄·NMe₃·C₆H₄·O·CO·NMeR(m) (I, R=Me; II, R=Ph) and physostigmine show an effect on isolated rabbit's intestine in a concn. of 1:54—7 million, whilst (I) and (II) are less toxic. Whereas physostigmine and (I) are antagonistic to curare, (II) has no effect. P. G. MARSHALL.

Digitalis. III. Composition of pharmaceutical preparations from the leaf powder of *D. purpurea* and *D. lanata*. IV. Cumulation of pharmaceutical preparations from leaves of *D. purpurea* and *D. lanata* in relation to their content of pure glucosides. V. Function of saponins in pharmaceutical preparations of *D. purpurea*. R. A. HOEKSTRA. VI. Function of mucilaginous substances in pharmaceutical preparations from *Digitalis* leaves. R. A. HOEKSTRA and H. E. J. TEN KLEIJ (Arch. exp. Path. Pharm., 1931, 163, 1—34, 35—45, 46—65, 355—365).—

III. *Digitalis* preps. have been quantitatively fractionated as follows: (1) material pptd. by native protein, digitoxin and lanadigin, (2) the part of the residue sol. in CHCl₃, gitalin and lanatoxin, (3) the part of the residue insol. in CHCl₃, bigitalin and lanatalin, and (4) in the case of *D. lanata* a saponin-like fraction, glucoside IV. Very considerable variations in composition may occur in different extracts, so that the pharmacological assay of the total extract does not adequately represent its properties.

IV. The cumulation vals. of the 7 pure glucosides present in *Digitalis* preps. have been determined. From these results the cumulation vals. for the various extracts may be calc. and partial agreement with the empirical cumulation vals. found by Van Esveld has been obtained.

V. Relatively large concns. of saponin increase the acute toxic action of *Digitalis* glucosides, whilst smaller concns. increase their cumulation. The saponins present in pharmaceutical preps. in this way account largely for the discrepancy already mentioned between the calc. and empirical cumulation vals.

VI. The extracts made from *D. purpurea* and probably also those made from *D. lanata* contain mucilages which inhibit the cumulation of the glucoside. Mucilage from *Tubera saleb* has not this effect. W. O. KERMACK.

Pharmacological detection and determination of lobeline. F. REINARTZ (Arch. exp. Path. Pharm., 1931, 163, 279—294).—Certain colour reactions of lobeline and the ultra-violet absorption spectrum of a solution of its hydrochloride are described. Lobeline in small quantities is best determined pharmacologically, the narcotised white mouse or preps. of leech being used as test objects. A method is given for the detection of lobeline in corpses. W. O. KERMACK.

Reversible coagulation in living tissue. VI, VII. W. D. BANCROFT and J. E. RUTZLER, jun. (Proc. Nat. Acad. Sci., 1931, 17, 570—574, 575—579).—VI. With carnivorous animals the action of histamine is increased by an anæsthetic, whilst the opposite effect is manifested in herbivorous animals. Swelling experiments show that the superior cervical ganglia of rabbits are peptised by NaCNS and agglomerated by histamine dihydrochloride. Ephedrine and NaCNS antagonise histamine *in vivo*. Reversible coagulation of proteins probably accounts for the skin reactions produced by agglomerating agents.

VII. Strychnine causes convulsions by agglomeration of certain proteins in the spinal cord. Methods are discussed whereby tetanic convulsions due to strychnine may be checked. W. R. ANGUS.

Influence of *d*-ψ-cocaine on the hypertensive action of adrenaline. F. MERCIER (Compt. rend., 1931, 193, 883—885).—*d*-ψ-Cocaine does not increase the hypertensive effect of adrenaline. C. C. N. VASS.

Relative efficiency of avertin, amytal, chloral, dial, and isopropylallylbarbituric acid as basal anæsthetics. G. B. KLEINDORFER and J. T. HALSEY

(J. Pharm. Exp. Ther., 1931, 43, 449—456).—Avertin and amytal exert an additive effect on volatile anaesthetics when used in doses of 16–20% of the min. lethal dose without any effect on respiration. Dial and isopropylallylbarbituric acid (allonal) exhibit a similar effect on anaesthesia, but have a depressor action on respiration. P. G. MARSHALL.

Action of the atophan preparation "Erycon" [2-anisylquinoline-4-carboxylic acid] in stimulating uric acid excretion. I. N. SUGIHARA and K. IN. II. N. SUGIHARA and M. YAMAGAMI. III. N. SUGIHARA and P. H. RI. IV. N. SUGIHARA and P. H. RI (Keijo J. Med., 1931, 2, 385—401, 410—424, 452—461, 462—468).—I. No difference is apparent in the effect of subcutaneous injection of "erycon" (0.1 g. per kg. body-wt.) into normal, splanchnicotomised, and vagotomised rabbits. Cutting the splanchnicus causes an increase in blood-uric acid and a decrease in urinary uric acid, whilst cutting the vagus results in decreases in both cases.

II. Cutting the splanchnicus and vagus of rabbits causes in the former case a decrease, and in the latter an increase, in the uric acid content of the bile. In both cases small increases in the vol. of the bile are obtained. Injection of "erycon" (0.2 g. per kg. body-wt.) into normal, splanchnicotomised, and vagotomised animals causes in all cases an increase of uric acid in the bile, the vol. remaining the same.

III. Subcutaneous injection of "erycon" increases the uric acid concn. in the urine and carotid blood of dogs, but these effects are not parallel. In rabbits injected with "erycon" the concn. of uric acid in arterial and venous blood increases, and the differences in the concns. in various veins and arteries of normal animals become more pronounced.

IV. After cutting both splanchnics in rabbits, the uric acid concn. in the blood of the portal and hepatic veins increases with a return to the normal val. The subcutaneous injection of "erycon" (0.2 g. per kg. body-wt.) into splanchnicotomised rabbits increases the uric acid in the portal and hepatic veins, the difference being more pronounced than in normal animals. A. LAWSON.

Sulphæmoglobinæmia after use of "pyridium." A. A. H. VAN DEN BERGH and F. E. REVERS (Deut. med. Woch., 1931, 57, 706—708; Chem. Zentr., 1931, i, 3258—3259).—Simultaneous ingestion of the urinary disinfectant "pyridium" and $MgSO_4$ often causes sulphæmoglobinæmia and cyanosis owing to intestinal production of H_2S . A. A. ELDRIDGE.

Toxicity of gossypol. I. Response of rats to gossypol administration during avitaminosis. W. D. GALLUP (J. Biol. Chem., 1931, 93, 381—405).—Gossypol given intraperitoneally is more toxic than that administered orally or by stomach tube. Normal rats and rats avitaminotic with respect to vitamins-A, -B complex, and -D are almost equally sensitive to intraperitoneal injections of gossypol. Rats on low vitamin-A diet succumb more readily to gossypol given by stomach tube or as a diet constituent than do normal rats. Removal of excess Ca from the gossypol-containing diet of rachitic rats is fatal.

A. COHEN.

Toxicity of gossypol. II. Effect of gossypol on the apparent digestibility of foods, and the rat's gastrointestinal absorption of glucose. W. D. GALLUP and R. REDER (J. Biol. Chem., 1931, 94, 221—232; cf. A., 1928, 794).—Doses of 7 and 11 mg. daily have no effect on the coeff. of digestion: their effect on the intestinal absorption of glucose is doubtful, indicating that gossypol poisoning may not be directly due to nutritional failure. H. DAVSON.

Pharmacology and pharmacodynamics of ointments. VII. Resorption of salicylic acid from ointments containing free salicylic acid, salicylates, and salicylic esters. C. MONCORPS (Arch. exp. Path. Pharm., 1931, 163, 377—392).—After inunction, under uniform conditions, of ointments containing equiv. quantities of salicylic acid or of its esters, the quantity absorbed through the skin and secreted in the urine depends very much on the particular prep. The nature of the vehicle employed and the method of prep. of the ointment are of importance as well as the nature of the salicylic acid constituent. When salicylic esters are used, these may be absorbed and secreted in the urine as such.

W. O. KERMACK.

Effect of aluminium chloride on the respiration of isolated kidney tissue. J. LEIBOWITZ (Biochem. Z., 1931, 242, 441—450; cf. A., 1931, 982).—The respiration of the tissue is irreversibly reduced by the higher concns. of $AlCl_3$, but, as previous results had shown, the lower concns. of the salt increase the respiration. There is, however, a cumulative effect on repeated treatment. The sensitivity of the tissue to Al decreases with increasing alkalinity. The mechanism of action of $AlCl_3$ differs in nature from that of the alkaline-earth chlorides, although the effects produced may sometimes be the same in both cases.

W. MCCARTNEY.

Antagonistic actions of calcium and magnesium salts on the oxidation system of the brain cell. H. ZAIN (Arch. exp. Path. Pharm., 1931, 163, 267—278).—The oxidation of *p*-phenylenediamine by finely-divided ox brain-tissue in 0.9% NaCl solution is increased by $CaCl_2$, and decreased by $MgCl_2$.

W. O. KERMACK.

Excretion of bromide in the urine. E. FREY (Arch. exp. Path. Pharm., 1931, 163, 393—398).—After the administration of NaBr to rabbits or cats the ratio of Cl' to Br' in the urine is approx. the same as that in the plasma so that the kidney appears not to distinguish between the two ions.

W. O. KERMACK.

Bromide in the cerebrospinal fluid. E. FREY (Arch. exp. Path. Pharm., 1931, 163, 399—400).—The ratio of Br' to Cl' in the cerebrospinal fluid of dogs and cats after oral administration of NaBr is approx. the same as in the plasma.

W. O. KERMACK.

Absorption of calcium preparations. F. WOKES (J. Pharm. Exp. Ther., 1931, 43, 531—550).—The toxic dose of $MgSO_4 \cdot 7H_2O$ given subcutaneously in mice is little greater than that required to produce narcosis; 1.0 mg. per g. will narcotise 41% and 1.5 mg. 80% of the mice. Continued injection of sub-lethal doses decreases equally the sensitivity to both nar-

cotic and toxic actions. Oral administration of Ca salts reduces the sensitivity to MgSO_4 and the extent of this reduction affords a measure of the Ca absorption. $\text{Ca}(\text{ClO}_3)_2$ reduces the proportion of narcotised animals from 80% to 11% when 0.3 mg. per g. is given. The absorption of Ca lactate is increased by addition of Na lactate, whilst saponin fails to affect the absorption of $\text{Ca}(\text{ClO}_3)_2$. CaCl_2 is the most readily absorbed Ca salt. P. G. MARSHALL.

Distribution and deposition of medicinal iron preparations. G. WALLBACH (Z. ges. exp. Med., 1931, 75, 353—377; Chem. Zentr., 1931, i, 3140).—The spleen is largely concerned in the deposition of Fe after administration of hæmoglobin, ferrum citricum, and FeCl_3 , but the liver is the centre of the metabolism of Fe ingested with food. A. A. ELDRIDGE.

Tin compounds in the chemotherapy of experimental *Staphylococcus* infections. J. A. KOLMER, H. BROWN, and M. J. HARKINS (J. Pharm. Exp. Ther., 1931, 43, 515—519).— NH_2Ph chlorostannate was the most toxic (M.L.D. 0.02 g. per kg. in rabbits), whilst several other Sn compounds had a M.L.D. of 0.2 g. per kg. None had any beneficial therapeutic effect in *S. aureus* infections, although blood cultures were negative. P. G. MARSHALL.

Periodic classification and chemotherapy. V. FISCHL (Z. angew. Chem., 1931, 44, 932—933).—Theoretical. No relationship appears to exist between the sp. therapeutic action of an element and its position in the periodic classification.

J. W. BAKER.

Metabolic changes produced by irradiation. IX. Effect of irradiation on the reducing substances in blood. L. PINCUSSEN and S. YOKOTA (Biochem. Z., 1931, 241, 398—402).—Irradiation of rabbits with a Hg-quartz lamp causes the amount of reducing substances in their blood which are removed by treatment with CuSO_4 and $\text{Ca}(\text{OH})_2$ to increase. Since it is not the amount of hexosephosphates and perhaps also not that of glucose which increases, and since irradiation also causes decrease in the amount of P found after the CuSO_4 - $\text{Ca}(\text{OH})_2$ treatment, an increase in the amount of other substances containing P probably takes place.

W. MCCARTNEY.

Some aspects of the chemistry of enzymes. O. FERNANDEZ (Bull. Soc. chim., 1931, [iv], 49, 1436—1460).—A lecture.

Pyocyanine, an accessory respiratory enzyme. G. A. H. FRIEDHEIM (J. Exp. Med., 1931, 54, 207—221).—Pyocyanine largely (24-fold) increases the respiration of living cells owing to reversibility of its oxidation and reduction. The effect is not species-sp.; it depends on the presence of another respiratory enzyme sensitive to KCN and CO. The catalytic effect of pyocyanine is restricted to the oxidation of substances closely associated with the bacterial body.

CHEMICAL ABSTRACTS.

o-Quinones as enzyme models. B. KISCH (Biochem. Z., 1931, 242, 1—20).—"Omega," the oxidation product of adrenaline, catalyses the oxidative deamination of glycine but not of other NH_2 -acids, the action being enzyme-like in specificity.

The influence of temp., p_{H} , duration of experiment, and amount of catalyst in the reaction is investigated. The quinone obtained by oxidation of pyrocatechol catalyses the deamination of glycine with the same specificity as omega. Resorcinol, benzoquinone, quinol, phloroglucinol, homogentisic acid, guaiacol, veratrol, inositol, and ethylene glycol have no action. The specificity is a function of the o-quinone group and omega is regarded as an adrenaline-quinone. The influence of substituent groups in the pyrocatechol on the deaminising power is investigated.

P. W. CLUTTERBUCK.

Mercuric chloride as an activator of the o-quinone enzyme model. B. KISCH (Biochem. Z., 1931, 242, 21—25).—Catalysis of the oxidative deamination of glycine by pyrocatechol and adrenaline is very considerably, by gallic acid scarcely at all, and by hydroxyquinol, adrenalone, diethylaminoacetylpyrocatechol, dihydroxyphenylalanine, and pyrogallol not accelerated by addition of HgCl_2 . With 0.025*M*-glycine and 0.001*M*-catalyst, optimal activation at p_{H} 6.9—8.0 is obtained with 0.0003*M*- HgCl_2 .

P. W. CLUTTERBUCK.

Tyramine oxidase. II. Course of the reaction. M. L. C. BERNHEIM (J. Biol. Chem., 1931, 93, 299—309).—The oxidation of tyramine by liver extracts (A., 1928, 1055) is now found to involve three enzyme systems. Fresh extracts in acid medium cause the uptake of 40 per mol. of tyramine; a quinone is suggested as the oxidation product. The system effective in alkaline medium causes an uptake of 10. The corresponding aldehyde is formed, which condenses with unchanged tyramine to form a Schiff's base. The most stable system exists in aged or diluted extracts, operates in alkaline or acid medium, and oxidises tyramine to *p*-hydroxyphenylacetic acid, 20 being consumed. The isolation of the latter acid is described. This reaction is not inhibited by 0.05*M*-pyrophosphate, but 0.05*M*-KCN confines the O_2 uptake to 1 atom per mol. of tyramine.

A. COHEN.

Tolidine and toluidine as peroxidase reagents. III. A. CASOLARI (Biochim. Terap. sperim., 1929, 16, 520—523; Chem. Zentr., 1931, i, 3706).—o-Tolidine is a good reagent for blood and fresh milk; o-, m-, and p-toluidine also react, the colours being reddish-violet; red, gradually becoming violet; and orange with subsequent turbidity, respectively.

A. A. ELDRIDGE.

Enzymes and light. XIX. Peroxidase. L. PINCUSSEN and T. HAMMERICH (Biochem. Z., 1931, 241, 384—391).—The activity of peroxidase from horseradish is greatly reduced by radiations from a quartz lamp, the extent of the effect being almost proportional to the intensity of the light used. During irradiation the $[\text{H}^+]$ plays no part, although the optimum for the effect of the light is in the acid region. Radiations from a "vitalux" lamp have no effect on the activity of the peroxidase.

W. MCCARTNEY.

Determination of starch-liquefying power. T. CHRZASZCZ (Biochem. Z., 1931, 242, 130—136).—The use of more powerful malt extracts in the usual method of Lintner and Sollied (B., 1903, 826) in order to hasten the reaction leads to inaccuracy. A

simple method of determining starch-liquefying power is described which gives accurate results and permits the use of a wide range of enzyme concns.

P. W. CLUTTERBUCK.

Separation and action of the two malt-amylases. Starch and its relation to glycogen. G. A. VAN KLINKENBERG (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 893—905; cf. A., 1890, 998).— α -Amylase was prepared from malt by extraction with aq. KH_2PO_4 followed by fractional pptn. with EtOH, and β -amylase from barley, the latter prep. being freed from traces of the α -enzyme by EtOH. Using sol. potato-starch as substrate, sugar-formation by the enzymes was followed in citrate buffer at 40°. The α -amylase had an optimum reaction of p_H 5.75—5.85 and β -amylase p_H 4.55—5.15. $\alpha\beta$ -Maltose partly inhibited the hydrolysis of starch by α - or β -amylase, whilst β -maltose inhibited the hydrolysis by β -amylase to a greater extent than that by α -amylase. The β -amylase formed 64% of the theoretical amount of maltose, at which point the I-reaction still persisted. The course of hydrolysis by β -amylase is also characteristic, 36% of the theoretical maltose formation taking place with a velocity far greater than that of the remainder. Glycogen forms a suitable substrate for α -amylase but not for β -amylase, and hence is an α -starch. F. O. HOWITT.

Influence of amino-acids on the hydrolysis of starch by Cumbu amylase. D. NARAYANAMURTI and C. V. R. AYYAR (J. Indian Chem. Soc., 1931, 8, 645—650).—Alanine has an accelerating effect on the hydrolysis of starch by Cumbu amylase (A., 1929, 1488) at all the concns. studied; the extent of the effect varies somewhat with p_H . Urea has an accelerating effect which gradually diminishes with time, whilst tyrosine, phenylalanine, tryptophan, arginine, hippuric acid, and glutamic acid cause an initial activation which is followed by an inhibition.

H. BURTON.

Specificity of invertases. H. PRINGSHEIM, H. BORCHARDT, and F. LOEW (Z. physiol. Chem., 1931, 202, 23—31).—A taka-maltase and a maltase from *Aspergillus Wentii* hydrolysed maltose, but had no action on α -methylglucoside at any p_H , although yeast-maltase hydrolysed the α -glucoside more rapidly than maltose. This is contrary to Weidenhagen's hypothesis (A., 1930, 499). Raffinase was absent from a strain of *Penicillium purpurogenum*; the raffinase obtained from *A. Wentii* hydrolyses raffinose only to melibiose and fructose.

J. H. BIRKINSHAW.

β -h-Fructosidase [invertase]. I. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1931, 81, 501—508).—Adopting some of the methods of Willstätter and others, the author has worked out a method for preparing invertase of high purity from yeast involving 7—8-fold enrichment of the invertase content of the yeast by means of sucrose solutions, followed by fractional autolysis, rejection of the first autolysate, pptn. of the main autolysate with tannin, washing of the ppt. with ice-cold H_2O , elution of the enzyme from the ppt. with 1% $(\text{NH}_4)_2\text{HPO}_4$, and final pptn. with COMe_2 . The solid prep. thus obtained from 14 kg. of enriched yeast

contained nearly half of the total invertase of this yeast, and was more than 1000 times as active as the yeast before enrichment. J. H. LANE.

Inhibitory action of certain products on the enzymic hydrolysis of sucrose. H. COLIN and A. CHAUDUN (J. Chim. phys., 1931, 28, 546—555).—Glucose, fructose, glycerol, MeOH, EtOH, urea, NH_2Ph , and alkalis (under certain conditions) retard or inhibit the hydrolysis of sucrose. The action of NH_2Ph is particularly marked. E. S. HEDGES.

Formation of methylglyoxal from hexosephosphate in presence of animal tissues. H. INOUE (J. Biochem., Japan, 1931, 13, 369—387).—The enzyme responsible for the conversion was freed from glyoxalase by means of EtOH, towards which the latter is sensitive. An aq. extract of rabbit's liver, dialysed against distilled H_2O in a collodion bag, gave a high yield of methylglyoxal and no lactic acid. 100% conversion of hexosediphosphate into methylglyoxal is attained under optimal conditions.

CHEMICAL ABSTRACTS.

Effect of preservatives on digestion in man. W. KOENIG (Chem.-Ztg., 1931, 55, 934—935).—In the digestion of egg-albumin by pepsin *in vitro* the amount of undigested protein varied with the quantity of BzOH added. This effect was not due to variation in p_H nor to bacterial decomp. W. J. BOYD.

Equilibrium point in peptic synthesis. H. WASTENEYS and B. F. CROCKER (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 199—200).—The cessation of synthetic action of pepsin on a conc. peptic digest of egg-albumin (cf. A., 1925, i, 102, 472) is due to adsorption of the enzyme on the plastein ppt. and not to its inactivation, the pepsin being still available for either synthesis or hydrolysis on presentation of suitable conditions. F. O. HOWITT.

Proteases of animal tissues. VI. Nature of the proteases in lymph glands. VII. Cathepsin of horse lymph glands. P. RONA and H. KLEINMANN (Biochem. Z., 1931, 241, 283—315, 316—363).—VI. In addition to cathepsin, aq. and glycerol extracts of (horse) lymphocytes and of ox spleen contain trypsin, although it cannot be detected by using albumin or edestin as substrate because these substances are not sufficiently sensitive towards it. The trypsin can be detected in both acid and alkaline extracts, but since the tissues contain considerably less of it than of cathepsin, special methods must be used for the detection. Possibly the trypsin is derived from the decomp. of myelocytes in the tissue; it is not from the blood retained in the extracted tissue.

VII. With respect to its activity at various $[\text{H}^+]$ towards various substrates cathepsin from horse lymphocytes does not differ from that from other animal organs. By H_2S and HCN it is activated towards gelatin, but not towards caseinogen or albumin (from horse blood). Purification of cathepsin by adsorption on kaolin does not increase the activity towards gelatin or caseinogen. H_2S activates the purified material towards gelatin and not towards the other substrates, whilst HCN does not activate it towards any of them. The amount of cathepsin

in the lymphocytes is of the same order as it is in other animal parenchymatous organs.

W. MCCARTNEY.

Proteolytic enzyme in the seeds of *Phaseolus mungo*. L. N. C. NAG and H. N. BANERJEE (Trans. Bose Res. Inst. Calcutta, 1930—1931, 14—19).—Aq. extracts of ungerminated seeds of *P. mungo* contain neither a fibrin- nor a peptone-digesting enzyme. The germinated seeds have peptone- but no fibrin-digesting activity.

A. LAWSON.

Proteolytic enzymes of *Carica papaya*. N. C. NAG and H. N. BANERJEE (Trans. Bose Res. Inst. Calcutta, 1930—1931, 1—13, 20—25).—The fibrin-dissolving power of the juice of the fresh pawpaw fruit is optimal at its natural p_H (5—7), and papain prepared from the juice and the whole fruit by pptn. with EtOH is most active at p_H 9. Tryptophan is produced on autolysis of, and Witte peptone is digested by, the juice, showing the presence of an ereptase, but the prepared papain shows no protease reaction even in the presence of HCN beyond that of the peptonisation of fibrin. The juice shaken with kaolin at p_H 5.3—5.6 and centrifuged gives a liquid containing ereptase, being able in the presence of HCN to digest Witte's peptone, but not fibrin even in alkaline solution. The NaCl eluate of the kaolin contains peptase, being able to digest fibrin but not peptones.

A. LAWSON.

Histaminase. E. W. McHENRY and G. GAVIN (Trans. Roy. Soc. Canada, 1931, [in], 25, V, 101—109).—Dried, defatted ox-kidney serves as a source of histaminase. An extract of this powder by phosphate buffer at p_H 7.0—7.2, which inactivates a histamine solution in 24 hr. at 38°, exhibits a lag period of 4 hr. probably due to a preliminary formation of an enzyme-substrate complex. The second phase, as followed by depressor activity of the solution, is a unimol. reaction. Absence of O_2 inhibits the action of the enzyme, which is also inhibited by KCN and increased by PO_4^{3-} . A concentrate of the enzyme is prepared by saturation with $(NH_4)_2SO_4$ of the buffer extract conc. to one third vol. in a vac. The ppt. is dried, ground up with $CHCl_3$, centrifuged, and the top layer drained and air-dried.

F. O. HOWITT.

Kinetics of enzymic production of esters. P. RONA, R. AMMON, and H. FISCHGOLD (Biochem. Z., 1931, 241, 460—468).—When the mechanism of the synthesis of esters from alcohols and acids by the action of dry powder from the pancreas is followed it is found that cetyl butyrate and (in $COMe_2$ - Et_2O) cetyl palmitate can be prepared by this means. High concns. of butyric acid damage the enzyme, but oleic acid has no effect on it. The reactions investigated are inhibited by $COMe_2$ and by Et_2O .

W. MCCARTNEY.

Specific adenylypyrophosphatase. E. JACOBSEN (Biochem. Z., 1931, 242, 292—302).—Liver contains a phosphatase which attacks the complex pyrophosphate of blood and muscle, but not inorg. pyrophosphate. It can be separated from glycerol- and pyrophosphatase by means of EtOH. Muscle extracts have much less power to decompose complex pyrophosphates than have those of liver. The distributions in the organism of the sp. phosphatase and of glycerol-

phosphatase are quite different. Although the pyrophosphate content of the liver is very great, this pyrophosphate is converted very rapidly into orthophosphate after death.

W. MCCARTNEY.

Specificity of phosphatase. Borneol phosphate. K. P. JACOBSON (Compt. rend. Soc. biol., 1930, 105, 152—154; Chem. Zentr., 1931, i, 3363).—In Neuberg's prep. of "borneolphosphoric acid" (A., 1928, 88) primary and a secondary borneol orthophosphate are formed. The secondary ester is not attacked by phosphatase.

A. A. ELDRIDGE.

Enzyme which hydrolyses glucosemonosulphate: glucosulphatase. T. SODA and C. HATTORI (Bull. Chem. Soc. Japan, 1931, 6, 258—264).—The enzyme has been extracted from snails (*Eulota luhuana*, *E. quassita*, and *E. pelionphala*) and effects a 10% hydrolysis of glucosemonosulphate at 22—28° in a week, the optimum p_H being 7.

J. W. BAKER.

Purification of soya-urease by precipitation with acetone and carbon dioxide. J. ZAKOVSKI (Z. physiol. Chem., 1931, 202, 67—82).—An eight-fold concn. of soya-urease is attained by a preliminary pptn. of the 2% aq. extract with CO_2 and pptn. of the enzyme in the diluted H_2O - $COMe_2$ solution with CO_2 . The solid is eluted with H_2O .

J. H. BIRKINSHAW.

Crystalline urease. IV. Its "antitryptic" property. H. TAUBER and I. S. KLEINER (J. Gen. Physiol., 1931, 15, 155—160; cf. A., 1930, 1217).—The contradictory results of Waldschmidt-Leitz and Steigerwaldt (A., 1931, 521) are explained by the absence of a gum in their experiments; under such conditions urease is not inactivated by trypsin, which behaves as a protective colloid. The gum apparently prevents urease from forming an inactive trypsin compound by combining with it; urease is then digested by the active trypsin.

H. DAVSON.

Action of papain on urease preparations. J. ZAKOVSKI (Z. physiol. Chem., 1931, 202, 249—267).—Urease is not attacked by HCN-activated papain at 7, but is markedly weakened at p_H 4.4—5.5. The weakening by papain is activated by H_2S or cysteine, neither of which has an action on urease. The differences shown by two papain preps. on gelatin are mirrored in their power of weakening urease. The velocity of weakening of urease by papain-HCN is a linear function of urease concn. Change of papain concn. affects the velocity, but not in a linear fashion. The facts do not contradict the hypothesis of a direct action of papain on urease.

J. H. BIRKINSHAW.

Antiurease. J. S. KIRK and J. B. SUMNER (J. Biol. Chem., 1931, 94, 21—28).—The serum of rabbits injected with increasing amounts of cryst. urease possesses antiurease activity, a method for the determination of this dependent on the difference between the original activity of the urease and that after incubation with serum being described. Results of experiments using rabbits which showed no rise in blood- NH_3 after injection with 100 times the dose of urease fatal to normal animals are in agreement with the views of other workers, viz., that the toxic effect of urease is due to NH_3 . Rabbits are most rapidly immunised by simultaneous intra-

peritoneal injection of urease and antiurease. Serum of immunised rabbits immunises rabbits and guinea-pigs, and rabbits poisoned by urease are restored to normal by injections of antiurease. A. LAWSON.

Sugar tolerance of yeasts expressed in atmospheres. M. B. CHURCH (Science, 1931, 74, 492—493).—Yeasts apparently do not grow in solutions of mixed sugars of 79% concn. L. S. THEOBALD.

Factors determining the ergosterol content of yeast. II. Carbohydrate sources. O. N. MASENGALE, C. E. BILLS, and P. S. PRICKETT (J. Biol. Chem., 1931, 94, 213—219; cf. A., 1930, 1067).—The determination of the yields of dry yeast, and the lipins, N, and ergosterol in the latter, on inoculating culture media containing different sugars with *Saccharomyces cerevisiae*, shows that the ergosterol content is higher with di- and tri-hexoses than with monohexoses, and independent of the N and non-sterol lipin content, indicating that ergosterol is primarily a product of carbohydrate metabolism.

H. DAVSON.

Effect of hydrogen-ion concentration on the division rate of *Paramecium aurelia*. A. PHELPS (Science, 1931, 74, 395—396).—The division rate is practically unaltered between p_H 5.9 and 7.7 when a pure strain of bacteria is used as food. The changes with p_H observed by Darby are attributed to the use of mixed bacteria as food. L. S. THEOBALD.

Dependence of citric and oxalic acid accumulation by moulds on the nitrogen content of the medium. T. CHRZASZCZ and D. TIUKOV (Biochem. Z., 1931, 242, 137—148).—Citric acid is an intermediate product in the utilisation of carbohydrate and is not related directly to the nitrogenous metabolism. An optimal concn. of N exists for accumulation of citric acid which depends on the amount and form of the N. For inorg. N the optimum is lower than for org. N. Some moulds form citric acid by deamination without forming $H_2C_2O_4$. The production of this acid by deamination is characteristic of a particular group of moulds. Some moulds do not form $H_2C_2O_4$. P. W. CLUTTERBUCK.

Extra-cellular decomposition of fats by micro-organisms. H. OEFFNER (Bot. Archiv, 1931, 33, 172—198).—Triolein, linseed and walnut oils are decomposed by *Penicillium*. Intermediate products are probably γ - and δ -hydroxy-acids and their lactones. Unsaturated compounds are formed during the process. A. G. POLLARD.

Production of itaconic acid and mannitol by a new mould, *Aspergillus itaconicus*. K. KINOSHITA (Acta Phytochim., 1931, 5, 271—287).—*A. itaconicus* produces itaconic acid in a medium containing sucrose and KNO_3 . Gluconic and citric acids have also been isolated from the medium. The course of the reaction is suggested as: sugar \rightarrow gluconic acid \rightarrow citric acid \rightarrow aconitic acid \rightarrow itaconic acid. With sucrose and NH_4NO_3 , *d*-mannitol is formed, a max. quantity (dependent on the time) being isolated using 3% solution of $(NH_4)_2SO_4$. Sucrose may be replaced by fructose but not by glucose. F. R. SHAW.

***Aspergillus oryzae* enzymes.** T. HARADA (Ind. Eng. Chem., 1931, 23, 1424—1427).—The conditions of growth of *A. oryzae* on wheat bran for the prep. of diastase and certain properties of the latter are described. 20% NaCl is the best antiseptic for the preservation of diastase. Above 45° diastatic activity is destroyed rapidly; the optimum p_H rises with temp. but not linearly. The hydrolysis of starch is bimol., but tends to be reversible. The presence of other enzymes in the aq. extract of the mould is demonstrated. H. DAVSON.

Biological decomposition of plant materials. IV. Biochemical activities on straws of some cellulose-decomposing fungi. A. G. NORMAN (Ann. Appl. Biol., 1931, 18, 244—259; cf. A., 1930, 261).—The extent of the decomp. of all the straw constituents except lignin by the various fungi examined was roughly proportional to the apparent total loss of org. matter. The "N-factor" (N immobilised per 100 g. of straw) was not correlated with the loss of org. matter or of any particular constituent, but was characteristic of the species of fungus concerned. The "N-equiv." (i.e., N immobilised as bacterial protein per 100 g. of org. matter removed) gave some indication of the relative efficiencies of the different organisms. A. G. POLLARD.

Decrease in rate of oxygen consumption under the influence of visible light on *Sarcina lutea*. B. B. RUBENSTEIN (Science, 1931, 74, 419—420).—The rate of O_2 consumption by *S. lutea* at 37° is decreased by exposure to the light of a Mazda lamp; the presence of inorg. salts has little or no effect on the rate. L. S. THEOBALD.

Gum production by *Azotobacter chroococcum* and its composition. W. B. HAMILTON (J. Bact., 1931, 22, 249—254).—*A. chroococcum* growing in a carbohydrate medium produced a levorotatory gum. The more complex carbohydrates were more readily available for gum production than mono- or di-saccharides. Proteins (e.g., peptone) increased, but were not essential to, gum formation. The gum is of the carbohydrate class, does not produce reducing substances by boiling with acid, and is probably an araban. A. G. POLLARD.

Microbic multiplication. Influence of composition of liquid media on microbial growth (*B. pyocyaneus*). J. REGNIER and D. DAVID (Compt. rend., 1931, 193, 1119—1122).—Various media are compared with respect to their content of elements of metabolic significance, for which analytical data are given. The max. growth of *B. pyocyaneus* does not increase proportionately with the content of the medium. Reproductive ability is not maintained as long in rich media, e.g., Liebig broth, as in a simple aq. extract of meat. A. COHEN.

Manometric determination of anaerobic respiration (experiments with acetic acid bacteria). A. REID (Biochem. Z., 1931, 242, 159—169).—When methylene-blue (chloride) is reduced, e.g., with cysteine in neutral solution, to the leuco-base, HCl is set free. If the reaction takes place in HCO_3^- buffer, an amount of CO_2 equiv. to the reduced

dye is set free and can be measured manometrically. In this case the oxidation product (cystine) is neutral. If, in place of cysteine, living cells (AcOH bacteria) are used for the anaerobic reduction of the dye, the oxidation products are acid (CO_2 , AcOH, etc.) and more CO_2 is formed than 1 mol. per mol. of reduced dye. If benzoquinone is reduced with cysteine, the reduction and oxidation products are neutral and no CO_2 arises. If the quinone is reduced anaerobically with living cells, the oxidation products are acid and an amount of CO_2 equiv. to the oxidation product is liberated.

P. W. CLUTTERBUCK.

Physiology of acetic acid fermentation. II. Influence of potassium cyanide and of acetone. Dismutation. K. TANAKA (Acta Phytochim., 1931, 5, 239—266).—KCN does not affect the dehydrogenase action with EtOH as H-donor, but oxidative fermentation is strongly deactivated (cf. Wieland and Bertho, A., 1929, 219). When MeCHO is also present there is less deactivation of oxidative fermentation, due to cyanohydrin formation. COMe_2 -treated bacteria behave exactly as do those treated with KCN. COMe_2 -treated bacteria can also dismute MeCHO; dismutation is therefore simply dehydrogenation with MeCHO. Dehydrogenation with O_2 is quicker in acid than in neutral solution, but for dismutation the reverse holds. Dehydrogenation and dismutation depend on the same enzymic action, whilst oxidative fermentation differs from this.

F. R. SHAW.

Fission of arcaine by micro-organisms. II. F. LINNEWER (Z. physiol. Chem., 1931, 202, 1—7; cf. A., 1931, 1321).—Putrefactive organisms produce from arcaine two further bases isolated as the picrates: agmatine and carbamylagmatine (picrate, m.p. 183—185°; dipicrate; dinitrate, m.p. 155—157°). The latter was synthesised from agmatine sulphate and KCNO. Arcaine is not appreciably decomposed by the weak alkaline reaction prevailing during putrefaction.

J. H. BIRKINSHAW.

Decomposition of the capsular polysaccharide of pneumococcus type III by a bacterial enzyme. R. DUBOS and O. T. AVERY (J. Exp. Med., 1931, 54, 51—71).—A bacillus isolated from peat soil decomposes the polysaccharide aerobically or anaerobically between p_H 6.2 and 7.8 at room temp. or 37.5°; an endocellular enzyme isolated by autolysis of the bacterial cells has the same sp. action. Hence capsular polysaccharides are responsible for type-specificity.

CHEMICAL ABSTRACTS.

Resistance of dehydrated pneumococci to chemicals and heat. F. P. GAY, K. N. ATKINS, and M. HOLDEN (J. Bact., 1931, 22, 295—307).—Desiccated but still living pneumococci are not killed, in the absence of H_2O , by EtOH solutions of common disinfectants (phenols, I, heavy metal salts, HgCl_2).

A. G. POLLARD.

Comparison of the hæmolysis produced by β -hæmolytic streptococci in blood-agar with and without 1% glucose. H. PLUMMER and F. H. FRASER (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 125—130).—Of 233 cultures 53% failed to produce hæmolysis on glucose-blood-agar. 32% produced reduced

hæmolysis, whilst 15% produced equal hæmolysis in plain and glucose-blood-agar. Cultures from normal persons had a greater percentage showing hæmolysis in both media than those from sick persons.

F. O. HOWITT.

Comparison of two agar media for counting soil micro-organisms. H. L. JENSEN (J. Agric. Sci., 1931, 21, 832—843).—Counts of soil bacteria and *Actinomyces* on dextrose-caseinogen-agar were higher in the majority of cases than those on mannitol-asparagine-agar.

A. G. POLLARD.

Chemistry of the diphtheria bacillus. J. HIRSCH (Z. Hyg., 1931, 112, 660—667).—The N content of cultures of the bacteria did not alter appreciably with age. A more marked variation occurs in the P content. The proportion of the protein constituents (Van Slyke) is sufficiently characteristic to differentiate the organism from others.

A. G. POLLARD.

Stabilisation of diluted diphtheria toxin. P. J. MOLONEY and E. M. TAYLOR (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 149—151).—Gelatin in concns. down to 0.00125% has a stabilising action on the toxin with respect to the toxicity.

F. O. HOWITT.

Toxin production and intracutaneous virulence of recently isolated diphtheria cultures. E. W. MADER and K. C. HALPERN (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 153—158).—An examination of cultures from diphtheria cases and carriers. Less virulent cultures produce better toxin than do the more virulent.

F. O. HOWITT.

Effect of antiseptics on the antigenic value of diphtheria toxoid. C. J. FRASER and P. J. MOLONEY (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 131—147).—PhOH (0.1%) or "merthiolate" (0.02%) is an effective antiseptic for diphtheria toxoid and causes no appreciable decrease in antigenic val. "Mercuraphen" (0.005%) does not affect the toxoid, but has little antiseptic power. Incubation of purified toxoid containing 20% EtOH for 1 month produces no loss of immunising power.

F. O. HOWITT.

Theory of the constitution of antibodies. H. VINCENT (Compt. rend., 1931, 193, 798—801).

Protein-free suspensions of viruses. I Adsorption and elution of bacteriophage and fowl-pox virus. I. J. KLIGLER and L. OLITZKI. II. Cataphoresis experiments. I. J. KLIGLER, L. OLITZKI, and M. ASCHNER (Brit. J. Exp. Path., 1931, 22, 172—177, 178—182).—By adsorption on kaolin and elution with aq. NH_3 bacteriophage and fowl-pox virus can be separated from the associated proteins. Both coliphage and fowl-pox virus, when free from protein, are sensitive to acid reactions and carry positive or negative charges according to the reactions of the medium. The phage is amphoteric in acid and decidedly alkaline solutions, and chiefly negatively charged in neutral or mildly alkaline solutions. The fowl-pox virus is positively charged on the acid side and amphoteric in neutral solutions; it carries a negative charge in alkaline solutions.

CHEMICAL ABSTRACTS.

Eucopintoxin hydrochloride in the preparation of vaccine virus. N. E. McKINNON (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 117—120).—Eucopintoxin exhibits no bactericidal action when emulsified with vaccine pulp at room temp. and very little at lower temp., whilst its inferiority to PhOH-glycerol is not compensated by absence of destructive action on the virus.

F. O. HOWITT.

Concentrated anti-vaccinia serum. N. E. McKINNON and W. KNOWLES (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 121—124).—Isolation of the pseudo- and eu-globulin fractions of the plasma by "salting-out" methods resulted in a 5-fold concn. of the virucidal antibody in the former, whilst the latter contained only a small amount.

F. O. HOWITT.

Relation between chemical constitution and action on micro-organisms. XI. Di- and trihydroxy- or -alkyloxy-benzoic acids and esters. T. SABALITSCHKA [with H. TIETZ] (Arch. Pharm., 1931, 269, 545—566; cf. A., 1931, 1054).—The figures quoted in parentheses after the following substances are the ratios of the min. concn. of PhOH inhibiting fermentation of glucose by yeast to the min. concn. of the substance preventing fermentation under identical conditions; where G is appended, the tests were carried out in presence of glycerol: pyrocatechol (0.8); resorcinol (0.9) [Me ether (1)]; quinol (0.8); 4-hexylresorcinol (72.2); pyrogallol (0.6); phloroglucinol (0.1); hydroxyquinol (0.6); guaiacol (0.7); eugenol (6.1); vanillin (1.2); isovanillin (0.7G); veratraldehyde (less than 0.9G); 4-hydroxy-3-methoxybenzoic acid (3.1) [Me (1.7G); Et (7.3); Pr, b. p. 304—306°/760 mm., m. p. 43° (10.4); Pr^β, m. p. 113.5° (less than 11.2G); Bu, m. p. 48—49° (33.4G), and CH₂Ph, m. p. 33—34° (48G), esters]; protocatechuic acid (0.8) [Me (14) and Pr, m. p. 115° (8.1), esters]; veratric acid (6.8) [Me (less than 7.3G) and Pr, b. p. 175—177°/15 mm. (less than 278), esters]; 2:3-dihydroxybenzoic acid (3.8); 2:4-dihydroxybenzoic acid (3.8) [Et, m. p. 71—72° (13.6), and Pr, m. p. 39° (48.7), esters]; 2:5-dihydroxybenzoic acid (1.4) [Me (2.1) and Pr, m. p. 60° (7.3), esters]; 2:6-dihydroxybenzoic acid (3.8) [Pr ester, b. p. 178—182°/15 mm. (18.2)]; 3:5-dihydroxybenzoic acid (0.7) [Pr ester, m. p. 60—61° (5.1)]; 2-hydroxy-4-methoxybenzoic acid (6.3) [Pr ester, b. p. 153—155°/15 mm. (less than 26.1G)]; 2:4-dihydroxy-5-hexylbenzoic acid (88.6G) [Me ester, m. p. 101° (less than 357G)]; 2:4:6-trihydroxybenzoic acid (less than 1) [Me ester (3.7G)]; gallic acid (less than 0.5) [Me (less than 0.6); Pr, m. p. 146° (2.9), and Bu, m. p. 90° (7.6), esters]; 3:5-dihydroxy-4-methoxybenzoic acid (0.6) [Pr ester, m. p. 99° (4.2)], and Me 2:4:6-trihydroxy-3:5-dimethylbenzoate (less than 26.1G). H. BURTON.

Cortico-adrenal extract: its efficacy by mouth. S. W. BRITTON and H. SILVERTE (Science, 1931, 74, 440—441).—The increase in blood-sugar which accompanies the administration of the extract to adrenalectomised cats with symptoms of insufficiency affords a means of bio-assay. The extract is effective when given by mouth, but large doses are required. Adrenaline, glucose, and extracts prepared from tissues other

than adrenal have no effect on symptoms of adrenal insufficiency. The existence of two hormones in cortico-adrenal extract is postulated; the primary action of the life-preserving hormone appears to be that of maintaining a normal carbohydrate balance in the body.

L. S. THEOBALD.

"Sympathetic substances" from the gut and other organs of the toad. H. C. CHANG and Y. P. CHEN (Chinese J. Physiol., 1931, 5, 363—375).—The extraction of a "sympathetic substance" from the gastro-intestinal tract is described. Stimulation of the sympathetic nerve improves the yield. The substance has a pressor action, most marked in adrenal extracts, increases the heart-rate of the toad, but does not affect intestinal motility in dogs. Weaker extracts are obtained from the heart, lung, liver, and skeletal muscle.

A. COHEN.

Nutrition and the action of the thyroid gland. IV. Effect of the hormone of the gland when normal and special diets are given. V. Effect of meat diet on experimental hyperthyroidism. I. ABELIN (Biochem. Z., 1931, 242, 385—410, 411—423; A., 1931, 253).—IV. Experimental hyperthyroidism in rats can be kept in check (even when administration of thyroxine is continued) to a very great extent by giving suitable food. Such food also maintains the power of the liver and muscle to produce glycogen despite the continued administration of thyroxine (or thyroid preps.), whereas, with ordinary food, this power is greatly reduced or quite destroyed. It is possible that the special food, which is poor in meat, strengthens the anti-thyroid powers of the organism particularly in the liver and in the endocrine organs.

V. The detrimental effect of the consumption of meat in experimental hyperthyroidism can be counteracted to a large extent by choosing the other constituents of the food suitably (e.g., 30% of boiled meat with cod-liver oil, vegetable powder, egg yolk, etc.). Rats which receive daily injections of thyroxine can be maintained in relatively good health for 1½ months or longer on such diets, whereas other hyperthyroidised rats which receive meat diets rapidly develop symptoms of serious poisoning and die. As regards disorders of the basal and glycogen metabolism diet rich in meat is not so detrimental in hyperthyroidism as is the usual milk and vegetable diet, but, on the other hand, not so favourable as food containing protein, e.g., caseinogen. It is concluded that, in hyperthyroidism, disorders due to diet can be reduced or eliminated by food of appropriate composition.

W. MCCARTNEY.

Extraction of insulin and stability of various preparations. C. M. JEPHCOTT (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 183—186).—The conditions for the optimum extraction of insulin from ox pancreas by means of acid-EtOH mixtures were determined. Yields of 3000—3500 units per kg. were obtained. Purified insulin added to the minced pancreas was almost completely lost during extraction, whilst similar addition of crude material resulted in quant. recovery.

F. O. HOWITT.

Acetylation of crystalline insulin. A. F. CHARLES and D. A. SCOTT (Trans. Roy. Soc. Canada,

1931, [iii], 25, V, 187—191).—Cryst. insulin yields an Ac derivative containing 13.6% Ac groups, 98% of the original potency being lost. Isoelectric pptn. of this product yields one of 7.0% Ac groups, indicating an adsorption or complex formation with AcOH to the extent of approx. 6.6% (cf. A., 1928, 675, 1160; 1930, 1320). Exposure of the purified acetylated insulin to dil. NaOH at p_H 9.56 at 4° for 1 week results in a recovery of 25% of the original potency.

F. O. HOWITT.

Insulin. VI. Optical behaviour of insulin and its derivatives. W. KUHN, H. EYER, and K. FREUDENBERG. VII. Homogeneity of insulin preparations. W. DIRSCHERL. VIII. Chemistry of insulin. K. FREUDENBERG, W. DIRSCHERL, and H. EYER. IX. Action of proteolytic enzymes on insulin. Comparison of hydrolysis and destruction of activity. K. FREUDENBERG, W. DIRSCHERL, H. EICHEL, and E. WEISS. X. Insulin. K. FREUDENBERG and W. DIRSCHERL (Z. physiol. Chem., 1931, 202, 97—115, 116—127, 128—158, 159—191, 192—206; cf. A., 1930, 646).—VI. Insulin shows an absorption band at 280 m μ very similar to that given by tyrosine and cystine. Inactivation of insulin by alkali, acids, or methylation followed by demethylation produces no change in absorption: inactivation by CH_3O , H_2O_2 , α -C $_6$ H $_4$ Cl-CHO, deamination, or photochemical action affects the absorption. The change on irradiation is probably due to aldehyde formation. The rotation-dispersion of insulin is similar to that of tyrosine and cystine; the active group probably contains at least one asymmetric C atom.

VII. The initial hypoglycaemia observed after injection of many insulin preps. is not produced by cryst. insulin. By the method of Döngemans (Arch. exp. Path. Pharm., 1928, 128, 44), unstable insulin preps. were obtained with $\frac{1}{4}$ times the activity of the cryst. material, which, however, is probably the purest stable prep. Insulin is adsorbed by Al(OH) $_3$ prep. C $_7$.

VIII. In the inactivation of insulin by dil. NaOH 0.16% of NH $_3$ is liberated. There is no increase in NH $_2$ -N. On treatment with hot dil. HCl, liberation of NH $_3$ precedes inactivation; the NH $_3$ therefore arises from portions of the mol. other than the active group. The regeneration of esterified insulin proceeds better with amorphous than with cryst. material and is associated with a second and irreversible reaction of the active group. The latter is esterified by diazomethane. Na or Mg amalgam at acid reaction inactivates insulin and removes 0.06—0.08% of NH $_3$ from the mol. A further similar amount is liberated by alkali. Inactivation by aromatic aldehydes consists of an O transfer. The NH $_3$ liberated by alkali is reduced to 0.07—0.08%. If this amount represents 1 equiv. the mol. wt. of cryst. insulin is 20,000. Deamination by HNO $_2$ is associated with, but not directly related to, inactivation.

IX. Enzymes which hydrolyse the protein portion of the insulin mol., e.g., pepsin, trypsin-kinase, papain, produce inactivation; trypsin (without kinase), amino-polypeptidase, and dipeptidase have no effect. With pepsin complete inactivation occurs with an increase in NH $_2$ -groups of about 0.4%, with papain 1.4%, with trypsin-kinase more than 4%. Inactivation is at first more rapid than hydrolysis.

Cryst. insulin shows only 0.75% increase in NH $_2$ -N for $\frac{1}{2}$ inactivation and an amorphous prep. 2.8% for complete inactivation. Papain liberates the two alkali-sensitive N groups as NH $_3$ from cryst. insulin, but no NH $_3$ from the alkali-inactivated product. Variation of p_H or of the amount of papain does not affect the relation between hydrolysis and inactivation.

X. Review and discussion. J. H. BIRKINSHAW.

Inactivation of crystalline insulin by cysteine and glutathione. V. DE VIGNEAUD, A. FITCH, E. PERABEK, and W. W. LOCKWOOD (J. Biol. Chem., 1931, 94, 233—242).—Cysteine is more potent in deactivating insulin than is glutathione; the reaction is considered to be the change from disulphide to thiol. and is irreversible and independent of Fe. The re-oxidised inactive insulin gives no heat ppt. and is insol. in liquid NH $_2$ Ac, unlike the active form.

H. DAVSON.

Action of insulin in the eviscerated spinal animal. C. H. BEST, L. IRVING, and H. C. FOSTER (Trans. Roy. Soc. Canada, 1931, [iii], 25, V, 93—95).—A further attempt to prepare a balance sheet of the glucose disappearing and that accounted for by oxidation, glycogen storage, and changes in tissue-sugar concn. in the spinal eviscerated animal (cf. A., 1926, 870). The R.Q. when corrected for changes in the CO $_2$ content of blood and muscle approximates to unity when adequate amounts of glucose and insulin are administered. Under these conditions large amounts of glycogen are deposited in the muscles and the balance leaves no room for the formation of other carbohydrate compounds.

F. O. HOWITT.

Pharmacology of insulin-free pancreatic extracts and Frey's circulatory hormone. A. H. ELLIOT and F. R. NUZZUM (J. Pharm. Exp. Ther., 1931, 43, 463—475).—An average increase of 30% in the coronary flow in rabbits was observed by perfusing with insulin-free pancreatic extracts, but no increase in heart rate occurred. This extract also abolished the pressor response to adrenaline. The Frey hormone, prepared from normal urine, has similar pharmacological properties and is probably distinct from choline, histamine, and adenylic acid. Both hormones are beneficial in the treatment of angina pectoris.

P. G. MARSHALL.

Sexual hormones. A. BUTENANDT (Z. angew. Chem., 1931, 44, 905—908).—A review of the chemistry of the follicular and testicular hormones. Parallel with the follicular hormone, the testicular hormone is sol. in certain solvents, stable towards dil. acids and alkalis at 100°, and is distillable in a vac.; on the other hand, whilst the follicular hormone is acid in character, the male hormone is neutral yet sol. in dil. alkali. Testicular hormone is prepared from a crude oil from male urine (cf. A., 1930, 254). Repeated hydrolysis of the oil (20—30 mg. per unit) followed by treatment with org. solvents and aq. EtOH gives an oil with 3 units per mg. Further purification by adsorption and pptn. yields an oily concentrate from which NH $_4$ OH yields a small amount of active cryst. material, m. p. 215°. Regeneration from the oxime gives a cryst. product, m. p. 165°, which contains only about 5% of the

hormone. Repeated crystallisation from aq. EtOH and sublimation at 80–85°/0.0001 mm. finally results in a cryst. substance, m. p. 178°, with a yield of 15 mg. from 25,000 litres of urine. This substance, active in doses of 0.0001 mg., possesses a CO and a OH group and has the composition $C_{16}H_{26}O_2$.

F. O. HOWITT.

Occurrence and action of the female sexual hormone. H. SCHWERTFEGGER (Arch. exp. Path. Pharm., 1931, 163, 487–492).—An œstrin-like substance has been found in the coelenterate, *Actinia equina*, and in arthropods (hornet and spider). Progynon, an œstrin prep., has an inhibiting effect on the movement of the isolated uterus from various animal species.

W. O. KERMAK.

Effect of the removal of female sex glands on the calcium and potassium content of the blood. H. SUZUKI (Keijo J. Med., 1931, 2, 332–344).—Removal of one or both ovaries or subcutaneous injection of “agomensin,” “sistomensin,” or “oophormin” into normal or castrated rabbits causes in each case decreases in serum-Ca and increases in serum-K with a tendency to return to the normal vals. after 5 weeks.

A. LAWSON.

Anterior pituitary hormone from urine of pregnancy. F. G. FISCHER and L. ERTEL (Z. physiol. Chem., 1931, 202, 83–96).—The purification of crude preps. from urine of pregnancy of the hormone stimulating the immature ovary and the chemical reactions of the purified product are described. The behaviour corresponds best with that of the “mucoids.”

J. H. BIRKINSHAW.

Antagonism of menoformone and hormones of the anterior pituitary lobe. S. E. DE JONGH and E. LAQUEUR (Pflüger's Archiv, 1931, 227, 57–70; Chem. Zentr., 1931, i, 3252).—Stimulation of sexual development of the infantile mouse by the hormone of the anterior pituitary lobe is retarded but not arrested by administration of menoformone; only the stimulation of the seminal vesicles is affected. The inhibitory action of menoformone can be completely suppressed by the pituitary hormone.

A. A. ELDRIDGE.

Carotenase. Transformation of carotene into vitamin-A in vitro. H. S. OLCOTT and D. C. McCANN (J. Biol. Chem., 1931, 94, 185–193; Science, 1931, 74, 414; cf. Moore, Capper, A., 1930, 962, 1321).—The minced livers, or their aq. extracts, of vitamin-A-free rats, when incubated with carotene in Et laurate, produce vitamin-A. This property is destroyed by heat, indicating the presence of an enzyme, *carotenase*.

H. DAVSON.

Relation of bile to the intestinal absorption of vitamin-A in the rat. W. SCHMIDT and C. L. A. SCHMIDT (Univ. Calif. Pub. Physiol., 1930, 7, 211–212).—Absorption of vitamin-A can take place from the gastro-intestinal tract of the rat in the absence of most, if not all, of the bile from the intestines.

CHEMICAL ABSTRACTS.

Determination [of vitamin-A] in cod-liver oil. B. BLEYER, F. SCHLEMMER, and W. MÜLLER-PARCHAM (Arch. Pharm., 1931, 269, 566–581).—Details are given for the colorimetric determination

of vitamin-A with $SbCl_3$ in $CHCl_3$ using a Hellige-Autenrieth colorimeter; the vals. obtained agree with those found biologically.

H. BURTON.

Antineuritic vitamin. I. Albino mice as test animals for antineuritic concentrates. W. FREUDENBERG and L. R. CERECEDO (J. Biol. Chem., 1931, 94, 207–212).—The Jansen-Donath prep. of concentrates from rice polishings (A., 1926, 644; 1929, 1344) was modified by the use of Lloyd's reagent in place of acid clay as adsorbent. Mice react to the concentrates similarly to pigeons and rats, a daily dose of 0.025 mg. being sufficient.

H. DAVSON.

Physiological functions of vitamins. R. R. WILLIAMS and W. H. EDDY (Carnegie Inst. Wash. Yearbook, 1929, 28, 377–385; 1930, 29, 389–395).—The four factors constituting vitamin-B are discussed. By electrodialysis of yeast autolysate, products which stimulate the growth of yeast were obtained at p_H 3.7 (β -bios; Ac derivative, m. p. 154°) and p_H 8 (α -bios). Hydrolysis of β -bios with HCl affords inositol. Sunflower seed contains much vitamin-B₃. The metabolism of yeast probably involves a group of factors. CHEMICAL ABSTRACTS.

Occurrence of vitamin-C in two varieties of potatoes grown under similar conditions. J. E. RICHARDSON, D. DOUGLASS, and H. MAYFIELD (Potato Assoc. Amer. Proc., 1929–1930, 16, 69–73).—Bliss Triumph potatoes had a higher antiscorbutic effect than Netted Gem, but after cooking the reverse held. The presence of a volatile inhibitor in the latter is postulated.

CHEMICAL ABSTRACTS.

Use of fractional electrolysis in the fractionation of the “bios” of Wildiers. R. J. WILLIAMS and J. H. TRUESDALE (J. Amer. Chem. Soc., 1931, 53, 4171–4181).—By the use of fractional electrolysis of extracts of rice bran, yeast, malt, sprouts, and milk, the “bios” of Wildiers has been separated into two supplementary fractions. The acid factor (accumulates in the anode cell) is readily dialysed through all the membranes tested, whilst the basic factor dialyses only slowly through collodion treated with 40% EtOH, and practically not at all through the other membranes. The active materials are org. in nature, since ignition causes loss of activity; the ash from the factor derived from yeast imparted a slight improvement to the synthetic medium for Wildiers' yeast. Preliminary work indicates that Narayanan's yeast needs one factor not required by Wildiers'. The theory of the electrolytic method, and possible applications to the study and concn. of vitamins, hormones, and enzymes, are discussed.

C. J. WEST (6).

Determination of vitamins-A and -D. P. SCHULTZER (Dansk Tidsskr. Farm., 1931, 5, 177–198).—Vitamin-A is determined by the curative method and vitamin-D by the preventive method, rats being employed.

H. F. HARWOOD.

Standardisation of vitamin-D by the line test. F. J. DYER (Quart. J. Pharm., 1931, 4, 503–516).—A “scale of healing” of rats rendered rachitic by a standard diet free from vitamin-D and then given various known doses of the vitamin was represented by seven progressive grades as shown by the line

test. Using this as a standard, curves correlating dosage with degree of healing were constructed. The use of these curves for the assay of vitamin-*D* is indicated. F. O. HOWITT.

Separation of the antirachitic from the toxic factor in the irradiation products of ergosterol. A. WINDAUS, P. BUSSE, and G. WEIDLICH (*Z. physiol. Chem.*, 1931, 202, 246—248; cf. *A.*, 1931, 881).—The vitamin, on heating or hydrogenation, is converted into a new substance which is antirachitically inactive but still toxic. J. H. BIRKINSHAW.

Gall bladders of chicks in a vitamin-*D*-deficient condition. W. C. RUSSELL and D. F. CHICHESTER (*Science*, 1931, 74, 437—438).—Vitamin-*D* deficiency is accompanied by enlarged gall bladders and an increased vol. of bile. L. S. THEOBALD.

Effect of large doses of irradiated ergosterol on nitrogen, calcium, and phosphorus metabolism in rats. R. KERN, M. F. MONTGOMERY, and E. U. STILL (*J. Biol. Chem.*, 1931, 93, 365—380).—Large daily doses of irradiated ergosterol cause considerable deposition of Ca in the kidneys of growing rats on a normal diet, the females being affected to a greater extent than males. Ergosterol irradiated in EtOH has a greater influence on Ca metabolism than that irradiated dry or in Et₂O. Urinary Ca increases and faecal Ca and P decrease. N excretion is affected mainly by food intake resulting from the vitamin administration. The proportions of Ca, P, and CO₃ in the leg bones remain normal. A. COHEN.

Source of excess calcium in hypercalcaemia induced by irradiated ergosterol. A. F. HESS, H. R. BENJAMIN, and J. GROSS (*J. Biol. Chem.*, 1931, 94, 1—8).—In view of the conclusions of Jones, Rapoport, and Hodes (*A.*, 1931, 773) that the source of excess Ca in hypercalcaemia of dogs induced by irradiated ergosterol was the food, and not the tissue, as indicated by Hess, Weinstock, and Rivkin (*Proc. Soc. Exp. Biol. Med.*, 1930, 27, 298), the effect of irradiated ergosterol on the serum-Ca of dogs was again studied under conditions identical with those of Jones *et al.*, results being obtained in agreement with later work of the latter author (*A.*, 1931, 1338), viz., that the source of serum-Ca in hypercalcaemia is the tissue. Hypercalcaemia in dogs was greatly reduced by intravenous injection of NaHCO₃, this resulting in an excess of Ca and P in the lungs and kidneys. A. LAWSON.

Permeability. V. Irradiated ergosterol and inorganic serum-phosphate. A. SOLE (*Biochem. Z.*, 1931, 242, 349—365; *A.*, 1931, 117).—The resorption of P in the intestine of the rabbit is not affected by intravenous administration of ergosterol, and consequently such administration produces hyperphosphatemia in rabbits which have fasted for long periods and have empty intestines. The hyperphosphatemia which follows parenteral injection of irradiated ergosterol is due to various changes in the amount and state of combination of the P in the various sections of the blood-stream and is reflected in the inorg. P content of the serum in these

sections. The extent of these changes has been determined. W. MCCARTNEY.

Antirachitic efficiency of winter sunlight in Chicago. J. T. HAUCH and M. E. HANKE (*Ind. Eng. Chem.*, 1931, 23, 1398—1402).—February Chicago sunlight transmitted through commercial ultra-violet glass is inadequate to prevent rickets in rats fed on a rickets-producing diet. The ultra-violet transmissions of various glasses are compared. H. DAVSON.

Antirachitic vitamin of radicles [of barley]. I—III. A. SCHITTENHELM and B. EISLER (*Z. ges. exp. Med.*, 1931, 75, 737—744, 745—757, 758—766; *Chem. Zentr.*, 1931, i, 3255).—Radicles of barley contain a substance which is antirachitic in absence of exposure to light of short wave-length. In rachitic rats the N metabolism is deranged; the N balance is negative, and the utilisation of food, even of the radicles, is disturbed. The active sterol mixture from barley radicles grown in the dark contains activated ergosterol. A. A. ELDRIDGE.

Assimilation of carbon dioxide. H. KAUTSKY and A. HIRSCH (*Naturwiss.*, 1931, 19, 964).—This has been studied by the absorption of ultra-violet light by leaves and measurement of the fluorescence. Three stages are distinguished: (1) rapid initial increase in fluorescence corresponding with chlorophyll-CH₂O-peroxide formation, (2) gradual decrease in fluorescence during assimilation, and (3) a steady stage of min. fluorescence. These stages are well marked at 30°, but at 0° or after HCN poisoning stages (2) and (3) do not occur. P. G. MARSHALL.

Rates of assimilation and increase of substance of the sea algae in diluted sea-water and behaviour on resalting. I. Phases of the poisonous action and the question of reversibility. II. Types of functional salt action. C. MONTFORT (*Ber. deut. bot. Ges.*, 1931, 49, 49—58, 59—66).—The photosynthetic activity of various species of sea algae when suspended in sea-H₂O diluted with fresh H₂O is in general first stimulated and subsequently depressed. Different species are distinguished by the magnitudes and time relationships of the two effects. When replaced in sea-H₂O, recovery takes place, provided that the depression has not been too great, but species show marked differences in respect of the limiting depression compatible with recovery. The algae are usually less susceptible in hypotonic solutions in cold (7—8°) than in warmer H₂O (17—18°). W. O. KERMACK.

Respiration of healthy and leaf roll potatoes. T. WHITEHEAD (*Nature*, 1931, 128, 967).—Differences in the respiration of normal and infected plants are recorded. L. S. THEOBALD.

Unequal effect of oxygen concentration on the velocity of [plant cell] oxidation in loci of different electric potential and glutathione content. E. J. LUND (*Protoplasma*, 1931, 13, 236—258).—The concn. of substances reacting as glutathione is a max. in the young, actively-growing, electropositive ends of stems and roots. The distribution of the concn. of these substances corresponds with the distribution of rates of O₂ consumption, CO₂

production, methylene-blue reduction, and electric potential. Oxidisable substances are present in greater amounts in the apical than in the basal ends of *Obelia* stems. A. G. POLLARD.

Composition of fruit-bud and -spur tissues of Wealthy apples under different conditions of nutrition. A. J. HEINICKE (Proc. Amer. Soc. Hort. Sci., 1931, 27, 190—198).—In bud tissues where the N content is high the amount of K and P also tends to be high, whilst the total carbohydrate is low. New spur growth contains less N, K, and P, but more carbohydrate. CHEMICAL ABSTRACTS.

Seasonal changes in the composition of Stayman apple trees. II. Nitrogen. J. T. SULLIVAN and H. R. KRAYBILL (Proc. Amer. Soc. Hort. Sci., 1931, 27, 220).—Total and sol. N decreased from terminal growth to the trunk in both bark and wood. Above ground the bark is higher and below ground lower in sol. N. Between December and February the N content of all parts increases. CHEMICAL ABSTRACTS.

Effect of seasonal temperatures on composition of kale (*Brassica oleracea*, var. *acephala*). R. L. CAROLUS (Proc. Amer. Soc. Hort. Sci., 1931, 27, 502—508).—Reducing substances are most abundant in the petioles, but scarce in the stem after cold weather. Sucrose and hydrolysable carbohydrate increase with fall in temp. CHEMICAL ABSTRACTS.

Relation of catalase activity to temperature, respiration, and nitrogen fertilisation in Grimes Golden apples. P. L. HARDING (Proc. Amer. Soc. Hort. Sci., 1931, 27, 37—42).—Catalase activity increases with addition of N with immediate or deferred storage at -1° and 2° and with continuous storage at 10° . The activity is independent of respiratory intensity at -1° and 2° , but not at 10° . CHEMICAL ABSTRACTS.

Seasonal distribution of reductase in the various organs of an apple tree. S. H. ECKERSON (Contr. Boyce Thompson Inst., 1931, 3, 405—412).—The ability of the tree to reduce nitrates was low in summer (min. during 5 weeks after flowering), high in autumn and winter, low in February, and rose rapidly to a max. in early spring. High reductase activity in autumn and winter was localised in the fine roots and, in early spring, in fine roots and buds. Leaves were poor in reductase at all times. A. G. POLLARD.

Enzyme content of trees during the winter rest period. S. MANSKAJA and M. SCHILINA (Biochem. Z., 1931, 240, 276—285).—The wood fibres, bark, and buds of the bird cherry, elder, and cornel contain amylase throughout the whole winter rest period (Nov.—April) and those parts of the last-named tree also contain catalase. The activity of the enzymes varies with the part of the tree from which they are obtained and with the time of year at which it is investigated. At the beginning of spring a great increase in the activity of both enzymes occurs in all cases. W. MCCARTNEY.

Properties of plant waxes in relation to climate and habitat. J. B. MCNAIR (Amer. J. Bot., 1931, 18, 518—525).—The m. p., mol. wt., and empirical

formula of the hydrocarbon, alcohol, and ester constituents of 232 plant waxes found in 84 plant families are classified and shown to bear a direct relationship to the climatic conditions of their natural habitats. A. G. POLLARD.

Properties of alkaloids in relation to climate and habitat. J. B. MCNAIR (Amer. J. Bot., 1931, 18, 416—423).—Inter-relationships between the m. p., mol. wt., nos. of H, C, and O atoms per mol., and toxicity of alkaloids, and climatic conditions are examined. A. G. POLLARD.

Influence of period of vegetation and development of plant on the alkaloidal content of *Hyoscyamus niger*, L. Z. F. KLAN (J. Amer. Pharm. Assoc., 1931, 20, 1163—1175).—Determination of the alkaloidal content of all parts of the plant at all stages of its growth shows that with the growth of the germinating plant the quantity of alkaloids in its organs decreases and, in decreasing order of their alkaloidal content, the parts of the plant are as follows: root (both of annual and biennial plants), flowering tops, fruits, leaves, and stems. E. H. SHARPLES.

Pyrethrum flowers: quantitative study of their development. F. TATTERSFIELD (Ann. Appl. Biol., 1931, 18, 602—635).—The pyrethrin content of pyrethrum flowers increased, both relatively and absolutely, from the small bud stage to maturity. The % of pyrethrin fell after pollination. A. G. POLLARD.

Changes in carbohydrate content of White Bush squash during maturation and storage. H. B. CORDNER and W. A. MATTHEWS (Proc. Amer. Soc. Hort. Sci., 1931, 27, 520—523).—The free reducing substance increases with age. Storage at $2-4^{\circ}$ conserves the total carbohydrate content. CHEMICAL ABSTRACTS.

Effect of different nutrient solutions on the structure, composition, and quality of peas. C. B. SAYRE and B. R. NEBEL (Proc. Amer. Soc. Hort. Sci., 1931, 27, 221—226).—Each part of the plant has a higher Ca content when grown in a solution rich in Ca; the Ca content decreases as the K content increases. CHEMICAL ABSTRACTS.

Behaviour of assimilating plants towards ammonium nitrate. D. N. PRIANISCHNIKOV and V. S. IVANOVA-SKOSIREVA (Ann. Acad. Agron. Petrovsk, 1928, No. 2, 7—16).—At all concns. NH_3 was assimilated more rapidly than NO_3' . CHEMICAL ABSTRACTS.

Influence of carbohydrate supply on behaviour of seedlings towards ammonium nitrate. D. N. PRIANISCHNIKOV and V. S. IVANOVA (Ann. Acad. Agron. Petrovsk, 1928, No. 2, 277—286).—Etiolated seedlings during early stages assimilate NH_3 in preference to NO_3' ; in later stages the reverse holds. CHEMICAL ABSTRACTS.

Effect of nitrate applications on the soluble carbohydrate in apples. E. F. HOPKINS and J. H. GOURLEY (Proc. Amer. Soc. Hort. Sci., 1931, 27, 32—36).—The effect is slight. CHEMICAL ABSTRACTS.

Physico-chemical mechanism of amylogen condensation. A. MAIGE (Compt. rend., 1931, 193,

602—603).—A discussion of the process of deposition of starch in plants. W. O. KERMACK.

Microchemistry of the starch grains and amyloplasts in potato tubers. F. W. KUDRZYCKA (Rocz. Farm., 1930, 8, 29—129; Chem. Zentr., 1931, i, 3478).—Apart from polysaccharides the amyloplast and starch grain have a very similar composition. The amyloplast consists of a glucoprotein containing glucose and maltose. In the stroma are found: maltose, lipins, peroxidase, tyrosinase, phenolase, chlorophyllase, and oxidoreductase, K, inorg. Mg, S, Si, and a little Ca. The protein is composed of tyrosine, histidine, tryptophan, arginine, and probably also asparagine and aspartic acid. The protein remaining on the starch grain contains more free NH_2 -acid. Within the starch grain are present: org. Mg, P, S, Si, and small quantities of protein.

A. A. ELDRIDGE.

Starch. Limit of enzymic decomposition, and the amylase complement. H. PRINGSHEIM, H. BORCHARDT, and H. HUPPER (Z. Ver. deut. Zucker-Ind., 1931, 81, 633—643). R. WEIDENHAGEN (*ibid.*, 644—646). H. PRINGSHEIM (*ibid.*, 647).—I. A criticism of Weidenhagen and Wolf (A., 1931, 653). The prep. of an almost non-reducing stable dextrin, and proof that it yields maltose on hydrolysis, are not new (A., 1924, i, 1142). Further experiments are described showing that the conversion of 1% solutions of sol. starch by amylase, as measured by Cu^{++} -reducing power, is carried further in presence than in absence of autolysed yeast-juice free from maltase.

II. No claim to priority respecting the stable dextrin was intended. In the new experiments described above the increased reducing power in presence of yeast-juice is considered too small in most cases to be evidence of an amylase complement acting as claimed by Pringsheim and Beiser.

III. A rejoinder.

J. H. LANE.

Origin of starch in the reserve organs of plants. H. BELVAL (Bull. Soc. d'Encour., 1931, 130, 605—628).—Leaves of the Gramineæ contain only sucrose and its products of hydrolysis, although the sheath is richer in reducing sugars at the expense of sucrose. The facts are considered as evidence that sucrose is formed in the leaves prior to the production of simple hexoses. In wheat there is also a production of fructosides from the sucrose. In the stalks of wheat, but not of maize or rice, there is present along with glucose and fructose a non-reducing laevorotatory sugar other than sucrose, which is sol. in 65% EtOH. At maturity this laevorotatory polysaccharide is present only in traces. The rotatory power of the sol. carbohydrates gradually changes during development from negative to positive, and the rotation after acid hydrolysis more nearly approaches that of invert sugar. Sucrose is the first recognisable sugar in the leaves of the banana, from which dextrans are absent at all stages of development. Carbohydrates accumulate as starch in the fruit. The leaves of *Lycoris radiata* contain laevorotatory sugars at all stages of development, whilst those of *L. squamigera*, Max., contain only small quantities in the later stages of growth. Extraction

of the roots of *L. squamigera* with 90% EtOH yields a solution from which a fructoside, *lycoroside*, separates, mol. wt. 1300, formula $\text{C}_{48}\text{H}_{80}\text{O}_{40}$, decomp. gradually above 173° , $[\alpha] -34^\circ$. A second fructoside, mol. wt. about 600, is obtained from the mother-liquors from lycoroside and is probably identical with asphodeloside.

P. G. MARSHALL.

Evolution of carbohydrates during the formation of the seed of two varieties of pea. M. BRIDEL and C. BOURDOUIL (Compt. rend., 1931, 193, 949—951).—In the seeds of *Pisum sativum*, L., var. early d'Arras, there is initially an appreciable amount of sucrose together with some reducing sugars, but no stachyose. With the progressive synthesis of starch, the sucrose content decreases, the reducing sugars disappear, whilst during the later stages stachyose is formed. Ripening is brought about more by an increase in the insol. matter than by loss of H_2O . In the second variety, Delicious, stachyose appears simultaneously with starch. Before ripening the starch content reached only 7.23%, whereas in the other variety it reached 20.6%.

C. C. N. VASS.

Carbohydrate composition of protected and unprotected raspberry canes. J. C. SNYDER and H. W. RICHEY (Proc. Amer. Soc. Hort. Sci., 1931, 27, 146—150).—In the spring the carbohydrate content is higher in unprotected canes.

CHEMICAL ABSTRACTS.

Carbohydrate composition of Dunlap strawberry plants. H. W. RICHEY and E. C. ASBURY (Proc. Amer. Soc. Hort. Sci., 1931, 27, 179—183).—Young plants have a slightly higher monosaccharide and disaccharide content than old ones. The polysaccharides increase as the season advances.

CHEMICAL ABSTRACTS.

Condition of chlorophyll in the plant. S. HILPERT, H. HOFMEIER, and A. WOLTER (Ber., 1931, 64, [B], 2570—2577).—Treatment of green leaves with 0.1N-NaOH causes immediate dissolution of yellow and brown materials, whilst subsequently dark green extracts with very marked red fluorescence are obtained. Isolated and truly dissolved chlorophyll is not appreciably affected by this treatment. The green substances of the plant extract are pptd. with the pectates by CaCl_2 and the dried Ca salts give a dark yellow solution with aq. MeOH or COMe_2 , in which the colouring matter has the solubility characteristics of carotene. NaH_2PO_4 or AcOH liberates from the salts an acid closely similar to isochlorophyllin. Its mode of production differs from its formation from isolated chlorophyll, but the possibility of the intervention of chlorophyllase is excluded, since the behaviour of the leaves is not altered by previous boiling. Treatment of green leaves with 0.1N-NaOH removes proteins, but there is no direct parallelism between extraction of chlorophyll and protein. Pre-treatment of the leaves with neutral CH_2O retards hydrolysis of the proteins below 55° , but facilitates removal of the dye. It is concluded that chlorophyll in the chloroplasts of plants differs in its solubility relationships and in chemical properties from that removed from the plant by org. solvents. The difference cannot be attributed solely to the state of subdivision. The action of CH_2O

indicates a relationship to the proteins, and the invariable presence of a carotenoid companion in the aq. alkaline solutions indicates that the chlorophyll complex in the leaves is greater than that of the chemical individual. The view that chlorophyll in the plant is in true solution in the lipins cannot be maintained.

H. WREN.

Acidity and colour changes in tomatoes under various storage temperatures. E. S. HABER (Iowa State Coll. J. Sci., 1931, 5, 171—184).

CHEMICAL ABSTRACTS.

Production of ethyl alcohol and acetaldehyde by fruits in relation to the injuries occurring in storage. II. Injuries to apples and pears occurring in the presence of oxygen and absence of accumulations of carbon dioxide in the storage atmosphere. M. THOMAS (Ann. Appl. Biol., 1931, 18, 60—74).—Production of MeCHO and EtOH does not occur in stored apples while the tissue is healthy, but follows the appearance of "internal breakdown" or "soft scald," especially during low-temp. ($>0^{\circ}$) storage. Relations between zymases following storage injury, invasive poisoning by EtOH or MeCHO, and the CO_2 content of the internal atm. of the diseased fruit are discussed.

A. G. POLLARD.

Assimilation of nitrogen by tobacco. A. B. BEAUMONT, G. J. LARSINOS, P. PIEKENBROCK, and P. R. NELSON (J. Agric. Res., 1931, 43, 559—567).—Using yield data, growth characteristics, and chemical composition of leaf as criteria it is concluded that in sterile cultures nitrate-N is most readily assimilated by Havana tobacco. Urea, NH_4 salts, asparagine, and cystine are assimilated to a smaller extent, but other NH_2 -acids and amides, including arginine, alanine, glycine, leucine, NH_2Ac , and cyanamide, remain unassimilated. Similarly cottonseed meal or its hydrolysed products are not taken up. The cumulative toxicity of assimilated NH_3 -N is held to be due in part at least to improper metabolism. The need in the field for conditions favourable for adequate ammonification and nitrification is emphasised.

W. G. EGGLETON.

Nitrogen metabolism of seaweeds. Glutamic acid peptides. P. HAAS and T. G. HILL (Biochem. J., 1931, 25, 1472—1475).—Aq. extracts of certain brown seaweeds give a marked biuret reaction the intensity of which diminishes with the depth of immersion at which the weeds grow. By clearing the aq. extract of *Pelvetia canaliculata* with EtOH and basic Pb acetate and precipitating with $\text{Hg}(\text{OAc})_2$ an octapeptide of glutamic acid was obtained. No similar product has been found in the red or green weeds.

S. S. ZILVA.

Protein crystals in species of *Cladophora*. E. CHEMIN (Compt. rend., 1931, 193, 742—745).—Minute crystals occurring in *C. pellucida*, *C. prolifera*, and *C. rupestris* consist of protein. F. O. HOWITT.

[Alkaloids of] *Lunasia amara*, var. *costulata*. E. H. WIRTH (Pharm. Weekblad, 1931, 68, 1011—1020).—Two alkaloids only could be isolated: lunacrine, $\text{C}_{16}\text{H}_{20}\text{O}_3\text{N}$, m. p. 115.5 — 116° , and lunasine, $\text{C}_{16}\text{H}_{21}\text{O}_5\text{N}_2$, m. p. 188 — 189° . The chemical, physical, and pharmacological properties are described.

S. I. LEVY.

Alkaloids of Chinese gelsemium, Kou Wen, *Gelsemium elegans*, Bth. T. Q. CHOU. **Physiological properties.** C. PAK and H. C. HOU (Chinese J. Physiol., 1931, 5, 345—352).—The isolation and some chemical and physiological properties of the following alkaloids from the stems, roots, and leaves are described: *koumine*, $\text{C}_{20}\text{H}_{22}\text{ON}_2$, m. p. 170° , $[\alpha]^{25}_D -265^{\circ}$ (1% solution in EtOH) [*hydrochloride*, m. p. 255° (decomp.); *hydrobromide*, m. p. 269° (decomp.)]. *Kouminine* (amorphous), m. p. about 115° [*hydrochloride* (inactive in H_2O) and *hydrobromide*, m. p. above 300°]. *Kouminicine* (impure; levorotatory *hydrochloride*). *Kouminidine*, m. p. 200° (*hydrochloride*; *hydrobromide*). A. COHEN.

Urea and ureides in higher plants. III. Occurrence of ureides. Determination of free and combined urea. G. KLEIN and K. TAUBOCK (Biochem. Z., 1931, 241, 413—459).—In most plants part or all of the urea present occurs as ureides (probably of aldehydes) which are not attacked by urease. Methods are described by which the free and combined urea can be determined. In fungi the amount of free urea may exceed the amount of combined. The amount and condition (free or combined) of the urea in the various parts of higher plants vary according to the stage of growth and age.

W. MCCARTNEY.

Constitution of asebotin. Its identity with phloridzin. M. BRIDEL and A. KRAMER (Compt. rend., 1931, 193, 748—750).—Asebotin (cf. A., 1883, 215, 349; 1912, ii, 380), m. p. 137.5° (Maquenne block), from the leaves of *Kalmia latifolia*, L., yields on acid hydrolysis asebogenol, m. p. 274° , which on hydrolysis by $\text{Ba}(\text{OH})_2$ yields in the same way as "phloretol," the hydrolytic product of phloridzin, phloroglucinol, and *p*-hydroxycoumaric acid, thus establishing the identity of asebotin with phloridzin (cf. A., 1930, 1474).

F. O. HOWITT.

Occurrence of sugar alcohols in marine algae. Dulcitol. P. HAAS and T. G. HILL (Biochem. J., 1931, 25, 1470—1471).—The dry tissue of *Bosstrychia scorpioides* was extracted with boiling 60% EtOH, cleared with basic Pb acetate, and the dry residue extracted again with boiling abs. EtOH. Dulcitol crystallised from the syrup. S. S. ZILVA.

Survey of anthocyanins. I. G. M. ROBINSON and R. ROBINSON (Biochem. J., 1931, 25, 1687—1705).—An extensive phylogenetic survey of anthocyanins. The great changes in the colour of varieties in a species are not due to variation in p_H of the cell-sap, but to changes in the nature of the anthocyanins brought about by the formation of weak additive complexes with sp. co-pigments which intensify and modify the colour. The complexes dissociate at high temp. and by the action of solvents. Sometimes the variation in colour may be due to different anthocyanins.

S. S. ZILVA.

Relationship between physiological activity and dye formation in plants. III. Growth and anthocyan formation in *Abutilon avicennae*. H. KOSAKA (J. Dept. Agric. Kyushu, 1931, 3, 99—119).—Anthocyan pigment formation varies inversely with the linear growth of the stalk, which in turn is

controlled by the extent of the accumulation of nutrient substances. P. G. MARSHALL.

Chemical examination of the marking-nut (*Semecarpus anacardium*, Linn.). P. P. PILLAY and S. SIDDIQUI (J. Indian Chem. Soc., 1931, 8, 517—525).—The Et₂O extract of the pericarp of the marking-nut contains *semecarpol* (I) (0.1%), *bhilawanol* (II) (46%), and a tarry corrosive residue (III). Subsequent extraction of the pericarp with EtOH yields tannic acid, an acid sol. in Et₂O, and one insol. in Et₂O. (I), solid below 25°, b. p. 185—190°/2.5 mm., is phenolic (green FeCl₃ colour) and is reduced in abs. EtOH by H₂ in the presence of Pt-black to a product, C₁₇H₂₇OH, m. p. 51—52°; it absorbs 1 mol. of Br in cold CHCl₃ and thus contains one ethylenic linking. (II), C₂₁H₃₀(OH)₂, solid below 5°, b. p. 225—226°/3 mm., 213—214°/1 mm., inactive (Ac₂ derivative, b. p. 230°/2 mm.; Me₂ ether, b. p. 218°/3.5 mm.; *dinaphthylurethane*, m. p. 138—140°), gives with FeCl₃ in EtOH a green colour changing immediately to a black ppt., and a violet-red colour on subsequent addition of KOH; it is thus an *o*-dihydric phenol; on dry distillation it yields pyrocatechol, other phenols, and hydrocarbons. Oxidation of the diacetate of (II) by KMnO₄ in aq. COMe₂-AcOH affords acids giving the colour reactions of *o*-catechuic acid. Hydrogenation of (II) in abs. EtOH in the presence of Pt-black gives *tetrahydrobhilawanol* (IV), m. p. 57—58° [Ac₂ derivative, m. p. 51°; Bz₂ derivative, m. p. 59—60°; Me₂ ether, m. p. 36—37°; nitro- and dinitro-methyl ether (the latter by HNO₃ of *d* 1.52, but not by HNO₃ of *d* 1.48), m. p. 71—72° and 83°, respectively], which on oxidation with KMnO₄ in aq. COMe₂ gives palmitic acid. (IV), its Bz₂ and Me₂ derivatives are identical with hydrourushiol and its derivatives, respectively (A., 1922, ii, 262). (II) is, therefore, 3-*n*-pentadecadienylpyrocatechol. (III) (mol. wt. nearly 1000) gives no cryst. derivatives, and on dry distillation at atm. pressure yields high-boiling phenols and non-phenols, but no pyrocatechol; it probably consists of a mixture of complex phenols, but is considered not to have been formed by polymerisation of (II).

R. S. CAHN.

Chemical composition of *Lemma* as a characteristic of the species. V. VERNADSKY and A. VINOGRADOV (Compt. rend., 1931, 193, 560—561).—The composition of *Lemma* is characteristic for the species and independent of locality of cultivation. The order of abundance of the chemical elements is in general the same for all species. Two types of species exist, one rich in C and poor in H₂O, the other poor in C and rich in H₂O. W. O. KERMAK.

Determination of carbon in plant tissues. R. R. LE G. WORSLEY and F. J. NUTMAN (Ann. Bot., 1931, 45, 693—707).—Combustion apparatus in which the plant material is introduced directly into the preheated tube is described. Combustion is complete in 5 min. H may be determined in the same apparatus. The Hagedorn-Jensen method for determining blood-sugar is modified to deal with larger quantities of sugar. Invert sugars from sucrose showed a slightly different reducing power from that of

pure glucose. In presence of starch the end-point of the titration is rather less definite. A. G. POLLARD.

Determination of the tension of carbon dioxide and oxygen in small amounts of liquid. A. BECK (Biochem. Z., 1931, 244, 218—221).—The author's method (A., 1928, 1292) is slightly modified in order to avoid the difficulty in transferring the equilibrated bubble into the intermediate vessel.

P. W. CLUTTERBUCK.

Dish for toxicity tests. A. S. DANIELS (Ind. Eng. Chem. [Anal.], 1931, 3, 358). E. S. HEDGES.

Determination of iodine in organic products. G. PFEIFFER (Biochem. Z., 1931, 244, 280—282; cf. A., 1931, 134).—Modifications in the method and apparatus previously described are given for the micro-determination of I in oils or fats or in material very rich in cellulose. W. MCCARTNEY.

Determination of iodine in biochemical material. J. SCHWABOLD and B. HARDER (Biochem. Z., 1931, 240, 441—453).—Minute amounts of I in any kind of biochemical material can be determined in the apparatus described by combustion of the org. matter in O₂ in a closed tube, absorption of the I in K₂CO₃ solution, oxidation to iodate with Cl₂, and titration (after concn. if necessary) of the whole or of an aliquot part of the solution with 0.002 or 0.001*N*-Na₂S₂O₃ solution. Br in the amounts likely to occur does not interfere. W. MCCARTNEY.

Micro-determination of sodium in biological materials. R. A. McCANCE and H. L. SHIPP (Biochem. J., 1931, 25, 1845—1848).—The authors' method (A., 1931, 926) is applied to various body-fluids and solid tissues. By employing suitable protein precipitants the necessity of incineration, except in the case of organs, can be avoided. S. S. ZILVA.

Colorimetric determination of potassium. H. R. D. JACOBS and W. S. HOFFMAN (J. Biol. Chem., 1931, 93, 685—691).—K is pptd. from the fluid to be examined as the cobaltinitrite (A., 1921, ii, 412), the ppt. dissolved in hot H₂O, treated with choline chloride and K₄Fe(CN)₆, and the resulting green solutions are compared with suitable standards. Determinations on human blood-sera and urines are given. F. O. HOWITT.

Source of error in nitrogen and phosphorus determinations on filtrates obtained after precipitation of tissue colloids by trichloroacetic acid or other strong acids. H. D. KAY (J. Biol. Chem., 1931, 93, 727—732).—In deproteinisation of tissue extracts by CCl₃-CO₂H or HgCl₂+HCl and when the acid is in contact with the lipins present for a period exceeding a few min., hydrolysis of the latter occurs, resulting in considerable error when the non-protein-N, choline, NH₂-N, or acid-sol. phosphoric ester is determined. F. O. HOWITT.

Destruction of organic matter. E. KAHANE.—See this vol., 71.

Micro-determination of carbon. II. E. SCHADENDORFF and M. K. ZACHERL.—See this vol., 72.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

FEBRUARY, 1932.

General, Physical, and Inorganic Chemistry.

General expression for intensity of hydrogen lines. L. McLEAN (*Nature*, 1932, 129, 25).

L. S. THEOBALD.

Supposed anomalous terms of [spectrum of] helium. E. MAJORANA (*Nuovo Cim.*, 1931, 8, 78—83; *Chem. Zentr.*, 1931, ii, 195—196).—Two new lines ($1s2p^3P_{012}-2p2p^3P_{012}$ and $1s2s^1S_0-2s2s^1S_0$) are recorded.

A. A. ELDRIDGE.

Second spark spectrum of boron, B III, in the region 5000—2000 Å. B. EDLÉN (*Z. Physik*, 1931, 72, 763—766).—14 new lines in the extreme ultraviolet appeared due to a Li-like system, and from them a term system was deduced for the region 5000—2000 Å.

A. B. D. CASSIE.

Excitation of the arc spectrum of nitrogen. K. R. MORE and O. E. ANDERSON (*Physical Rev.*, 1931, [ii], 38, 1995—1999).—The strong $N\text{ I}$ lines were as intense as the moderately strong A lines in the arc spectrum of N_2 excited in mixtures of A and N_2 . The probable excitation mechanism is discussed.

N. M. BLIGH.

New atmospheric oxygen band at 7710 Å. R. MECKE and W. BAUMANN (*Z. Physik*, 1931, 73, 139—146).—At great depths of atm. the sun's spectrum shows absorption due to a $^3\Sigma-^1\Sigma$ transition of O_2 .

A. B. D. CASSIE.

Spectra of gases appearing in the early stages of the spark. E. MATUYAMA (*J. Opt. Soc. Amer.*, 1931, 21, 792—799).—A study of the broadening of the lines due to gases which appear before the electrode spark lines in discharges in air, O_2 , and H_2 .

N. H. HARTSHORNE.

Neon-helium bands. M. J. DRUYVESTEYN (*Nature*, 1931, 128, 1076—1077).—Two bands, observed near 4000 Å. in the negative glow of Ne-He mixtures, are possibly to be attributed to a compound such as NeHe.

L. S. THEOBALD.

Intensity measurements in the neon column. W. ELENBAAS (*Z. Physik*, 1931, 72, 715—723).—Intensity relations between lines of the principal series were studied for different electric currents, densities of the gas, and cross-sections of the column.

A. B. D. CASSIE.

Continuous and "forbidden" series in the sodium arc spectrum. H. BARTELS (*Z. Physik*, 1931, 73, 203—215).

A. B. D. CASSIE.

D-Line fluorescence of sodium at higher pressures. A. JABLONSKI and P. PRINGSHEIM (*Z. Physik*, 1931, 73, 281—288).—The polarisation of fluorescence D-radiation from Na vapour corresponding

with 230° was unaffected by magnetic fields up to 80 gauss.

A. B. D. CASSIE.

Oscillator density for D-lines. R. LADENBURG and E. THIELE (*Z. Physik*, 1931, 72, 697—699).—The number of dispersing electrons per atom effective for the Na D-lines is 0.35 and 0.70 for the D_1 and D_2 lines, respectively, and the life of the two resonance levels is 1.48×10^{-8} sec.

A. B. D. CASSIE.

Zeeman effect in quadrupole lines of alkalis. E. SEGRE and C. J. BAKKER (*Z. Physik*, 1931, 72, 724—733; cf. A., 1931, 1203).— $^2S-^2D$ lines were investigated for Na and K in a magnetic field; the results agree with Rubinowicz's theory of radiation by quadrupoles (cf. A., 1930, 653).

A. B. D. CASSIE.

Auto-ionisation in the alkaline-earth metals and the inert gases. H. E. WHITE (*Physical Rev.*, 1931, [ii], 38, 2016—2020).—Certain characteristics of the spectra of Ca, Sr, Ba, Kr, and Xe are explained on the process of auto-ionisation suggested by Shentstone (cf. A., 1931, 1204).

N. M. BLIGH.

Band spectrum of AsH. G. E. KIMBALL and J. R. BATES (*Nature*, 1931, 128, 969).—As contained in the negative electrode of a C. arc in an atm. of H_2 at a potential of 110 volts gave two typical hydride bands, origins at 32,380.2 and 31,636.9 cm^{-1} , and a band probably due to As_2 with the head at 31,802.6 cm^{-1} . The electronic transition is probably of the type $^1\Sigma-^1\Sigma$.

L. S. THEOBALD.

Fluorescence of diatomic selenium vapour in the green and yellow regions of the spectrum. J. GENARD (*Bull. Acad. roy. Belg.*, 1931, [v], 17, 1235—1240).—The green and yellow fluorescence spectrum of Se_2 vapour excited by the 4047 and 4359 Å. lines from a high-power Hg arc has been investigated spectroscopically.

J. W. SMITH.

Transmission bands of silver. S. SCHUBIN (*Z. Physik*, 1931, 73, 273—280).—The broad transmission band of Ag near 3200 Å. is consistent with the quantum-mechanical theory of metals.

A. B. D. CASSIE.

Fluorescence of diatomic tellurium vapour excited by mercury lines. J. GENARD (*Bull. Acad. roy. Belg.*, 1931, [v], 17, 1241—1248).—The resonance spectrum of Te_2 vapour excited by the Hg lines 4046.7, 4078, 4359, 5461, and 6235 Å. has been investigated.

J. W. SMITH.

Spark spectra of iodine. L. BLOCH and E. BLOCH (*Ann. Physique*, 1931, [x], 16, 503).—Errors in an earlier paper (A., 1929, 617) are corrected.

Nuclear moment of caesium. W. SCHÜTZ (Naturwiss., 1931, 19, 1007).—An error in the calculation of Barth and Schütz (A., 1931, 1204) is indicated. Corrected vals. for intensity ratio and nuclear moment are 1.41 and $5/2$, respectively.

W. R. ANGUS.

Bands in the spectrum of barium hydride. A. SCHAAFSMA (Nature, 1931, 128, 1042).—Ba in an atm. of H_2 gave band-heads at 6634, 6689, 6850, and 6923 Å. all shaded towards the violet. The calc. moment of inertia indicates that the bands should be ascribed to BaH.

L. S. THEOBALD.

Arc spectrum of gold. J. C. McLENNAN and A. B. McLAY (Proc. Roy. Soc., 1931, A, 134, 35—41).—The terms of Au I and their vals. based on zero val. for the deepest, 6s8, are recorded. Classified wave-lengths and intensities are tabulated.

L. L. BIRCUMSHAW.

Hyperfine structure of spectral lines. II. K. MURAKAWA (Z. Physik, 1931, 73, 366—375).—The hyperfine structure of Hg I was investigated, and is arranged into hyperfine terms showing nuclear moment zero for the even isotopes, $1/2$ for 199, and $3/2$ for 201. Every electron in at. nuclei cannot have $1/2$ units of spin momentum.

A. B. D. CASSIE.

Analysis of the first spark spectrum of mercury. B. VENKATESACHAR and T. S. SUBBARAYA (Z. Physik, 1931, 73, 412—418).—New 2D and 4P terms have accounted for 76 HgI lines.

A. B. D. CASSIE.

Hyperfine structure of 4916 Å. (Hg I). B. VENKATESACHAR and L. SIBAIYA (Naturwiss., 1931, 19, 1041—1042).

W. R. ANGUS.

Structure of the mercury line 5461. E. LAU (Ann. Physik, 1931, [v], 12, 66—68).—With new apparatus the structure of the Hg 5461 line is different from that usually accepted. The structures of the line from a cooled arc and from a discharge tube containing H_2 are compared.

A. J. MEE.

Mercury line spectrum in fluorescence. (LORD) RAYLEIGH (Nature, 1931, 128, 905).—The lines 3650, 3126, and 2967 Å. are still emitted when Hg vapour is excited by the resonance line alone from a Hg arc. Stepwise absorption thus cannot explain the process by which the vapour is raised to the 3^3D_{321} state. The emission of these lines continues in a rapid stream of vapour even when it has passed out of the region directly illuminated. The results are probably connected with the known ionisation of the vapour by the resonance line.

L. S. THEOBALD.

Spark spectrum of mercury. J. C. McLENNAN, A. B. McLAY, and M. F. CRAWFORD (Proc. Roy. Soc., 1931, A, 134, 41—47).—A classified list of wave-lengths of Hg II involving many-electron terms is given.

L. L. BIRCUMSHAW.

Zeeman effect of a forbidden line. E. SEGRÈ and C. J. BAKKER (Nature, 1931, 128, 1076).—An investigation of the Hg line λ 3680 Å.

L. S. THEOBALD.

Hyperfine structure of mercury hydride bands. S. MROZOWSKI (Z. Physik, 1931, 72, 776—784).—

The HgH bands near 4520, 4394, 4219, and 4017 Å. were investigated with crossed Lummer-Gerke plates.

A. B. D. CASSIE.

Hyperfine structure of spectrum lines of lead arc in the visible and ultra-violet regions. W. MOHAMMAD and P. N. SHARMA (Phil. Mag., 1931, [vii], 12, 1106—1110).—Only the 2s level possesses structure; measurements are recorded.

H. J. EMELEUS.

Hyperfine structure of spectral lines. K. MURAKAWA (Z. Physik, 1931, 72, 793—797).—Hyperfine structure due to Pb I, Pb II, Zn I, Mg I, and Sn I suggests nuclear angular momentum zero for Zn, Mg, Sn, and Pb^{208} , and $\frac{1}{2}$ for Pb^{207} .

A. B. D. CASSIE.

Wave-length of the green auroral line determined by the interferometer. L. VEGARD (Nature, 1932, 129, 23).—The wave-length found is 5577.340 (or 5)X, in agreement with Babcock's val. of 5577.350 for the green line which appears in night sky luminescence.

L. S. THEOBALD.

Graphical representation of some band [spectroscopical] results. R. RYDBERG (Z. Physik, 1931, 73, 376—385).

A. B. D. CASSIE.

Nuclear spin and hyperfine structure in band spectra. E. HULTHÉN (Nature, 1932, 129, 56—57).—A discussion.

L. S. THEOBALD.

Different kinds of light excitation in the gaseous discharge. E. LAU and O. REICHENHEIM (Ann. Physik, 1932, [v], 12, 52—65).—As a result of improvements in the method of observing excitation spectra it has become possible to investigate light emissions which arise from causes other than electron collision. Effects due to the dissociation of H_2 into one excited and one unexcited atom were observed. Light emission due to irradiation was studied, and it was found that the concn. of atoms in the excited, but not metastable, state may be as great as that of the metastable atoms.

A. J. MEE.

Spectra of B stars. O. STRUVE (Astrophys. J., 1931, 74, 225—267).—Absorption lines for stars of type O9 to B8 are recorded and the elements present given.

L. S. THEOBALD.

Possible explanation of the difference in wave-lengths of the spectral lines of a given element produced on the sun and on the earth. F. SANFORD (Science, 1931, 74, 412—413).

L. S. THEOBALD.

New mirror spectrometer (monochromator) with single and double dispersion for the region 0.2—4 μ . C. LEISS (Z. Physik, 1931, 72, 822—828).—A spectrometer of the Wadsworth type is described; the mirrors have a particularly high reflecting power, and the Czerny disposition is used.

A. B. D. CASSIE.

Light emission of metallic vapours by excitation in the positive column. H. KREFFT (Physikal. Z., 1931, 32, 948—950).—Certain relationships were found between the light emissions of the alkali metals, connected with their positions in the periodic table. For Cs the recombination spectrum is weakest and it increases with decreasing at. no. The widening of series lines due to the Stark effect is also variable

in the same sense. The results obtained are general for all metal vapours with doublet series.

A. J. MEE.

Emission bands of polar aurora in spectrum of night sky. J. DUFAY (Compt. rend., 1931, 193, 1106—1108).—Eight new bands were observed, as well as 13 previously known. The bands may or may not occur in auroral spectra.

C. A. SILBERRAD.

Intensity of interference of rapid cathode rays, and simple interference apparatus for demonstration purposes. F. KIRCHNER (Physikal. Z., 1931, 32, 969—971).—The different types of electron interference diagrams for thin polycryst. layers and thin single crystals are compared. The angular range for electron reflexion is greater than for X-rays, and for very thin layers is considerably greater than the reflexion angle itself. An apparatus suitable for demonstration is described.

A. J. MEE.

Angular intensity distribution of continuous X-ray spectrum. IV. Stellar opacity coefficient. Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 17, 89—110).—Mathematical.

A. J. MEE.

Absolute values of X-ray wave-lengths and the fundamental atomic constants. M. SIEGBAHN and M. SODERMAN (Nature, 1932, 129, 21—22).—Two methods for fixing the scale of X-ray wave-lengths in cm. are described. Definite vals. will be given when exposures under varied conditions with different gratings have been made.

L. S. THEOBALD.

Structure of soft X-ray lines. W. V. HOUSTON (Physical Rev., 1931, [ii], 38, 1797—1801).—The lines produced by the bombardment of a solid target are broader than those emitted by a vapour, as the upper level is not sharp. The line shapes and widths for Be calc. from the free and bound electron models are compared.

N. M. BLIGH.

Upper atomic-number limits for satellites of the X-ray line $L\beta$. R. D. RICHMYER (Physical Rev. 1931, [ii], 38, 1802—1807).—The X-ray spectral region of the line was investigated photographically for elements of at. no. 50, 51, 52, 53, 56, 58, and 60. The at.-no. ranges of the 5 satellites have, in all but one case, clearly-defined upper limits (approx. at. limit 53). The explanations of previously reported lines beyond these limits are discussed. A new wave-length table is given.

N. M. BLIGH.

Dependence of the K-spectrum of sulphur, excited by X-rays, on chemical linking. A. FAESSLER (Z. Physik, 1931, 72, 734—743).—The $K\alpha$ spectrum of S in compounds was excited by X-rays instead of by electron bombardment, and showed former results to be partly due to heat and electrical effects of the electrons; the α -components are displaced to longer wave-lengths in sulphides, and to shorter wave-lengths in sulphates.

A. B. D. CASSIE.

Determination of atom factors in the region of anomalous dispersion. R. GLOCKER and K. SCHÄFER (Z. Physik, 1931, 73, 289—311).—The atom factor of Fe dust between 0.7 and 2.3 Å. changes, not only in abs. val., but also in angular distribution

as the K-absorption edge is approached. Atom factors were determined for W and Au for wave-lengths longer than the L-edge.

A. B. D. CASSIE.

Field- and photo-effect at outer boundary surfaces. R. SUHRMANN (Physikal. Z., 1931, 32, 929—937).—Experiments with photo-cells with very thin layers, sometimes unimol. layers of alkali metals, are described. An explanation of the selective effect is given, and a large effect of field is noted on surfaces emitting electrons.

A. J. MEE.

Red displacement of photo-ionisation of alkali atoms on adsorption by negative salt surfaces. J. H. DE BOER and M. C. TEVES (Z. Physik, 1931, 73, 192—199).—The drop in energy required for photo-emission by alkali atoms on adsorption by salts of negative surface potential is due to formation of negative alkali ions rather than to any conductivity electron effect.

A. B. D. CASSIE.

Photo-electric and thermionic emission from cobalt. A. B. CARDWELL (Physical Rev., 1931, [ii], 38, 2033—2040).—Results on the variation of the photo-electric sensitivity and long-wave limit with extended outgassing, temp. change, and structural alteration, and the effect of the last-named on the thermionic emission, are reported.

N. M. BLIGH.

Photo-electric properties of tantalum. A. B. CARDWELL (Physical Rev., 1931, [ii], 38, 2041—2048).—Experimental.

N. M. BLIGH.

Determination of the photo-electric threshold for tungsten by Fowler's method. A. H. WARNER (Physical Rev., 1931, [ii], 38, 1871—1875).—Photo-current per unit intensity curves for two different W surfaces plotted by Fowler's method (cf. A., 1931, 1106) are in satisfactory agreement with theory.

N. M. BLIGH.

Emission of secondary electrons from tungsten. A. J. AHEARN (Physical Rev., 1931, [ii], 38, 1858—1870).

N. M. BLIGH.

Initiation of ionisation of inert gases by alkali ions. O. BEECK and C. MOUZON (Ann. Physik, 1931, [v], 11, 858—862).—Ionisation, often very sharp, of inert gases by positive alkali ions begins at very different potentials between 70 and 400 volts.

A. B. D. CASSIE.

Electron temperatures in inert gases. R. SEELIGER and R. HIRCHERT (Ann. Physik, 1931, [v], 11, 817—857).—Langmuir's electron temp. is definite and reproducible in He, Ne, and Ar up to pressures of 10 mm.; it falls rapidly with increasing pressure of the gas, and reaches an approx. steady val. between 5 and 10 mm.; it also falls with increasing c.d., this fall being greater the smaller is the gas pressure. At all pressures and currents the electron temp. is greatest in He and least in Ar.

A. B. D. CASSIE.

Elastic collisions. J. S. TOWNSEND (Proc. Roy. Soc., 1931, A, 134, 352—356).—Polemical. Criticism by Atkinson with reference to the mean loss of energy of an electron in collisions (A., 1928, 809) and statements of Bullard and Massey with reference to the variation of effective cross-section of atoms with electron velocity (A., 1931, 542) are discussed.

L. L. BIRCHMISHAW.

Electron exchange phenomena in the excited atom. R. WHIDDINGTON and J. E. ROBERTS (Nature, 1931, 128, 966).—In the case of He no evidence of a transition corresponding with $1S-2S$ singlet or triplet has been obtained (cf. A., 1931, 1107). L. S. THEOBALD.

Lateral space distribution of X-ray photo-electrons. P. KIRKPATRICK (Physical Rev., 1931, [ii], 38, 1938—1942).—Results from 752 condensation track photographs for photo-electrons ejected from A by partly polarised X-rays of mean wave-length 0.53 Å. are in good agreement with quantum predictions. N. M. BLIGH.

Gas concentration of electron radiation. W. ENDE (Physikal. Z., 1931, 32, 942—945).—Experiments described agree in the main with the explanation given by Johnson (J. Opt. Soc. Amer., 1922, 6, 701) of this phenomenon. A. J. MEE.

Energy loss by medium-velocity electrons in nitrogen and carbon monoxide. E. RUDBERG (Ann. Physik, 1931, [v], 11, 802—816).—Max. in curves of energy loss by electrons of 200—2000 volts when traversing N_2 and CO appear at voltages corresponding with absorption wave-lengths of the optical spectrum; i.e., optical selection rules apply to transitions caused by these electrons. A. B. D. CASSIE.

Electron scattering in helium. S. WERNER (Proc. Roy. Soc., 1931, A, 134, 202—210).—The scattering of 40—300 volts electrons at a fixed angle of 90° has been measured. The experimental scattering is much greater at low velocities than that calc. from Mott's formula (A., 1930, 974), but agreement is found above 100 volts. L. L. BIRCUMSHAW.

Photo-electrons and negative ions. E. M. WELLS (Proc. Roy. Soc., 1931, A, 134, 427—444; cf. A., 1931, 1347).—The view that during the passage of electrons through a gas some of them become attached to mols., giving rise to negative ions, is shown to be untenable. L. L. BIRCUMSHAW.

Negative ions in hydrogen and water vapour. W. W. LOZIER (Physical Rev., 1930, [ii], 36, 1417—1418).—Negative ions have been observed among the positive ions produced in H_2 by electron impact (this vol., 14); their production is confined to a narrow range of electron velocities and is increased by the presence of H_2O vapour. Possible mechanisms of formation are discussed. L. S. THEOBALD.

Mobilities of atmospheric large ions. R. K. BOYLAN (Proc. Roy. Irish Acad., 1931, A, 40, 76—85).—Curves were obtained by two methods for air at Dublin. Saturation was not shown at a voltage corresponding with the mobility of the Langevin ion. Ionisation increased by 28—200% at saturation voltage. The existence of large ions of higher and lower mobilities than that of the Langevin ion is indicated. N. M. BLIGH.

Production of heavy high-speed ions without the use of high voltages. D. H. SLOAN and E. O. LAWRENCE (Physical Rev., 1931, [ii], 38, 2021—2032).—By successive acceleration in a series of metal tubes synchronised with an oscillating electrical potential, 1,260,000 volt singly-charged Hg ions were produced. N. M. BLIGH.

Mobility of positive ions in helium. I. Helium ions. A. M. TYNDALL and C. F. POWELL (Proc. Roy. Soc., 1931, A, 134, 125—136; cf. A., 1930, 1336).—An improved apparatus is described, by means of which the mobility of positive ions of He in pure He has been found to be 21.4 cm./sec./volt/cm. at $20^\circ/760$ mm. The speed of the ions is proportional to E/p , where E is the field in volts/cm. and p the pressure in mm., over a range of E/p from 0.3 to 4.2. L. L. BIRCUMSHAW.

Atoms traversing magnetic fields of varying orientation. P. GUTTINGER (Z. Physik, 1931, 73, 169—184). A. B. D. CASSIE.

Relative abundance of the chemical elements in white dwarf and its electrification. S. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 307—310).—The dissociation equilibrium of the various elements in white dwarfs is discussed. W. R. ANGUS.

At. wt. of fluorine. E. MOLES (Nature, 1931, 128, 966—967).—A crit. discussion of the vals. found by previous investigators. The at. wt. of F, probably, should not exceed 19.000. L. S. THEOBALD.

At. wt. of xenon. R. WHYTLAW-GRAY, H. S. PATTERSON, and W. CAWOOD (Proc. Roy. Soc., 1931, A, 134, 7—19).—Using a sensitive quartz micro-balance, a comparison of the balancing pressures of O. and Xe has been made. The ratio was determined for two densities corresponding with pressures of Xe of about 153 and 80 mm., respectively. The at. wt. is found to be 131.26 ± 0.01 , in good agreement with Aston's mass-spectrograph val. 131.27 ± 0.04 . L. L. BIRCUMSHAW.

Chart of radioactive elements indicating their structure. I. W. D. HACKH (Science, 1931, 74, 490—492).—The structure of the nucleus and the electron shell of the radioactive isotopes is indicated. L. S. THEOBALD.

Resonance in atomic disintegration processes. E. STEUDEL (Naturwiss., 1931, 19, 1044).—Pose's results on the at. disintegration of Al (cf. A., 1931, 279) could not be verified. W. R. ANGUS.

Theory of collisions of α -particles and light nuclei. E. GUTH and T. SEEL (Physikal. Z., 1931, 32, 941—942).—Theoretical. In general there is a greater number of scattering phenomena to be expected on the basis of the quantum mechanics theory than on that of classical theory. A. J. MEE.

Range of the α -particles from uranium II. S. BATESON (Canad. J. Res., 1931, 5, 567—571).—Using a scintillation method the range of the α -particles from U II is 3.29 ± 0.08 cm. at 15° and 760 mm. The experimental procedure and purification of U_3O_8 which was used as source are discussed. The range is in good agreement with the val. of Laurence (A., 1928, 684). The period of U II is shown to be 28,000 years, which is much less than the val. obtained by direct measurement (A., 1931, 891). W. R. ANGUS.

Interaction energy of two α -particles at close distances, determined from the anomalous scattering in helium. H. M. TAYLOR (Proc. Roy. Soc., 1931, A, 134, 103—125).—The distance between

the centres of two α -particles at which their interaction energy ceases to be that given by the Coulomb law is 3.5×10^{-13} cm. approx. L. L. BIRCUMSHAW.

Anomalous scattering of α -particles by hydrogen and helium. H. M. TAYLOR (Nature, 1932, 129, 56).—Calc. and observed vals. for scattering in H₂ and He are in good agreement.

L. S. THEOBALD.

Scattering of α -particles by light elements. W. RIEZLER (Proc. Roy. Soc., 1931, A, 134, 154—170).—The scattering of α -particles through large angles by Be, B, C, and Al shows large deviations from that predicted on the assumption of Coulomb forces between the particles, and the deviation increases rapidly with the velocity of the α -particle. The results obtained are predicted by the wave mechanics. An approx. val. is found for the size of the scattering nuclei.

L. L. BIRCUMSHAW.

γ -Spectrum of thorium-C' and the Gamow theory of α fine structure. L. MEITNER and K. PHILIPP (Naturwiss., 1931, 19, 1007).—The two γ -spectrum lines, energies 40.8 and 279 kv., have been detected. The results contradict the Gamow theory of α fine structure.

W. R. ANGUS.

Monochromatic de Broglie molecular ray waves. I. ESTERMANN, R. FRISCH, and O. STERN (Z. Physik, 1931, 73, 348—365).—De Broglie waves due to mol. rays were rendered monochromatic by two methods: reflexion at a LiF crystal surface, and by selection of rays of one velocity by a rotating toothed wheel. The wave-length was in each case measured by reflexion at a second LiF crystal surface.

A. B. D. CASSIE.

Appearance of spatial quantisation. T. E. PHIPPS and O. STERN (Z. Physik, 1931, 73, 185—191).

A. B. D. CASSIE.

Triatomic or monatomic hydrogen. G. R. SCHULTZE (J. Physical Chem., 1931, 35, 3186—3188; cf. A., 1931, 805).—The characteristics of activated H do not necessarily point to the presence of H₃; another explanation of the activity is possible (cf. *ibid.*, 440).

C. T. SNELL (c).

Experimental proof of the spin of the photon. (SIR) C. V. RAMAN and S. BHAGAVANTAM (Indian J. Physics, 1931, 6, 353—366).—The depolarisation observed with light scattered by gases or liquids is more closely in accord with that anticipated on the spinning photon theory than on the classical theory.

J. W. SMITH.

Collision problems involving large interactions. O. K. RICE (Physical Rev., 1931, [ii], 38, 1943—1960).—Mathematical.

N. M. BLIGH.

Evaluation of the matrix components for helium. L. P. SMITH (Physical Rev., 1931, [ii], 38, 1961—1968).—Mathematical.

N. M. BLIGH.

Structure of the nucleus and its total moment of momentum. S. D. BRYDEN, jun. (Physical Rev., 1931, [ii], 38, 1989—1994).—Theoretical.

N. M. BLIGH.

Mass of the proton. (SIR) A. EDDINGTON (Proc. Roy. Soc., 1931, A, 134, 524—532).—Mathematical. By a development of the geometrical theory the mass

of the proton as well as that of the electron can be calc. from the recession of the spiral nebulae.

L. L. BIRCUMSHAW.

Ultra-violet absorption of aqueous solutions of chlorides. R. TREHIN (Compt. rend., 1931, 193, 1089—1091; cf. A., 1931, 19).—The absorption spectra of NaCl, KCl, LiCl, BaCl₂, and SrCl₂ between λ 2816 and 1990 Å. are similar, but different from that of HCl save in very dil. solution. In more conc. solutions the metallic cations in association with H₂O and Cl⁻ modify the absorption differently from H⁺. Sufficiently conc. solutions of LiCl show a max. absorption.

C. A. SILBERRAD.

Optical investigation of perylene and its derivatives. III. Ultra-violet absorption spectrum. H. CONRAD-BILLROTH (Z. physikal. Chem., 1931, B, 15, 1—17; cf. A., 1929, 487).—The ultra-violet absorption spectra of perylene and 11 derivatives consist of two groups of bands, one of which is to be ascribed to the benzenoid linking and the other to the linking between two rings. The optical data have thus made it possible to derive electronic formulæ for the three quinones examined. From the spacing of the perylene bands nuclear frequencies of 1330, 920, and 300 cm.⁻¹ are deduced, and by means of these vals. it has been possible to obtain an equation giving the max. in the spectrum of the hydrocarbon, and, with different coeffs., the max. in the spectra of its derivatives.

R. CUTHILL.

Normal vibrations of carbonate and nitrate ions. A. C. MENZIES (Proc. Roy. Soc., 1931, A, 134, 265—277).—Dennison's method (A., 1926, 222) has been used to calculate the frequencies of the normal modes of vibration of the CO₃ and NO₃ ions. A characteristic equation is obtained differing from Nielsen's. The consts. in the formulæ have been calc. from infra-red and Raman effect data for calcite and NaNO₃. The magnitude of the binding forces between the central and outer atoms suggests that they are appropriate to the second excited state of CO and NO, respectively.

L. L. BIRCUMSHAW.

Vibrations of pentatomic tetrahedral molecules. H. C. UREY and C. A. BRADLEY, jun. (Physical Rev., 1931, [ii], 38, 1969—1978).—Andrews' suggestion (cf. A., 1930, 1345) for the choice of restoring forces along and perpendicular to the chemical linkings is tested. The agreement of calc. and observed vals. of vibrational frequencies with this choice of forces is unsatisfactory. A correction for repulsive forces between corner atoms secures better agreement.

N. M. BLIGH.

Emission spectrum of carbon dioxide. H. D. SMYTH (Physical Rev., 1931, [ii], 38, 2000—2015).—Complete data for the range 6500—1400 Å. and a partial analysis are reported.

N. M. BLIGH.

Faint branches in the OH bands. G. M. ALMY and G. D. RAHRER (Physical Rev., 1931, [ii], 38, 1816—1817; cf. A., 1930, 1074).—Weak branches detected photographically are identified by comparison of observed and calc. wave nos.

N. M. BLIGH.

Far infra-red. J. STRONG (Physical Rev., 1931, [ii], 38, 1818—1826).—Using a new instrument (cf.

A., 1931, 996) for the range 20—150 μ , data are reported for reflectivities of rough surfaces, galena, β -magnesia, zincite, stibnite, corundum, sphalerite, molybdenite, and cuprite, transmissivities of KBr, KI, a layer of KCl evaporated on a lacquer film, a thin film of amorphous quartz, liquid CCl_4 , and powdered Al and Cu, and emission of liquid and solid NaCl near the m. p. N. M. BLIGH.

Infra-red spectrum and the molecular configuration of N_2O . E. K. PLYLER and E. F. BARKER (Physical Rev., 1931, [ii], 38, 1827—1836).—Data for the vibration spectrum and rotational analysis are given. The non-symmetrical linear mol. form $\text{N}:\text{N}:\text{O}$ is indicated. The single Raman line 1281 cm^{-1} is observed. N. M. BLIGH.

Infra-red absorption bands of hydrogen cyanide in gas and liquid. F. S. BRACKETT and U. LIDDEL (Smithsonian Misc. Coll., 1931, 85, No. 5, 1—8).—Of the 15 bands observed for the liquid between 1 and 2 μ , 14 are combinations or harmonics of the fundamentals proposed by Badger and Binder (A., 1931, 667). With the saturated vapour at 22.5° the bands $2\nu_1$, $3\nu_1$, and $2\nu_1 + \nu_2$ were observed as doublets, no Q branch being present. Badger and Binder's val. of moment of inertia, and their conclusions regarding arrangement of atoms etc., are confirmed. CHEMICAL ABSTRACTS.

Infra-red radiation of the terrestrial atmosphere. J. DEVAUX (Compt. rend., 1931, 193, 1207—1209).—Using a specially designed spectrograph with rock-salt prisms and a radiometer, radiation of the zenith sky has been compared with that of a black body at known temp. A wide band at 8—14 μ and a narrow one at 5 μ are attributed to H_2O and perhaps CO_2 ; a small secondary max. at 10 μ is probably due to O_3 at a moderate temp.

C. A. SILBERRAD.

Laminary reflexion gratings for infra-red investigation. C. H. CARTWRIGHT (J. Opt. Soc. Amer., 1931, 21, 785—791).—The intensity distributions of laminary reflexion gratings are given, and several methods of making them and a new method of making an echellette grating are described.

N. H. HARTSHORNE.

Molecular scattering of light. (SIR) C. V. RAMAN (Indian J. Physics, 1931, 6, 263—273).—Nobel lecture. J. W. SMITH.

Circular polarisation of Raman lines. A. KASTLER (Compt. rend., 1931, 193, 1075—1078).—The fact that the Raman lines produced by circularly polarised light, when viewed longitudinally, are inversely polarised, and when viewed transversely depolarised (cf. A., 1931, 668, 997), implies theoretically that Q lines should behave in reverse, P and R lines in similar fashion. This is in accordance with the selection rules for the Raman lines, which require that $\Delta=0$ (Q lines) or ± 2 (P and R lines), the privileged direction being that of the polarisation of the incident beam (cf. this vol., 107).

C. A. SILBERRAD.

Circular polarisation of Raman lines. A. CORRON (Compt. rend., 1931, 193, 1078—1079).—The effect on the Raman lines produced in PhNO_2

by the indigo line of Hg, of a magnetic field of 48,300 gauss normal to both incident and diffused beams, is to increase the intensity of the lines 1112, 1342, and 1587 cm^{-1} when vibrations are parallel to the field, and of 1112 and 1587 when normal thereto. The diffused line (4916 and 5461) are unaffected.

C. A. SILBERRAD.

Relative intensities of Stokes and anti-Stokes lines in the Raman spectrum. S. C. SIKKAR (Indian J. Physics, 1931, 6, 295—303).—The ratio of the intensities of the Raman lines of frequencies $\nu + \nu_{mn}$ and $\nu - \nu_{mn}$ in the case of the two CCl_4 lines $\nu_{m1} = 1368 \times 10^{10}$ and 945×10^{10} respectively is represented more accurately by the expression $\{(\nu + \nu_{mn})/(\nu - \nu_{mn})\}^4 \cdot e^{-h\nu_{mn}/kT}$ as given by Placzek's theory than by the Boltzmann factor alone.

J. W. SMITH.

Raman effect in gases. I. Experimental results. II. Theoretical considerations. S. BHAGAVANTAM (Indian J. Physics, 1931, 6, 319—330, 331—344).—The Raman effect in H_2 , O_2 , N_2 , CO_2 , N_2O , C_2H_2 , H_2S , and SO_2 has been studied at pressures up to 50 atm. The frequencies are in good agreement with those reported by previous authors. Lines representing vibrational transitions are usually well polarised, whereas those from rotational transitions are imperfectly polarised. Above a certain pressure the fine structure disappears. This crit. pressure corresponds with the state where the frequency of mol. rotation is the one quantum state.

II. The theory of Raman scattering, both rotational and vibrational types, is discussed, and comparison is made between theory and observation for the intensity and polarisation of light scattered by diat. mols.

J. W. SMITH.

New Raman bands of water. E. SEGRE (Atti R. Accad. Lincei, 1931, [vi], 13, 929—931).—In the Raman spectrum of H_2O excited by the 2537 Å. Hg line a band with a max. at 140 cm^{-1} has been found. It is attributed to oscillations in polymerised H_2O mols.

O. J. WALKER.

Raman band of water. G. BOLLA (Nature, 1932, 129, 60).—The reported peculiarity of the Raman band of H_2O (A., 1931, 1353) may be produced or essentially modified by interference in the spectrograph used.

L. S. THEOBALD.

Raman spectra of some inorganic chlorides. S. VENKATESWARAN (Indian J. Physics, 1931, 6, 275—285).—The Raman spectra of SO_2Cl_2 , S_2Cl_2 , PCl_3 , POCl_3 , and BCl_3 have been studied, and the structures of these mols. are discussed. The frequency 1290 cm^{-1} is attributed to $\text{P}:\text{O}$.

J. W. SMITH.

Raman spectrum of ammonia in solution at various concentrations. V. RICCA (Atti R. Accad. Lincei, 1931, [vi], 14, 197—200).—Aq. solutions of NH_3 salts do not show any Raman lines which can be attributed to NH_4^+ . Aq. solutions of NH_3 give a Raman spectrum identical with that of liquid NH_3 . So far no lines characteristic of NH_4OH have been found.

O. J. WALKER.

Circular polarisation of Raman lines. W. HANLE (Ann. Physik, 1931, [v], 11, 885—904).—Polarisation of Raman radiation due to a circularly

polarised primary was investigated for CCl_4 , CHCl_3 , C_6H_6 , PhMe , MeOH , EtOH , and $\text{CH}_3\text{Pr}^s\text{CH}_2\text{OH}$; corresponding vibrations in different substances show the same circular polarisation. A. B. D. CASSIE.

Raman effect and chemical constitution: the cyclopropane nucleus. R. LESPIEAU, M. BOURGUEL, and R. WAKEMANN (Compt. rend., 1931, 193, 1087—1089).—*cyclo*Propane has Raman lines at 1188, 3011, and 3028 cm^{-1} and bands with centres at 867, 1439, and 3076, disagreeing with Yates' (cf. A., 1931, 545) but in fair agreement with Bhagavantam's (cf. A., 1930, 1237) calculations. Comparison with the Raman spectra of its Me, Me₂, Me Et, Me Pr, Ph, and Ph₂ derivatives shows that the C-C linking in the C₃ nucleus is characterised by a strong line near 1188 (1208, 1214, 1209 and 1221, 1207 and 1221, 1221, 1227, respectively), increasing in frequency with increased mol. wt., and is a doublet when there are two different substituents. The C-H linking is characterised by a line, or pair of lines, between 2999 and 3028, and a band between 3061 and 3076, resembling the ethylenic spectrum. C. A. SILBERRAD.

Raman effect and nature of allenic linkings. M. BOURGUEL and L. PIAUX (Compt. rend., 1931, 193, 1333—1335).—The Raman spectrum of allene gives no indication of lines or bands characteristic of either double or triple linkings (cf. A., 1930, 978; this vol., 7); it consists of strong lines at 1074 and 3000, and indistinct bands at 1440 and 3073. Propyl-, butyl-, and $\alpha\alpha$ -dimethyl-allenes give similar results, the changes accompanying substitution being similar to those in the *cyclo*propanes (cf. preceding abstract). It is concluded that the linkings in allene cannot be ethylenic." C. A. SILBERRAD.

Raman spectrum of formic acid. S. PARTHASARATHY (Indian J. Physics, 1931, 6, 287—293).—A crit. study has been made of the Raman spectrum of HCO_2H . The characteristic frequencies and the effects on these of heating, addition of H_2O , and polarisation are described. J. W. SMITH.

Raman spectra of some organic crystals and solutions. P. KRISHNAMURTI (Indian J. Physics, 1931, 6, 309—317).—The Raman spectra of NH_4OAc , $\text{Cd}(\text{OAc})_2$, $\text{Zn}(\text{OAc})_2$, $\text{Pb}(\text{OAc})_2$, $\text{H}_2\text{C}_2\text{O}_4$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, C_2Cl_6 , $\text{CO}(\text{NH}_2)_2$, and hexamethylenetetramine have been studied. The changes in the frequencies have been examined with $\text{Pb}(\text{OAc})_2$, $\text{CO}(\text{NH}_2)_2$, and hexamethylenetetramine when dissolved in H_2O . The last-named shows considerable changes in the C-H frequencies, suggesting hydrate formation, but shows little change in CCl_4 or Et_2O solution. The C=O frequency does not appear in the spectra of the acetates and $\text{CO}(\text{NH}_2)_2$. The possibility of the latter existing in an enol form is discussed. J. W. SMITH.

Raman effect of benzene and toluene under high dispersion and resolving power. L. E. HOWLETT (Canad. J. Res., 1931, 5, 572—579).—The Raman spectra of C_6H_6 and PhMe under high dispersion are compared with previous results. With both liquids a no. of new lines have been found; these arise from separation into components of previously observed lines or are entirely new.

W. R. ANGUS.

Raman effect in aldehydes. S. S. LU (Sci. Rep. Tsing Hua Univ., 1931, 1, 25—32).—Data for PhCHO , heptaldehyde, and furfuraldehyde are reported and discussed. N. M. BLIGH.

Raman effect in certain organic compounds. M. E. HIGH (Physical Rev., 1931, [ii], 38, 1837—1844).—Comparisons are made for *n*- and *iso*-forms, and the effect of shifting substituents from the *o*- to the *m*- and *p*-positions is investigated. Data are reported for Pr_2O , Pr^s_2O , amyl ether, propyl, butyl, amyl, and methyl propionate, *o*-, *m*-, and *p*-chlorotoluene, tolyl Me ether, chloronitrobenzene, and nitrotoluene. Some comparisons with infra-red data are made. N. M. BLIGH.

Raman effect and the carbon-halogen linking. W. D. HARKINS and H. E. BOWERS (Physical Rev., 1931, [iii], 38, 1845—1857).—Raman data are reported for allyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec*-, and *tert*-butyl, and *n*- and *iso*-amyl bromides. For halides, the effect of the length of the mol. and branching and their relation to the fundamental frequencies, force consts., and characteristic frequencies associated with the C-halogen linking are examined.

N. M. BLIGH.

Cathode luminescence of diamond. M. V. JOHN (Indian J. Physics, 1931, 6, 305—308).—The luminescence produced when three small diamonds were bombarded by cathode rays has been examined spectroscopically. One yielded a continuous spectrum extending throughout the visible region with a marked band at 4157 Å., in the same position as the fluorescence band observed by Bhagavantam in the Raman spectra (A., 1930, 1345). Another diamond showed slight absorption at this wave-length, whilst a third gave only a strong continuous spectrum.

J. W. SMITH.

Close connexion between extinction of fluorescence and retardation of photochemical reactions. K. WEBER (Z. physikal. Chem., 1931, B, 15, 18—44).—The effectiveness of anions in reducing the fluorescence of aq. Na naphthionate decreases in the order NO_3^- , I^- , Br^- , Cl^- , SO_4^{2-} , and thus diminishes as the hydration increases. Cu^{++} , Ni^{++} , and Ag^+ also have a considerable effect, but the alkali and alkaline-earth ions are practically indifferent. The rate at which Lauth's violet is bleached in aq.-MeOH solution in presence of diethyl- β -allylthiocarbamide as acceptor rises rapidly towards a limiting val. as the concn. of the latter is increased, and at the same time the temp. coeff. falls. Quinol, pyrogallol, and PhOH retard the bleaching and also reduce the fluorescence of Na naphthionate, the relative efficiencies being similar in each case. It is therefore concluded that the part played by these substances in both processes depends on their deactivating power on collision. At high concns. electrolytes either accelerate the bleaching somewhat or retard it only slightly, but with small concns. of some salts there is a pronounced retardation. It is therefore inferred that all electrolytes have an accelerating influence, but that with those salts which also have a retarding action this predominates at low concns. The activating effect is ascribed to the electrolyte increasing the activity of the reactants by increasing the amount of radiation

absorbed, a view which is supported by observations on the effect of electrolytes on the absorption spectrum of Lauth's violet. R. CUTHILL.

Fluorescence and free neutral radicals. W. A. WATERS (*Nature*, 1931, 128, 905—906).—Evidence supporting the view that fluorescence is associated with the re-formation of stable valency linkings from previously activated mols. is advanced.

L. S. THEOBALD.

Luminescence of zinc compounds. A. KUTZNIGG (*Z. anorg. Chem.*, 1931, 201, 323—328).—Fluorescence colours of ZnO prepared in various ways, and of some basic Zn salts, are described.

F. L. USHER.

Emission of praseodymium in alkaline-earth phosphors. I. H. EVERT (*Ann. Physik*, 1932, [v], 12, 107—136).—Phosphors containing sulphides and fluorides of Ca, Sr, and Ba, CaO, SrO, Al_2O_3 , and sulphates of Ca and Sr, respectively, together with Pr were prepared, and the spectra of the emitted lights mapped. The results agree with the theory already developed.

A. J. MEE.

Visible phosphorescence of fluorspar, excited by Schumann rays. E. LAU and O. REICHENHEIM (*Ann. Physik*, 1932, [v], 12, 69—70).—The phosphorescence is found only at the surface of the fluorspar, corresponding with the small penetration of the rays. The emission spectrum is composed of three pairs of bands.

A. J. MEE.

High efficiencies of emission from oxide-coated filaments. B. J. THOMSON (*Physical Rev.*, 1930, [ii], 36, 1415—1417).—High efficiencies of electron emission for filaments of Ni, coated with $BaCO_3$ and $SrCO_3$, are reported.

L. S. THEOBALD.

Thermionic emission and electrical conductivity of oxide cathodes. A. L. REIMANN and L. R. G. TRELOAR (*Phil. Mag.*, 1931, [vii], 12, 1073—1088).—The thermionic current from the core metal is carried through the oxide coating mainly by Ba, Sr, or Ca ions, and re-emitted thermionically.

H. J. EMELEUS.

Electrodeless conductivity measurements. W. BRAUNBECK (*Z. Physik*, 1931, 73, 312—334).—Induced eddy currents may be used to determine the conductivity of liquid metals and alloys. Examples given are Cu and Hg at 400°.

A. B. D. CASSIE.

Variation of the electrical conductivity of molten bismuth with content of bismuth chloride. W. BRAUNBECK (*Z. Physik*, 1931, 73, 335—347).—The influence of dissolved Cl on the electrical conductivity of Bi is small; 7½ at.-% of Cl did not reduce the conductivity to ½ its original value.

A. B. D. CASSIE.

Conductivity of compressed metallic powders. C. KANTOROWICZ (*Ann. Physik*, 1931, [v], 12, 1—51).—The resistance of metal powders of different particle size was found under pressures up to 4200 atm. The resistance is different from that of the compact metal. The powder changes under pressure, probably solidifying, and this accounts for a relatively complex relationship between the resistance and the conditions of the experiment. The resistance is not const., but varies with time. For increasing

pressure the resistance is given by $1/R = c\sqrt{P} + C$, where c and C are consts. depending on the previous treatment of the powder. For the same previous treatment, the pressure-resistance curves are reproducible. They are irreversible. Ohm's law is not satisfied. The temp. coeff. of resistance is negative for $P=0$, but for higher pressures is negative for rising temp. and positive for falling temp. Coherer action is sometimes shown at high pressures.

A. J. MEE.

Dielectric constant of commercial nitrogen at high pressures. J. W. BROXON (*Physical Rev.*, 1931, [ii], 38, 2049—2050; cf. this vol., 3).—The variation of $(K-1)$ with the pressure, for N_2 (99% pure), up to 167 atm., was investigated.

N. M. BLIGH.

Dipole moments of molecules with mutually independent (ideally decoupled) dipole groups. L. EBERT and K. HOJENDAHL (*Z. physikal. Chem.*, 1931, B, 15, 74—78).—It is deduced theoretically and verified from experimental data that the total dipole moment of a mol. which has two similar independent polar groups each of moment μ , say at the ends of a very long aliphatic chain, is $\sqrt{2}\mu$.

R. CUTHILL.

Change in dielectric constant of thin layers of ZnS-Cu phosphors on illumination with different wave-lengths of light. E. BREUNIG (*Ann. Physik*, 1931, [v], 11, 863—884).—The spectral distribution of increase in dielectric const. of layers $56-80 \times 10^{-4}$ cm. thick of ZnS-Cu phosphors follows closely the distribution of wave-lengths exciting phosphorescence.

A. B. D. CASSIE.

Electric moment and molecular structure. VI. **Variation of electric moment with temperature.** C. P. SMYTH, R. W. DORRTE, and E. B. WILSON (*J. Amer. Chem. Soc.*, 1931, 53, 4242—4260; cf. A., 1931, 1112).—The calculation of the energy of a system of dipoles rotating about a common axis, either in terms of the classical or the wave mechanics, leads to the conclusion that the moment may vary with temp. The electric moments of CH_2Cl-CH_2Cl and CH_2Cl-CH_2Br vary markedly with temp., whilst that of $EtOAc$ shows no significant variation, probably because of the high mutual potential energy of the dipoles. The moment of Et succinate increases from 0° to 180°, probably because increasing vibrational energy enables more and more mols. to open out to an extended structure, the moment at 180° being identical with those of the very long-chain dicarboxylic acid esters. The moment of a mol. containing two or more dipoles, the axes of which may alter their positions relative to one another, may be affected by both temp. and environment (solvent).

H. F. JOHNSTONE (c).

Dielectric constants and molecular polarisations of binary liquid mixtures. W. GRAF-FUNDER and E. HEYMANN (*Z. Physik*, 1931, 72, 744—762).—Using an improved resonance method the dielectric consts. of a series of binary liquid mixtures have been measured and the corresponding mol. polarisations calc. Mixtures of two polar liquids show no anomalies other than those shown where only one of the liquids is polar. The results are discussed with reference to so-called association.

J. W. SMITH.

Physics of the nitrobenzene "Kerr" cell. III. Distribution of a strong electrical alternating field in the nitrobenzene Kerr cell. IV. Accuracy of Kerr's law for nitrobenzene in strong alternating electric fields. F. HEHLGANS (Physikal. Z., 1931, 32, 951—957, 971—974; cf. A., 1931, 1220).—III. Experiments with alternating fields show that the field distribution in the PhNO_2 Kerr cell is always homogeneous. With impure PhNO_2 , however, the field distribution was not homogeneous.

IV. For pure PhNO_2 in strong alternating electric fields Kerr's law holds. A. J. MEE.

Theory of Kerr effect in wave mechanics. T. NEUGEBAUER (Z. Physik, 1931, 73, 386—411).

Refraction and dispersion of gaseous hydrocarbons. S. FRIBERG (Z. Physik, 1931, 73, 216—222).—Refraction and dispersion of wave-lengths between 5800 and 2300 Å. were measured for C_3H_8 and C_3H_6 , and the results are fitted to Cauchy dispersion formulæ: dispersion of these gases is very susceptible to impurities. A. B. D. CASSIE.

Refractive index of fused sodium nitrate. E. VAN AUBEL (Bull. Acad. roy. Belg., 1931, [v], 17, 1158—1160).—Assuming a mean val. of 11.54 for the mol. refraction of liquid NaNO_3 to hold up to the crit. temp. and using the val. 0.625 calc. from viscosity data for the crit. density, the refractive index of NaNO_3 at its crit. point is 1.127, in good agreement with the vals. found for other substances at the crit. point (A., 1912, ii, 1013). J. W. SMITH.

Nature of valency linkings and circular dichroism. J. P. MATHIEU (Compt. rend., 1931, 193, 1079—1081).—A solution of acid Cr^{III} tartrate prepared by dissolving not more than 1/3 g.-atom of Cr [as $\text{Cr}(\text{OH})_3$] in 1 mol. of tartaric acid, when first prepared, is bluish-violet, contains the Cr as a coloured Cr^{III} cation, and exhibits normal rotatory dispersion, with no circular dichroism. On keeping, the colour slowly changes to deep violet, the Cr passing into a coloured complex anion no longer precipitable by NH_3 , the dispersion increases and becomes anomalous, and circular dichroism appears, probably proportionally to the amount of the complex anion formed. In the first case the chromophore is united by a heteropolar, in the second by a homopolar, valency (cf. A., 1925, ii, 1119). C. A. SILBERRAD.

Rotatory magnetic polarisation of liquids and liquid mixtures. J. VERHAEGHE (Bull. Acad. roy. Belg., 1931, [v], 17, 1221—1234).—The rotatory magnetic power of quinoline and of mixtures of quinoline with C_6H_6 and CCl_4 has been measured. The results are discussed. J. W. SMITH.

Optically active properties of inorganic compounds. W. KUHN and A. SZABO (Z. physikal. Chem., 1931, B, 15, 59—73).—In aq. solution K Cr tartrate has a strong absorption band at 3700 and a weak band at 5960 Å., but the circular dichroism and anomalous rotation are confined to the latter. The anisotropy factor is not, however, const. over the whole band, which indicates that in respect of the electron transitions giving rise to it the band is far from being homogeneous. The connexion between the dichroism and the rotation may be expressed

satisfactorily by the equation deduced previously (A., 1930, 980). A survey of the available data shows that in their optically active properties inorg. compounds closely resemble org. compounds. The rotation of an inorg. compound is normally contributed in the main by a comparatively weak absorption band which represents only a small fraction of the total absorptive power of the compound. An instance of optical superposition among Co compounds is reported. R. CUTHILL.

Theory of homopolar valency in polyatomic mols. M. BORN (Angew. Chem., 1932, 45, 6—8).—A theoretical discussion in terms of electron spins.

E. S. HEDGES.
Valency variation and at. structure. M. GOMBERG (Science, 1931, 74, 553—557).—An address.

L. S. THEORALD.
State of molten salts. P. WALDEN (Z. physikal. Chem., 1931, 157, 389—421).—It is found empirically that for the molten tetra-alkylammonium picrates at $140^\circ \lambda c = \text{const.}$, where λ is the equiv. conductivity and c the temp. coeff. of the conductivity. A similar relation is valid for the molten alkali chlorides, bromides, and iodides at 800° , and the val. of $\lambda\sqrt{M}$ at the m. p., where M is the mol. wt., is also const. for these compounds. At the m. p., $\lambda\eta\sqrt{M}$, where η is the viscosity, has the val. 10.5 for molten KNO_3 , NaNO_3 , NaCl , KCl , and NaOH , and the picrates in aq. and non-aq. solution at infinite dilution give the same figure. It is therefore deduced that the molten salts are completely dissociated. Utilising the relations $l_{\text{pi}}\eta = \text{const.}$ for the conductivity l_{pi} of the picrate ion, and $l_{\text{cat}}\eta\sqrt{M_{\text{cat}}} = \text{const.}$ for the conductivities, l_{cat} , of the tetra-alkylammonium ions, it has been possible to calculate the equiv. conductivities at the m. p. of the picrates, and a similar calculation has been made for alkali salts. The results indicate that the molten salts are practically completely ionised. With the picrates of the mono-, di-, and tri-alkylammonium bases, however, the degree of dissociation at the m. p. varies from 0.65 to 0.95.

R. CUTHILL.
Calculation of molecular lattice dimensions from resonance forces. E. CREMER and M. POLANYI (Z. physikal. Chem., 1931, B, 14, 435—442).—Assuming that the energy of a mol. lattice is equal to the difference between an attraction potential, which varies with the intermol. distance in accordance with London's theory (A., 1931, 149), and a repulsion potential, which is due to quantum mechanical resonance and can be calc. from optical data, it has been possible to calculate the intermol. distance in the lattices of H_2 , HCl , HBr , and HI . R. CUTHILL.

Relation between b. p. and chemical constitution. II. K. BILLIG (Svensk Kem. Tidskr., 1931, 43, 281—293).—The manner in which the association factor K_f (cf. this vol., 13) diminishes as the degree of association rises is illustrated by reference to $(\text{H}_2\text{O})_x$, and the relevant vals. of K_f are employed to calculate the percentage of associated mols. in the fatty acids. It is shown that with these compounds association takes place through principal valencies. For derivatives of the fatty acids conditions are more complicated; with open-chain esters and acid anhydrides

the auxiliary valencies are the principal means of association, whereas with ring compounds such as lactones the principal valency type of association preponderates. The latter type is found also for H_2O , and it is shown that the 4 valency linkings of O must be directed towards the corners of a tetrahedron, as in the case of the C atom; the mol. of $(\text{H}_2\text{O})_6$ thus resembles that of C_6H_6 . Various other types of 6-membered ring are discussed, including those of NH_3 , N_2H_4 , and the heterocyclic ring formed by N_2H_4 , H_2O , and those of the O compounds of N and the org. NO_2 -compounds. This type of ring formation is very general, although in the case of inorg. compounds the rings are not stable and break down when the substance vaporises.

II. F. GILLBE.

An aspect of co-ordination. J. KENNER (Nature, 1931, 128, 1000—1001).—Theoretical.

L. S. THEOBALD.

Specific heat of ferromagnetics and Ewing's model of the magnetic atom. J. R. ASHWORTH (Nature, 1931, 128, 1003).—A discussion.

L. S. THEOBALD.

Ferromagnetic moment and the periodic system. C. SADRON (Compt. rend., 1931, 193, 1070—1073; cf. A., 1931, 791).—The magnetic moments (in Weiss magnetons) of the following elements in solid solution in Ni or Co are: Cu 2.09, Au 2.3, Si 17.8, Sn 18.0, V 23.9, Sb 24.4. They support the conclusion, previously arrived at, that elements in the same column of the periodic table have the same moment. Ru is an exception, the moment being 11, that of pure Fe, and not that of Fe in Ni (14). Assuming the foregoing to hold, the moments of elements in the line of Fe plotted against at. no. show an ascending (Cu—V) and a descending (V—Ni) branch with intervals of approx. 5 and 4 magnetons, respectively, save between Si and Ti.

C. A. SILBERRAD.

Magnetic behaviour of cobalt atoms. H. VATTER (Z. Physik, 1931, 73, 260—272).—A method for obtaining at. rays of metals of high m.p. is described. The greatest moment of Co is 5.8 Bohr magnetons.

A. B. D. CASSIE.

Magnetic moment of quadrivalent cobalt. (Mlle.) A. SERRES (Compt. rend., 1931, 193, 1327—1328).—The magnetic susceptibility of MgCoO_3 (cf. A., 1896, ii, 647) has been determined from -182.7° to 549.4° . $1/\chi$ is related linearly to temp. above 233° , the Curie point is -164.5° abs., the Curie const. 4.261, and the magnetic moment of Co^{IV} 29 experimental magnetons.

C. A. SILBERRAD.

Magnetic properties of iron above the Curie point. L. NÉEL (Compt. rend., 1931, 193, 1325—1326).—By determining the ferromagnetic (0_f) and paramagnetic (0_p) Curie points and the Curie const. (c) for a series of Fe—Sn (87.21—92.23% Fe) and Fe—Si (89.72—97.04% Fe) alloys and extrapolating the vals. for β -Fe (which when unalloyed changes to γ -Fe before the required temp. is attained) are deduced as 0_f 772°, 0_p 815°, c 0.02256. C. A. SILBERRAD.

Paramagnetic susceptibility of chromic chloride and its hexahydrates. J. W. SHIH (Sci. Rep. Tsing Hua Univ., 1931, 1, 83—91).—Using $\text{Mn}_2\text{P}_2\text{O}_7$ as the standard substance for comparison

the vals. $\times 10^6$ obtained per g. were: for the anhyd. salt 44.5, for $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ 24.0, and for $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ 12.6. N. M. BLIGH.

Theory of magnetisation curves of isotropic ferromagnetics in medium and strong fields. R. GANS (Physikal. Z., 1932, 33, 15—17).

Variations of atomic moment in paramagnetic substances. Magnetic states and different varieties of the same ion. G. FOEX (J. Phys. Radium, 1931, [vii], 2, 353—375).—The bent graphs obtained by plotting the inverse of the coeff. of magnetisation against the temp., and the different magnetic moments shown by different samples of the same substance within the same temp. range, are discussed on the basis of the data for many paramagnetic substances. N. H. HARTSHORNE.

Diamagnetism of free electrons in metals. P. Y. CHOU (Sci. Rep. Tsing Hua Univ., 1931, 1, 1—7).—Mathematical. N. M. BLIGH.

Magnetic properties of gold-iron alloys. J. W. SHIH (Physical Rev., 1931, [ii], 38, 2051—2055).—The change in susceptibility with temp. and composition was investigated for alloys containing 0.07—10 wt.-% Fe. Alloys containing 0.1—5% Fe are paramagnetic. N. M. BLIGH.

Classification of paramagnetic atoms, molecules, and ions according to field and temperature. E. C. WIERSMA (Wis. en Natuurkund. Tijdschr., 1930, 5; Chem. Zentr., 1931, i, 2442—2443).—Three groups, viz., (i) weakly paramagnetic metals such as Na, K, Pt, and Pd with susceptibility practically independent of temp., (ii) paramagnetic gases, O_2 and NO , and (iii) salts such as NiSO_4 , CrCl_3 , FeCl_3 , and those of Co, are distinguished. The extent to which the Curie-Weiss law holds for each group is discussed. L. S. THEOBALD.

Diamagnetism of liquid mixtures. J. FARQUHARSON (Nature, 1932, 129, 25).—The susceptibility-concn. curve for CHCl_3 - COMe_2 mixtures shows a max. at equimol. proportions and two minima, but the departure from additivity is 3—4%. The two ends of the curve show a slight rise in diamagnetism. The susceptibilities found are -0.60×10^{-6} for COMe_2 , and -0.498×10^{-6} for CHCl_3 . L. S. THEOBALD.

Parachor measurements applied to the study of the constitution of polysulphides, polyselenides, and mixed chains of sulphur and selenium. A. BARONI (Atti R. Accad. Lincei, 1931, [vi], 14, 28—32; cf. A., 1929, 1270).—Parachor measurements have been made of various Et_2 sulphides, selenides, and sulphoselenides. These indicate that compounds containing 3 atoms of S or Se have a straight chain. This becomes branched in the tetrasulphide and converted into a ring of 3 S atoms in the two isomeric pentasulphides. O. J. WALKER.

Capillarity. XVI. Capillary rise of liquids between parallel plates. K. SCHULTZE (Kolloid-Z., 1931, 57, 277—285).—The capillary rise of H_2O between parallel glass plates is independent of the width of the plates (in accordance with the usual formula) when this exceeds 2 mm.; when the width of the plates is between 2.0 and 0.4 mm. the capillary

rise decreases as the width of the plates is reduced, and the distance apart is kept const. When the plates are of unequal width, that of the narrower plate determines the rise, but the rise is greatest when two identical plates are used. The effect of increasing the width of the plates increases as the distance between the plates is decreased.

E. S. HEDGES.

Densities and partial molal volumes of ammonia for the amines of calcium and barium chlorides. L. J. GILLESPIE and H. T. GERRY (J. Amer. Chem. Soc., 1931, 53, 3962—3968; cf. A., 1921, ii, 116; 1927, 92).—Determinations of d^{25} have been made with the aid of new methods which do not necessitate the isolation of the pure ammine and are suitable for use with compounds having such high decomp. pressures that the ordinary methods are inapplicable.

W. C. FERNELIUS (c).

Aitken condensation nuclei. A. R. HOGG (Nature, 1931, 128, 908).

L. S. THEOBALD.

Two forms of molecular hydrogen. A. CAMPETTI (Nuovo Cim., 1931, 8, xvii—xxvii; Chem. Zentr., 1931, ii, 190).—A resume. A. A. ELDRIDGE.

Diffuse scattering of X-rays from sylvine at low temperature. G. E. M. JAUNCEY and G. G. HARVEY (Physical Rev., 1931, [ii], 38, 1925—1931).—Intensities of wave-length 0.43 Å. scattered in the angle range 25—90° at 90° and 300° abs. are compared, and the relation thereto of temp. effect and the structure factor is investigated.

N. M. BLIGH.

Intensity of total scattering of X-rays by monoatomic gases. Y. H. WOO (Sci. Rep. Tsing Hua Univ., 1931, 1, 55—67; cf. A., 1930, 1334; 1931, 665).—Theoretical.

N. M. BLIGH.

Absorption of soft X-rays in gases. R. G. SPENCER (Physical Rev., 1931, [ii], 38, 1932—1937).—Absorption coeffs. of air, A, and O₂ in the range 1.5—7 Å. and in the immediate neighbourhood of the K absorption limit are in agreement with the absorption law.

N. M. BLIGH.

Use of ionisation determination methods with X-rays. W. STOCKMEYER (Ann. Physik, 1932, [v], 12, 71—106).—Ionisation is proportional to absorbed energy. The proportionality factors for EtBr and SO₂ are determined, these being frequently used in ionisation chambers because they absorb X-rays more strongly than air. For EtI₃ the absorption is determined for different wave-lengths, as there is a distinct change in the factor for wave-lengths shorter than the K-limit of Br.

A. J. MEE.

Dispersion of X-rays in calcite. L. A. PARDEE (Physical Rev., 1931, [ii], 38, 1808—1815).—The K α_1 line from a Mo target was used; (1— δ) was $(2.001 \pm 0.009) \times 10^{-6}$. The intensities of radiation reflected from calcite mirrors in the neighbourhood of the crit. angle were in fair agreement with theory.

N. M. BLIGH.

Growth of crystals. F. STÖBER (Chem. Erde, 1931, 6, 453—467).—A discussion of certain anomalies in the growth of crystals for which explanations are offered (cf. A., 1931, 1028, 1030).

L. J. SPENCER.

Crystallisation of lead nitrate. Effect of foreign substances in the mother-liquor. P.

GAUBERT (Bull. Soc. franç. Min., 1930, 53, 157—171; Chem. Zentr., 1931, i, 2433).—Crystals of Pb(NO₃)₂ grow more quickly in the presence of methylene-blue, but without a change of form. The coloured crystals show clear striations on the cubic faces, whilst a cubic-octahedral combination from pure solution shows in the coloured solution a quicker growth at the octahedral faces. Sr(NO₃)₂ crystals are coated with Pb(NO₃)₂ from a coloured solution of the latter and show its characteristics. Ba(NO₃)₂ grows in Pb(NO₃)₂ solution, but is coloured with difficulty. When methylene-blue is suspended in the solution the Pb(NO₃)₂ crystallises in platelets especially at higher temp., but at lower temp., cubes can appear. With rosolic acid, elongated octahedra formed on certain cubic faces make the crystals appear to be orthorhombic.

L. S. THEOBALD.

Change of the distance between adjacent atoms in certain elements and alloys which results when the cubic face-centred lattice changes to the cubic body-centred or hexagonal lattice. H. PERLITZ (Acta Comm. Univ. Tartuensis, 1931, 72 pp.).—Calculations have been made from published data on various metals, binary and ternary alloys, and steels. The calc. change is in general due exclusively to change of the co-ordination no. and type. It ranges from —1.3% to —3.3% (mean 2.25%) for transition from the face-centred to the body-centred cubic lattice, and from —1.1% to +5.1% for transition from the densest cubic to the densest hexagonal lattice; for the second case it tends to zero as the axial ratio of the hexagonal lattice approaches 1.633.

H. F. GILLBE.

A two-dimensional space lattice? R. C. MENZIES (Nature, 1931, 128, 907).—When 10% KI solution is added to a saturated, aq. solution of dimethyl-thallium iodide or when a warm aq. solution is cooled, part of the Tl compound separates on the surface in a regular pattern; each crystal is equidistant from 6 others. The effect is transient.

L. S. THEOBALD.

A two-dimensional space lattice? W. BAKER (Nature, 1931, 128, 1078).—An explanation of the unusual crystallisation (cf. preceding abstract) is advanced, and similar cases are recorded.

L. S. THEOBALD.

Specific surface properties of molecular fields. Structure of active charcoals and the inversion of surface effects and heats of activation. II. B. V. ILJIN and J. P. SEMANOV (J. Gen. Chem. Russ., 1931, 1, 567—568).—The presence of 1% of graphite added to active C can be detected by X-ray spectrum methods; this amount of graphite suffices to cover only 20% of the total surface with a unimol. layer, showing that the inversion of Traube's series exhibited by certain charcoals not giving the graphite lines cannot be due to graphitisation of their surface.

R. TRUSZKOWSKI.

Structure of ferromagnetic ferric oxide. J. THEWLIS (Phil. Mag., 1931, [vii], 12, 1089—1106).—Ferromagnetic Fe₂O₃ is cubic; unit cube 8.4 Å.; 12 mols. Fe₂O₃ in unit cube; space-group O⁶ (or O⁷) or T⁴. The structure is very similar to that of Fe₃O₄ (cubic; unit cube 8.4 Å.; 8 mols. Fe₃O₄ in unit cell). Fe and O atoms occupy the same positions as in

Fe_3O_4 . The possible arrangements of the extra 4 O atoms are discussed. H. J. EMELEUS.

Magnetic properties and crystalline structure of different varieties of anhydrous cobalt sulphate. R. HOCART and (Mlle.) A. SERRES (Compt. rend., 1931, 193, 1180—1182).—X-Ray examination of Chatillon's two varieties of CoSO_4 , of magnetic moment 25 and 26 magnetons (cf. A., 1928, 454), and of the variety obtained by Klobb (cf. A., 1892, 941), also of moment 26 magnetons, shows that the structures of the two latter are identical—orthorhombic, a 4.6, b 6.7, c 8.4 Å., 4 mols. in unit cell—whilst that of the first is identical as regards shape and dimensions of the unit cell, but differs in the arrangement of the atoms therein. C. A. SILBERRAD.

Structure of compounds of sulphur with iodides. I. Compounds of sulphur with tri-iodides. E. HERTEL (Z. physikal. Chem., 1931, B, 15, 51—57).—Both $\text{CHI}_3\cdot 3\text{S}_8$ and $\text{AsI}_3\cdot 3\text{S}_8$ crystallise in the trigonal system with the probable space-group C_{3v} , and the dimensions of the unit cell, which in each case contains 1 mol., are a 14.1, b 24.4, c 4.44, and a 14.2, b 24.6, c 4.48 Å., respectively. The S_8 mols. in these compounds are probably three-dimensional systems, with the min. symmetry C_2 . The f.p. diagrams show that AsI_3 and CHI_3 are not miscible in the solid state, whereas $\text{AsI}_3\cdot 3\text{S}_8$ and $\text{CHI}_3\cdot 3\text{S}_8$ are miscible in all proportions.

R. CUTHILL.

Crystal structure of potassium tantalum and potassium niobium heptafluorides and of potassium titanium hexafluoride. F. ZAMBONINI (Bull. Soc. franç. Min., 1930, 53, 443—468; Chem. Zentr., 1931, i, 2451).— K_2TaF_7 is monoclinic with $a:b:c=0.6718:1:0.9198$, β $90^\circ 15'$, and d 4.056; K_2NbF_7 , monoclinic, has $a:b:c=0.6711:1:0.9209$, β $89^\circ 48'$, and d 3.21. Anhyd. K_2TiF_6 , trigonal, d^{15} 3.012, shows weak double refraction; it is isomorphous with $(\text{NH}_4)_2\text{TiF}_6$ and $(\text{NH}_4)_2\text{SnF}_6$. L. S. THEOBALD.

Bismuth thiocarbamide compounds. C. GOTTFRIED and H. STEINMETZ (Veroff. Kaiser Wilhelm-Inst. Silikatforsch., 1929, 2; Chem. Zentr., 1931, i, 2435).—The compound, $\text{BiCl}_3\cdot 3\text{CS}(\text{NH}_2)_2$, has a 13.29, c 7.02, r 14.81 Å.; 1 mol. per unit rhombohedron; space-group C_3^2 ; $\text{BiCo}(\text{CN})_6\cdot 6\text{CS}(\text{NH}_2)_2$ has a 13.92, c 12.48, r 9.13 Å.; 1 mol. per unit rhombohedron; space-group probably D_{3d}^5 . $[\text{Bi}\cdot 6\text{CS}(\text{NH}_2)_2][\text{X}(\text{CN})_6]$, where X is Cr and Fe, have been obtained. Microcryst. ppts. are formed in Bi salt- $\text{CS}(\text{NH}_2)_2$ solutions with $\text{K}_3\text{Co}(\text{NO}_2)_6$, $\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3$, and $\text{K}_3\text{Cr}(\text{CNS})_6$; the oxalate compound contains 6 mols. of $\text{CS}(\text{NH}_2)_2$ to 1 atom. of Bi. L. S. THEOBALD.

Crystal lattice of calcium metaborate. W. H. ZACHARIASEN (Proc. Nat. Acad. Sci., 1931, 17, 617—619).— CaB_2O_4 is orthorhombic with 4 mols. per unit cell; a 6.19, b 11.60, c 4.28 Å., space-group $Pnca$ (V_4).

N. H. HARTSHORNE.

Spinel. IV. Manganese and cadmium sulphochromites. L. PASSERINI and M. BACCAREDDA (Atti R. Accad. Lincei, 1931, [vi], 14, 33—37; cf. A., 1931, 289).—These two compounds crystallise in the cubic system with a lattice of the spinel type. MnCr_2S_4 , a 10.045 ± 0.005 Å., v 1013.56×10^{-24} c.c.,

$d_{\text{calc.}}$ 3.736, $d_{\text{obs.}}$ 3.44; CdCr_2S_4 , a 10.190 ± 0.005 , v 1058.09×10^{-24} c.c., $d_{\text{calc.}}$ 4.295. O. J. WALKER.

Sulpho-salts with spinel structure. G. NATTA and L. PASSERINI (Atti R. Accad. Lincei, 1931, [vi], 14, 38—43; cf. preceding abstract).—The spinel type structure of linnæite is confirmed; a 9.41 ± 0.01 Å. (cf. A., 1927, 502). ZnCr_2S_4 also belongs to the spinel type; a 9.92 ± 0.02 , v 976.10×10^{-24} c.c., $d_{\text{calc.}}$ 4.05.

O. J. WALKER.

Lattice dimensions of spinels. G. L. CLARK, A. ALLY, and A. E. BADGER (Amer. J. Sci., 1931, [v], 22, 539—546).—Results are tabulated. C. W. GIBBY.

Relationship between structures of argentite and acantite. J. GARRIDO (Anal. Fis. Quim., 1931, 29, 505—513).—Published data indicate that acantite possesses a pseudocubic structure, whilst argentite has a multiple lattice of dimensions similar to those of the acantite lattice; the structure of synthetic Ag_2S is similar. The structural relationships and stability conditions are discussed. H. F. GILLBE.

Crystal structure of argentite and acantite. J. PALACIOS and R. SILVA (Anal. Fis. Quim., 1931, 29, 514—515).—A criticism of Garrido's conclusions (cf. preceding abstract). H. F. GILLBE.

Structure of the phenacite-dioptase group. Phenacite, Be_2SiO_4 . C. GOTTFRIED (Jahrb. Min. Beil.-Bd., 1927, A, 55, 393—400; Chem. Zentr., 1931, i, 2452).—Rotation diagrams about [001] and [211] give for Be_2SiO_4 , a 12.49, c 8.26 Å., 18 mols. in the hexagonal unit cell; space-group C_6^2 . Willemite, a 14.14, c 9.58 Å., troostite, a 14.21, c 9.62 Å., and dioptase, a 14.66, c 7.83 Å., have the same space-group and no. of mols. per unit cell.

L. S. THEOBALD.

Crystal structure of marcasite. M. J. BUEGER (Amer. Min., 1931, 16, 361—395).—The unit cell has a 3.37, b 4.44, c 5.39 Å.; space-group V_1^2 . Marcasite appears to be composed of Fe and S in the at. state with almost identical radii (1.12 Å.).

CHEMICAL ABSTRACTS.

Crystal structure of rubidium azide. W. BÜSEM, P. ROSBAUD, and P. GÜNTHER (Z. physikal. Chem., 1931, B, 15, 58).—The structure advocated by Pauling (A., 1930, 983) is accepted. R. CUTHILL.

Structure of the azides. E. BERGMANN and W. SCHÜTZ (Nature, 1931, 128, 1077—1078).—Sutton's conclusions (A., 1931, 1359) are criticised; an open-chain structure for the azides is preferred. The dipole moments of Ph, *p*-chlorophenyl, and *p*-bromophenyl azides are 1.55, 0.47, and 0.64×10^{-18} e.s.u., respectively. L. S. THEOBALD.

Crystal structure of an organic molecular compound of the type AB_2 . E. HERTEL and K. SCHNEIDER (Z. physikal. Chem., 1931, B, 15, 79—83).—The crystals of the compound of stilbene with 2 mols. of *s*-trinitrobenzene belong to the triclinic system and the unit cell has a 12.7, b 15.4, c 7.7 Å., and contains 2 mols. R. CUTHILL.

Hysteresis effects in magnetostriction. A. SCHULZE (Ann. Physik, 1931, [v], 11, 937—948).

Hall effect and superconductivity. I. KIKOIN and B. LASAREV (Nature, 1932, 129, 57—58).—

Superconductors show a relatively small val. of the Hall coeff. L. S. THEOBALD.

New method of investigating the modes of vibration of quartz crystals. J. A. STRONG (Nature, 1932, 129, 59). L. S. THEOBALD.

Allotropic modification of solid barium. E. RINCK (Compt. rend., 1931, 193, 1328—1330).—Pure Ba is acted on by CO_2 , and must be distilled in A. The twice-distilled metal has m. p. $710 \pm 2^\circ$, d_4^{25} 3.74. The cooling and resistance-temp. curves show discontinuities at 375° , the α variety being stable below, the β above, that temp. (cf. A., 1931, 416). C. A. SILBERRAD.

Allotropism of phosphorus. V. N. IPATIEV, A. A. VVEDENSKI, and A. V. FROST (J. Gen. Chem. Russ., 1931, 1, 632—640).—The sp. heat and inflammation point of red P increase with rise of temp. at which it was prepared, from 2.17 and 330° at 315° to 2.34 and 450° at 589° . The sp. heat of red P is unaffected by varying the pressure at which it was prepared from 1 to 220 atm. Red P is probably violet P adsorbed on white P. R. TRUSZKOWSKI.

Superconductivity at high frequencies. J. C. McLENNAN, A. C. BURTON, A. PRIT, and J. O. WILHELM (Nature, 1931, 128, 1004).—Pb and Sn become superconducting with currents of frequencies of the order 10^7 per sec. The transition temp. are lowered as frequency is increased. L. S. THEOBALD.

Thermodynamic properties of dichlorodifluoromethane, a new refrigerant. IV. Specific heat of liquid and vapour and latent heat of vaporisation. R. M. BUFFINGTON and J. FLEISCHER. V. Correlation, checks, and derived quantities. R. M. BUFFINGTON and W. K. GILKEY (Ind. Eng. Chem., 1930, 23, 1290—1292, 1292—1294; cf. A., 1931, 675).—IV. Measurements of the sp. heat of CCl_2F_2 at atm. pressure in a flow calorimeter at 0° , 25.8° , and 49.9° indicate that it follows the equation $C_p = 17.0 + 0.0279t$ g.-cal. per mol. The heat capacity of the liquid measured by the method of mixtures at 17° is 30.3 g.-cal. per mol., and by using an electric heating method is 25.4 at -43° . The latent heat of vaporisation as determined by an electrical heating method is 4880 g.-cal. per mol. at -29.8° (the b. p.), 4100 at 23° , and 3960 at 28° . Using Kundt's method the ratio C_p/C_v for the vapour at 25° and atm. pressure is found to be 1.139.

V. Data previously recorded are summarised and cross-checked with one another. J. W. SMITH.

Explosion method for the determination of specific heats of gases at high temperatures. B. LEWIS (J. Amer. Chem. Soc., 1931, 53, 4227—4228).—Sp. heat determinations were made with mixtures of H_2 and O_2 , the velocity of the detonation wave being made the same in all mixtures by addition of suitable amounts of A or He, or mixtures of the two. The effect on the sp. heats of variations in the type, size, and material of the diaphragm pressure indicator and the explosion chamber is also investigated. C. J. WEST (c).

Nature of liquids. L. G. CARPENTER (Nature, 1932, 129, 60).—It is shown that the sp. heats of the

elements near the m. p. support the previously expressed view (A., 1931, 1360; this vol., 14) that liquids, especially near the m. p., resemble solids more nearly than gases. L. S. THEOBALD.

Determination of the internal latent heats of vaporisation of liquids. N. DE KOLOSOVSKI and I. S. MESHENIN (Bull. Soc. chim., 1931, [iv], 49, 1461—1465, and J. Gen. Chem. Russ., 1931, 1, 616—619).—A known wt. of liquid is allowed to evaporate from a continuously-evacuated vessel contained in an adiabatic calorimeter. From the internal latent heat thus determined the total latent heat is calc. for various temp. for Bu°OH , CHCl_3 , CCl_4 , C_6H_6 , PhMe , PhEt , and $\text{C}_6\text{H}_5\text{N}$. C. W. DAVIES.

M. p. of butyl ether. R. C. ARCHIBALD (J. Amer. Chem. Soc., 1931, 53, 4452).—The m. p. is $177.8 \pm 0.2^\circ$ abs. C. J. WEST (c).

Rational unit in thermal conduction. P. VERNOTTE (J. Phys. Radium, 1931, [vii], 2, 376—380).—A discussion. The name "fourier" for the unit of thermal conduction is preferred, the heat being measured in joules. N. H. HARTSHORNE.

Thermal conductivity of inert gases. M. CURIE and A. LEPAPE (J. Phys. Radium, 1931, [ii], 2, 392—397).—A more detailed account of work already noted (this vol., 13).

Thermal conductivities of certain approximately pure metals and alloys at high temperatures. L. C. BAILEY (Proc. Roy. Soc., 1931, A, 134, 57—76).—The thermal conductivities of a number of metals and alloys have been determined by the guard-tube method. The conductivity of Al reaches a max. at about 225° and then decreases to 550° ; Ag reaches a min. at about 400° and then increases to 575° . The val. for Zn decreases gradually and continuously from -170° to 370° , whilst Cd shows an abrupt fall and rise near 50° , after which the normal steady decrease occurs. The conductivity of brass increases linearly with rise of temp. up to 125° , after which it tends to become const. at 0.335 up to 450° . With platinum, the val. increases linearly with rise of temp. Support is obtained for the view that the conductivity of a metal increases as the degree of purity is increased.

L. L. BIRCUMSHAW.

Thermal conductivities of the saturated hydrocarbons in the gaseous state. W. B. MANN and B. G. DICKINS (Proc. Roy. Soc., 1931, A, 134, 77—96).—The thermal conductivities and temp. coeffs. of CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , $n\text{-C}_5\text{H}_{12}$, and $n\text{-C}_6\text{H}_{14}$ have been determined by the hot-wire method. A hyperbolic curve is obtained by plotting the thermal conductivity at 0° against the mol. wt., the relation between the two being given by $(K_0 - 0.00002227) \times (M - 5.53) = 0.0005241$. Plotting the temp. coeff. against the mol. wt. gives a curve which passes through a max. L. L. BIRCUMSHAW.

Density and deviation from Avogadro's law of nitrous oxide. At. wt. of nitrogen. T. BATUECAS (Anal. Fis. Quim., 1931, 29, 538—551, and J. Chim. phys., 1931, 28, 572—586).—

N_2O , prepared by 10 different methods, had d 1.9804 ± 0.0001 g. per litre. At 0.667 and 0.333 atm. pressure the densities were 1.9746 and 1.9694, respectively; the factor $1+\lambda$ is therefore 1.0085, a val. which differs by more than 0.1% from previous determinations. The compressibility of N_2O is 112×10^{-6} and the calc. at. wt. of N is 14.007. (Cf. A., 1931, 1222.) H. F. GILLBE.

Vapour pressure, surface tension, and density of osmium tetroxide. E. OGAWA (Bull. Chem. Soc. Japan, 1931, 6, 302—317).—The v. p. of OsO_4 over the range $15-130^\circ$ has been redetermined by means of a glass spring manometer. From these data, the m. p. ($40.6-40.7^\circ$), b. p. (131.2°), heats of sublimation (11,640 g.-cal.), vaporisation, and fusion (1540 g.-cal.), Trouton's const. (21.5), parachor (157.7), and crit. temp. (405°) are calc. OsO_4 is a normal liquid above 75° , slight association occurring at lower temp. Krauss' statement (A., 1925, ii, 894) that solid OsO_4 exists in two forms was not confirmed.

D. R. DUNCAN.

Determination of the coefficient of cubical expansion of solid benzoic acid by means of a gas-filled dilatometer. E. R. SMITH (Bur. Stand. J. Res., 1931, 7, 903—905).—The coeff. of cubical expansion of $BzOH$ between 15° and 30° , determined by the method described, is 0.00052 per degree.

E. S. HEDGES.

Isotherms of hydrogen, carbon monoxide, and their mixtures. D. T. A. TOWNEND and L. A. BHATT (Proc. Roy. Soc., 1931, A, 134, 502—512; cf. A., 1929, 1227).—The isotherms of H_2 , CO, and mixtures of the two in the mol. proportion 2:1, 1:1, and 1:2 have been determined at 0° and 25° over a pressure range extended up to 600 atm. Each isotherm is expressed in the form $pv_A = a + bp + cp^2 + dp^3$, the vals. of the consts. being tabulated. The observed deviations from the "additive vol." and "additive pressure" laws are discussed. Between pressures of about 300 and 470 atm. the mixtures are less compressible than either of the constituent gases.

L. L. BIRCUMSHAW.

Relation between viscosity and the constitution of hydrocarbons of high mol. wt. G. HUGEL (Chim. et Ind., 1931, 26, 1282—1288).—The viscosity of cyclic hydrocarbons is greater than that of paraffins of equal mol. wt. The introduction of side-chains to acyclic hydrocarbons has little or no influence on the viscosity; the introduction of Me into cyclic hydrocarbons has a sp. effect, although not always in the same direction. Non-saturation has scarcely any effect on the viscosity of acyclic hydrocarbons, but the viscosity of unsaturated cyclic hydrocarbons is increased by saturation. In any series the max. viscosity appears to be attained by the saturated cyclic hydrocarbon.

E. S. HEDGES.

Theory of the viscosity of liquids. E. L. LEDERER (Kolloid-Beih., 1931, 34, 270—338).—From thermodynamic considerations a formula for the dependence of the viscosity of a pure liquid on temp. has been deduced, and, by reference to the data for more than 160 liquids, is shown to represent their behaviour with considerable accuracy. The following deductions were also made: the crit. kinematic

viscosity is practically the same for all liquids; the heat of association is an accurate measure of mol. association and its variation with temp.; the Trouton-Pictet rule is valid for the association of liquids which are not associated in the vapour phase; the internal pressure of liquids and solids can be calc.; there is at least a qual. connexion between viscosity, constitution, mol. cohesion, and dipole moment. A formula connecting pressure and viscosity has also been obtained, and agrees well with the data for a number of liquids, even including H_2O . The theoretical basis of Arrhenius' empirical formula for the viscosity of "ideal mixtures" and the quant. deviations from this formula by "real mixtures" are given. The heat of mixing can be calc. if no other change of internal energy, such as hydration energy, is involved. It is probable that the theory can also be applied to solutions of electrolytes.

M. S. BURR.

General equations of energy and entropy of gases. T. C. HUANG (Sci. Rep. Nat. Tsing Hua Univ., 1931, 1, 93—102).—A more detailed account of work already noted (A., 1931, 793).

Viscosity of gases at high pressures. Viscosity of nitrogen to 1000 atm. A. MICHELS and R. O. GIBSON (Proc. Roy. Soc., 1931, A, 134, 288—307).—Details are given of a transpiration method by means of which results are obtained for the viscosity of N_2 at 25° , 50° , and 75° up to 1000 atm.

L. L. BIRCUMSHAW.

Aluminium-manganese system of alloys. A. J. BRADLEY and P. JONES (Phil. Mag., 1931, [vii], 12, 1137—1152).—X-Ray powder photographs show the existence of $Al-Mn$, Al_3Mn , a range of solid solutions with 50—60% Mn, and solid solutions of Al in α - and β -Mn. No indication of Mn_3Al was found. The solution of Al in β -Mn lowers the α - β transition point so much that the β -lattice becomes stable at room temp.

H. J. EMELEUS.

Alloys of zinc and manganese. N. PARRAVANO and V. CAGLIOTI (Atti R. Accad. Lincei, 1931, [vi], 14, 166—169).—X-Ray spectra for alloys containing up to 33.06% Mn show the existence of γ -, ϵ -, and η -phases analogous with those of brass. The hexagonal ϵ -phase is stable between 33% and 24% Mn at room temp., and between 24% and 12.5% Mn at higher temp. The γ -phase exists between 22.26% and 8.09% Mn and has a body-centred cubic lattice with 52 atoms in the unit cell. The η -phase consists of solid solutions of about 1% Mn in Zn, but is unstable.

O. J. WALKER.

X-Ray study of alloys of silver with bismuth, antimony, and arsenic. II. S. J. BRODERICK and W. F. EHRET (J. Physical Chem., 1931, 35, 3322—3329; cf. A., 1931, 1223).—X-Ray examination of the system Ag-As substantially confirms Heike and Leroux's thermal diagram (A., 1916, ii, 248). Whereas Ag is practically insol. in As, Ag dissolves about 5% of As, the lattice parameter increasing from 4.076 to 4.080 Å. At higher temp. there is formed a β -phase with about 7.5% As, and having the hexagonal close-packed structure. The axial ratio is 1.633 and the side of the unit cell 2.891 and the

height 4.722 Å. The crystal structures met with in the Ag-As, Ag-Sb, Ag-Bi, and related systems are discussed. I. J. PATTON (c).

Complex systems with iron. IV. System chromium-carbon (and iron-chromium-carbon). E. FRIEMANN and F. SAUERWALD (Z. anorg. Chem., 1931, 203, 64-74).—Equilibria in the systems Cr-C and Fe-Cr-C have been investigated. The existence of Cr_7C_3 is very probable, although the formula Cr_6C_2 is a possible alternative. The solubility of C in solid Cr is less than 0.03%. The m. p. of Cr is lowered greatly by the presence of N. The formation of nitride begins at 1000°. E. S. HEDGES.

Internal friction of molten metals and alloys. IV. Internal friction of silver and silver-copper alloys. W. RADECKER and F. SAUERWALD (Z. anorg. Chem., 1931, 203, 156-158).—The internal friction of molten Ag-Cu alloys is related linearly to the composition. E. S. HEDGES.

Solid solutions between alkali halides. A. BARONI (Atti R. Accad. Lincei, 1931, [vi], 14, 215-217).—X-Ray examination by the Debye method shows that KCl and KI are not miscible in the solid state. X-Ray data for the systems KCl-KBr and KBr-KI show that true equilibrium is reached if the mixtures are obtained from solutions. O. J. WALKER.

Viscosity of mixtures of tin tetrachloride with aromatic hydrocarbons. I, II. F. DE CARLI (Atti R. Accad. Lincei, 1931, [vi], 14, 120-124, 200-205).—I. The viscosities of 0-100% mixtures of PhMe with SnCl_4 have been measured at 20° and 30°. PhMe differs from C_6H_6 in its tendency to form association complexes with SnCl_4 ; no definite compound is indicated, however.

II. The viscosities of mixtures of *m*-xylene and of ψ -cumene with SnCl_4 have been determined at 20° and 30°. The data suggest that C_6H_6 homologues associate with SnCl_4 at room temp. The association is almost destroyed, however, at 30°. O. J. WALKER.

Partial pressure isotherms. I. W. D. BANCROFT (J. Physical Chem., 1931, 35, 3160-3185).—Association, dissociation, and heat effects resulting from dilution and solvation increase the apparent mol. wt. of one component and lower that of the other except when combination is in an equimol. ratio. A tendency to form two liquid layers increases the partial pressures and apparent mol. wts. of both components, but in all the systems studied the increase is negligible in very dil. solutions and important only in conc. solutions. MeOH, EtOH, and PrOH in H_2O and in C_6H_6 , and EtOH in PhMe show abnormally high mol. wts. for both components. In C_6H_6 the order of apparent polymerisation is $\text{MeOH} > \text{EtOH} > \text{PrOH}$, whereas in H_2O it is the reverse. The true polymerisation coeff. of liquid H_2O , MeOH, and EtOH is less than 2. In the system H_2O -glycerol the deviations of the H_2O isotherm from the ideal curve are small and negative. Addition of anhyd. CaCl_2 or NaI separates MeOH- C_6H_6 solutions into two liquid layers, but does not separate EtOH- C_6H_6 solutions. In the system COMe_2 -MeOH the tendency

to form two liquid layers is not the chief cause of anomalous behaviour. R. H. CHERRY (c).

System water-ethyl alcohol-acetic acid-ethyl acetate. MION (Compt. rend., 1931, 193, 1330-1333).—The limiting compositions of ternary mixtures of (1) H_2O , EtOH, and EtOAc, and (2) H_2O , AcOH, and EtOAc are recorded; data for the quaternary mixtures are also given.

C. A. SILBERRAD.
Solubility of oxygen in iron. H. ESSER (Z. anorg. Chem., 1931, 202, 73-76).—Microscopical examination of specimens of Fe containing O_2 , after quenching from temp. between 950° and 1200°, shows that the solubility of O_2 in solid Fe is very small, <0.02%. This result agrees with previous calculations (A., 1931, 1128). The O_2 dissolved in the molten metal separates probably as FeO, which also is very sparingly sol. in Fe. H. F. GILLBE.

Solubility of lithium chloride in water. J. A. N. FRIEND and A. T. W. COLLEY (J.C.S., 1931, 3148-3149).—Data are given from 0° to 95°. The transition point $\text{LiCl} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{LiCl} \cdot \text{H}_2\text{O}$ occurs at about 18°. D. R. DUNCAN.

Solubility of iodine in aqueous salt solutions. A. VON KISS and A. URMANCZY (Z. anorg. Chem., 1931, 202, 172-190).—The solubility of I in various K, Na, Li, Mg, Ca, and Ba salt solutions has been determined. In absence of KI the solubility in nitrate and sulphate solutions diminishes with increase of the salt concn., whilst in chloride solutions it increases to a max. at about 0.3-0.4N and then diminishes. In presence of KI (0.025N) the solubility falls continuously with increasing salt concn. The difficulty of calculating the thermodynamic equilibrium consts. of the complex iodide ions is discussed. The vals. of the equilibrium const., expressed in terms of activities, the activity of I', and the ratio of the activities of I_3' and I', have been calc. H. F. GILLBE.

Solubility of calcium hydroxide in aqueous salt solutions. J. JOHNSTON and C. GROVE (J. Amer. Chem. Soc., 1931, 53, 3976-3991).—The solubility at 25° in H_2O is 19.76 millimol. per 1000 g. In solutions of LiCl, NaCl, KCl, CsCl, SrCl_2 , BaCl_2 , NaBr, KBr, NaI, NaNO_3 , NaNO_2 , NaClO_3 , NaClO_4 , and NaOAc the solubility passes through a max. with increasing salt concn., except for BaCl_2 , and then decreases to a val. which is sometimes less than that for pure H_2O . L. P. HALL (c).

Germanium. VIII. Germanium dioxide. R. SCHWARZ and E. HUF (Z. anorg. Chem., 1931, 203, 188-218).—Data for the solubility of GeO_2 in H_2O are discordant. New determinations show that the solubility has no significance unless the ratio $\text{GeO}_2/\text{H}_2\text{O}$ is given. GeO_2 is partly molecularly dissolved and partly colloiddally dispersed; the ion HGeO_3' is responsible for peptisation, stabilisation, and dissolution. The crystalloidal portion is supersaturated and gradually diminishes with time. The solubility of GeO_2 is less the higher is the temp. of ignition. Two cryst. forms and one amorphous form have been recognised. The particles of GeO_2 hydrosol are negatively charged and not very stable, tending to

go into true solution (the reverse behaviour of SiO_2 sol). When left undisturbed, the sols separate into periodically-spaced layers having different particle-densities. The dissociation const. of H_2GeO_3 from conductivity measurements is 0.5×10^{-7} . Dialysis of NaOH-GeO_2 mixtures with a cellophane membrane suggests the existence of the ion Ge-O^- .

E. S. HEDGES.

Solubility relations of the isomeric dihydroxybenzenes. W. H. WALKER, A. R. COLLETT, and C. L. LAZZELL (*J. Physical Chem.*, 1931, 35, 3259—3271).—The solubilities in COMe_2 , Et_2O , EtOH , and H_2O are considerable, but in CHCl_3 , C_6H_6 , and CCl_4 are small. The solubility curves for the *o*- and *m*-isomerides in EtOH , COMe_2 , and Et_2O fall below the ideal curve deduced from the variation with temp. of the mol. heat of fusion, whereas the solutions in the non-polar solvents deviate in the opposite direction; with H_2O the deviations are only slight. The solubility curve of quinol in COMe_2 exhibits a discontinuity at 62° and 33 mol.-%, and compound formation is said to be indicated. C. T. SNELL (c).

Rhythmic precipitation of stearic acid from alcoholic and ethereal solutions. A. KUTZELNIGG (*Kolloid-Z.*, 1931, 57, 292—293).—Stearic acid crystallises from hot EtOH solution (100 g. in 70 c.c.) and from saturated Et_2O solution in concentric ring systems. Spiral forms were also observed. Substances forming periodic crystallisation structures are said to have a high temp. coeff. of solubility. The phenomenon is believed to be caused by the liberation of heat of crystallisation. E. S. HEDGES.

Partition of iodine between carbon disulphide and water. G. HERRERO (*Anal. Fis. Quím.*, 1931, 29, 616—620).—The results agree with recorded data.

H. F. GILLBE.

Crystals produced by solidification of a fused substance containing dyes in solution. P. GAUBERT (*Compt. rend.*, 1932, 194, 109—111; cf. A., 1931, 672).—The dyes (1—20%) were added to various easily fusible colourless org. substances capable of considerable undercooling. When crystallisation occurs near the ordinary m. p. the crystals are colourless, but at lower temp. they are coloured, homogeneous, polychroic, and fluorescent in ultra-violet light. Different modifications of the same substance, e.g., vanillin (cf. A., 1923, i, 154), are differently affected as regards tint, rate of change, and relative amount.

C. A. SILBERRAD.

Activated and van der Waals adsorption of ammonia and of certain other gases. N. W. TAYLOR (*J. Amer. Chem. Soc.*, 1931, 53, 4458—4459).—The belief that activated adsorptions and desorptions are fairly general (A., 1931, 1366) is supported by the literature. Catalytic promoters may serve to provide a mechanism for low activation energy steps by which hysteresis effects are eliminated.

C. J. WEST (c).

Gaseous adsorption. II. Heat of adsorption curve for hydrogen on platinum. E. B. MANTED and N. HASSID (*J.C.S.*, 1931, 3313—3318).—The heat of adsorption or desorption is almost const., irrespective of the amount of H_2 already adsorbed.

D. R. DUNCAN.

Relative adsorbability of acids by activated carbon and the mass effect of the adsorbents. S. ROYCHOUDHURY (*Kolloid-Z.*, 1931, 57, 308—311).—Deviations from the adsorption isotherm in the adsorption of various acids by C (particularly from sugar) are recorded. The adsorption of a series of org. acids bears no relation to the relative solubilities or dissociation consts. In many cases the curves cut each other.

E. S. HEDGES.

Hydrolytic adsorption by activated carbon. S. ROYCHOUDHURY and J. N. MUKHERJEE (*Kolloid-Z.*, 1931, 57, 302—307).—Activated C, prepared in different ways, acquires an increasingly positive charge with repeated washing. Negatively-charged animal charcoal adsorbs alkali but not acid, whilst the positively-charged material adsorbs both. H^+ , OH^- , Cl^- , and SO_4^{--} can all be adsorbed at the solid side of the interface.

E. S. HEDGES.

Activated charcoal. S. ROYCHOUDHURY and J. N. MUKHERJEE (*Z. physikal. Chem.*, 1931, 157, 435—441).—Frumkin's theory of the adsorption of electrolytes by activated charcoal is criticised on the basis of an investigation of the charge on the charcoal.

R. CUTHILL.

Activated charcoal. A. FRUMKIN, R. BURSTEIN, and P. LEWIN (*Z. physikal. Chem.*, 1931, 157, 442—446).—Objections to the gas electrode theory of the adsorption of electrolytes by activated charcoal (cf. preceding abstract) are refuted.

R. CUTHILL.

Discontinuities in adsorption isothermals. A. J. ALLMAND and L. J. BURRAGE (*J. Amer. Chem. Soc.*, 1931, 53, 4453—4454).—The hypothesis of Benton and White (A., 1931, 1005) regarding discontinuities in adsorption isotherms is discussed.

C. J. WEST (c).

Kinetics of adsorption processes. A. R. UBBELOHDE and A. EGERTON (*Proc. Roy. Soc.*, 1931, A, 134, 512—523).—The adsorption of H_2 on charcoal at the temp. of liquid O_2 has been studied by an improved and accurate dynamic method. The rate of establishment of equilibrium on desorption is very high. The difference in the viscosities of 50% and 75% mixtures of *o*- and *p*- H_2 is less than 0.3%. The influences of the rotational state of the adsorbed mols. on the discontinuities in the isotherm and the adsorption potential are discussed.

L. L. BIRCUMSHAW.

Adsorption of ions, particularly of radioelements and dyes, by salt-like compounds. K. FAJANS and T. ERDEY-GRÜZ (*Z. physikal. Chem.*, 1931, 158, 97—151).—The adsorption of positively-charged dye ions by Ag halides is increased by a negative charge on the adsorbent, and diminished by a positive charge; negatively-charged dye ions show the reverse behaviour. Adsorption may, however, occur even if the adsorbent is uncharged, or has a charge of the same sign as that on the adsorbate. In a group of anions of similar constitution the adsorbability of the various ions runs parallel with the smallness of the solubility of the compounds which they form with the Ag of the adsorbent (cf. A., 1921, ii, 386). The adsorption of Th-B⁺ from solution in dil. HNO_3 by various Ag salts and the effect of added electrolytes have been studied. Adsorption of the

anion of the electrolyte leads to increased adsorption of Th-B'', whereas adsorption of the cation has the reverse effect. Th-B'' is adsorbed by Ag salts even when the adsorbent is free from excess of either of its ions or positively charged by excess of Ag'. The adsorbability of Pb'' and IO₃' is greater on AgIO₃ than on AgBr. The results show that Fajans' adsorption rule (A., 1913, ii, 1919) and Hahn's rule (A., 1926, 1092) are not of general applicability. It is probable that the adsorption of ions on salt-like compounds is influenced by the surface area of the adsorbent, the presence of foreign electrolytes (primarily through their effect on the charge of the surface), the solubility of the compound of the ion being adsorbed with the oppositely-charged ion of the adsorbent, the relative size and deformability of the ions participating, considerations of isomorphism, and by whether the ions being adsorbed are those of a radioactive element present in minute concn. or are ions of other elements present in weighable amount. In general a salt-like adsorbent free from excess of either of its ions readily adsorbs an ion from aq. solution only if that ion forms with the oppositely-charged ion of the adsorbent a sparingly sol. or only slightly dissociated compound. Further, the adsorption of an ion is increased by the adsorption of another ion with charge of opposite sign and reduced by adsorption of an ion with charge of the same sign.

R. CUTHILL.

Chemical and electrical processes at metal surfaces charged with gas. R. SUHRMANN (Z. anorg. Chem., 1931, 203, 235—244).—A discussion of published work on the effect of mol. layers of gases on the thermoelectric and photo-electric emission of metals, and the relation to heterogeneous catalysis.

E. S. HEDGES.

Surface activity of salts of the higher fatty acids. A. LOTTERMOSER and W. TESCH (Kolloid-Beih., 1931, 34, 339—372).—The variation of surface tension with concn. for solutions of Na salts of higher fatty acids has been studied at 20° and 65°. At 65° a min. is obtained which appears at a lower concn. as the no. of C atoms in the acid increases. Addition of free fatty acid also lowers the concn. of min. σ . The vals. obtained depend on the previous treatment of the solution, especially at 20°. The addition of NaOH or Na₂CO₃ at 60° increases the surface tension and alters the form of the concn.- σ curve. There is no appreciable adsorption of soap by added lamp-black.

M. S. BURR.

Slippage in a non-Newtonian liquid. M. REINER (J. Rheology, 1931, 2, 337—350).—A 1.71% solution of cellulose nitrate in Bu phthalate is a non-Newtonian liquid which appears to slide on a glass wall. The fluidity increases with the age of the solution. This type of system is treated mathematically.

E. S. HEDGES.

Quasi-laminar capillary flow. R. L. PEEK, jun., and W. R. ERICKSON (J. Rheology, 1931, 2, 351—369).—A mathematical treatment of the physical conditions under which flow through capillaries may be steady and yet not parallel to the axis of the tube. The conclusions reached do not account for all the anomalies observed in the viscosity of colloidal solu-

tions, and it is suggested that mol. orientation may be involved.

E. S. HEDGES.

Dynamics of membrane permeability in relation to ion-distribution. S. K. LIU (Kolloid-Z., 1931, 57, 285—292).—Mathematical.

E. S. HEDGES.

Ultrafiltration. I. Ultrafiltration of electrolytes from alkali caseinogenate solutions. D. M. GREENBERG and M. GREENBERG (J. Biol. Chem., 1931, 94, 373—382).—Data showing the electrolyte concn. in filtrates from mixtures of alkali caseinogenate with corresponding inorg. alkali salts support the view that a Donnan membrane equilibrium is involved in their ultrafiltration.

A. COHEN.

Osmosis in systems containing liquids of constant composition. V. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 823—830; cf. A., 1931, 795).—Mathematical.

W. R. ANGUS.

Specific permeability of capillary systems. E. MANEGOLD and R. HOFMANN (Biochem. Z., 1931, 243, 51—66).—The sp. permeability of a capillary system is discussed and the vals. for a collodion membrane are determined by the use of H₂O and aq. solutions of capillary-active substances. The vals. vary with the nature of the dissolved substance. The mechanism of the action of permeability regulators is discussed.

P. W. CLUTTERBUCK.

Electrostatic explanation of the phenomenon of flotation. B. KAMIENSKI (Nature, 1932, 129, 59—60).—The potential of unattackable electrodes such as Pt, PbS, and Acheson graphite is reduced when the electrodes are wetted by an emulsion of dielectrics in H₂O. Zn electrodes, not being inert, change their potential but little.

L. S. THEOBALD.

Electrocapillary curves of mixtures of normal alcohols with water, and adsorption of alcohol molecules at mercury surface. C. OCKRENT (J. Physical Chem., 1931, 35, 3354—3366).—The curves for the complete series of mixtures of MeOH, EtOH, and PrOH with H₂O and some BuOH-H₂O mixtures have been measured. The calc. areas of alcohol mols. at the p.d. where max. adsorption occurs agree fairly well with those calc. from insol. alcohol films on H₂O. Up to fairly high concns. the alcohols appear to form a unimol. layer at the charged Hg surface, and are oriented in the same way as at the air-H₂O interface. In solutions of various alcohols H₂O appears to raise the interfacial tensions at polarisations more positive than -0.6 volt and lower them at more negative polarisations. These effects may be ascribed to large liquid junction potentials or to a positive adsorption of H₂O at negative polarisations, which increase as the homologous series is ascended.

F. L. BROWNE (c).

Kinetics of coagulation at boundary surfaces. H. FREUNDLICH and R. VON RECKLINGHAUSEN (Z. physikal. Chem., 1931, 157, 325—341).—The mechanical coagulation, i.e., coagulation by stirring, of a CuO sol occurs at the liquid-gas interface, since it does not take place if the stirring is such that the surface of the liquid is not disturbed or renewed. When the sol is stirred in a similar way with l-

bromonaphthalene or Hg, the first result is the formation of an emulsion stabilised by the CuO, and the rate at which CuO is removed from the sol changes as stirring proceeds. Ultimately, however, mechanical coagulation at an approx. const. rate starts at the Hg-IL₂O interface. R. CUTHILL.

Alkali aluminium silicates. II. Ammonium permutites and their derivatives and an attempted chemical classification of the permutites. III. Hydrolysis of permutites. E. GRUNER [in part with E. HIRSCH] (Z. anorg. Chem., 1931, 202, 337—357, 358—371).—II. Cation exchange has been studied in the permutites of the type $m\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3 \cdot p\text{SiO}_2 \cdot q\text{H}_2\text{O}$, where $m:n:p:q = 1:1:2:2$, $1:1:3:4$, and $1:1:4:4$. With these, NH_4Cl yields respectively

$0.5(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2 \cdot 2.5\text{H}_2\text{O}$ (A),
 $(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ (B), and
 $(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ (C). $\text{N}_2\text{H}_4 \cdot \text{HCl}$ gives similar products. B and C behave normally with NaCl, but A gives rise to $0.5\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2 \cdot 2.5\text{H}_2\text{O}$, whereas it forms the original permutite with NaOH. N_2H_4 is eliminated from N_2H_5 -permutites by H_2O_2 , which forms a mol. compound in which H_2O_2 can be replaced by H_2O , NH_3 , or SO_2 . By treatment in a sealed tube with excess of NaOH permutites with more than 2 mols. of SiO_2 are converted into the 1:1:2:2 type. The reactions observed can best be explained by considering the simplest permutite to be a salt of the dibasic acid $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{H}_2$, the permutites with higher proportions of SiO_2 being regarded as solid solutions of the parent substance with H_4SiO_4 or H_2SiO_3 .

III. When Ag-permutites of the simplest type are treated with dil. K_2CrO_4 , the solid is coloured red and contains CrO_4^{2-} in excess of the amount corresponding with the observed cation exchange. With excess of K_2CrO_4 the cation exchange is complete, and the Ag_2CrO_4 formed remains attached to the permutite. This and other similar reactions are attributed to hydrolysis of the permutite, which has been directly measured, and amounts, under the conditions used, to 33%. F. L. USHER.

Examination of protein films. A. HUGHES, J. SCHULMAN, and E. K. RIDEAL (Nature, 1931, 129, 21).—Proteins such as egg-albumin, gliadin, and glutenin can be made to spread in the form of highly-dispersed, uniform films on the surface of H_2O by the method described. Preliminary results of the examination of aq. protein systems by the method of surface potentials are described. L. S. THEOBALD.

Association of aromatic nitroso-compounds in solution. D. L. HAMMICK [with W. S. ILLINGWORTH, W. A. M. EDWARDS, and (Miss) E. EWBANK] (J.C.S., 1931, 3105—3111).—Mol. wts. in C_6H_6 have been determined cryoscopically. PhNO and its *m*- and *p*-derivatives are only slightly associated (mean = 2.3% bimol.), but *o*-substitution favours association (mean for di-*o*-derivatives = 61.9%). Probably a dipole aggregate is first formed and this passes over into an oxyazoxy-structure. D. R. DUNCAN.

Action of boric acid and borates on rotatory power of glucose, galactose, and fructose. E.

DARMOIS and (Mlle.) R. PEYROUX (Compt. rend., 1931, 193, 1182—1185).—The variations in rotatory power of solutions containing glucose and a Na borate (cf. A., 1930, 69) increase with the alkali content of the borate. With NaBO_2 $[\alpha]$ first diminishes, becoming negative, passes through a min., and then rises to a limiting val., whilst the dispersion increases; the velocity of the changes increases with rise of temp. It is inferred that a laevorotatory complex of borate and glucose, probably $\text{Na}_2[(\text{BO}_2)_2 \cdot \text{C}_6\text{H}_{12}\text{O}_6]$, is formed, the changes in $[\alpha]$ being due to variations in the relative amounts of this and of glucose. At 20° $K = [\text{glucose}][\text{borate}]/[\text{complex}] = 0.21$. Similar results were obtained with galactose and fructose.

C. A. SILBERRAD.

Influence of electrolytes on the dielectric constant of water. I. Experimental method. II. Uni-univalent salts. R. T. LATTEY and W. G. DAVIES (Phil. Mag., 1931, [vii], 12, 1111—1136).—The dielectric const. of aq. solutions of KCl, NaCl, NaF, and NaIO_3 , determined by the voltage tuning method, is greater than that of H_2O . The increase is proportional to the concn. of dissolved salt, and is the same for equiv. concns. of each uni-univalent salt examined within the error of experiment.

H. J. EMELEUS.

Viscosity of dilute solutions of strong electrolytes. W. E. JOY and J. H. WOLFENDEN (Proc. Roy. Soc., 1931, A, 134, 413—427).—The viscosities of aq. solutions of KCl, KClO_3 , RbNO_3 , and HNO_3 (concn. range N — $0.002N$) have been measured at 18° , and in all cases, in agreement with the theory of Jones and Dole (A., 1929, 1385), the viscosity is greater than that of H_2O . The Falkenhagen-Dole theory (A., 1929, 1389) is confirmed by the limiting slopes of the viscosity-concn. curves and their temp. coefficients. L. L. BIRCHUMSHAW.

Two varieties of aqueous solutions of a cobaltous salt: relation of magnetic state to concentration. A. LALLEMAND (Compt. rend., 1931, 193, 1323—1325).—The solutions of CoCl_2 with const. (a) and variable (b) magnetic susceptibility described by Trümpler (Diss., Zürich, 1917), are obtained (a) by preventing contact between the dissolving crystals ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and conc. solution, e.g., by continual agitation, and (b) by preparing in the first instance a very conc. solution, subsequent dilution having no effect. The magnetic moment of the "variable" solutions is practically independent of the concn., but the Curie point rises from -18° for C 0.072 to -7° for C 0.0125, the mol. field being thus a function of C (cf. A., 1928, 454). C. A. SILBERRAD.

Colloidal theory of van der Waals gases. S. RAY (Kolloid-Z., 1931, 57, 259—266).—Theoretical. E. S. HEDGES.

Properties of aerosols. S. C. BLACKTIN (Nature, 1931, 138, 968). L. S. THEOBALD.

Theory of the electrification of aerosols. H. S. PATTERSON (Phil. Mag., 1931, [vii], 12, 1175—1182).—Calculation shows that for slightly charged aerosols the fraction of particles charged should increase with time, and for aerosols highly charged initially should remain const. Calc. and experimental vals. agree

for NH_4Cl , stearic acid smoke, and for MgO from burning Mg . H. J. EMELÉUS.

Highly polymerised compounds. LVII. Viscosity measurements with solutions of long thin molecules. H. STAUDINGER and E. OCHIAI (Z. physikal. Chem., 1931, 158, 35—55; cf. A., 1930, 571).—At 20° the sp. viscosity (relative increase in viscosity caused by the solute), η_{sp} , of CCl_4 solutions of long straight-chain paraffins, aliphatic esters, and ketones and $\text{C}_5\text{H}_5\text{N}$ solutions of fatty and dicarboxylic acids is given by $\eta_{sp}/c = ny + x$, where c is the quotient of the concn. in g. per litre by 14 (the mol. wt. of the CH_2 group), n the no. of C atoms in the mol., y a const. characteristic of the CH_2 group, and x a const. which is zero for paraffins but depends on the nature of the group containing O in the other compounds. This equation, which is valid only if n exceeds 9, shows that the solute mols. are long thin structures in the dissolved as in the cryst. state. For CCl_4 solutions of straight-chain fatty acids $\eta_{sp}/c = 2ny + x$, indicating that, as in the solid state, the acid mols. are linked end to end in pairs. The introduction of a double linking into a fatty acid scarcely affects η_{sp}/c . Aliphatic esters with straight chains have larger sp. viscosities than isomerides with branched chains. Ring structure markedly increases the viscosity.

R. CUTHILL.

Viscosity of suspensions of elongated particles, and their interpretation by space-filling. R. EISENSCHITZ (Z. physikal. Chem., 1931, 158, 78—90).—Theoretical. Calculation of the viscosity, η , of a suspension of elongated ellipsoidal particles on lines similar to those followed in Einstein's theory of the viscosity of a suspension of spherical particles has shown that $\eta/\eta_0 - 1 = 1.15va/\{\pi Vb \log(2a/b)\}$, where η_0 is the viscosity of the dispersing medium, V the vol. of the suspension, and v the total vol. of the suspended particles, the semi-axes of which are a and b . This equation agrees satisfactorily with the data for the viscosity of solutions of long-chain paraffins (A., 1930, 571). The fact that the viscosity of a suspension deviates from the requirements of Einstein's theory in so far as it depends, not only on v , but also on the nature of the suspended particles does not prove therefore that the dispersed particles occupy a larger vol. than corresponds with their dimensions.

R. CUTHILL.

Suspension effect of Wiegner and Palmann. I. Activity of the adsorbed ions. J. M. ALBAREDA Y HERRERA (Anal. Fis. Quim., 1931, 29, 643—650).—The variation of the suspension effect in acid and alkaline suspensions of clays with variation of the p_H of the disperse medium has been studied, and the activities of the adsorbed ions have been calc.

H. F. GILLBE.

Theory of the micellar state in relation to the idea of complexity in chemistry. G. MALFITANO and M. CATOIRE (Kolloid-Z., 1931, 57, 266—276).—The micelle is treated as a structural chemical unit in the series: atom, mol., complex mol., micelle.

E. S. HEDGES.

General colloid chemistry. XXV. Dependence of the properties of aluminium hydroxide sols on the colloid equivalent. F. MUTTONE and

W. PAULI (Kolloid-Z., 1931, 57, 312—324).—The colloid equiv. is the no. of mols. corresponding with a single free charge of the oppositely-charged ion. The colloid equiv. of $\text{Al}(\text{OH})_3$ sols is increased by boiling, whilst the viscosity increases and the activity coeff. of the oppositely-charged ion (Cl') decreases strongly. The changes are caused by the formation of secondary particles. With increasing colloid equiv. the electrophoretic velocity falls to a min. and then slowly rises; the viscosity behaves similarly. The activity coeff. of Cl' falls steadily as the colloid equiv. is reduced. There is a relation between viscosity and the free charge. The flocculation vals. of egg- and serum-albumin are low for small colloid eqivs., but increase markedly and later fall as the colloid equiv. increases.

E. S. HEDGES.

Diffusion in alkaline copper solutions. V. L. RICKETTS and J. L. CULBERTSON (J. Amer. Chem. Soc., 1931, 53, 4002—4008).—Equations giving rates of diffusion for certain boundary conditions are deduced and utilised to distinguish between colloids and complexes in certain alkaline hydroxy-org. Cu systems. The diffusion coeff. of the glycerol-Cu complex into agar gel is comparable with those of many crystallisable salts.

R. H. CHERRY (c).

Migration studies with ferric oxide sols. II. Negative sols. F. HAZEL and G. H. AYERS (J. Physical Chem., 1931, 35, 3148—3159; cf. A., 1931, 1232).—The conversion of positive Fe_2O_3 sols into negative sols by means of $\text{K}_4\text{Fe}(\text{CN})_6$ is related to the p_H of the medium. The sols lose their stability when the particles migrate with a velocity between about -2.0 and $+2.0 \mu$ per sec. per volt per cm., vals. which correspond with the crit. potentials. The isoelectric point of the sol is not determined uniquely by its p_H . The effect of K^+ , Ba^{++} , Al^{+++} , and Th^{++++} on the migration velocity of negative sols is illustrated.

F. SAUNDERS (c).

Flow of colloids which show anomalous viscosity. H. KROEPFELIN (J. Rheology, 1931, 2, 385—391).—Measurements of the distribution of velocity of flow of colloidal solutions at different points in a tube of circular cross-section indicate that the properties of solids play no important part in the anomalies.

E. S. HEDGES.

Highly-polymerised compounds. LVIII. Streaming double refraction of protein solutions. G. BOEHM and R. SIGNER (Helv. Chim. Acta, 1931, 14, 1370—1403).—The applicability of streaming double refraction measurements to the investigation of mol. aggregation has been studied. In ordinary colloidal solutions streaming anisotropy is caused principally by the orientation of elongated particles, which may be either mols. or micelles. Proteins may be classified according to the form of the mols. in solution, as indicated by refraction measurements: in solutions of ovalbumin and myogen the particles are spherical, and in solutions of myosin elongated, whilst in solutions of ovoglobulin they form long threads; gelatin solutions appear to contain short rod-shaped particles. Deformation of the particles as a consequence of reaction may be detected by the measurements, but no evidence in support of

Meyer's theory of muscular contraction is afforded by measurements with ovoglobulin and polyacrylic acid. H. F. GILLBE.

Inactivation, viscosity, and p_H value of gum arabic solution. S. A. SCHOU and J. M. OLSEN (Dansk Tidsskr. Farm., 1932, 6, 6—16).—The viscosity shows a nearly const. max. between p_H 4 and 10; above and below these limits it decreases rapidly (cf. A., 1928, 706). The addition of 0.5% of "nipagin" has no effect on the viscosity. The viscosity decreases if the solution is heated at 100° for 30 min., and the acidity increases slightly at the same time, but there appears to be no definite relation between the two. The decrease in viscosity on heating is not merely transitory, as out of 5 samples only 2 showed a slight subsequent increase again after 14 days. The use of gum arabic solution as a protective colloid in the prep. of a camphor suspension has been studied. H. F. HARWOOD.

Solutions of cellulose [derivatives]. J. DUCLAUX and F. HIRATA (J. Chim. phys., 1931, 28, 537—545).—Solutions of cellulose in $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, cellulose nitrate in COMe_2 , PhNO_2 , $\text{C}_6\text{H}_{11}\text{OAc}$, or COMeEt , cellulose trinitrate in COMeEt , cellulose acetate in COMe_2 , and cellulose triacetate in $\text{C}_2\text{H}_5\text{Cl}_4 + \text{EtOH}$ have no measurable permanent rigidity, although the viscosity of some of these solutions is 10^7 times that of H_2O . The time of relaxation of 6% cellulose nitrate in PhNO_2 is 170 sec.

E. S. HEDGES.

Concentrations at which coagulative power of certain organic substances is maximal. B. JIRGENSONS (Z. physikal. Chem., 1931, 158, 56—64).—The coagulative action of PhOH , COMe_2 , and various alcohols on starch and egg-albumin sols rises with increasing concn. of coagulant, and attains a max. at a concn. which is a linear function of the dielectric const. of the coagulant and increases with it. The max. is sometimes followed by a min.

R. CUTHILL.

Periodic precipitation in the absence of colloids. J. W. MCBAIN (Nature, 1931, 128, 1042).—Attention is directed to the work of Morse and Pierce (A., 1904, 14; 1930, 1117) in which periodic pptn. in the absence of a gel has been observed.

L. S. THEOBALD.

Spiral precipitation. (MILLER) S. VEIL (Compt. rend., 1931, 193, 1337—1339).—The method previously described (cf. A., 1930, 1516) occasionally gives rise to spirals, in which case \log (distance between successive spirals measured along a radius vector from centre of drop) varies linearly with the ordinal no. of the spiral (cf. A., 1914, ii, 631; 1930, 1117).

C. A. SILBERRAD.

Analogue of the acclimatisation phenomenon in the protection of arsenious sulphide sol by gelatin. A. J. RAO (J. Indian Chem. Soc., 1931, 8, 621—622).—When gelatin is added drop by drop to As_2S_3 sol, the protected sol is less stable towards electrolytes than when the protective colloid is added rapidly.

E. S. HEDGES.

Pectography and the constitution of colloidal solutions. E. S. HEDGES (Chem. and Ind., 1932,

25—26).—The work of Bary (A., 1928, 705, 1186, *et seq.*) on the deposits produced by the desiccation of colloidal solutions of metallic hydroxides and sulphides, and dyes is discussed. The production of banded deposits is explained in terms of Hedges' general theory of the formation of periodic structures (A., 1930, 1261). The crit. condition is provided by the free electrolyte in the colloidal solution, which, by evaporation in the surface, reaches a concn. at which it coagulates the colloid. Successive bands of deposit are formed each time the concn. of electrolyte reaches the crit. val. for coagulation.

E. S. HEDGES.

Colloid chemistry of gliadin separation phenomena. H. L. B. DE JONG and W. J. KLAAR (Trans. Faraday Soc., 1932, 28, 27—68; cf. B., 1930, 31, 787; 1931, 177).—The separation is continuous and there is no evidence that a crit. charge of the particles is involved. The relative viscosity, η , of aq. sols at 25° increases with concn. of EtOH and COMe_2 to a max. with 48 vol.-% and 44 vol.-%, respectively, and the difference in relative viscosity in the presence of equiv. quantities of univalent electrolytes is almost zero at these max., where a reversal of the lyotropic series occurs. The vals. of η for 44% COMe_2 sols decrease with increasing concn. of uni- and bi-valent ions. The small differences between vals. of η for 44% COMe_2 sols containing equimol. concn. of KCl and KI increase with protein concn., and for const. protein concn. the differences increase with concn. of salt until the sol is discharged. The difference is max. with sols of max. viscosity and min. at the isoelectric point as well as with higher $[\text{H}^+]$.

The results are interpreted on the assumption that ionic adsorption influences the boundary potential and mol. adsorption causes the lyotropic effects. The latter in certain EtOH and COMe_2 media is the same, or zero, for electrolytes of the same valency.

J. G. A. GRIFFITHS.

Relation of proteins to colloids and electrolytes. W. PAULI (Naturwiss., 1932, 20, 28—37).—A lecture.

Swelling. IV. Adsorption of hydrochloric acid by hide and the related swelling. A. LOTTER-MOSER and H. THIELE (Kolloid-Z., 1931, 57, 343—353; cf. A., 1931, 1232).—The adsorption of HCl by cow-hide (deprived of hair) is reversible, but the accompanying swelling is partly irreversible. The liquid inside the hide is not pure H_2O , but has the same composition as the surrounding swelling liquid. This fact must be considered in adsorption measurements.

E. S. HEDGES.

Swelling of pine-wood cellulose through electrolytes and organic substances in aqueous solution. C. G. SCHWALBE and O. FISCHER (Kolloid-Z., 1931, 57, 338—343).—The swelling of pine-wood cellulose in H_2O is increased by alkalis and decreased by acids. Small amounts of alcohols or COMe_2 increase the swelling, but further quantities have no further effect. Carbohydrates and NH_2 -acids increase the swelling in proportion to their concn.

E. S. HEDGES.

Hydrogels. XI. System $\text{SiO}_2\text{--H}_2\text{O}$. XII. System $\text{SnO}_2\text{--H}_2\text{O}$. A. SIMON and P. RATH (Z.

anorg. Chem., 1931, 202, 191—199, 200—204).—XI. A method is described for the determination of the v. p.-temp. curves of hydrated SiO_2 , prepared by the action of HCl on hydrated Na silicate at low temp.; if anhyd. acid is used, anhyd. SiO_2 is formed immediately, and it is necessary to have sufficient H_2O present to form a hydrate of HCl . The decomp. isobars show the existence of $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, $\text{SiO}_2 \cdot 1.5\text{H}_2\text{O}$, and $\text{SiO}_2 \cdot \text{H}_2\text{O}$; $\text{SiO}_2 \cdot 0.5\text{H}_2\text{O}$ probably exists, but there is no evidence of $\text{SiO}_2 \cdot 2.5\text{H}_2\text{O}$.

XII. Similar measurements with the product obtained by the action of 98% HNO_3 on Na stannate demonstrate the existence of $\text{SnO}_2 \cdot 3\text{H}_2\text{O}$ and $\text{SnO}_2 \cdot \text{H}_2\text{O}$; the heats of formation of those compounds are about 15.5 and 30 kg.-cal., respectively, compared with 14 and 26.5 kg.-cal. for $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SiO}_2 \cdot \text{H}_2\text{O}$, respectively. The results are compared with those for other elements of the fourth group.

H. F. GILLBE.

Difference between the X-ray spectra of gelatin sol and gelatin gel. J. R. KATZ, J. C. DERKSEN, and W. F. BON (Rec. trav. chim., 1931, 50, 1138; cf. A., 1931, 971).—X-Ray spectra of a conc. gelatin- H_2O mixture at 55° (sol) and at 20° (gel) are reproduced.

C. W. DAVIES.

Influence of organic substances on the formation of jellies of thorium arsenate, phosphate, and molybdate. S. PRAKASH (Z. anorg. Chem., 1931, 201, 301—313; cf. A., 1929, 1235).—Gelatinisation of all three substances is retarded by glycerol and accelerated by carbamide. The action of glycine is sp. The results are discussed.

F. L. USHER.

Role of cations in the gelation of pectin sols. S. GLUCKMANN (Kolloid-Z., 1931, 57, 330—338).—Determinations of ash and OMe content, p_H , viscosity, particle size, and gelation under the influence of the chlorides of Li, Na, K, Mg, Ca, Ba, and Al have been made with pectin sols. The tendency to gelate depends on the valency and degree of hydration of the cation. The results support the crystallisation theory of gelation.

E. S. HEDGES.

Ageing phenomena of chromic hydroxide gel. K. KLANFER and F. PAVELKA (Kolloid-Z., 1931, 57, 324—330).—The course of ageing of gelatinous $\text{Cr}(\text{OH})_3$ has been followed by determining its solubility in AcOH , $\text{H}_2\text{C}_2\text{O}_4$, H_3BO_3 , oleic acid, and KOH . The solubility was found to decrease steadily with age. There is a discontinuity between 50° and 80°, and the H_2O content of the gel varies with temp. in a similar way.

E. S. HEDGES.

Thixotropic behaviour of thorium jellies. S. PRAKASH and N. N. BISWAS (J. Indian Chem. Soc., 1931, 8, 549—555).—The molybdate and phosphate jellies are highly thixotropic, whilst Th arsenate jellies are thixotropic when freshly prepared. The time of thixotropic setting is almost const. for the clear jellies, but with opalescent, agglomerated jellies, such as Th arsenate, it decreases on repetition. The thixotropic time is less than the original time of setting and is greater for dil. jellies than for conc. jellies. The effect of shaking is to set free the structurally-imbedded liquid of the jelly. Glycerol and sucrose act as peptising agents and increase the setting

and thixotropic times. Glycine in small quantities decreases the thixotropic time, but has a stabilising influence at higher concns. K_2SO_4 decreases the setting and thixotropic times.

E. S. HEDGES.

Gels. I. Syneresis of silica gel. II. Effect of hydrogen-ion concentration on syneresis of silica gel. D. G. R. BONNELL (Trans. Faraday Soc., 1931, 28, 1—11, 12—19; cf. A., 1930, 1519).—I. Apparatus for determining the velocity of syneresis and the composition of the exuded liquid is described. At p_H 8 and SiO_2 concn. greater than 5%, the initial velocity and the final vol. of liquid increase with the concn., but below 5% the gels exude increasing quantities of liquid as the concn. falls. For the same p_H and SiO_2 concn., the acid used in the prep. of the gel affects the velocity of syneresis and the vol. of liquid exuded increases in the order AcOH , HCl , H_2SO_4 . No change of total vol. accompanies the syneresis of either acidic or alkaline gels. The setting time and the induction period increase with decreasing concn.

II. Gels at p_H between 3 and 11 have been investigated. At the highest p_H vals. the SiO_2 content of the exuded liquid increases with the initial concn. of the gel. The total vol. of liquid exuded is minimal at p_H 8 and increases more rapidly with increase than decrease of p_H . The initial velocity of syneresis is maximal at p_H 8. The setting time and period of induction increase as the p_H recedes in either direction from 8, independently of the acid used. The results indicate an isoelectric point between p_H 7.5 and 8.0 for 6.5—9% SiO_2 gels at 20°. The vol. of liquid exuded increases with rise of temp.

J. G. A. GRIFFITHS.

Preparation and properties of artificial sponges of cellulose. E. HUBERT (Kolloid-Z., 1931, 57, 253—258).—Photomicrographic examination reveals that the natural sponge is a 3-dimensional network, the rubber sponge is a solid foam, and the viscose sponge is a combination of these forms, the walls of the cells containing capillary pores, whilst the spaces contain a capillary network. The porosity and H_2O -retaining capacity of the viscose sponge vary with the concn. of viscose solution used and with the solubility of the salt added. Viscose sponges shrink considerably (25—40%) on drying, but regain their original vol. in a few sec. in H_2O .

E. S. HEDGES.

Temperature at which unbound water is completely frozen in a biocolloid. J. L. ST. JOHN (J. Amer. Chem. Soc., 1931, 53, 4014—4019).—From the observation that a temp. of -12.6° is sufficient to freeze all the "free" (freezable) H_2O in a hydrophilic biocolloid, whereas the remaining H_2O ("bound" H_2O) is not frozen at -12.5° to -35° , it is inferred that the average amount of bound H_2O in the thick part of egg-white is about 20%. An improved formula for the calculation of free H_2O is given.

C. J. WEST (c).

Theory of the Ludwig-Soret effect. B. BRUZZI (Z. physikal. Chem., 1931, 157, 422—434).—From thermodynamic considerations and the theory of stationary heat flow it is found that $\sigma = -(1/NT)(\partial c_p / \partial N) / (\partial^2 S / \partial N^2)$, where σ is the Soret coeff. for the

component of a solution having the mol. fraction N , c_p the partial mol. sp. heat, S the partial mol. entropy, and T the temp. For a dil. solution this becomes $\sigma = -(1/RT)\partial c_p/\partial \log_e N$, which agrees satisfactorily with available experimental data. The Soret effect proves to be a special case of a general dynamic effect, and is analogous to the Peltier, Seebeck, and Hittorf effects. R. CUTHILL.

Calculation of degrees of dissociation of weak electrolytes. W. H. BANKS (J.C.S., 1931, 3341—3342).—In solving the equation $\alpha = \Lambda/\Lambda_\infty$, where Λ is the conductivity and Λ_∞ the sum of the ionic mobilities, Λ_∞ can be calc. directly from the expression $\Lambda_\infty = \sqrt{[\Lambda_0^2 - 2b(\Lambda_0\Delta C)]}$. Here C is the equiv. concn., and b the Onsager slope for the electrolyte. C. W. DAVIES.

Application of Debye's electrolytic theory to concentrated solutions. G. SCATCHARD (Physikal. Z., 1932, 33, 22—32).—An extension of the Debye-Hückel theory of strong electrolytes to include non-ionic forces. The equation deduced explains variation of osmotic and activity coeffs. A. B. D. CASSIE.

Electrolytic dissociation of acids in salt solutions. III. Dissociation constants of certain acids and activity relations of their ions in sodium and potassium chloride solutions. E. LARSSON and B. ADEL (Z. physikal. Chem., 1931, 157, 342—362).—Previous investigation (A., 1931, 1368) has been extended to other acids. The substitution of Me, Ph, or OH groups in a normal fatty acid affects the vals. of $-\log \phi$ and $-\log \psi$ only if the substituent is introduced into the α -position. Substitution of OH in the o - or m -position to the CO_2H group in BzOH has no effect. The vals. of ϕ and ψ for a carboxylic acid depend on the effective radius of the anion, which, whilst it is determined essentially by the CO_2' group, may be affected by the presence in the ion of certain atoms or groups, particularly strongly polar groups, and the more so the nearer these are to the CO_2' group. At the same time, other ions exert an influence: the ions of NaCl and KCl deform the acid anions. R. CUTHILL.

Iodine. J. LANZA (Anal. Fis. Quím., 1931, 29, 621—642).—Study of solutions and crystals of alkali polyiodides, and of the f.-p. depression, electrical conductivity, transport, absorption spectra, and behaviour towards animal C of aq. solutions of I, suggests that I is not truly sol. in H_2O , but is sol. in, e.g., KI. H. F. GILLBE.

Lead chamber process. I. System nitrosyl-sulphuric acid-sulphuric acid-water. E. BERL and H. H. SAENGER (Z. anorg. Chem., 1931, 202, 113—134).—The v. p. of solutions of HSO_5N in 64—80% H_2SO_4 solutions has been determined by a static method at temp. between 30° and 150°. The calc. latent heat of evaporation, of HSO_5N rises from 8223 g.-cal. in 64% H_2SO_4 solution to 12,383 g.-cal. in the 80% acid; there is an abrupt discontinuity in the λ -concn. curve at about 73% H_2SO_4 . The v. p. of the solutions is very greatly increased by addition of HNO_3 . H. F. GILLBE.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. XIII.

Silicic acids and dissolved hydrated silica in alkaline and acid solutions. G. JANDER and W. HEUKESHOVEN (Z. anorg. Chem., 1931, 201, 361—382; cf. A., 1931, 183).—From data relating to the diffusion and ultra-violet absorption of Na silicate solutions of different p_{H} , and to the solubility of silicic acid in mineral acids, it is inferred that SiO_3'' exists only when the $[\text{H}^+]$ is less than that of $N\text{-NaOH}$. It is readily hydrolysed to give $2\text{OH}^+ + \text{Si}_2\text{O}_5''$, which latter is stable between p_{H} 13.5 and 10.9. At lower p_{H} silicic acid is largely polymerised and tends to separate from its solutions, the part remaining in true solution being of a more basic character than mono- or disilicic acid. Its conversion into the latter is shown by thermometric or conductometric titration with NaOH . F. L. USHER.

Exceptional isotherm at 0° of the system palladium-hydrogen. L. J. GILLESPIE and J. H. PERRY (J. Physical Chem., 1931, 35, 3367—3370).—The isotherm is apparently an extension of the normal isotherm into the metastable region. The highest pressure observed was 110 mm., the solid phase containing about 0.95 atom of H per atom of Pd. F. D. ROSSINI (c).

Redetermination of thermal dissociation eq. equilibria of inorganic compounds. I. Dissociation equilibrium of calcium carbonate by means of a high-temperature vacuum balance. S. TAMARU, K. SROMI, and M. ADATI (Z. physikal. Chem., 1931, 157, 447—467).—Measurements of the dissociation pressure, p , at 614—891° are in good agreement with those of Andrussov (A., 1925, ii, 803). The relation between p and T is given by $\log p = -39,670/4.575T + 10.385$, or, more exactly, by $\log p = -9220/T + 1.70 \log T - 0.00149T + 1.443 \times 10^{-7}T^2 + 7.181$. A vac. spring balance utilising a coiled quartz fibre and suitable for high-temp. work is described. R. CUTHILL.

Complex-chemical behaviour of lithium. II. Lithium halides with ethylamine or propylamine. A. SIMON and H. KIMMERLE (Z. anorg. Chem., 1931, 202, 385—402; cf. A., 1929, 431).—Tensimetric measurements show the existence of the following compounds (temp. of decomp. in parentheses): LiCl with 1 (−5°) and 3 (−37°) mols.; LiBr with 1 (59°), 2 (31°), and 4 (−12°) mols.; LiI with 0.5 (135°), 2 (76°), and 4 (22°) mols. NH_4Et ; LiCl with 1 (29°), 2 (11°), and 4 (−25°) mols.; LiBr with 1 (69°), 2 (46°), and 4 (4°) mols.; LiI with (128°), 2 (93°), and 4 (38°) mols. NH_4Pr . Heats of formation are calc. and the valency isobars discussed. F. L. USHER.

Fused products of $\text{Cr}_2\text{O}_3\text{-SiO}_2$ system. Y. YAMAGUCHI and H. NAKAZAWA (Bull. Chem. Soc. Japan, 1931, 6, 285—289).—By fusing together SiO_2 and Cr_2O_3 at 1700—2000°, glasses of various colours are produced. The influence of composition, temp. of fusion, rate of cooling, and reheating on the colour has been investigated and the products have been examined microscopically. D. R. DUNCAN.

Freezing of solutions. VI. Freezing of mixtures of di- and tetra-symmetrically substituted derivatives of ethane. J. TIMMERMANS and (MME.) VESSELOVSKY (Bull. Soc. chim. Belg., 1931, 40, 504—

517).—The equilibrium in binary mixtures of numerous derivatives of C_2H_6 has been deduced from f. p.-composition curves. Binary mixtures of halogenated derivatives generally form ideal solutions having a simple eutectic when the halogen atoms are identical, but when different halogens are present in the two components mixed crystals are formed. On the other hand, binary mixtures of *s*-di- with tetra-substituted derivatives form equimol. compounds, whether the substituent radicals are halogens or otherwise. A stereochemical explanation of the formation of these compounds is given. E. S. HEDGES.

Binary systems comprising carbamide with metallic nitrates. W. J. HOWELLS (J.C.S., 1931, 3208—3212).—Thermal diagrams indicate the existence of the compounds $LiNO_3 \cdot 2CO(NH_2)_2$, m. p. 126° , and $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$, m. p. 151.5° . No compounds are formed with NH_4NO_3 , $NaNO_3$, KNO_3 , or $TiNO_3$, but association occurs in solution.

D. R. DUNCAN.

Oxide hydrates and active oxides. XLIX. System lanthanum trioxide-water. G. F. HUTTIG and M. KANTOR (Z. anorg. Chem., 1931, 202, 421—428; cf. A., 1931, 1235).—Isobaric dehydration curves for a number of specimens of hydrated La_2O_3 and X-ray diagrams indicate the existence of a stable cryst. $La_2O_3 \cdot 3H_2O$, which is converted on dehydration into amorphous $La_2O_3 \cdot H_2O$. 0.5 mol. H_2O is still retained after heating at 700° . The dehydration curve closely resembles that of hydrargillite.

F. L. USHER.

Polytherms of ternary systems containing water, alkali sulphate, and a sulphate of the vitriol type. IV. A. BENRATH (Z. anorg. Chem., 1931, 202, 161—171).—The solubilities of $ZnSO_4 \cdot H_2O$ and $CoSO_4$ have been redetermined. The transition temp. $ZnSO_4 \cdot 6H_2O \rightleftharpoons ZnSO_4 \cdot H_2O$ is 55.5° (lit. 70°). $CoSO_4 \cdot H_2O$ is formed only very slowly, the transition temp. being about 71° . Isotherms ($0-100^\circ$) for the systems $ZnSO_4-(NH_4)_2SO_4-H_2O$, $ZnSO_4-Tl_2SO_4-H_2O$, $MgSO_4-Tl_2SO_4-H_2O$, $CoSO_4-Na_2SO_4-H_2O$, and $Na_2SO_4-Na_2SO_4-H_2O$ have been determined. The only double salts observed are $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $ZnSO_4 \cdot Tl_2SO_4 \cdot 6H_2O$, $MgSO_4 \cdot Tl_2SO_4 \cdot 6H_2O$, $CoSO_4 \cdot Na_2SO_4 \cdot 4H_2O$, and $Na_2SO_4 \cdot Na_2SO_4 \cdot 4H_2O$. Of these, only the first-named dissolves congruently throughout the whole temp. interval.

H. F. GILLBE.

Systems strontium oxide-arsenic pentoxide-water and lead oxide-arsenic pentoxide-water at 25° (acid range), and a basic strontium arsenate. H. V. TARTAR, M. R. RICE, and B. J. SWEO (J. Amer. Chem. Soc., 1931, 53, 3949—3956).—Equilibrium diagrams for the two systems defining the existence at 25° of the two acid Sr arsenates and the two acid Pb arsenates are given. The prep. of a basic Sr arsenate, $[Sr_3(AsO_4)_2]_3 \cdot Sr(OH)_2$, is described.

M. G. MOORE (c).

Formation of barium silicates from barium carbonate and silicic acid in the solid state. G. GRUBE and R. TRUCKSESS (Z. anorg. Chem., 1931, 203, 75—96).—The equilibrium pressure of CO_2 in each stage of reaction between $BaCO_3$ and SiO_2 has been measured. Four stages are recognised and their

approx. heats of reaction have been determined as follows: $BaO + SiO_2 = BaO \cdot SiO_2 + 26$ kg.-cal.; $BaO \cdot SiO_2 + BaO = 2BaO \cdot SiO_2 + 21$ kg.-cal.; $2BaO \cdot SiO_2 + BaO = 3BaO \cdot SiO_2 + 13$ kg.-cal.; $3BaO \cdot SiO_2 + BaO = 4BaO \cdot SiO_2 + 4$ kg.-cal. E. S. HEDGES.

Desulphurisation of steel. G. TAMMANN and H. O. VON SAMSON-HIMMELSTJERNA (Z. anorg. Chem., 1931, 202, 329—336).—The occurrence or non-occurrence of a reaction between FeS and various oxides and carbonates has been deduced from the form of the heating curves obtained by heating FeS with each of the substances examined. Positive effects were obtained with CaO , BaO , and PbO . When Fe containing FeS is heated at 1700° with Pb, a part of the S is removed as PbS , but no desulphurisation occurs when the content of S is below 0.014%.

F. L. USHER.

Equilibria between metals and slags in melts. I. Equilibrium $FeO + Mn \rightleftharpoons Fe + MnO$ at $1550-1560^\circ$. W. KRINGS and H. SCHACKMANN (Z. anorg. Chem., 1931, 202, 99—112).—The equilibrium const. $k = [Mn] \cdot (FeO) / [Fe] \cdot (MnO)$, where $[Fe]$ and $[Mn]$ are concns. in the metal phase and (FeO) and (MnO) those in the slag phase, is 0.0032 ± 0.0005 at $1550-1560^\circ$. The mass-action and Nernst partition laws are valid. The results are discussed in relation to the influence of impurities and the dissociation of silicate in the melts. H. F. GILLBE.

Phase boundary surfaces, phase boundary lines, and phase boundary points. W. OSTWALD (Z. physikal. Chem., 1931, 158, 91—96).—The theoretically possible types are enumerated, and other types of boundary strata are pointed out.

R. CUTHILL.

Third law of thermodynamics. W. H. RODEBUSH (Physical Rev., 1930, [ii], 35, 210).—A discussion.

L. S. THEOBALD.

Energy diagrams of the hydrogen halides in the gaseous state and in aqueous solution. P. J. VAN RYSELBERGHE (J. Physical Chem., 1931, 35, 3371—3378).—By combining data for heats of dissociation, ionisation, solvation, and dissolution, the energy of mutual polarisation of H and halogen atoms is calc. to be about 1 volt-electron.

F. D. ROSSINI (c).

Methods and apparatus in use at the Bureau of Physico-Chemical Standards. V, VI. Heats of combustion. M. BECKERS (Bull. Soc. chim. Belg., 1931, 40, 518—570).—Apparatus and technique for the precise measurement of heats of combustion are described. The measured heat of combustion of salicylic acid is 5237.2 g.-cal., and in consideration of the results of other investigators, the standard val. recommended is 5237.5 g.-cal. (15°) per g. of acid weighed in vac. The greatest deviation from this val. is 0.015%. Salicylic acid is recommended as a second standard provided that the technique is such as to ensure complete combustion (in respect of which it is less satisfactory than $BzOH$). The objection that salicylic acid also exists in an unstable form is refuted by showing that if an unstable modification exists (which is doubtful) it is converted into the stable form by pressure in making the pastille. E. S. HEDGES.

Heat of absorption of hydrogen by palladium-black at 0°. L. J. GILLESPIE and H. A. AMBROSE (J. Physical Chem., 1931, 35, 3105—3110).—The internal energy increase in the reaction $H_2 + 4Pd = 2Pd_2H$ is -8740 g.-cal.₁₅, which gives -9280 g.-cal.₁₅ for the increase in heat content. These vals. agree with the vals. from v.-p. data. The average composition of the two solid phases formed corresponds with the formula Pd_2H . F. D. ROSSENI (c).

Free energies of formation and heats of formation of thallium amalgams. C. E. TEETER, jun. (J. Amer. Chem. Soc., 1931, 53, 3917—3927).—Mol. free energies of formation at 20° and 40° have been calc. from published o.m.f. data. The heats of formation at 20° and 30° are positive. L. P. HALL (c).

Heats of dissolution, heats of formation, and free energies of formation of cadmium amalgams. C. E. TEETER, jun. (J. Amer. Chem. Soc., 1931, 53, 3927—3940; cf. A., 1928, 710).—The heats of dissolution in Hg of Cd-rich amalgams at 25° have a max. negative val. at 22.5% Cd, representing a physical transition point and not a compound, since at 30° the max. is shifted to 24% Cd. Mol. heats of formation calc. from these thermal data do not agree with those calc. from o.m.f. temp. coeffs. Mol. free energies at 25° have been calc. from the recorded e.m.f. L. P. HALL (c).

Hydrazine. Mobility of hydrazinium ion at 25°. E. C. GILBERT (J. Amer. Chem. Soc., 1931, 53, 3956—3962).—The conductivities at 25° of several N_2H_4 salts have been determined. At low concn. the slope of the curve obtained by plotting Λ against \sqrt{C} is quite close to that calc. from the Onsager equation (A., 1927, 517). The mobility of the hydrazinium ion at 25° is 58.6—59.1.

W. C. FERNELIUS (c).

Dispersion of the electrical conductivity of some aqueous and non-aqueous electrolyte solutions. II. GAERTNER (Physikal. Z., 1931, 32, 919—926).—Variation of conductivity with the frequency of applied potential was determined for aq. solutions of $CaCrO_4$, $MgCrO_4$, $Ca_2Fe(CN)_6$, and for solutions of $MgSO_4$ in glycerol and MeOH; addition of 4% of H_2O to glycerol gave a large change in the time of relaxation. A. B. D. CASSIE.

Electromotive force of cell $Zn(s)|ZnSO_4(m)|PbSO_4(s)|Pb(s)$. Experimental determination of the temperature coefficient of the ion size parameter in the theory of Debye and Hückel. I. A. COWPERTHWAITE and V. K. LA MER (J. Amer. Chem. Soc., 1931, 53, 4333—4348).—E.m.f. measurements have been made at concns. of 0.0003—0.01M and at 0—50°, the results being compared with those predicted by the first approx. equation of the Debye-Hückel theory and by the Gronwall, La Mer, and Sandved extension. The simple Debye theory requires negative ionic sizes, which change rapidly with temp. and concn., whilst the parameter α of the extended theory remains const. at 3.64 Å.

M. DOLE (c).

Theory of glass electrode. M. DOLE (J. Amer. Chem. Soc., 1931, 53, 4260—4280).—The H electrode function of thin glass films is attributed to their

selective permeability towards H^+ or the mobility of H^+ across the interface glass-aq. solution. The deviations of the glass electrode potentials from the theoretical H electrode potentials in alkaline solution are attributed to an appreciable mobility of Li^+ , Na^+ , and K^+ across the interface. Quant. agreement with this theory is obtained on application of the Henderson liquid-junction equation up to p_H 12 if it is also assumed that the H^+ mobility increases relatively to that of Li^+ , Na^+ , or K^+ as the p_H rises. The mobility through the interface may depend on the nature of the Helmholtz double layer. The experimental results agree with the equation $\log(e^{pH_{theor}} - 1) = A + np_H$, where A and n are consts. and ΔE is the deviation of the glass electrode potential from its theoretical val.

M. DOLE (c).

Acid standard cells of the unsaturated type. Y. ISHIBASHI and T. ISHIZAKI (Rev. Sci. Instr., 1931, [ii], 2, 785—796).—The solubility of $CdSO_4$ in dil. H_2SO_4 , and the connexion between e.m.f. and concn. of $CdSO_4$ and H_2SO_4 have been determined. Acid unsaturated cells are reproducible to 0.00003 volt. Hysteresis is small. A cell with an electrolyte containing 43.0% $CdSO_4$ and 0.05N-acid gives an e.m.f. of 1.08840 volt at 20°, and has practically no temp. coeff.

C. W. GIBBY.

Correlation between rate of oxidation and potential in iron systems. L. MICHAELIS and C. V. SMYTHE (J. Biol. Chem., 1931, 94, 329—340).—Comparison of the normal oxidation-reduction potentials at const. p_H of a series of salts and cyanide complexes of Fe referred to the H electrode shows that the autoxidizability of the Fe^{++} compound increases as the potential becomes more negative. Davidson's val. of 0.491 volt for $Na_3[Fe(CN)_5H_2O]$ (A., 1928, 1330) places this compound in an anomalous position in the series; reinvestigation yields a lower val. compatible with its relative autoxidizability.

A. COHEN.

Discontinuous variation in e.m.f. of photo-electric cells containing a coloured liquid. A. GRUMBACH and F. TABOURY (Compt. rend., 1931, 193, 1178—1180).—With a cell similar to that described previously (cf. A., 1929, 1393), the electrolyte containing 0.052 g. of acid fluorescein and 6 mols. of H_2SO_4 per litre, and a new method of measurement, the results are irregular, save that there is a marked tendency for the e.m.f. to assume one or other of a series of vals. given by $V = nV_1$, n being a whole no., and $V_1 = 1.3 \times 10^{-3}$ volt. An electrolyte containing 0.018 g. of fluoran and 8.4 mols. of H_2SO_4 per litre gives similar results. C. A. SILBERRAD.

Law of equidistance in photo-electric cells. A. GRUMBACH and F. TABOURY (Compt. rend., 1932, 194, 84—86; cf. preceding abstract).—Capillary and quadrant electrometers give similar results with H_2O and with solutions of acid fluorescein and Congo-red. This similarity obtains whether the cell is illuminated or not. The effect is attributed to alternate formation and removal of adsorbed unimol. layers by the electrode. C. A. SILBERRAD.

Influence of electrolytes on photo-electric phenomena. R. AUDUBERT (Compt. rend., 1932, 194, 82—84).—Using electrodes of CuI , Cu_2O , CuO ,

Ag_2S , AgI , and Hg_2I_2 , the influence on the photo-electric effect of aq. K_2SO_4 buffered by mixtures of citric acid and Na_2HPO_4 of p_{H} 9—2.8 shows that positive photo-potential is raised and negative lowered by a diminution in p_{H} , and conversely. The effects for 24 other salts of various metals show that the negative potential of an electrode exhibiting such in aq. K_2SO_4 is increased in an oxidising and diminished in a reducing solution; in all cases the effect is diminished by increased concn. of cations. The results support the author's theory (cf. A., 1931, 999). C. A. SILBERRAD.

Limits of gaseous explosions. M. NEUMANN and A. SERBINOFF (*Nature*, 1931, 128, 1040—1041).—For a certain range of temp. 3 pressure limits of ignition exist for a stoichiometric mixture of CH_4 and O_2 . Details are given for such a mixture in a cylindrical quartz vessel 3 cm. in diameter.

L. S. THEOBALD.

Flame temperatures of mixtures of air with methane and oxygen, with methane and hydrogen, and with methane and acetylene. G. W. JONES, B. LEWIS, and H. SEAMAN (*J. Amer. Chem. Soc.*, 1931, 53, 3992—4001; cf. A., 1931, 572).—Flame temp. for mixtures in various proportions have been determined, the max. temp. in each case being reached with a mixture slightly on the rich side. The max. flame temp. of any mixture of CH_4 and H_2 with CH_4 and C_2H_2 can be calc. by the additive principle from the max. flame temp. of the constituent mixtures. R. H. CHERRY (c).

Rate of formation of bromine chloride from its elements in the gas phase. W. JOST (*Z. physikal. Chem.*, 1931, B, 14, 413—420).—At room temp. the reaction is bimol. and homogeneous, with a heat of activation of about 14 kg.-cal. R. CUTHILL.

System iodine-excess of sodium hydroxide. E. CARRIÈRE and JULLIARD (*Compt. rend.*, 1931, 193, 1426—1428).—The formation of IO' is accelerated by increase of alkali and by rise of temp., whilst the transformation into IO_3' is little affected by either. At 50° the formation of IO' is practically instantaneous. The results agree with those of Schwicker (cf. A., 1895, ii, 213). C. A. SILBERRAD.

Saponification of di-esters M. RITCHIE (*J.C.S.*, 1931, 3112—3125).—Vals. are reported of k_1 and k_2 , the first and second stage velocity coeffs., for Et succinate, malonate, and substituted malonates in H_2O and H_2O -EtOH mixtures at 0°, 15°, and 25°. Two general ways of calculating k_1 from the data are developed; k_2 was calc. from measurements on the mono-ester by the classical bimol. equation. Increasing EtOH content reduces k_1 and k_2 , which tend to zero for pure EtOH, and also reduces k_1/k_2 .

C. W. DAVIES.

Kinetic salt effect in methyl alcohol solutions. Reaction between sodium bromoacetate and sodium methoxide. A. N. KAPPANNA and H. W. PATWARDHAN (*J. Indian Chem. Soc.*, 1931, 8, 541—548).—The rate of reaction of $\text{CH}_2\text{Br}-\text{CO}_2\text{Na}$ with NaOMe in MeOH solution at 50° and 60° increases with increasing ionic concn. in accordance with Brönsted's theory, but the results do not agree even

approx. with the Debye-Hückel theory. The temp. coeff. of the bimol. velocity coeff. is independent of the ionic concn., but has a much higher val. (3.273) than is usual for aq. solutions. The reaction velocity is increased by adding NaBr. E. S. HEDGES.

Kinetics of the inversion process in dilute solutions of sucrose in presence of hydrochloric acid. A. N. KAPPANNA and J. G. SHRIKHANDE (*J. Indian Chem. Soc.*, 1931, 8, 557—569).—The inversion of sucrose in dil. solution at 35° and 45° has been followed by chemical analysis. At const. concn. of HCl (0.1N) the velocity coeff. increases with the concn. of sucrose (0.002924M—0.2924M), but not so greatly as the rate of increase of a_{H^+} . The temp. coeff. is 3.505, independently of the concn. When the concn. of sucrose is const. at 0.02924M, the velocity coeff. is proportional to the concn. of HCl up to 0.01N and then increases at a greater rate. The velocity coeff., V , up to 0.12N-HCl is expressed by $0.434V = 1.376 \times 10^{-2} + 0.84 \times 10^{-2}C$, where C is the concn. of HCl. The effect of KCl, NaCl, and LiCl (0.10—3.0N) on the velocity coeffs. is expressed by $k - k_0 e^{aC}$, where a , the characteristic const., is 0.135 for KCl, 0.1564 for NaCl, and 0.1767 for LiCl. The increase in a_{H^+} does not account for the effect of the neutral salts. E. S. HEDGES.

Significance of velocity measurements in relation to the benzene substitution problem. D. H. PEACOCK (*Nature*, 1932, 129, 57).—Mainly a discussion. In the reaction between *o*-, *m*-, or *p*-toluidine and CH_3PhCl the energy of activation of the *o*- is higher than that for the *p*-compound.

L. S. THEOBALD.

Origin of explosive wave in mercury fulminate. M. PATRY and P. LAFFITTE (*Compt. rend.*, 1931, 193, 1339—1342).—By using trains of fulminate of definite rectangular cross-section and ignited as before (cf. A., 1931, 1020) it is found that the distance from the point of ignition at which an explosive wave is formed is, for the same cross-section, greater as the height is less, that no such wave is formed if the cross-section is less than 30 sq. mm., and that the velocity of the wave increases with, but not proportionally to, the cross-section.

C. A. SILBERRAD.

Dilution theory of detonation. I. A. J. DUFF (*J. Inst. Petrol. Tech.*, 1931, 17, 697—737).—A mathematical study of the auto-ignition theory of "pinking."

N. H. HARTSHORNE.

Behaviour of atomic hydrogen. III. Mercury hydride. A. KLEMENC and F. PATAT (*Z. physikal. Chem.*, 1931, 158, 65—77).—The vals. for the $v. p.$ of Hg at 7—10° obtained by the gas-saturation method when H_2 under a pressure of 1 atm. or a mixture of H_2 and N_2 in which the partial pressure of the H_2 is 1—2 mm. is used as the inert gas and the evaporating Hg is irradiated with the light from a Hg-vapour lamp are the same as those obtained with pure N_2 without irradiation. It is concluded that the velocity coeff. of the unimol. decomp. of HgH must be of the order of 10^{11} mols. per c.c. per sec., and that the reactions in the system Hg- H_2 under the influence of the resonance line 2536 Å. are brought about by at. H, not by HgH. R. CUTHILL.

Reactions in the solid state at high temperatures. IX. Variation of the reaction velocity with the relative proportions and method of preparation of the components and with the presence of admixtures. W. JANDER and E. HOFFMANN (Z. anorg. Chem., 1931, 202, 135—153).—The velocities of the reaction between BaCO_3 and SiO_2 and between CaCO_3 and MoO_3 have been studied under varying conditions of origin and purity of the reactants and in presence of 5% of TiO_2 or CaF_2 , or of WO_3 or NaCl , respectively. Variation of the method of prep. of the reactants is without influence on the amount of energy, q , necessary to produce migration of the atoms in the lattice, although it alters the number of points at which diffusion takes place; the presence of admixtures produces small variations of q and considerable change of the number of active centres. q is dependent on the relative proportions of the reactants only if more than one compound is formed in the system. H. F. GILLBE.

Passivity of iron. U. R. EVANS (Nature, 1931, 128, 1062—1065).—A summary.

L. S. THEOBALD.

Influence of metallic impurities on the rate of dissolution of base metals. G. TAMMANN and F. NEUBERT (Z. anorg. Chem., 1931, 201, 225—244).—The rate of evolution of H_2 from dil. acids by Zn, Fe, or Al can be expressed by $v=at+bt^2$, where v is the vol. liberated at time t . The const. a is characteristic of the base metal and is not affected by impurities, whereas b represents the accelerating influence of local galvanic elements, and usually increases with increasing concn. of a nobler metal, with the exception of Si or Sn in Al. The rate of dissolution of Fe-C alloys is almost const. until the pearlite concn. is exceeded, when the rate increases rapidly with C content. Zn and Fe dissolve in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at a const. rate which is but little affected by foreign metals. F. L. USHER.

Attack of platinum and tungsten by iodine. G. VAN PRAAGH and E. K. RIDEAL (Proc. Roy. Soc., 1931, A, 134, 385—404).—The metals were in the form of wire, the Pt being 0.007 cm. and the W 0.005 cm. in diameter. With Pt no surface attack occurs at relatively low temp., but dissociation of mol. I takes place at about 1300° abs. At I attacks Pt at 1400°, forming volatile PtI and PtI_2 . The abs. rates of the reactions are discussed and the heat of adsorption of at. I in Pt is calc. to be 53,700 g.-cal. per mol. The emissivity of Pt is unaltered by the action of I up to 1700° abs.; therefore this method cannot detect the unimol. adsorbed layer of the complex PtI formed at all temp. below 1560° abs. The difference between the metals was anticipated from the difference between their work functions. At low temp. W is attacked by I, but at high temp. dissociation of I occurs more readily on the Pt.

L. L. BIRCUMSHAW.

Topochemistry of corrosion and passivity. II. Investigation of initial step in corrosion of soft iron. E. PIETSCH, B. GROSSE-EGGEBRECHT, and W. ROMAN (Z. physikal. Chem., 1931, 157, 363—388; cf. A., 1931, 1374).—A homogeneous surface of soft Fe brought in contact with aq. H_2O_2

at room temp. becomes passive, and neither rusts nor decomposes the H_2O_2 . Addition of AcOH or barbituric acid has no effect, but rusting starts some time after addition of HCl. When the passive Fe is immersed in boiled-out H_2O rust appears, after a period of induction, at the grain boundaries, and spreads autocatalytically over the grain surfaces. The wt. of Fe dissolved from a homogeneous surface by dil. H_2SO_4 is a linear function of the length of grain boundary in the surface. It is therefore concluded that the initial step in corrosion is the adsorption of the corroding medium at grain boundaries or other active linear discontinuities, such as the boundary between the Fe and an indifferent substance of high surface tension, e.g., paraffin wax. It is suggested that in rusting the H_2O is adsorbed and the OH is drawn into a closer resonance union with the Fe than with the H, which leads to the formation of $\text{Fe}(\text{OH})_2$. In presence of H_2O_2 the active centres are blocked by adsorbed O, formed by a minute decomp. of H_2O_2 , the adsorption of H_2O thus being prevented. An Fe surface which is not homogeneous, i.e., has been insufficiently polished, or contains cavities, is attacked by H_2O_2 at once, presumably because it possesses centres sufficiently active to adsorb H_2O as well as O. R. CUTHILL.

Reactions between gas and solid. I. Velocity of absorption of moisture by quicklime. T. AONO (Bull. Chem. Soc. Japan, 1931, 6, 294—301).—The velocity of absorption of H_2O from damp air by CaO has been studied under various conditions of humidity and temp. The first product of the reaction is $\text{Ca}(\text{OH})_2$, which then adsorbs more H_2O . D. R. DUNCAN.

Decomposition of hydrogen peroxide by traces of metallic salts. H. TATU (Tiba, 1931, 9, 473—477).—Ca salts had practically no effect. In neutral solution the decomp. after 21 days with additions of 0.05 or 0.10 g. per litre (2.5% H_2O_2), respectively, of metals was: Cu 72.4, 76.4; Mn 43.2, 49.6; Fe 50.4, 66.4%. In acid solution it was: Cu 38.4, Mn 22, Fe 81.2%. In alkaline solution decomp. in presence of Mn is practically complete in 20 min.

CHEMICAL ABSTRACTS.

Interaction between copper oxide and neutral salt solutions. M. P. V. IYER (J. Indian Chem. Soc., 1931, 8, 613—618).—When CuO is shaken with neutral salt solutions, OH^- is adsorbed primarily and the complex reacts with the neutral salt with the liberation of alkali. The total amount of alkali liberated is 1.3904×10^{-6} g.-ion per g. of CuO. The nature of the cation has little influence on the amount of alkali liberated, but the valency of the anion is important and follows the series $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. The liberation of alkali is closely connected with the electrokinetic behaviour of CuO in contact with different electrolytes. E. S. HEDGES.

Catalytic effect of ferricyanide in the oxidation of unsaturated compounds by oxygen. G. P. WRIGHT, J. B. CONANT, and S. E. KAMERLING (J. Biol. Chem., 1931, 94, 411—413).—In Na_2CO_3 solution oleic acid is not oxidised by ferricyanide in the absence of O_2 , neither is ferrocyanide oxidised by O_2 in the same medium. The catalytic oxidation

of oleic acid (A., 1931, 758) is therefore not a cyclic process, in which the latter reduces ferricyanide, and the ferrocyanide produced is re-oxidised. The oxidation may be a chain reaction initiated by ferrieyanide.

A. COHEN.

Constitutional factors controlling prototropic changes in carbonyl compounds. I. Relative speeds of enolisation of acetone and bromoacetone and the effect of the acid catalyst. E. D. HUGHES, H. B. WATSON, and E. D. YATES (J.C.S., 1931, 3318—3324).—The mechanism of bromination is the same for bromoacetone and COMe_3 , so velocity measurements give the speed of enolisation. This is greater for the Br-compound in absence of catalyst, but is far less accelerated by acid. On the assumption that enolisation involves (a) ionisation of an α -H atom and (b) co-ordination of the CO-oxygen with H_2O or H_3O^+ , the two effects are explained by electron drift; the Br favours process (a), but hinders the co-ordination with a positive group.

C. W. DAVIES.

So-called autoxidation of cysteine. C. A. ELVEHJEM (Science, 1931, 74, 568—569).—A criticism (cf. A., 1931, 1246). The so-called autoxidation of cysteine may be due to the presence of Cu.

L. S. THEOBALD.

Reaction of active nitrogen with hydrogen atoms at metal surfaces. J. K. DIXON and W. STEINER (Z. physikal. Chem., 1931, B, 14, 397—406; cf. A., 1930, 1378).—The formation of NH_3 from active H and N is greatly accelerated by an Fe, Ni, or Cu surface, whereas the rate of formation of N_2H_4 is considerably reduced. The most satisfactory explanation of the reaction is that some of the adsorbed H atoms recombine, but others react with N atoms impinging on the surface from outside, $\text{N} + \text{H} = \text{NH}$. The NH mols. then undergo the reactions $\text{NH} + \text{H}_2 = \text{NH}_3$, $\text{NH} + \text{NH} = \text{N}_2 + \text{H}_2$, $\text{NH} + \text{H} = \text{N} + \text{H}_2$, $\text{NH} + \text{N} = \text{H} + \text{N}_2$, $\text{NH} + \text{H} = \text{NH}_2$, of which the first is the most probable, and the NH_2 formed in the last reacts as follows: $\text{NH}_2 + \text{NH}_2 = \text{N}_2\text{H}_4$, $\text{NH}_2 + \text{H} = \text{NH}_3$. The yield of NH_3 is independent of the area of catalyst surface.

R. CUTHILL.

Oxide hydrates and active oxides. XLVII. Active states of metallic oxides. E. ROSENKRANZ (Z. physikal. Chem., 1931, B, 14, 407—412; cf. A., 1931, 1235).—The activity in catalysing the decomp. of MeOH and of aq. AgNO_3 of ZnO which has been partly converted into ZnO by heating is not a linear function of the ZnO content, but may pass through a max. and fall again as the proportion of ZnO increases. These observations are taken to mean that the ZnO formed directly from the ZnC_2O_4 is unstable, and passes through a series of states of differing activity before reaching the final stable state.

R. CUTHILL.

Blanc's alumina. N. PARRAVANO (Mem. R. Accad. Ital., 1930, 1; Chem. Zentr., 1931, i, 2521; cf. A., 1930, 437).— Al_2O_3 obtained by prolonged heating of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at 350—450° (Blanc's alumina) is a good catalyst for converting EtOH into Et₂O. EtOH is unchanged, however, when Al_2O_3 in which the at. distances have been reduced by heating is used.

L. S. THEOBALD.

Catalytic oxidation of sulphur dioxide in the presence of tin vanadate. E. B. MAXTED and N. J. HASSID.—See B., 1932, 20.

[Catalytic] preparation of acetic acid from methyl alcohol and carbon monoxide. E. A. SHILOV.—See B., 1932, 12.

[Catalytic] synthesis of methyl alcohol from carbon monoxide and hydrogen under pressure. V. A. PLOTNIKOV and K. N. IVANOV.—See B., 1932, 11.

Oxidation of ethyl alcohol by air in presence of carbon-copper catalysts. MARTINEAU (Compt. rend., 1931, 193, 1189—1192).—A catalyst prepared by action of aq. NH_3 on an intimate mixture of C with Cu hydroxide or carbonate, drying at 140°, and heating at 250° in a covered vessel to liberate Cu, brings about oxidation of EtOH to MeCHO by air at 63°, the max. catalytic activity being observed with a ratio Cu:C of 1:2—3 according to the temp. Activated C or Cu alone or in admixture does not bring about the oxidation below 110°.

H. A. PIGGOTT.

Catalytic oxidation of ethyl alcohol. A. R. DAY (J. Physical Chem., 1931, 35, 3272—3279; cf. A., 1930, 1381).—In the vapour-phase oxidation of EtOH with a Ag catalyst the presence of a small quantity of Sm_2O_3 in the catalyst slightly increases the yield of MeCHO at a low catalyst temp. Higher yields were obtained in a one-step oxidation than have previously been attained by similar methods. The yield was 79.5% with a catalyst at 370° containing 2.7858 g. Ag and 0.0075 g. Sm_2O_3 .

F. L. BROWNE (c).

Vapour-phase esterification in presence of silica gel. H. C. TIDWELL and E. E. REIN (J. Amer. Chem. Soc., 1931, 53, 4353—4358; cf. A., 1924, ii, 667).—The esterification of EtOH and AcOH has been studied at 150—300°. The limiting conversion obtained with an equimol. mixture of alcohol and acid was approached from the other side of the equilibrium point by the hydrolysis of an acetate- H_2O mixture, the average conversion being about 85% at 150° and 75% at 300°. These data indicate that the equilibrium const. varies somewhat with temp.

C. J. WEST (c).

Beryllium. III. Electrolysis of solutions of beryllium compounds in liquid ammonia. H. S. BOOTH and G. G. TORREY (J. Physical Chem., 1931, 35, 3111—3120; cf. A., 1931, 1249).—Be obtained by electrolysis of solutions of BeCl_2 or $\text{Be}(\text{NO}_3)_2$ in liquid NH_3 is so pure that it can be dissolved in ordinary reagents only with difficulty. The decomp. voltage of the BeCl_2 solution is approx. 3.5 volts.

I. J. PARTON (c).

Electrodeposition of metals from anhydrous ammonia. H. S. BOOTH and M. MENAHEM (J. Physical Chem., 1931, 35, 3303—3321).—Cu, Ag, Au, Be, Zn, Cd, Hg, Tl, Sn, Pb, As, Cr, Mn, Fe, Ni, Co, Pd, and Pt can be successfully deposited from anhyd. NH_3 solutions at the b. p. Al, Th, Bi, Sb, Mo, and W do not deposit either at the b. p. or at room temp. under pressure. A cell for high-pressure electrodeposition is described.

R. H. CHERRY (c).

Electrodeposition of iron, copper, and nickel alloys from cyanide solution. I. L. E. STOUT and C. L. FAUST.—See B., 1932, 66.

Effect of mercury in zinc cyanide plating solutions. M. DE K. THOMPSON and W. E. CHARLES.—See B., 1932, 66.

Stability of cadmium cyanide plating solutions. S. WERNICK.—See B., 1932, 67.

Reaction at the quinhydrone electrode in methyl alcohol. A. MACFARLANE (J.C.S., 1931, 3212—3218).—The rate of fall in potential of the quinhydrone electrode in MeOH solutions of HCl is explained by a slow oxidation of the HCl to Cl_2 by dissolved O_2 . This is followed by substitution: $\text{Cl}_2 + \text{Q} \rightarrow \text{HCl} + \text{QCl}$, and $\text{QCl} + \text{HQ} \rightleftharpoons \text{HQCl} + \text{Q}$, where Q and HQ are respectively benzoquinone and quinol.

C. W. DAVIES.

Reactions in the brush discharge. A. P. DAVIS (J. Physical Chem., 1931, 35, 3330—3352).— COMe_2 is entirely converted into gaseous products, the principal reaction being $\text{COMe}_2 = \text{C}_2\text{H}_6 + \text{CO}$; H_2 , C_2H_4 , and C_2H_2 are formed by decomp. of the C_2H_6 . The COMe_2 undergoes little condensation, but yields keten by pyrolysis. From C_6H_6 , which forms gas much more slowly than COMe_2 , there are obtained a resinous substance, $(\text{C}_6\text{H}_5)_n$, and Ph_2 , without, however, the H eliminated in the formation of these compounds appearing as such in the products of reaction.

R. H. CHERRY (c).

Chemical action in the glow discharge. VIII. Effect of cathode material. P. D. KUECK and A. K. BREWER (J. Physical Chem., 1931, 35, 3207—3213; cf. A., 1931, 919).—The rate of synthesis of H_2O and of NH_3 in the negative glow is in general directly proportional to the normal cathode falls of potential for the various metals used as cathodes, which is attributed to an increase in positive ion production with increased electron acceleration. The anode material has no effect on the rate of reaction.

P. H. EMMETT (c).

Chemical action of the electric discharge. V. Influence of the nature of the electrodes on the production of nitric oxide in the electric arc. E. BRINER, J. CORBAZ, and C. WAKKER (Helv. Chim. Acta, 1931, 14, 1307—1314).—By coating the platinum electrodes with paraffin mixed with BaCO_3 or CaCO_3 , and heating, adherent oxide deposits are obtained and the yield of NO (per kv.-amp.-hr.) is increased by 20—40%. Ni electrodes could not be similarly covered. With a Li phosphate deposit the increase of yield is up to 71%. The yields obtained with Cu and Ag electrodes are increased by 50—70% if the electrodes are alloyed with Li or Ca (0.8—4%).

H. F. GILLBE.

Photochemical kinetics of hydrogen-chlorine reaction. Formation of hydrogen chloride on absorption of light in the banded region of the chlorine spectrum. E. HERTEL (Z. physikal. Chem., 1931, B, 14, 443—456).—The reaction velocity is given by $dx/dt = k[\text{H}_2][\text{Cl}_2]\{n[\text{H}_2] + p[\text{Cl}_2] + q[\text{HCl}]\}$, where $n=1$, $p=3$, and $q=0.5$, which becomes $dx/dt = k_1[\text{H}_2][\text{Cl}_2]^2$ when there is a great excess of Cl_2 , and $dx/dt = k_2[\text{H}_2]^2[\text{Cl}_2]$ when the H_2 is present

in great excess. The yield per quantum is of the order of 10^4 — 10^5 . O_2 retards the reaction, the velocity equation becoming $dx/dt = \{k[\text{Cl}_2]^2/[\text{O}_2]\}\{n[\text{H}_2] + p[\text{Cl}_2] + q[\text{HCl}]\}$. The general velocity equation may be deduced by assuming that the primary reaction is the formation of excited Cl_2 mols. by absorption of light. A small fraction of these is dissociated by impact with H_2 , Cl_2 , and HCl mols., the efficiencies of which in effecting dissociation are in the ratio 1:3:0.5. The Cl atoms then react as follows: $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$, $\text{H} + \text{Cl}_2 = \text{HCl} + \text{Cl}$. If O_2 terminates the reaction chains by combining with the H atoms, the observed velocity equation is accounted for.

R. CUTHILL.

Photochemical formation of ozone sensitised by zinc oxide. G. JUNG and E. KUNAU (Z. physikal. Chem., 1931, B, 15, 45—50).—The photochemical formation of O_3 from O_2 in presence of ZnO (B., 1922, 392) occurs only when the ZnO has been prepared by ignition of $\text{Zn}(\text{NO}_3)_2$ and contains a little undecomposed nitrate. $\text{Zn}(\text{NO}_3)_2$ sensitises the reaction if hydrated, but not if anhyd. The sensitisation has no relation to the visible luminescence of ZnO .

R. CUTHILL.

Reaction $5\text{As}_2\text{O}_3 \rightarrow 3\text{As}_2\text{O}_5 + 4\text{As}$ as a pyrochemical and photochemical process. G. G. REISSAUS (Z. angew. Chem., 1931, 44, 959—962).—The mechanism of the thermal conversion of arsenite into arsenate is invariably based on the reaction $5\text{As}_2\text{O}_3 \rightarrow 3\text{As}_2\text{O}_5 + 4\text{As}$, and does not involve direct oxidation by atm. O_2 . In air, As_2O_3 is formed subsequently from the As liberated, and then undergoes further decomp.; the As thus acts as an O carrier. By heating As_2O_3 or an arsenite under pressure or in vac., pure As may be prepared. Commercial Pb arsenite, as well as specimens prepared by ordinary methods in the laboratory, are not photosensitive, but a dry mixture of PbO and As_2O_3 is remarkably sensitive, As being liberated in the reaction. It is probable that the salt as ordinarily prepared is $3\text{Pb}(\text{OH})_2 \cdot \text{As}_2\text{O}_3$, since if it is prepared from As_2O_3 and PbO in the "nascent" state, e.g., by heating $\text{Pb}(\text{OH})_2$ with As_2O_3 and dil. NaOH solution, it is photosensitive. No other metallic arsenite has been found to be photosensitive.

H. F. GILLBE.

Photographic emulsion; silver ion-gelatin equilibrium. B. H. CARROLL and D. HUBBARD (Bur. Stand. J. Res., 1931, 7, 811—825).—Measurements of the equilibrium between Ag^+ and gelatin by means of a Ag electrode have shown a strong selective combination of Ag^+ with gelatin. In the photographic emulsion, the gelatin may cause large changes in $[\text{Ag}^+]$. No combination of gelatin with $\text{Ag}(\text{NH}_3)_2^+$ was observed. Prolonged washing of AgBr - or AgCl -gelatin emulsions causes appreciable hydrolysis of the Ag halide, leaving an excess of Ag in combination with the gelatin.

E. S. HEDGES.

Chemical reactions induced by light. III. VECCHIOTTI and G. ZANETTI (Gazzetta, 1931, 61, 798—802).—In a mixture of PhMe and PhNO_2 after exposure to sunlight for 5 months in a sealed tube NH_3 , Ph and azoxybenzene are found in addition to BzOH and p -aminophenol (A., 1930, 1180). The

mechanism of the reaction is explained. No reaction is caused by the sun's heat when light is excluded.

E. E. J. MARLER.

Danger of explosion of alkali chlorates, especially sodium chlorate, from strong mechanical shocks. LENZE, METZ, and RUBENS (Jahrb. Chem.-tech. Reichsanst., 1931, 8, 1—3; Chem. Zentr., 1931, i, 2446).—Pure NaClO_3 and KClO_3 are not exploded by intense blows or by rubbing. In contact, but not necessarily mixed, with inflammable org. matter explosions can be produced by such means.

L. S. THEOBALD.

Principles of genetic development of material. VI. Reactions within small bodies. Copper complexes. V. KOHLSCHÜTTER [with H. NITSCHMANN] (Helv. Chim. Acta, 1931, 14, 1215—1246).—The influence of temp. and concn. on the reaction between Cu and $\text{C}_2\text{O}_4^{2-}$ has been studied, together with the effect of the subsequent gradual addition of one of the reactants. The varieties of appearance and particle size of the ppts. are described. The pptn. is accelerated by H_2SO_4 , without change of the cryst. form, but other additions cause a change of form. Some of the ppts. appear as somatoids, others as well-defined crystals, and others as amorphous powders, but the X-ray diagrams are all identical. The somatoids are probably developed from gel droplets, and the same may be true of the cryst. types, although the formation of these from the somatoids has not been observed. The production of the various forms is not a progressive process; each form is produced independently from the original materials. Formation of $\text{Cu}(\text{OH})_2$ from the somatoids takes place without change of form, but the cryst. forms are destroyed during this process; somatoid $\text{Cu}(\text{OH})_2$ may be reconverted into somatoids of CuC_2O_4 . If the $\text{Cu}(\text{OH})_2$ is treated with 10% H_2O_2 , and the resulting $\text{CuO}_2 \cdot \text{H}_2\text{O}$ reconverted into $\text{Cu}(\text{OH})_2$, a much more reactive material is obtained, owing to destruction by the H_2O_2 of the central structure of the somatoid. Similar experiments have been made with $\text{Cu}(\text{OH})_2$ derived from schonite and from basic nitrate and carbonate. The comparative catalytic activities of specimens of $\text{Cu}(\text{OH})_2$ of different origins on the decomp. of H_2O_2 have been determined; the activity is governed, not merely by the particle size, but also by the internal structure of the particles; it is scarcely influenced by the nature of the envelope. The activity of the somatoids diminishes as the particles age, owing to structural changes, and is altered also by destruction of the internal orientation by mechanical means. The reaction involves the reversible formation of a Cu peroxide. The general nature of reactions within small particles, as opposed to reactions at the surface and in the bulk of the material, is discussed.

H. F. GILLBE.

Comparison of copper oxalate and polymethylene precipitates. H. W. KOHLSCHÜTTER (Helv. Chim. Acta, 1931, 14, 1246—1249).—A discussion of the preceding paper in relation to other published work (cf., e.g., A., 1931, 198).

H. F. GILLBE.

Fluoroberyllates and their analogy with sulphates. I. N. N. RÅY (Z. anorg. Chem., 1931,

201, 289—300).—A close analogy of fluoroberyllates with sulphates is indicated by the physical properties of corresponding salts. Isomorphism of the Ba salts has been established by X-ray analysis. The following compounds are described: $\text{Li}_2\text{BeF}_4 \cdot \text{H}_2\text{O}$, d_4^{20} 1.944; Rb_2BeF_4 , d_4^{20} 3.243; Cs_2BeF_4 , d_4^{20} 4.213; Ti_2BeF_4 , d_4^{20} 6.650; BaBeF_4 , d_4^{20} 4.170; PbBeF_4 , d_4^{20} 6.135; Ag_2BeF_4 ; $\text{N}_2\text{H}_5\text{BeF}_4$; $(\text{NMe}_4)_2\text{BeF}_4$; $\text{NMe}_4\text{HBeF}_4$. F. L. USHER.

Azides of the alkaline-earth metals. HAYD, GOETZE, SELLE, KOENEN, SCHMIDT, and BECHER (Jahrb. Chem.-tech. Reichsanst., 1931, 8, 102—108; Chem. Zentr., 1931, i, 2447).—An investigation of the explosibility of Ca, Ba, and Sr azides under different conditions shows that Ca azide is a much stronger explosive than those of Ba and Sr, which are approx. equal. Dry Ba azide can be transported in cardboard boxes in quantities up to 500 g., and with a H_2O content of 10% it is no longer a dangerous explosive.

L. S. THEOBALD.

Synthesis of β -calcium metasilicate (wollastonite) by a reaction between solids. H. EHRENBURG (Z. physikal. Chem., 1931, B, 14, 421—434).—The formation of wollastonite on heating compressed pastilles of a mixture of calespar and amorphous SiO_2 at 750—1000° has been demonstrated by X-ray examination.

R. CUTHILL.

Hydrothermal synthesis of calcium silicates under ordinary pressure. II. S. NAGAI (J. Soc. Chem. Ind. Japan, 1931, 34, 418—422B; cf. B., 1932, 25).—Hydrothermal treatment of a $3\text{CaO} : 1\text{SiO}_2$ mixture for 1 hr. at temp. between 600° and 1100° gives $3\text{CaO} \cdot 2\text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$, the proportion of the latter increasing with rise of temp. to approx. 100% at 900°. A 1 : 2 mixture under these conditions gives $\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot 2\text{SiO}_2$, the proportion of the latter reaching 100% between 900° and 1000°, above which some $2\text{CaO} \cdot \text{SiO}_2$ is formed. Treatment of a 1 : 1 mixture for 5 hr. at 900° and 1000° partly decomposes the $2\text{CaO} \cdot \text{SiO}_2$ first formed into a less basic product, whilst under the same conditions 2 : 1 and 3 : 1 mixtures yield $2\text{CaO} \cdot \text{SiO}_2$ almost exclusively.

N. H. HARTSHORNE.

Decomposition of tricalcium silicate in the temperature range 1000—1300°. E. T. CARLSON (Bur. Stand. J. Res., 1931, 7, 893—902).—The decomp. of $3\text{CaO} \cdot \text{SiO}_2$ into $2\text{CaO} \cdot \text{SiO}_2$ and CaO , measured by determining the free CaO , is greatest at about 1175°; at 1300° it is almost negligible. The decomp. appears to be autocatalytic, the rate being increased by the presence of CaO or $2\text{CaO} \cdot \text{SiO}_2$. Exposure to moist air promotes the decomp. Freshly-ignited $3\text{CaO} \cdot \text{SiO}_2$, containing a min. amount of free CaO , decomposes very slowly. Gypsum accelerates the decomp., probably through the formation of CaO by dissociation.

E. S. HEDGES.

Calcium chromo-, selenio-, and sulpho-aluminates. (Mlle.) FORET (Compt. rend., 1931, 193, 1423—1425).—The double salts $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaA}_2 \cdot 30\text{H}_2\text{O}$, where $\text{A} = \text{CrO}_4$, SeO_4 , or SO_4 (cf. A., 1915, ii, 50), are obtained by methods similar to those previously described (cf. A., 1930, 1386, 1537). On mixing clear solutions of calcium

aluminate, CaA_2 , and Ca(OH)_2 , the cryst. double salt is pptd. $[\text{CaO}]$ should be $>3[\text{Al}_2\text{O}_3]$, $[\text{CaA}_2] < 30[\text{Al}_2\text{O}_3]$, $[\text{CaCrO}_4] < 0.05M$, and $[\text{CaSeO}_4] < 0.32M$. The phase relations are discussed. C. A. SILBERRAD.

Double compound of aluminium chloride with hydrogen cyanide. L. E. HINKEL and R. T. DUNN (J.C.S., 1931, 3343).—HCN and finely-divided AlCl_3 give the compound $\text{AlCl}_3 \cdot 2\text{HCN}$ as a white solid unstable in moist air and sol. in dry Et_2O .

C. W. DAVIES.

Double sulphates of metals of the rare earths and of the alkali metals. XIV. Sulphates of praseodymium and sodium. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1931, [vi], 14, 69—71; cf. A., 1930, 1387).—The solubility isotherm at 25° shows that only two double sulphates are formed, $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $4\text{Pr}_2(\text{SO}_4)_3 \cdot 5\text{Na}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$. Some properties of these compounds are described. O. J. WALKER.

Thermal decomposition of the oxalates and nitrates of lanthanum, cerium, praseodymium, neodymium, and samarium in an atmosphere of carbon dioxide. T. SOMIYA and S. HIRANO (J. Soc. Chem. Ind. Japan, 1931, 34, 459—461b).—Decomp. proceeds according to the schemes

$\text{M}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O} \rightarrow \text{M}_2(\text{C}_2\text{O}_4)_3 \rightarrow [\text{M}_2(\text{C}_2\text{O}_4)_3] \rightarrow$
 $[\text{M}_2\text{O}_3, 2\text{CO}_2] \rightarrow \text{M}_2\text{O}_3 \cdot \text{CO}_2 \rightarrow \text{M}_2\text{O}_3$, and $\text{M}(\text{NO}_3)_3 \rightarrow$
 $\text{MO}(\text{NO}_3) \rightarrow \text{M}_2\text{O}_3 \cdot \text{CO}_2 \rightarrow \text{M}_2\text{O}_3$, where M is La, Pr, Nd, or Sm. The temp. of decomp. of $\text{M}_2\text{O}_3 \cdot \text{CO}_2$ rises with increasing basicity of M. $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3$ are converted into CaO_2 .

N. H. HARTSHORNE.

Activation of carbon by means of carbon dioxide. P. P. KOSAKOVITSCH and M. A. ISMAILOV (Kolloid-Z., 1931, 57, 294—302).—The activation of C by CO_2 is greatest after a certain duration of treatment, further treatment reducing the activity. The optimal duration is decreased by rising temp. and increasing velocity of the CO_2 stream. Differences in the behaviour of sugar- and wood-charcoals can be ascribed to the variation of ash content and porosity. Small quantities of Al_2O_3 accelerate the reaction between C and CO_2 , but greater amounts have less influence, probably through forming a protective film. E. S. HEDGES.

Halogen compounds of non-metals. I. Silicon tetrabromide. II. Boron tribromide. E. POHLAND (Z. anorg. Chem., 1931, 201, 265—281, 282—288).—I. SiBr_4 exists in a tetragonal modification, m. p. 2.4° , and a cubic, m. p. 5.2° . Density, refractive index, and heat of formation have been redetermined, and the chemical behaviour towards various compounds has been studied.

II. Physical consts. of BBr_3 have been redetermined and its chemical reactivity has been examined. Compounds $\text{BBr}_3 \cdot \text{HCN}$, m. p. 70° , and $\text{BBr}_3 \cdot \text{AgCN}$, indicating the co-ordination no. 4 for B, have been prepared. F. L. USHER.

Titanium nitride. S. UMEZU (Proc. Imp. Acad. Tokyo, 1931, 7, 353—356).—When fine-grained TiO_2 was heated with C in a slow stream of N_2 at different temp. for 1—4 hr., the % reduction to Ti_2O_3 reached a max. of about 43 at 1100° , above which it decreased

and the % formation of TiN increased to about 90 at 1300° . These yields were lower when a coarser TiO_2 was used. TiO is much more readily converted into TiN by a stream of N_2 than is Ti_2O_3 .

N. H. HARTSHORNE.

Action of ammonia and amines on germanium tetraiodide. T. KARANTASSIS and L. CAPATOS (Compt. rend., 1931, 193, 1187—1189).— GeI_4 is prepared by dissolving GeO_2 in hot conc. aq. HI, and crystallising the evaporated product from CHCl_3 . By passing NH_3 into, or adding liquid NH_3 to, a CCl_4 solution of the other amines to, a CCl_4 solution of GeI_4 the following compounds are obtained: $\text{GeI}_4 \cdot 8\text{NH}_3$; $\text{GeI}_4 \cdot 6\text{NH}_4\text{Et}$; $\text{GeI}_4 \cdot 10\text{NH}_4\text{Et}_2$; $\text{GeI}_4 \cdot 5\text{NEt}_3$; $\text{GeI}_4 \cdot 4\text{NH}_2\text{Ph}$; $\text{GeI}_4 \cdot 6(o\text{-C}_6\text{H}_4\text{Me})\text{NH}_2$; and $\text{GeI}_4 \cdot 10\text{C}_9\text{H}_7\text{N}$. All are white cryst. powders except the quinoline compound, which is yellow.

C. A. SILBERRAD.

Preparation of lead disulphide by reaction between lead mercaptides and sulphur. W. E. DUNCAN and E. OTT (J. Amer. Chem. Soc., 1931, 53, 3940—3949; cf. A., 1930, 1405).—Lead disulphide, PbS_2 , a brown solid, is formed by the action of S on sec.-butyl Pb mercaptide in C_6H_6 solution, the ratio S : Pb being greater than 7. It decomposes into PbS and S at room temp., and with HCl yields H_2S_2 .

M. G. MOORE (c).

Lead suboxide. P. PASCAL and P. MINNE (Compt. rend., 1931, 193, 1303—1305).—That the product obtained by the decomp. of PbC_2O_4 in vac. at 275° (cf. A., 1917, ii, 141) is Pb_2O is confirmed by the fact that the magnetic susceptibility ($\times 10^6$) thereof is -0.09 as compared with -0.12 and -0.19 , the susceptibilities of Pb and PbO , respectively. Reduction of PbO by $\text{NHPh} \cdot \text{NH}_2$ (cf. A., 1928, 721) yields a mixture of Pb and Pb_2O . C. A. SILBERRAD.

Mechanism of precipitation processes. VII. Thiocyanate compounds of lead. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1931, 202, 62—72).—Pptn. of KCNS solution with a 10% excess of Pb(OAc)_2 solution yields, irrespective of concn. and temp., Pb(OH)CNS ; in acid solution, or if the ratio Pb(OAc)_2 : KCNS is less than 2, Pb(CNS)_2 is pptd. If Pb(CNS)_2 is boiled with NH_4OAc solution, Pb(OAc)CNS , and ultimately Pb(OH)CNS , are formed. The latter is stable at $50\text{--}60^\circ$, but is partly hydrolysed by H_2O at 100° and in sunlight it slowly decomposes into PbS. The solubility of Pb(CNS)_2 at 25° is 0.5347%, and is 25 times that of Pb(OH)CNS . The ppt. obtained with H_2SO_4 and Pb(CNS)_2 always contains CNS' (0.7—1.3%), but the quantity diminishes with time. Solutions of $\text{Na}_2\text{C}_2\text{O}_4$ and Pb(CNS)_2 yield almost pure PbC_2O_4 , but the ppt. gradually absorbs a considerable quantity of CNS' from the solution; a compound $\text{Pb(CNS)}_2 \cdot \text{PbC}_2\text{O}_4$ is formed under certain conditions. H. F. GILLBE.

Formation of fluorophosphoric acid from phosphoric acid and aqueous hydrofluoric acid. W. LANGE and G. STEIN (Ber., 1931, 64, [B], 2772—2783; cf. A., 1929, 764).—The equilibrium $\text{H}_3\text{PO}_4 + \text{HF} \rightleftharpoons \text{H}_2\text{PO}_4\text{F} + \text{H}_2\text{O}$ has been investigated at 20° by withdrawal of aliquot portions of the mixture after definite intervals, neutralising, and cautiously adding dil. AgNO_3 , whereby Ag_3PO_4 is exclusively

and quantitatively pptd. In H_2O the equilibrium is independent of the use of anhyd. or 90% H_3PO_4 . Increasing amounts of H_2O initially decrease the formation of H_2PO_3F to an unusual extent, but below a certain concn. (initially about 60% H_3PO_4) further addition of H_2O has no unusual activity and appears to influence the equilibrium in accordance with the law of mass action. With increasing amounts of 41% HF there is initially increase in the amount of H_2PO_3F formed from anhyd. H_3PO_4 . At a definite concn. the increase ceases abruptly and subsequently the amount of H_3PO_4 decreases slightly and then remains const. It appears that conc. H_3PO_4 contains a modification (? neutral, undissociated mols.) which reacts with HF according to an unknown law and passes when diluted with H_2O into other forms (? ions) of which at least one reacts with HF according to the law of mass action. With KH_2PO_4 and increasing amounts of 41% HF the PO_3F'' concn. increases slowly and ultimately becomes const. $Na_3P_2O_7$ and HF yield H_2PO_3F , but it remains undecided whether reaction is due to the P_2O_7 ion or whether hydrolysis precedes the change. KF and KH_2PO_4 do not react in dil. or conc. solution or in alkaline solution. The bimol. nature of the change $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$ is established, but the equation is regarded as purely schematic, since in solutions of conc. H_3PO_4 and HF very different types of mols. and ions are present which exert mutual influence.

H. WREN.

Theory of the sulphuric acid chamber reaction. W. J. MULLER.—See B., 1932, 20.

Dehydration of selenious acid. N. RAE (J.C.S., 1931, 3342—3343).— H_2SeO_3 when kept over P_2O_5 at room temp. is converted (completely in 50 days) into SeO_2 .

C. W. DAVIES.

Chromium halides. II. System chromium-iodine. Preparation and behaviour towards hydrogen of chromous iodide. F. HEIN and I. WINTNER-HOLDER (Z. anorg. Chem., 1931, 202, 81—98).—Pure CrI_2 , m. p. 790—795°, has been prepared by heating electrolytic Cr with an excess of I in N_2 or vac. at 1150—1200°, and removing the excess of I from the product by heating at 200°. Two forms, viz., greyish-white and dark brown, exist. CrI_2 has an appreciable decomp. pressure at 400—700°, but in presence of a trace of I vapour this is strongly depressed, and rises only very slowly with rise of temp. I reacts with CrI_2 , although not very readily, at 300°, but a product containing more than 91% of CrI_3 could not be obtained. I reacts vigorously with pyrophoric Cr at 300°, with partial formation (67%) of CrI_3 . Attempts to obtain decomp. pressure-temp. curves for the two iodides are described.

H. F. GILLBE.

Action of hydrogen sulphide on chromates. II. Hydrogen chromate. H. B. DUNNICLIFF and G. S. KOTWANI (J. Physical Chem., 1931, 35, 3214—3236; cf. A., 1929, 282).—When H_2S is passed into aq. CrO_3 the solution becomes dull purple, then dark brown, when it contains colloidal S and $Cr(OH)_3$, Cr''' , sulphate, and CrO_3 . The sulphate is initially ionic, but after a time half of it has become co-ordinated, and after further action of H_2S a brown

solid containing a co-ordinated sulphatochromium sulphate together with S and $Cr(OH)_3$ separates, the $Cr(OH)_3$ reacting with CrO_3 to form an oxide Cr_5O_9 or CrO_2 . The liquid phase then contains SO_4'' , $Cr(OH)_3$, CrO_3 , and colloidal S. After prolonged passage of H_2S the solid phase becomes pale green, containing one or more co-ordinated Cr sulphates, $Cr_2(S_2O_3)_3$ (probably co-ordinated), S, and $Cr(OH)_3$, whilst the only ion in the liquid is HS' or S'' .

L. KELLEY (c).

Synthesis of chromic thiocyanate complexes of heavy metals. D. M. TSAMADOS and A. C. BOUZUAZOU (Praktika, 1929, 4, 113—117; Chem. Zentr., 1931, ii, 208).—The compounds $Bi[Cr(CNS)_6]$ and $Sb[Cr(CNS)_6] \cdot H_2O$ are described.

A. A. ELDRIDGE.

Bromine pentafluoride. O. RUFF and W. MENZEL (Z. anorg. Chem., 1931, 202, 49—61).— BrF_5 , m. p. -61.3°, b. p. 40.5°, has been prepared by heating BrF_3 with F, at 200°; the reaction is complete and the yield is about 87.5%. At room temp. BrF_5 is a colourless fuming liquid having $d_{4-496} = 0.00346T$; the v. p. is given by $\log_{10} p = 8.0716 - 1677.7/T$. It reacts explosively with H_2O , but the controlled reaction results in the production of, probably, $BrOF_3$; with NaOH solution, NaF, $NaBrO_3$, NaBr, and O_2 are formed. The behaviour of a mixture of BrF_5 and Br on distillation suggests that a fluoride lower than BrF_3 exists. The action of BrF_5 on many elements and some compounds is described.

H. F. GILLBE.

Manganic dithiocarbamates. L. CAMBI and A. CAGNASSO (Atti R. Accad. Lincei, 1931, [vi], 14, 71—74).—The prep. and properties of the following manganic dithiocarbamates are described:

$(C_5H_{10}NCS_2)_3Mn$; $[(C_4H_9)_2NCS_2]_3Mn$; $[(C_2H_5)_2NCS_2]_3Mn$. They are very analogous to those of the corresponding Fe^{III} compounds.

O. J. WALKER.

Potassium rheni-iodide. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (J.C.S., 1931, 3218—3220).—Potassium per-rhenate with excess of KI and boiling aq. HI gives on cooling the compound K_2ReI_6 . This is hydrolysed by H_2O , but can be recryst. in solvated form from $COMe_3$. It is quite stable up to 200°, but above 300° in dry N_2 the quant. reaction $K_2ReI_6 \rightarrow 2KI + Re + 4I$ occurs.

C. W. DAVIES.

Tervalent rhenium and its behaviour on oxidation. W. MANCHOT, H. SCHMID, and J. DUSING (Ber., 1931, 64, [B], 2905—2908; cf. A., 1931, 810).—Reduction of K_2ReCl_6 by Zn and acid or in H_2SO_4 at a Hg cathode affords evidence of the existence of Re^{III} . With air or O_2 the solution thus obtained gives dark, wine-red liquids in which Re^V appears present. In acid solution K_2ReCl_6 does not bleach indigotinsulphonic acid or reduce $KMnO_4$, whereas in alkaline solution it is readily autoxidised. The crude brown product obtained by Enke (*loc. cit.*) behaves towards oxidation and reduction like K_2ReCl_6 .

H. WREN.

Ferromagnetic ferric oxide. A. GIRARD and G. CHAUDRON (Compt. rend., 1931, 193, 1418—1421).—Magnetisation-temp. curves are given for lepidocrocite (a) natural, or prepared (b) by slow oxidation

of $\text{Fe}(\text{OH})_2$, (c) by hydrolysis of NaFeO_2 , (d) by rusting Fe in a saline solution, in air, and in vac. In air (b) is dehydrated at about 250° , and transformed from ferromagnetic into stable Fe_2O_3 at 525° . (c) is dehydrated at about 140° with formation of a more stable ferromagnetic Fe_2O_3 unchanged at 600° . In vac. (a), (b), and (d) are dehydrated at about 250° ; the Fe_2O_3 then begins to dissociate with formation of Fe_3O_4 (cf. A., 1930, 1100; 1931, 324).

C. A. SILBERRAD.

Differentiation of the various forms of ferric oxide and hydrated oxide. III. Hydrated ferric oxide from iron pentacarbonyl. W. H. ALBRECHT and E. WEDEKIND (Z. anorg. Chem., 1931, 202, 205—208).— $\text{Fe}(\text{OH})_3$ may be prepared by treating a solution of $\text{Fe}(\text{CO})_5$ in Et_2O with aq. H_2O_2 and extracting the mixture with H_2O ; traces of $\text{Fe}(\text{CO})_5$ may be removed with Et_2O . The yellow product obtained on ultra-filtration is the α -hydrate; on ageing by heating at 100° with H_2O it becomes red, the lattice begins to break down, and the magnetic susceptibility increases considerably. The prep. was free from Fe^{II} , and the aged product presumably contained other hydrates of unknown structure.

H. F. GILLBE.

Metal carbonyls. X. Iron carbonyl halides. W. HIEBER. 1. Substitutions in iron tetracarbonyl halides [with G. BADER and K. RIES]. 2. Trimeric iron carbonyl bromide [with E. BECKER] (Z. anorg. Chem., 1931, 201, 329—336; cf. A., 1931, 1255).—1. $\text{Fe}(\text{CO})_4\text{I}_2$ reacts at 30° with $\text{EtS}[\text{CH}_2]_2\text{SEt}$ to give the compound $(\text{EtS}[\text{CH}_2]_2\text{SEt})\text{Fe}(\text{CO})_4\text{I}_2$. Both this and the corresponding bromide form red crystals. The chloride is decomposed at -10° with total loss of CO. With *o*-phenanthroline cryst. dicarbonyl-*o*-phenanthroline ferrous bromide has been prepared, the chloride being formed only below -10° .

2. $[\text{Fe}(\text{CO})_4]_3$ reacts with excess of Br at 0° to give a mixture of 3 mols. of $\text{Fe}(\text{CO})_4\text{Br}_2$ with 1 mol. of the compound $[\text{Fe}(\text{CO})_3\text{Br}]_3$. The analogy of the carbonyl ferrous halides with the corresponding Pt^{II} compounds is discussed.

F. L. USHER.

Metal carbonyls. XI. Iron carbonyls substituted by ethylenediamine and a new mode of formation of iron carbonyl hydride. W. HIEBER and F. LEUTERT (Ber., 1931, 64, [B], 2832—2839; cf. A., 1931, 1255).—Ethylenediamine monohydrate and $\text{Fe}(\text{CO})_5$ react readily according to the scheme: $\text{Fe}(\text{CO})_5 + \text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{O} = \text{Fe}(\text{CO})_4\text{H}_2 + \text{NH}_2\text{C}_2\text{H}_4\text{NHCO}_2\text{H}$, reaction ceasing at room temp. after separation of the carbamic acid. $\text{Fe}(\text{CO})_4$ and $\text{C}_2\text{H}_4(\text{NH}_2)_2$ immediately evolve gas and yield a dark red solution. Reaction depends on the disproportionations $2\text{Fe}(\text{CO})_4 = \text{Fe}(\text{CO})_5 + \text{Fe}(\text{CO})_3$ and $3\text{Fe}(\text{CO})_4 = \text{Fe}(\text{CO})_5 + 2\text{Fe}(\text{CO})_3 + \text{CO}$, these changes being facilitated since $\text{Fe}(\text{CO})_5$ reacts with the diamine (see above) and $\text{Fe}(\text{CO})_3$ is stabilised by it. In a similar manner compounds containing $\text{Fe}(\text{CO})_2$ can arise from $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$, thus $2\text{Fe}(\text{CO})_4 = \text{Fe}(\text{CO})_5 + \text{Fe}(\text{CO})_2 + \text{CO}$ and $3\text{Fe}(\text{CO})_3 = \text{Fe}(\text{CO})_5 + 2\text{Fe}(\text{CO})_2$. Addition of H_2O to the red solution at 40° causes pptn. of the compound $\text{Fe}_4(\text{CO})_{12}\text{en}_3$, immediately decomposed by air to $\text{Fe}(\text{CO})_4$, FeO , and $\text{C}_2\text{H}_4(\text{NH}_2)_2$.

In absence of O_2 decomp. occurs with pptn. of the stable $\text{Fe}_2(\text{CO})_9\text{en}_2$. If a mixture of $\text{Fe}(\text{CO})_4$ and $\text{C}_2\text{H}_4(\text{NH}_2)_2$ is heated at 60 – 80° , the compound $\text{Fe}_2(\text{CO})_9\text{en}_2$ separates, whilst $\text{Fe}(\text{CO})_5$ simultaneously produced, undergoes the "base reaction." Up to this stage, only CO is evolved, whereas at higher temp. the gas is accompanied by H_2 in consequence of the auto-decomp. of the hydride, $2\text{Fe}(\text{CO})_4\text{H}_2 = \text{Fe}(\text{CO})_5 + \text{Fe}(\text{CO})_3 + 2\text{H}_2$. The final result of the reactions is that only $\text{Fe}(\text{CO})_2$ compounds remain in solution at 145° which cannot be further degraded without complete decomp. and separation of Fe. The isolation of the compounds $\text{Fe}_4(\text{CO})_{12}\text{en}_3$ and $\text{Fe}_2(\text{CO})_9\text{en}_2$ is described. Treatment of the last-named substance with dil. acids proceeds according to the equation $\text{Fe}_2(\text{CO})_9\text{en}_2 + 8\text{H}^+ + \text{Fe}(\text{CO})_4\text{H}_2 = \text{Fe}^{++} + 3(\text{en} \cdot 2\text{H}^+)$. The volatile hydride is condensed at -180° . At room temp. or when passed through EtOH or glycerol it is decomposed: $2\text{Fe}(\text{CO})_4\text{H}_2 = \text{Fe}(\text{CO})_5 + \text{Fe}(\text{CO})_3 + 2\text{H}_2$.

II. WREN

Phosphides of heavy metals. II. Action of hypophosphite on nickel and cobalt salts. R. SCHOLDER and H. L. HAKEN (Ber., 1931, 64, [B], 2870—2877).—Reaction between Ni salts and hypophosphite occurs only in neutral or alkaline solution, leading to mixtures of Ni and Ni phosphides, the composition of which varies greatly with experimental conditions. The P content of the product is at a max. when the final solution is acid. Contrary to Paal (A., 1931, 1374), the products are ultimately sol. in boiling HCl or AcOH. Cautious treatment with HCl leaves Ni_2P as a definite compound, whereas treatment with AcOH leaves Ni_3P_2 , transformed by HCl into Ni_2P . Dissolution of Ni_2P in HCl occurs according to the equation $\text{Ni}_2\text{P} + 4\text{HCl} + 3\text{H}_2\text{O} = 2\text{NiCl}_2 + \text{H}_3\text{PO}_3 + 7\text{H}$. The Ni-P compounds cannot be regarded as true phosphides, but are intermetallic substances. Reaction between Co salts and hypophosphite almost invariably occurs in initially neutral or alkaline solution, provided the concn. of the hypophosphite is sufficiently great, although the yields from neutral solutions are very small in consequence of the solvent action of the liberated acid. Hence $\text{Co}(\text{OAc})_2$ is more suitable than the Co salts of strong acids. In alkaline solution in presence of KCN neither Co nor Ni is pptd. The best yields of a mixture of Co and Co phosphide is obtained by the action of KH_2PO_3 on a solution of KOH, K tartrate, and $\text{Co}(\text{OAc})_2$ in H_2O . The mixtures are magnetic, more or less readily autoxidised, and retain H_2O tenaciously. Reaction with HCl gives CoCl_2 , H_3PO_3 , and H_2 ; PH_3 is produced at most in traces. Restricted action of acids causes very marked enrichment of the residues in P. The existence of intermetallic compounds CoP , Co_2P , and Co_3P or Co_5P is probable.

H. WREN.

Indirect analysis. E. RINCK (Bull. Soc. chim., 1931, [iv], 49, 1465—1467).—The indirect analysis of a mixture of constituents which cannot be quantitatively separated (e.g., K, Rb, Cs) is impossible when their number exceeds two, since the system of equations obtained is indeterminate.

C. W. DAVIES.

Condensation gas analysis and its extension to adsorption in silica gel at low temperature. G. KUHN.—See B., 1932, 7.

Testing the reaction of distilled water. E. THUOG (Science, 1931, 74, 633—634).—Pure H_2O in equilibrium with the atm. has p_H 5.6—5.8. The amount of acid, and especially NH_3 , in laboratory air may be high enough profoundly to modify the p_H of distilled H_2O . Neutral bromocresol-purple is an excellent indicator for testing the p_H of distilled H_2O by the method described. In the absence of CO_2 and NH_3 the p_H of pure H_2O rises to 7.

L. S. THEOBALD.

Conductometric studies. II. Influence of alcohol in conductometric titrations and on indicators. W. POETHKE (Z. anal. Chem., 1931, 86, 399—422; cf. A., 1931, 1256).—Corrections to be applied in the titration of a weak acid with NaOH in the presence of different proportions of neutral EtOH have been determined for naphthol-, phenol-, and thymol-phthalein as indicators. The first-named is the most suitable. The effect of neutral salts has also been studied. In conductometric titrations EtOH does not affect the "neutrality" point, but the latter is sensitive to neutral salts, especially when the concn. of EtOH is high.

F. L. USHER.

Simple method of conductometric titration. N. RAE (J.C.S., 1931, 3143—3147).—The "Dionic" Water Tester replaces the usual electrical equipment.

C. W. DAVIES.

Measurement of p_H of liquids by means of a rotating electrode. P. L. DU NOUY (Compt. rend., 1931, 193, 1417—1418).—Hasselbach's (cf. A., 1911, ii, 182; 1913, ii, 379) and Clark's (cf. A., 1916, ii, 75) methods are modified by giving the electrode the form of a rotating disc (300—400 r.p.m.) half in the liquid and half in H_2 .

C. A. SILBERRAD.

Solutions for colorimetric standards. V. Systems proposed for use in the determination of p_H values. J. P. MEHLIG and M. G. MELLON (J. Physical Chem., 1931, 35, 3397—3414; cf. A., 1931, 699).—The light transmitted by solutions of various org. indicators and mixed solutions of coloured inorg. salts recommended as colorimetric standards in p_H determinations has been analysed spectrographically. The results show that solutions containing Co, Fe, and Cu salts are not satisfactory as standards for comparison with solutions of two-colour indicators, for an exact match cannot be obtained, and different observers may therefore arrive at different results. Mixtures of K_2CrO_4 and $K_2Cr_2O_7$ may, however, be used in conjunction with one-colour indicators, such as the nitrophenols, if proper precautions are taken.

W. T. HALL (c).

Salicylic acid as an alkalimetric standard. J. ROSICKY and J. TAMCHYNA (Chem. Listy, 1931, 25, 468—470).—Salicylic acid is preferred to $H_2C_2O_4$ or BzOH for the standardisation of alkali solutions.

R. TRUSZKOWSKI.

Determination of fluorine in phosphate rock and phosphatic slags. D. S. REYNOLDS and K. D. JACOB.—See B., 1932, 62.

Portable motor-driven impinger unit for determination of sulphur dioxide. R. B. SMITH

and B. S. T. FRIIS (J. Ind. Hygiene, 1931, 13, 338—342).—Apparatus for scrubbing a known vol. of air through NaOH solution for subsequent iodometric determination of SO_2 is described. F. L. USHER.

Exact determination of very small quantities of gases containing sulphur (H_2S , SO_2 , and CS_2) in the atmosphere when present together. J. BOESEKEN and H. D. MULLER (Rec. trav. chim., 1931, 50, 1117—1124).—The air is passed through three 1-dm. tubes containing respectively: finely-divided AgCl deposited on asbestos, to retain H_2S ; porous stone impregnated with MnO_2 , to retain SO_2 ; and porous stone impregnated with NaOEt, to retain CS_2 . The tubes are then heated separately in a stream of H_2 containing a little HCl, the S is converted into H_2S by ter Meulen's method and is determined with I. An accuracy of 0.01 mg. S per cu. m. is claimed, and is independent of the degree of dilution. For determining total S only, the third tube alone suffices.

C. W. DAVIES.

Determination of sulphate ions in water analysis. E. ROTHENBACH and H. ANTELMANN.—See B., 1932, 50.

Volumetric determination of sulphuric acid in water. B. PASCHKE.—See B., 1932, 50.

Oxidation of hydrothiocyanic acid by permanganate. W. ILLARIONOV (Z. anal. Chem., 1931, 87, 26—32).—The chief source of error in the titration of HCNS with aq. $KMnO_4$ in presence of H_2SO_4 is the loss of HCNS by the formation of a volatile complex with the HCN produced by the reaction. In calculating the result an experimentally determined decomp. coeff. should be employed. In presence of CN^- nearly all the $KMnO_4$ should be added at once and the titration completed by the addition of a further 3 or 4 drops. The same decomp. coeff. as before is then required.

M. S. BURR.

Determination of ammonium salts by the formaldehyde method. E. SORRENTINO (Atti III. Cong. Naz. Chim. pura Appl., 1929, 552—556; Chem. Zentr., 1931, ii, 279).—To 20—25 c.c. of solution (1 g. of salt) are added 5 c.c. of neutralised 40% CH_2O solution; titration is carried out with 0.2N- $Ba(OH)_2$ in presence of phenolphthalein. The free acid is titrated in a control using Me-red.

A. A. ELDRIDGE.

Determination of phosphorous and of hypophosphorous acid. L. WOLF and W. JUNG (Z. anorg. Chem., 1931, 201, 337—346).—Both H_3PO_3 and H_3PO_2 are oxidised by I in acid solution, whereas in $NaHCO_3$ solution only H_3PO_3 is oxidised. On this basis an iodometric method, which permits the two acids to be determined separately or when mixed, has been devised. $H_4P_2O_6$ exercises no disturbing effect.

F. L. USHER.

Argentometric method for determining hypophosphoric acid in presence of phosphates or phosphites. L. WOLF and W. JUNG (Z. anorg. Chem., 1931, 201, 347—352; cf. preceding abstract).—At p_H 1—2 Ag_3PO_4 is sol. and reduction of Ag salts by H_3PO_3 is inappreciable, whereas $H_4P_2O_6$ is quantitatively pptd. by excess of Ag^+ . A method for determining $H_4P_2O_6$, which is pptd. by excess of

AgNO_3 from a solution acidified with H_3PO_4 or HCO_2H , is described. F. L. USHER.

Determination of phosphorous, hypophosphorous, hypophosphoric, and phosphoric acids. L. WOLF and W. JUNG (Z. anorg. Chem., 1931, 201, 353—360; cf. preceding abstracts).—All four acids when present together can be determined only by separating H_3PO_2 from the mixture before determining $\text{H}_4\text{P}_2\text{O}_6$. This is done by adding excess of $\text{Ba}(\text{NO}_3)_2$ to the neutral solution and separating the sol. $\text{Ba}(\text{H}_2\text{PO}_2)_2$. The methods already described may then be applied. F. L. USHER.

Elimination of the phosphate ion as $\text{Pb}_3(\text{PO}_4)_2$. J. BOUGAULT and E. CATTELAINE (Compt. rend., 1931, 193, 1093—1095).—The method, which enables phosphates to be removed from a solution containing Mn, Mg, Ca, Sr, and Ba, consists in adding aq. $\text{Pb}(\text{OAc})_2$ to the solution under investigation acidified with AcOH , the Pb remaining in solution being then removed. C. A. SILBERRAD.

Modified Gutzeit apparatus. G. H. DAVIS (Food Tech., 1931, 1, 145).—A H_2O jacket allows only dry AsH_3 to pass to the HgCl_2 paper.

E. B. HUGHES.

Arsenic testing by Gutzeit method. L. POINTING (Food Tech., 1931, 1, 146).—A scrubbing device removes H_2S from the AsH_3 and a brass union grips the HgCl_2 paper to localise the stain.

E. B. HUGHES.

Determination of carbon dioxide. C. J. SCHOLLENBERGER (Chemist Analyst, 1931, 20, No. 5, 10—14).—The carbonate is decomposed with dil. acids in an evacuated apparatus, the CO_2 being passed into standard $\text{Ba}(\text{OH})_2$, the excess of which is determined titrimetrically (thymolphthalein).

CHEMICAL ABSTRACTS.

Oxidimetric determination of sodium. H. GALL and K. H. HEINIG (Z. anorg. Chem., 1931, 202, 154—160).—The Na is separated as Na U Zn acetate, which is dissolved in dil. H_2SO_4 and filtered through a 6-cm. layer of electrolytic Cd to reduce the U^{VI} . Since up to 3% of the U may thus be reduced to U^{III} , the solution is then filtered, with free exposure to the air, to convert the U^{III} into U^{IV} . The solution is finally titrated with 0.1N- KMnO_4 . The error, with about 5 mg. NaCl, is about $\pm 0.5\%$. The method has the advantage that in the ppt. the U:Na ratio is always 3:1 and is not influenced by variations of the H_2O content. H. F. GILLBE.

Determination of potassium. R. K. KUZNETSOVA and M. F. ZAGORSKY (Udobr. Urozhai, 1931, 3, 364—370).—The K_2PtCl_6 is reduced with Mg in boiling aq. solution.

CHEMICAL ABSTRACTS.

Determination of small quantities of potassium. C. F. MILLER (Chemist-Analyst, 1931, 20, No. 5, 8—10).— K_2PtI_6 is formed from K_2PtCl_6 and KI and is determined colorimetrically in presence or absence of EtOH . For 50 in 10^6 the error is $\pm 5\%$. NH_4 salts, org. matter, and a large excess of acid must be absent.

CHEMICAL ABSTRACTS.

Volumetric method of determining potassium. AUSTERWEIL and LEMAY (Bull. Soc. chim., 1931, [iv], 49, 1541—1542).—The ppt. with Na cobaltinitrite

is dissolved in dil. HCl and the solution exactly neutralised; the Co is then pptd. with standard Na_2CO_3 and determined by a back-titration, after filtering, with HCl. C. W. DAVIES.

Determination of magnesia and alkalis after decomposition by hydrofluoric acid. F. BANN (Glashütte, 1931, 61, 170—171; Chem. Zentr., 1931, i, 2523).—The substance decomposed by HF is evaporated, taken up with HCl, and the heavy metals and CaO are determined as usual. Mg is pptd. with alkali-free, yellow HgO , the alkalis are weighed as sulphate and then separated by the perchlorate method.

L. S. THEOBALD.

Volumetric determination of copper. A. MALKOV (J. Chem. Ind. Russ., 1931, 8, No. 13, 44—46).—1—2 c.c. of solution are kept for 20—25 min. at room temp. with 0.5—1.0 c.c. of a solution containing 20 g. of K Na tartrate and 15 g. of KOH per 100 c.c., and with 1—3 c.c. of 1% fructose or invert-sugar, the washed ppt. of Cu_2O is dissolved in 20—30 c.c. of a solution containing 5 g. of $\text{Fe}_2(\text{SO}_4)_3$ and 20 g. of H_2SO_4 per 100 c.c., and Cu is determined by titration with KMnO_4 . This method can be applied in the presence of Pb, Sn, Fe, and Zn, when ≤ 5 mg. of Cu are present.

R. TRUSZKOWSKI.

Gravimetric determination of aluminium by the cyanate method. Separation from manganese and zinc. A. OKAC (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 135, 1—5).—The results given by Ripan's method (A., 1928, 499) are about 2% higher than the actual vals. The method can be applied in the presence of Mn and Zn provided that a considerable excess of NH_4Cl be present.

R. TRUSZKOWSKI.

Precipitation of manganese as dioxide and its use in quantitative separations. K. A. JENSEN (Z. anal. Chem., 1931, 86, 422—438).—An exhaustive study of the sorption of foreign metals by MnO_2 pptd. from acid solution by persulphates under various conditions shows that the method cannot be used for quant. separation of Mn from other metals, with the exception of Cr, Mg, Be, Al, and the alkali metals.

F. L. USHER.

Determination of manganese with potassium periodate. C. F. MILLER (Chemist-Analyst, 1931, 20, No. 5, 8).—The sample is dissolved in a mixture of conc. H_2SO_4 (15 c.c.), HNO_3 (20 c.c.), H_3PO_4 (10 c.c.), and H_2O (to 100 c.c.); 0.2—0.4 g. KIO_4 is added, the solution is boiled for 1 min., heated for 5—10 min. at 100° , and cooled, the MnO_4' being determined colorimetrically.

CHEMICAL ABSTRACTS.

Determination of manganese. R. G. HARRY (J.S.C.I., 1931, 50, 434—436r).—A review of the following methods is given: gravimetric (oxide, sulphide, sulphate, and pyrophosphate); volumetric (chlorate, Pattinson, persulphate, Volhard, bismuthate, and red lead); and colorimetric [$(\text{NH}_4)_2\text{S}_2\text{O}_8$, tetramethyldiaminodiphenylmethane, and KIO_4].

Determination of manganese by Knorre's method. R. G. HARRY (J.S.C.I., 1932, 51, 24r).—Knorre's method (A., 1902, ii, 108) in which the Mn is oxidised by means of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and pptd.

as hydrated MnO_2 was investigated in the presence of other metals equiv. in amount to 4% of each. In the presence of Cu, Pb, Zn, and Ca the method was entirely suitable. Ti, Sn, and Co seriously interfere; Bi, Sb, As, V, Cr, and Ni interfere to a small extent.

Use of zinc oxide in determination of cobalt and manganese. J. I. HOFFMAN (Bur. Stand. J. Res., 1931, 7, 883—892).—The addition of ZnO to a solution obtained by dissolving steel in HCl-HNO_3 or $\text{H}_2\text{SO}_4\text{-HNO}_3$ will ppt. all the Fe^{+++} , W, V, Cr, U, Zr, Ti, Al, P, As, Sn, and nearly all the Cu, Mo, and Si. Fe^{++} , W (if not previously oxidised), Cu, Mo, Sb, and Pb may be expected in the filtrate. Separation of Fe and certain other constituents of steel from Co and Mn by means of ZnO is satisfactory if double pptns. are made, but is not satisfactory for Ni. Small amounts of Na_2CO_3 in the ZnO are not objectionable and the temp. of pptn. has little influence. E. S. HEDGES.

Colorimetric determination of iron in drinking and effluent waters by means of sulphosalicylic acid. L. N. LAPIN and W. E. KILL.—See B., 1932, 50.

Use of bromate in volumetric analysis. VI. Determination of iron, using basic mercuric bromate. C. F. SMITH and H. H. BLISS (J. Amer. Chem. Soc., 1931, 53, 4291—4297; cf. A., 1931, 925).—The Fe^{III} solution is reduced at the b. p. with SnCl_2 in presence of HCl, avoiding excess of SnCl_2 . There are added at room temp. HgCl_2 , a mixed solution of CuSO_4 , $(\text{NH}_4)_3\text{AsO}_4$, and H_3PO_4 , and a solution of fuchsin, chrysoidine-R, Bordeaux, or naphthol-blue-black as indicator, and then 0.1N- $\text{Hg}(\text{OH})\text{BrO}_3$ is run in until the colour of the indicator is discharged. MeOH , EtOH , $\text{H}_2\text{C}_2\text{O}_4$ and succinic, citric, and tartaric acids do not interfere. W. T. HALL (c).

Detection of traces of vanadium. F. EPHRAÏM (Helv. Chim. Acta, 1931, 14, 1266—1269).—In alkaline solution the reaction $\text{V}^{IV} + \text{Fe}^{+++} \rightleftharpoons \text{V}^V + \text{Fe}^{++}$ proceeds from left to right. The solution in which V is sought is partly evaporated with HCl and to the cooled solution FeCl_3 and dimethylglyoxime solutions are added. On adding aq. NH_3 the depth of the red coloration produced is approx. proportional to the V content of the solution. The colour is transient, but may be preserved by covering the solution with, e.g., ligroin. Extreme care must be taken to exclude oxidising agents. Few metals interfere, but Co, Ni, Fe, Mn, or Cu, if present in quantity, should be removed with NaOH; CrO_4^{--} interferes. The limiting concn. is 1 in 4×10^5 . The oxidation of benzidine by NH_4 vanadate in AcOH solution provides a drop reaction for V, but the limiting concn. is only 1 in 2×10^4 . V yields with cecotheline a bluish-violet colour; by the drop method the limiting concn. is 1 in 2.5×10^4 . H. F. GILLBE.

Determination of bismuth as metal. E. RUFF and G. HAMANN (Z. anal. Chem., 1931, 87, 32—35).—In the gravimetric determination of Bi the metal pptd. by alkaline aq. CH_3CO may be obtained free from oxide if glycerol or Na K tartrate, preferably the former, is present. A short subsequent treatment with H_2 ensures accurate results. If Mg is used for pptn., Na K tartrate should be present to

neutralise the HCl and prevent the formation of BiOCl . The latter method is much more tedious than the former. M. S. BURR.

High-temperature laboratory electric furnace. W. WEYL and M. BROHowsKY (Chem. Fabr., 1931, 469).—The Pt or Pt-Rh heating element is wound on the inner surface of a tube of suitable refractory material; practically the whole of the heat radiated by the wire is thus utilised, and temp. of 1550—1600° may be attained and maintained const. for long periods. The apparatus is especially suitable for the study of, e.g., silicates in an oxidising atm.

H. F. GILLBE.
Measurement of very small thermal effects. W. SWIENTOSLAWSKI (Ann. Chim., 1931, [x], 16, 251—275).—Details are given of the adiabatic micro-calorimeters previously described (A., 1931, 593). Spurious thermal effects due, e.g., to traces of adsorbed H_2O may be a source of serious error. Heats of adsorption of C_6H_6 , EtOH , and CCl_4 by activated charcoal are given. Heats of vaporisation at 20° are: H_2O 581.1, C_6H_6 98.2, CHCl_3 66.8 \pm 0.3% g.-cal. per g. (cf. *ibid.*, 553). Sp. heats of radioactive minerals are recorded. J. G. A. GRIFFITHS.

Improved quartz mercury-vapour lamp. G. S. FORBES and L. J. HEIDT (J. Amer. Chem. Soc., 1931, 53, 4349—4350).—The lamp retains such advantages as operation under const. pressure, a highly conc. discharge, and ease of renewal without special vac. technique and eliminates cemented joints and objectionable capillaries used to check Hg oscillations.

H. F. JOHNSTONE (c).
Lustre-meter and spectrophotometer. H. BOFFEY and D. A. DERRETT-SMITH (J. Sci. Instr., 1931, 8, 356—360).—With this instrument angles of reflexion and incidence can be varied over a wide range, and the sample tested need not be cut.

C. W. GIBBY.
Method of grazing incidence for the determination of indices of refraction. A. BIOT (Ann. Soc. Sci. Bruxelles, 1931, 51, 185—191).—To obtain max. accuracy, the line of sight must be within 5° of perpendicularity to the face of the prism. The method cannot give an accuracy of more than 0.00002 in n .

C. W. GIBBY.
Automatically constant monochromatic illumination from a spark source. G. S. FORBES and F. P. BRACKETT (J. Amer. Chem. Soc., 1931, 53, 3973—3976).—The spark is formed between adjacent edges of two square bars supported at right angles to each other and moving in horizontal planes. Conduction and radiation of heat are so rapid that erosion is minimised, and the illuminating power is const. over long periods. H. F. JOHNSTONE (c).

Automatic colorimetry. W. KORDATZKI (Chem. Fabr., 1931, 485—486).—The apparatus automatically withdraws at regular intervals samples of solution for colorimetric control of p_{H} or for colorimetric testing for the presence of certain ions. The sample mixes with the indicator or testing solution and is then discharged automatically through a siphon.

E. S. HEDGES.
Double potentiometer for measurement of temperatures. C. SĂLCEANU (Bull. Acad. Sci.

Roumaine, 1931, 14, 87—88).—A variable voltage, tapped off from a potentiometer, is applied to a second potentiometer, on which the e.m.f. of a thermocouple is balanced. Temp. between 0° and 300° can be measured to 0.2°. C. W. GIBBY.

Automatic p_H recorder. C. MORTON (J.S.C.I., 1931, 50, 436—438t).—The solution under examination flows through a three-compartment cell, the e.m.f. of which fluctuates in unison with the changes in $[H^+]$ and the voltage variations are continuously recorded in p_H units. The two end chambers, into which the electrodes are inserted, contain the solution under test and a reference buffer solution, respectively, and the central chamber contains saturated KCl solution. A concn. cell is thus formed. By means of siphoning devices the intermittent flushing of the three chambers is rendered automatic.

Apparatus for determination of electrical conductivity. W. MUCHLINSKY (Chem. Fabr., 1931, 462—464, 469—472).—The volume of sound at the balance point may be reduced by using a.c. mains, instead of a buzzer, as the source of e.m.f. Suitable circuits are described, including one in which thermionic valves are used to obtain a const. note of adjustable frequency, and one in which a valve is used as the generator. A circular bridge wire and scale is described. For determination of the balance point the telephone is too insensitive, and suitable a.c. instruments are expensive; the current should therefore be rectified. The method of using thermionic valves and "dry" rectifiers is described. If a valve amplifier also is used, a cheaper and more stable galvanometer may be employed. Methods of preparing and mounting Pt electrodes are noted.

H. F. GILLBE.

Extraction apparatus for large quantities of solid material. F. FRIEDRICH (Chem.-Ztg., 1931, 55, 963).—The apparatus is made in sections with standard ground-glass joints, a jointed glass "chain" being included in the vapour tube for rigidity. Extraction vessels ranging in size from 30 c.c. to 20 litres are available. These are in two parts, for filling purposes, with a "stopper" or "plate" type ground-glass joint according to size. A simpler type of apparatus serves for cases where extraction may be performed in the hot and need not be exhaustive.

S. S. WOOLF.

Laboratory rectifying stills of glass. J. H. BRUUN and S. T. SCHICKTANZ (Bur. Stand. J. Res., 1931, 7, 851—882).—A set of all-glass rectifying stills, suitable for pressures between 1 atm. and about 50 mm., is described. The stills are provided with bubbling-cap columns containing 30—60 plates, and surrounded by a jacket provided with a series of independent electrical heating units in order to maintain adiabatic conditions. The reflux ratio may be adjusted and maintained const. A continuous b. p. apparatus is incorporated in the receiving system for the purpose of obtaining the true b. p. of the distillates. A still of the packed-column type for distillations at pressures less than 50 mm. is also described. Efficiency tests are given.

E. S. HEDGES.

Soda-lime tube substitute for standard solution bottles. A. B. KNOEBEL (Chemist Analyst, 1931, 20, No. 5, 20—21).—Moist air is introduced through NaOH solution in the first of two U-tubes.

CHEMICAL ABSTRACTS.

Drop recorder. O. S. GIBBS (Science, 1931, 74, 549; cf. A., 1929, 1415; 1931, 1026).

L. S. THEOBALD.

Device for holding ultra-filtration membranes. C. BREEDIS (Science, 1931, 74, 635).

L. S. THEOBALD.

Calculation of number and size distribution of spherical crystals in opaque materials by means of the circles obtained from a plane section. E. SCHEIL (Z. anorg. Chem., 1931, 201, 259—264).—Mathematical. F. L. USHER.

Magnetic spectrograph for β -rays emitted by feebly radioactive substances. G. OCCHIALINI (Atti R. Accad. Lincei, 1931, [vi], 14, 103—107).—The radioactive substance is placed on the inside wall of a flat cylindrical box at the centre of which a Geiger-Müller counter is placed coaxially. The pressure inside can be reduced to a suitable val., and the apparatus is placed in an electromagnetic field so that the lines of force are parallel to the axis of the cylinder. The velocity of the β -rays emitted by Rb is 0.62 c.

O. J. WALKER.

Small slow-combustion pipette for gas analysis. H. L. HARDEN (J. Sci. Instr., 1931, 8, 332).—Both leads to the Pt heating spiral enter in the same piece of glass tubing through a rubber bung at the bottom of the pipette.

C. W. GIBBY.

Safety siphon. R. READMAN (J. Sci. Instr., 1931, 8, 331).—The siphon is filled by squeezing a rubber bulb attached to a side tube at its highest point, the delivery end being closed by a tap.

C. W. GIBBY.

Mercury pumps used in connexion with gas-analysis apparatus. K. MELLANBY (J. Sci. Instr., 1931, 8, 330).—Hg is contained in a steel reservoir closed by a rubber diaphragm, and can be forced up by pressing on the latter with a plunger having coarse and fine screw movements.

C. W. GIBBY.

Gas holder for delivering known volumes of a dry gas at atmospheric temperature and pressure. G. W. ELLIS (J. Sci. Instr., 1931, 8, 316—319).—The construction of a calibrated glass gasometer is described.

C. W. GIBBY.

Apparatus for comparing the rate of dissolution of solid substances. V. COFMAN (Chem. and Ind., 1931, 1057—1058).—The solid substance is placed in a perforated boat attached to a hydrometer and the rate of dissolution is measured by the rate of rise of the hydrometer in the liquid. The apparatus is useful for comparing the behaviour of different specimens of colloidal substances, e.g., soap, and for measuring the rate of disintegration of compressed tablets.

E. S. HEDGES.

Constant-pressure device for an autoclave. D. H. MATHESON (Chemist-Analyst, 1931, 20, No. 5, 21—22).—An electrical device is described.

CHEMICAL ABSTRACTS.

Determination of diffusion coefficients. H. KROEPFELIN (Sitzungsber. physikal.-med. Soz. Erlangen, 1930, 62, 285—288; Chem. Zentr., 1931, ii, 141).—An apparatus is described. A. A. ELDRIDGE.

Sedimentation method for determining particle sizes, using an automatic [photographic] recorder. C. G. SUMNER (Trans. Faraday Soc., 1932, 28, 20—27).—The technique of Lambert and Wightman (A., 1925, ii, 1194) is improved. C_6H_6 is used as index liquid, and the evaluation of results is simplified. J. G. A. GRIFFITHS.

New high vacuum system. J. A. BECKER and E. K. JAYCOX (Rev. Sci. Instr., 1931, [ii], 2, 773—784).—A vac. of 2×10^{-8} mm. Hg can be obtained by using an oil diffusion pump backed by a pressure of 10^{-1} mm. and a charcoal trap instead of liquid air.

C. W. GIBBY.

History of the discovery of the critical state. W. KÖNIG (Ann. Physik, 1931, [v], 11, 985—986).

Chinese alchemy. J. R. PARTINGTON (Nature, 1931, 128, 1074—1075).—Historical.

L. S. THEOBALD.

Geochemistry.

Composition of the escaping gases from the Bare Spring (Cameroons Protectorate). A. LEPAPE and M. GESLIN (Bull. Soc. franç. Min., 1930, 53, 274—278; Chem. Zentr., 1931, i, 2453).—The spring, temp. 27°, emits 2.7 cu. m. every 24 hr. The H_2O contains Fe and Ca H carbonates and gives a residue of 0.91 g. per litre. The gases consist of 99.50% CO_2 , 0.05% O_2 , 0% H_2 , 0.00030% CH_4 , 0.00013% of higher hydrocarbons, 0.438% N_2 , 0.0091% A (+traces of Kr and Xe), and 0.00008% He+Ne. L. S. THEOBALD.

Gas-yielding wells in Hukagawa. N. MIYABE (Proc. Imp. Acad. Tokyo, 1931, 7, 344—347).—The evolution of gas containing a high % of CH_4 by three wells in Tokyo is possibly connected with a depression in the tertiary stratum and a subsidence of the surface in the vicinity. N. H. HARTSHORNE.

Classification and chemical composition of mineral waters. W. WERNAUSKY (Bull. Soc. franç. Min., 1930, 53, 417—442; Chem. Zentr., 1931, i, 2453).—The geochemical role of H_2O is discussed. Three main groups, fresh, salt, and thermal water, are further subdivided according to their contained gases and other relationships. L. S. THEOBALD.

Radioactivity of waters from heights in the Vosges. R. DELABY, R. CHARONNAT, and M. JANOT (Compt. rend., 1931, 193, 1434—1436).—Measurements of the radioactivity of 8 springs at heights of 1008—1424 m. show amounts of radon varying from 0.83 to 63.51 m μ c per litre, and 36.12 in the gases from one. Similar measurements for granites from the neighbourhood of some of the springs (1.5—17.5) show somewhat similar variations. Granite, quartz, feldspar, mica, and amphibole from the Ballon d'Alsace gave 17.5, 12.5, 8, 23, and 15.5 m μ c respectively, whilst the springs there gave 63.51 and 62.83. C. A. SILBERRAD.

Lead content of rocks. G. HEVESY and R. HOBIE (Nature, 1931, 128, 1038—1039; cf. following abstract).—The recorded determinations of Pb in samples representing 220 rocks give an average val. of 16×10^{-6} g. Pb per g. of rock, a larger val. than the 7.5×10^{-6} g. previously accepted (J. Wash. Acad. Sci., 1914, 4, 58). The greater part of rock-Pb is of non-radioactive origin; the higher Pb content of acid rocks, which compared with basic rocks also have a relatively high U and Th content, is due to the fact that Pb, like U and Th, has a marked affinity

for siliceous magmas. A comparison of the Pb content of basic and ultrabasic rocks with that of meteorites shows that the silicate shell of the earth received only a moderate share of the total Pb available for partition, and that this uneven distribution has been compensated only slightly by the formation of Pb by radioactive disintegration.

L. S. THEOBALD.

Lead content of rocks. A. HOLMES (Nature, 1931, 128, 1039—1040; cf. A., 1926, 449; 1929, 1263).—The significance of Hevesy and Hobbie's determinations (preceding abstract), which show that the previous val. of 7.5×10^{-6} g. per g. rock is no longer representative, is discussed. These results show that the total Pb in composite rocks is from 4 to 53 times that of the generated Pb. Considerations of at. wt. for Pb in granitic rocks show that there is no reason to doubt the conclusion that Pb ores have been derived from granitic and related magmas, provided that the age of the earth is not considerably greater than 16×10^8 years.

L. S. THEOBALD.

Radium in rocks. IV. Location and association of radium in igneous rocks. C. S. PRIGOT and H. E. MERWIN (Amer. J. Sci., 1932, [v], 23, 49—56; cf. A., 1929, 1035; 1931, 332).—The fractionation of a granite from Stone Mountain, Georgia, and of another from North Jay, Maine, both of high Ra content, showed that the Ra is associated much more with the micas than with the other components of the rock. The reason for this is not clear. Hot H_2O removes some of the emanation, but apparently neither the Ra nor the U, from most powdered specimens. The radioactivity is completely restored after 30 days.

N. H. HARTSHORNE.

Actinium problem. G. EISEN (Chem. Weekblad, 1931, 28, 714; cf. A., 1931, 1145).—The U contents and activities of certain minerals are recorded and discussed. H. F. GILLBE.

Probertite from Ryan, Inyo Co., California. W. F. FOSHAG (Amer. Min., 1931, 16, 338—341).—Probertite contains CaO 15.88, MgO 0.06, $Fe_2O_3 + Al_2O_3$ 0.38, Na_2O 9.00, B_2O_3 49.10, H_2O 25.64, insol. 0.20, total 100.26%; it has H about $3\frac{1}{2}$, d 2.135, n_a 1.517, n_p 1.525, n_g 1.544.

CHEMICAL ABSTRACTS.

Krausite. W. F. FOSHAG (Amer. Min., 1931, 16, 352—360).—The mineral, found with alunite, coquim-

bite, and in a transition zone between the latter and roemerite, voltaite, etc., contains insol. 0.92, CaO 0.12, FeO 0.24, Fe₂O₃ 24.94, K₂O 14.71, Na₂O 0.64, SO₃ 51.05, SiO₂ 2.19, H₂O 5.59, total 100.40%, corresponding with K₂SO₄.Fe₂(SO₄)₃.2H₂O. It has d 2.849, H 2.5; n_a 1.588, n_g 1.650, n_v 1.722.

CHEMICAL ABSTRACTS.

Castanite. A. F. ROGERS (Amer. Min., 1931, 16, 396—404).—Castanite, from Knoxville, California, triclinic, contains Fe₂O₃ 34.74, SO₃ 35.11, H₂O 30.31, insol. 0.22, total 100.21%; Fe₂O₃.2SO₃.8H₂O. It has n_a 1.553, n_g 1.643, n_v 1.657.

CHEMICAL ABSTRACTS.

Peculiarities of primary platinum ores from the Ural. A. G. BETECHTIN (Gorn. Zhur., 1930, 106, No. 1, 152—161).—The composition range of 14 ores was Pt 55.75—77.87, Fe 10.86—14.97, Cu 0.50—11.43, Ir 1.08—7.20, Ni 0.27—3.70%, with a little Pd, Rh, Ru, and Au. An increase in Ir is followed by a decrease in Cu; the same holds for Ni and Fe, but the Pt content does not decrease as Ir accumulates. Pt containing Cu exists in at least two modifications: admixture, and a Cu-Pt alloy on the outside of the Pt.

CHEMICAL ABSTRACTS.

Plateau basalt of west Greenland. H. NIELAND (Chem. Erde, 1931, 6, 591—612).—Petrographical descriptions and chemical analyses are given of an anorthoclase-trachyte and a picritic olivine-basalt from Svartenhuk. The differentiation of basaltic magma into andesitic and trachytic series is discussed.

L. J. SPENCER.

Geochemical role of sorption. W. NOLL (Chem. Erde, 1931, 6, 552—577).—The geochemical distribution of elements in the cycle of sedimentary rocks is governed more by the sorption properties of colloids than by the sizes of ions, as in cryst. rocks.

L. J. SPENCER.

Green-earths of southern Tyrol and other halmvrolitic iron silicates. K. HUMMEL (Chem. Erde, 1931, 6, 468—551).—The occurrences of green-earth between augite-porphyrato and Triassic limestone at Schlern and of celadonite between basalt and Eocene limestone at Monte Baldo are described in detail, with chemical analyses and optical determinations. These are compared with glauconite, chamosite, and other green chlorite-like minerals, and it is concluded that they have been formed by the submarine alteration of igneous rocks—a process which the author in 1922 named halmvrolysis. Owing to metamorphism, the green-earths of different geological periods show different characters and different refractive indices.

L. J. SPENCER.

Metamorphism of the ancient crystalline rocks of the Eastern Alps. H. WIESENER (Tsch. Min. Petr. Mitt., 1931, 42, 136—181).—The cryst. schists where intruded by the Aspang granite have undergone certain modifications. A so-called eclogite is an altered amphibolite, and the so-called diabase is a diorite-like differentiation product of the granite. Enstatite- and anthophyllite-olivine-rocks have been formed by the interaction of amphibolites and dolomite-marbles.

L. J. SPENCER.

Amphibolites of the southern Odenwald and their relation to diorites and granites. V. LEINZ

(Tsch. Min. Petr. Mitt., 1931, 42, 81—135).—Detailed petrographical descriptions with chemical analyses of these rocks are given. The amphibolites have been derived from diabase-tuffs, and are modified where they have been intruded by diorite and granite.

L. J. SPENCER.

Bixbyite from Chuhut [Argentina]. H. CORTI (Anal. Assoc. Quim. Argentina, 1931, 19, 109—116).—Analyses of various specimens are given; the composition varied between 3FeO.2MnO₂ and 4FeO.3MnO₂, with 2—4% of TiO₂. Other properties resembled those of bixbyite.

H. F. GILLBE.

Chemical and mineralogical composition of the rock of Pic de Teide. E. JEREMINE (Bull. Soc. franç. Min., 1930, 53, 210—215; Chem. Zentr., 1931, i, 2453).—The Alca Vista rock, described by Preiswerk as a soda-trachyte, is a phonolite; the other rocks of the Pic de Teide are phonolitic.

L. S. THEOBALD.

Identity of plancheite and shattuckite. Bisbeeite and katangite. A. SCHÖEP (Bull. Soc. franç. Min., 1930, 53, 375—393; Chem. Zentr., 1931, i, 2452—2453).—Plancheite from Katanga occurs in 3 different types and a formula cannot be given. Type 1, bluish-black with blue lustre, has the composition 36.03—36.63% SiO₂, 57.44—57.81% CuO, and 5.42—6.74% H₂O; hardness 6—7, d 3.94, n_v 1.811, and n_a 1.730. Shattuckite, 37.91% SiO₂, 55.31% CuO, and 5.83% H₂O, n_v 1.815 and n_a 1.752, is identical with this type. Type 2, light blue, hardness 2—3, d 3.2—3.3, n_v 1.700—1.725, n_a 1.640—1.665, contains more H₂O, less CuO, and some CaO. Type 3, n_v 1.660—1.685, n_a 1.525—1.665, contains no CaO, more CuO, and also Al₂O₃ and Fe₂O₃. Bisbeeite from Arizona is identical with this type. Katangite is a gel of hydrated Cu silicate which has the same composition and properties as chrysocolla, with which it is identical.

L. S. THEOBALD.

Natural and artificial ultramarines. F. M. JAEGER (Bull. Soc. franç. Min., 1930, 53, 183—209; Chem. Zentr., 1931, i, 2447—2448).—The ultramarines are stable towards alkalis but unstable towards acids. Na can be replaced by Li (bluish-violet), Rb, Cs, K, Tl (violet), Ag (light yellow), Mg (light blue), and other bivalent metals (colourless) by treatment in aq. solution at 100—120°. Replacement of S by Se or Te yields blood-red or yellow ultramarines, respectively. They possess hydraulic properties and resemble permutits in many respects. The substitution of Na by Ag leads to an equilibrium dependent on concn. and temp., and that of Ag by alkali goes more readily with iodides than with chlorides. Replaceability and reaction velocity increase with a decrease in at. wt. of the alkali metal. All these ultramarines yield spectrograms identical with those of nosean and hauynite. The centred cubic lattice has a 9.13 Å. The space groupings of the atoms certain of which appear to be "wanderers" are discussed.

L. S. THEOBALD.

Formulae of hauynite and cancrinite. L. H. BORGSTROM (Bull. Comm. geol. Finlande, 1931, No. 92, 51—57; Chem. Zentr., 1931, ii, 30).—If it is assumed that the Ca atom is replaced by Na instead of by Na₂, the formula and analysis are in accord. The nosean mol. then has the composition

$3\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8, \text{Na}_2\text{SO}_4$. Na cancrinite has the formula $3\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8, \text{Na}_2\text{CO}_3$, and Ca cancrinite the formula $3\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8, 2\text{CaCO}_3$; the two mols. form mixed crystals in all ratios. A. A. ELDRIDGE.

Elements and minerals of pegmatitic rocks. V. M. GOLDSCHMIDT (Nachr. Ges. Wiss. Göttingen, 1930, 370—378; Chem. Zentr., 1931, ii, 213).—A discussion. Besides distribution in magma according to SiO_2 content, there is also distribution according to the ratio $\text{Na}+\text{K}:\text{Al}$. A. A. ELDRIDGE.

Asphalt ring from Ur of the Chaldees. J. F. HACKFORD, S. LAWSON, and P. E. SPIELMAN (J. Inst. Petrol. Tech., 1931, 17, 738—740).—The composition and probable origin of the ring are given. N. H. HARTSHORNE.

Soils from Argolis. E. BLANGK and F. GIESECKE (Chem. Erde, 1931, 6, 578—586).—Mechanical and chemical analyses (bulk analysis and analysis of the portion sol. in HCl) are given of yellow, brown, and red earths (terra rossa) from various localities in Argolis, Greece. Analyses are also given of the underlying limestone from which these soils were derived. L. J. SPENCER.

Reactions of horizons in tropical soils. A. J. W. HORNBY (Nature, 1932, 129, 58).—The p_H of soil samples from different depths of red soils of south-central Africa are discussed. In virgin soil max. acidity occurs for a depth of 2—3 feet in a region generally coincident with a tendency to pan formation. L. S. THEOBALD.

Organic Chemistry.

Synthesis of hydrocarbons at ordinary pressure from mixtures of carbon monoxide and hydrogen. M. G. LEVI, C. PADOVANI, and M. BUSI (Atti III Cong. Naz. Chim. pura appl., 1929, 718—729; Chem. Zentr., 1931, i, 3631—3632).—By the use at 257—285° of catalysts of Fe, Co, and Cu containing Mn or Cr oxides, reduced in $\text{N}_2\text{—H}_2$ mixtures or in N_2 , yields of light liquid hydrocarbons up to 74.4 c.c. per cu. m. of gaseous mixture were obtained. A. A. ELDRIDGE.

Properties of conjugated compounds. XIV. Homogeneity of seven mono- and di-methylbutadienes and the influence of the position of alkyl substitution in these substances on refractivity. E. H. FARMER and F. L. WARREN (J.C.S., 1931, 3221—3235; cf. A., 1931, 1397).—The various methods of prep. of the methyl- and dimethylbutadienes are examined. B.-p. ranges, d , n , ϵ , and molar polarisation are recorded for the purest specimens and the optical data are discussed; the consts. vary most when the hydrocarbon can exist in geometrically isomeric forms. $\alpha\gamma$ -, $\alpha\delta$ -, and $\beta\gamma$ -Dimethyl- and β -methyl-butadiene add quantitatively to maleic anhydride; $\alpha\beta$ -dimethyl- and α -methyl-butadiene polymerise slightly and $\alpha\alpha$ -dimethylbutadiene completely when treated with maleic anhydride. 3-Methyl- and 3:4-dimethyl- Δ^4 -tetrahydrophthalic anhydride have m. p. 61° and 67°, respectively; the former with boiling H_2O gives the acid, m. p. 155°. R. S. CAHN.

Pyrogenic decomposition of a highly unsaturated hydrocarbon at high hydrogen pressure. R. ODA (J. Soc. Chem. Ind. Japan, 1931, 34, 386—388B).—Squalene, $\text{C}_{30}\text{H}_{50}$, b. p. 250—253°/1 mm., d^{15}_4 0.8601, I val. 370.35, is converted by H_2 at 450°/100 atm. (below which it is merely polymerised) into products of b. p. 39—260°; the lower fractions are olefines, the higher are terpenes, the I val. varying from 17.1 to 69.6. Fractions with much higher I val. (117—180 and 151—251) are obtained as by-products of polymerisation at 300° with and without H_2 pressure. C. HOLLINS.

Action of radon on unsaturated hydrocarbons. G. B. HEISIG (J. Amer. Chem. Soc., 1931, 53, 4460;

cf. A., 1931, 1252).—Vinylacetylene condenses to a white solid which becomes orange as the exposure to the action of α -particles continues; about 11 mols. of the hydrocarbon polymerise per ion pair and practically no H_2 and CH_4 are evolved. C_2H_6 condenses to a light mobile liquid, and the amount of H_2 and CH_4 evolved is slightly lower than with C_2H_4 ; somewhat less than 3 mols. condense per ion pair. The energy relations show that condensation of the saturated hydrocarbons is endothermal, whilst that of the unsaturated compounds is exothermal; the latter condensations have a higher M/N ratio. C. J. WEST (b).

Thermal polymerisation of acetylene in presence of zinc chloride. A. V. LOZOVOR (J. Gen. Chem. Russ., 1931, 1, 717—728).—Purified C_2H_2 was passed at 15 litres per hr. through a glass tube containing a 60—65-c.c. long layer of pumice + 5% ZnCl_2 at 420—430°; the gaseous products were 32% C_2H_2 , 2% isoolefines, 10% n -olefines, 12% H_2 , 41% CH_4 , C_2H_6 , etc. The unsaturated hydrocarbons identified were C_2H_4 , propylene, Δ^2 -propinine, allene, and butadiene. The liquid condensate (190 g. from 600 litres of C_2H_2) contained a small amount of olefines, C_6H_6 , PhMe, and C_{10}H_8 , but no paraffins or naphthenes. It is suggested that the propylene was formed from CH_4 and C_2H_2 and the butadiene from 2 mols. of C_2H_4 ; the formation of C_6H_6 takes place in two stages, the first being the combination of 2 mols. of C_2H_2 to $\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot$, which can either form divinyl or unite with C_2H_2 to give C_6H_6 . The propinine may be formed from propylene and then give rise to allene. G. A. R. KON.

[Friedel-Crafts syntheses in the aliphatic and hydroaromatic series.] J. VON BRAUN (Ber., 1931, 64, [B], 2869; cf. Hopff, this vol., 44).—Cases of occurrence of the Friedel-Crafts reaction with non-aromatic H have been recorded by the author (A., 1912, i, 435; 1928, 161). H. WREN.

Action of arylsulphonyl halides and esters on some metallic derivatives: syntheses in the acetylene series. R. TRUCHET (Ann. Chim., 1931, [x], 16, 309—419).—Arylsulphonyl chlorides and

CR:CNa react in Et₂O to give CR:CCl and Na arylsulphinates in 50–70% yield. Mg derivatives behave similarly, with smaller yields, but Ag and Cu derivatives of acetylenes do not react. The physical properties of α -chloro- Δ^8 -heptinene, b. p. 141–142°, d^{18}_{20} 0.918, Δ^8 -octinene, b. p. 61–62°/17 mm., d^{20}_{20} 0.972, Δ^8 -noninene, b. p. 75–77°/15 mm., d^{20}_{20} 0.906, and phenylacetylene, are described. The Cl does not react until the triple linking has been broken, differing from the Br- and I-derivatives. Hg salts cause the addition of H₂O (hexoyl chloride, b. p. 72–75°/20 mm.), I is added (C₅H₅Cl:CCl, b. p. 119–121°/2.5 mm.), NaOEt and KOEt give mixtures of the corresponding acids and esters, but CH₃(CO₂Et)₂ does not react. Na and Zn directly replace Cl either by the metal or by H, but do not dimerise the mol. Arylsulphonyl bromides and iodides behave similarly with CPh:CNa. The chlorides and RMgBr (R=Et, Me) give chiefly RCl and ArSO₂MgBr with some sulphoxides and sulphides, but no sulphones (cf. Wedekind and Schenck, A., 1921, i, 664; Hepworth and Clapham, J.C.S., 1921, 119, 1188), the latter being formed in secondary reactions. AcCl and acetylenes give chloroacetylenes and some CR:CCOMe. These reactions show that a metallic may be converted into a halogeno-derivative by direct replacement, and the action is very general between many metallic derivatives and certain halogenated compounds RX in which the H or RH or ROH has acidic properties.

The reaction R·SO₃R' + CR':CNa → CR':CR' + R·SO₃Na (R'=alkyl) has given in good yield the following: Δ^8 -noninene; Δ^7 -noninene, b. p. 155–157°, d^{20}_{20} 0.763; Δ^7 -decinene, b. p. 175–176°, d^{21}_{21} 0.765; Δ^8 -decinene, b. p. 74–75°/19 mm., d^{17}_{17} 0.772; phenylmethyl-, -ethyl-, -propyl-, b. p. 213–215°, d^{18}_{18} 0.911, -butyl-, b. p. 114–115°/14 mm., d^{17}_{17} 0.899, butylamyl-, b. p. 195–197°, d^{20}_{20} 0.785, and diamyl-acetylene, b. p. 103–104°/14 mm., d^{18}_{18} 0.790. The physical properties, including the parachor and absorption spectra, of these are given.

F. R. SHAW.

Fluorination of compounds of carbon (benzene and carbon tetrachloride with iodine pentafluoride, and carbon tetrachloride with fluorine). O. RUFF and R. KEIM (Z. anorg. Chem., 1931, 201, 245–258; cf. A., 1930, 1387).—IF₅ and C₆H₆ interact at room temp. to give HF, PhI, and charred material. Under similar conditions CCl₄ gives CCl₃F with Cl₂, ICl, and ICl₃. CCl₄ at its b. p. reacts with F₂ to give a mixture of CCl₃F, CCl₂F₂, chlorotrifluoromethane, and CF₄. Addition of I, As, Sb, W, or CoF₃ to the reaction mixture is desirable to avoid explosions. The following data are given: CCl₃F, b. p. 24–1°, d^{18}_{18} 1.72; CCl₂F₂, b. p. –28°, d^{18}_{18} 1.67; CClF₃, b. p. –80°, d^{130}_{130} 1.726.

F. L. USHER.

Preparation of chloropicrin. E. O. G. FRAHM (Rec. trav. chim., 1931, 50, 1125–1126).—A modification of the method of B.P. 142,878 (A., 1918, i, 521). CCl₃NO₂ is obtained in 95–98% yield by passage of Cl₂ at 0° into an aq. solution of Ca picrate containing Ca(OH)₂ in suspension.

H. A. PIGGOTT.

New hypnotic, ethyl- β -ethylbutylbarbituric acid, and some derivatives of β -ethylbutyl alcohol. E. FOURNEAU and J. MATTI (J. Pharm. Chim., 1931, [viii], 14, 513–522).— β -Ethylbutyl

alcohol with Ac₂O and 3 drops of H₂SO₄ gives the acetate, b. p. 63°/20 mm., with 48% HBr and H₂SO₄ the bromide (I), b. p. 143–144°/762 mm., and with 45% HCl and a little H₂SO₄ the chloride, b. p. 125–127°. (I) with NaI in COMe₂ gives the iodide, b. p. 160°/763 mm., and with Et sodiomalonate Et₂ (β -ethylbutyl)malonate, b. p. 140°/16 mm., which with NaOEt and EtBr yields Et₂ ethyl- β -ethylbutylmalonate (II), b. p. 158°/27 mm. (II) with carbamide and NaOEt affords ethyl- β -ethylbutylbarbituric acid, m. p. 125°, and an oil, whilst hydrolysis and distillation of the acid gives α -diethylhexoic acid, b. p. 145°/24 mm.; the Et ester, b. p. 106–107°/25 mm., of the latter acid with Na and dry EtOH gives α -diethylhexyl alcohol, b. p. 123–125°/43 mm. (acetate, b. p. 116–117°/25 mm.). Treatment of the Grignard reagent from (I) with isobutaldehyde gives β -methyl- ϵ -ethylheptan- γ -ol, b. p. 92°/28 mm. (acetate, b. p. 94–96°/24 mm.), together with other products, and with chloroacetone affords the chlorohydrin, which with NHMe₂ in C₆H₆ at 120–130° yields methyl-(β -ethylbutyl)(dimethylaminoethyl)carbinol, b. p. 115–116°/27 mm. The hydrochloride of the benzoate of the last-named compound has strong anaesthetic action on the tip of the tongue.

R. S. CAHN.

Attempts to resolve *n*-amyl alcohol (β -methylbutanol). F. VON FALKENHAUSEN (Biochem. Z., 1931, 242, 472–481).—Attempts to resolve the alcohol by way of the brucine and strychnine monoamyl phosphates, morphine monoamyl 3-nitrophthalate, the H tartrate and the α -bromo-*d*-camphor- α -sulphonate of α -amino- γ -methylbutane, the condensation product of the latter with hydroxymethylenecamphor, and in other similar ways were unsuccessful possibly because mixed crystals are produced.

W. MCCARTNEY.

Synthesis of pure optically active amyl alcohol. F. VON FALKENHAUSEN and C. NEUBERG (Biochem. Z., 1931, 242, 482–486; cf. A., 1929, 907).—By repeated recrystallisation of the product obtained from β -acetobromoglucose and *sec*-butylcarbinol in the manner previously described pure dl-amyl- β -D-tetra-acetylglucoside, m. p. 101–102°, is obtained. On hydrolysis this compound yields pure *d*-amyl alcohol, b. p. 128°, $[\alpha]^{20}_D$ –5.88°. β -dl-Amyl-*d*-glucoside has m. p. 89–90°.

W. MCCARTNEY.

Synthesis and characterisation of β -dimethylpentan- α -ol. T. CHU and C. S. MARVEL (J. Amer. Chem. Soc., 1931, 53, 4449).—MgBu⁸Br and MeCHO give 49% of CH₃Pr⁸·CHMe·OH, b. p. 129–131°; the bromide, b. p. 130–132°, of this with Mg and CH₃O give 30% of β -dimethylpentan- α -ol, b. p. 65–67°/18 mm., 160–162° (3-nitrophthalate, m. p. 154–155°).

C. J. WEST (b).

Configurative relationships of carbinols of the isobutyl series and of benzylethylcarbinol to the simple aliphatic carbinols. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1931, 94, 367–372).—The conclusion previously reached (A., 1931, 599) that configuratively related *n*- and *iso*-butylcarbinols rotate in the same direction is confirmed by the prep. of 1-methylisobutylcarbinol, b. p. 65–66°/60 mm. (α -naphthylurethane, m. p. 86–89°, $[\alpha]^{20}_D$ –3.72° in EtOH), from *d*-propylene oxide and MgPr⁸Br, and

of 1-ethylisobutylcarbinol, b. p. 63—64°/19 mm. (α -naphthylurethane, m. p. 77—79°, $[\alpha]_D^{25}$ -1.5° in EtOH), and 1-ethylbutylcarbinol, b. p. 66°/18 mm., α_D^{25} -0.9° (α -naphthylurethane, m. p. 74—75.5°), from d - α -butylene oxide (I) and MgPr²Br and MgPrBr, respectively. (I) is prepared from l - β -hydroxybutyl bromide and conc. NaOH at 90°, and is converted by aq. HBr into a 1-bromohydrin, b. p. 70—71°/23 mm. 1-Benzylethylcarbinol, b. p. 126°/27 mm. (α -naphthylurethane, m. p. 116—119°), from (I) and MgPhBr, is configuratively related to ethyl- n -alkylcarbinols rotating in the same direction (cf. A., 1930, 1178). H. BURTON.

Phytochemical reductions. Configurations of glycols obtained by reduction with fermenting yeast. P. A. LEVENE and A. WALT (J. Biol. Chem., 1931, 94, 361—366).— α -Hydroxy-aldehydes are not reduced so readily by fermenting yeast as the β -keto-alcohols, R·CO·CH₂·OH (A., 1927, 337). When reduction does occur, optically active glycols of the same configuration as those from the keto-alcohols are produced. Similar reduction of the γ -keto-alcohols, R·CO·CH₂·CH₂·OH, gives optically active glycols of opposite configuration. The optically active glycols result from true asymmetric reductions. Pentane- α - β -diol, b. p. 98—102°/13 mm., $[\alpha]_D^{25}$ +3.75° in EtOH (diphenylurethane, m. p. 97—98°), hexane- α - β -diol, b. p. 111°/12 mm., $[\alpha]_D^{25}$ +0.58° in EtOH, and 1-butane- α - γ -diol, b. p. 107—110°/23 mm., $[\alpha]_D^{25}$ -18.8° in EtOH (diphenylurethane, m. p. 127—128°), are obtained from α -hydroxy-valeraldehyde and hexaldehyde, and β -acetyethyl alcohol, respectively. d - β -Hydroxybutyric acid, obtained by reduction of acetoacetic acid (Friedmann, A., 1931, 1091), has the same configuration as the glycol formed from aldol.

H. BURTON.

Compounds of bivalent carbon. IV. Sodium-oxyethoxymethylene. H. SCHEIBLER [with E. BAUMANN] (Ber., 1931, 64, [B], 2914—2916; cf. A., 1927, 338; Adickes, A., 1931, 196).—The action of CO at 20°/80 atm. on NaOEt free from EtOH causes increase in wt. corresponding with production of about 30% of sodiumoxyethoxymethylene. The product is hydrolysed by H₂O to HCO₂Na and EtOH.

H. WREN.

Ethyl ethers of α -glycols. II. D. BADRAN (Bull. Soc. chim., 1931, [iv], 49, 1551—1555).—When dehydrated with P₂O₅ in presence of pyridine at 140°, the Et ethers of α -glycols, OH·CR₂·CHR'·OH, are converted into the olefinic Et ethers, CR₂·CR'·OEt, from which by hydrolysis with 20% H₂SO₄ the same ketones, CHR₂·COR', are obtained as are prepared in 40—50% yield by the action of HCO₂H, H₂C₂O₄, or 20% H₂SO₄ on the original α -glycol ethers. Thus γ -ethoxy- δ -propylheptan- δ -ol yields 90% of γ -ethoxy- δ -propyl- Δ^7 -heptene, b. p. 108—109°/17 mm., giving with Br (2 atoms) in CS₂ a dibromide which yielded no glycol with aq. Ba(OH)₂, did not react with NPhMe₂, and on distillation yielded a small fraction, b. p. 115—138°/15 mm. With O₃ in CHCl₃, γ -ethoxy- δ -propyl- Δ^7 -heptene gives the corresponding ethylene oxide, b. p. 120—121°/19 mm., hydrolysed by 10% H₂SO₄ to δ -hydroxy- δ -propylheptan- γ -one, b. p. 102—104°/24 mm. α -Ethoxy- α -phenyl- β -ethyl-

Δ^2 -butene, b. p. 134—135°/15 mm. (yield, 90%), similarly gives a Br-derivative yielding a fraction, b. p. 138—142°/18 mm. β -Ethoxy- α -diphenyl- Δ^2 -propene (90%), b. p. 141—147°/6.5 mm.; γ -ethoxy- δ -butyl- Δ^7 -octene (94%), b. p. 124—127°/16 mm.; and α -ethoxy- α -phenyl- β -butyl- Δ^2 -hexene, b. p. 165—167°/14.5 mm., are described. R. BRIGHTMAN.

Glycerophosphomolybdates. P. FLEURY (Compt. rend., 1931, 193, 1350—1352).—The optical activity of aq. solutions of NH₄ molybdomalate decreases following addition of Na₂ α - and β -glycerophosphates or of Na₂HPO₄ (cf. A., 1926, 778). Solutions of (NH₄)₂MoO₄ to which NaH₂PO₄ or Na α - or β -glycerophosphate is added become progressively alkaline until a const. val. is attained. Treatment with EtOH of appropriate solutions of β -glycerophosphate and MoO₃·2H₂O results in the separation of the cryst. salts, 2.5MoO₃· β (C₃H₇O₂)₂·Na₂PO₄·4H₂O and 2.5MoO₃· β (C₃H₇O₂)₂·K₂PO₄·2.5H₂O.

F. O. HOWITT.

isoPropylideneglucose 3-phosphate and its triphenylmethyl ester. K. JOSEPHSON (Svensk Kem. Tidskr., 1931, 43, 242—244; cf. A., 1930, 1166).—The suggested constitution of isopropylidene-glucose phosphate has now been confirmed by determination of the amount of COMe₂ liberated by the action of mineral acids and by the prep. of its CPh₃ derivative, m. p. about 130°, $[\alpha]_D^{25}$ -24.7° in COMe₂.

H. F. HARWOOD.

Reactivity of the mercapto-group. I. N. HELLSTRÖM.—See this vol., 26.

Bismuth derivative of sodium β -hydroxy- γ -thiolpropanesulphonate. A. LEULIER and M. JUVIN.—See this vol., 192.

Metallic derivatives of the enolic forms of monocarbonyl compounds. XIII. Course of the reaction of the Claisen-Darzens glycidic ester synthesis. H. SCHEIBLER and P. S. TUTUNDZITSCH (Ber., 1931, 64, [B], 2916—2920).—Condensation of CH₂Cl·CO₂Et with PhCHO in presence of NaOEt and Et₂O affords Et phenylglycidate (converted into phenylglycidic acid and thence into CH₂Ph·CHO) and a little α -chlorocinnamic acid. Other condensing agents give similar results and hence, contrary to Rutovski and Dajev (A., 1931, 604), the reaction is capable of a uniform interpretation involving the intermediate production of the ester enolate CHCl·C(OEt)·ONa. Similarly, furfuraldehyde, NaOEt, and CH₂Cl·CO₂Et afford *Na furyl-glycidate*, converted by conc. aq. tartaric acid in presence of Et₂O into *furylacetaldehyde*, a mobile oil which readily polymerises. CO(CH₂Ph)₂ is transformed into *dibenzylglycidic acid*, slowly converted by dil. H₂SO₄ into β -phenyl- α -benzylpropaldehyde, b. p. 140—150°/1 mm., which does not react with NH₃, NaHSO₃, NPh·NH₂, NH₂·CO·NH₂·NH₂, or NH₂OH, but gives an azine, m. p. 79°.

H. WREN.

Reaction of anhydrous sodium acetate with alkyl trichloromethyl carbonates. N. N. MELNIKOV and (MLLE.) E. A. SIDOROVA (J. Gen. Chem. Russ., 1931, 1, 740—742).—Ph, *p*-tolyl, and isoamyl CCl₃ carbonates with NaOAc yield Ac₂O and the corresponding alkyl acetate. It is suggested that the

aldehyde and γ -methyl- Δ^8 -butenal; it is less marked with CH_2O , but obvious at p_H 8–9. Leucyl-leucine and albumin are feeble accelerators. Primary and secondary aliphatic amines are active, but hippuric acid is ineffective. H. WREN.

Colour reaction of formaldehyde and ketones with sodium nitroprusside and hydroxylamine. P. PRATESI (Giorn. Chim. Ind. Appl., 1931, 13, 513).—Na nitroprusside solution (not too dil.) is treated with NH_4OH salt crystals and a few drops of 40% CH_2O solution. On adding about 2*N*-NaOH, a transient yellow coloration is first produced, and then a stable, intense violet-red coloration. Aliphatic ketones give a similar, but unstable, coloration.

T. H. POPE.

Preparation and determination of acraldehyde. E. V. ZAPPI and R. A. LABRIOLA (Anal. Assoc. Quím. Argentina, 1930, 18, 243–246).—Slight modifications in the prep. of acraldehyde (Org. Syntheses, 1926, 6, 1) are described. Acraldehyde may be determined by treatment with excess of NaHSO_3 and back-titration with I (Ivanov, A., 1911, ii, 419) or, less satisfactorily, by treatment with Br in CCl_4 or CHCl_3 and titration of excess of Br. R. K. CALLOW.

Polymerisation and condensation. VII. Polymerisation of α -hydroxy-aldehydes. P. A. LEVENE and A. WALTJ (J. Biol. Chem., 1931, 94, 353–360).— α -Hydroxy-propionaldehyde, -butaldehyde, and -valeraldehyde (dimeride, m. p. 145°), prepared by reduction of the ozonides of methyl-, ethyl-, and propyl-vinylcarbinols, respectively, with Zn dust and AcOH, are mobile liquids when freshly distilled; they polymerise readily at room temp. to viscous liquids which gradually deposit cryst. (dimeric) material. α -Hydroxyhexaldehyde (I), b. p. about 60°/1–2 mm. (ultra-violet absorption spectrum given), prepared similarly from Δ^8 -octen-3-ol, affords a dimeride, m. p. 150°, which when distilled at 0.5 mm. pressure regenerates (I). The rotations of d-, b. p. 70–75°/about 3 mm., and l-, b. p. 109–111°/25 mm., α -hydroxy-heptaldehydes, prepared from l- and d-amylnylcarbinols, respectively, increase considerably during the process of polymerisation. H. BURTON.

Preparation of keten. E. PEYTRAL (Compt. rend., 1931, 193, 1199–1200).—A small proportion of keten is obtained by passing vapours of Ac_2O through a Pt tube at 800°; removal of AcOH and unchanged Ac_2O by cooling to 0° gives a gas containing only 0.5–1% of impurities, mainly CO and C_2H_4 . H. A. PIGGOTT.

Reactions of carbon disulphide. II. Reaction with acetone. E. WERTHEIM (J. Amer. Chem. Soc., 1931, 53, 4037–4045; cf. A., 1926, 497).—Repetition of the work of Apitzsch (A., 1904, i, 510; 1905, i, 810; 1909, i, 46), in which COMe_2 was treated with solid KOH and CS_2 , gave evidence of the production of an acidic S compound, which could not be isolated. The reaction between CS_2 , COMe_2 , and Na is complex; the H_2 liberated is 98.2% of that required by the equation $\text{CH}_3\text{COMe-OH} + \text{CS}_2 + \text{Na} \rightarrow \text{CH}_3\text{COMe-OCS}_2\text{Na} + \text{H}$. The part insol. in Et_2O - COMe_2 consists largely of Na trithionate (obtained in about 50% yield), and the Et_2O - COMe_2 filtrate with

BzCl gives the Bz derivative, m. p. 155–156° (Ag salt), of acetonebiscarbithioic acid; with NaOMe this yields the Me ether, m. p. 150–151°, of the enol form of the acid. The filtrate also contained a little mesityl oxide. When the filtrate was acidified, a salmon compound, probably acetone- α -biscarbithioic acid, m. p. 84–85° (Ag salt), which has a disagreeable, faecal odour, was pptd.; this loses H_2S when suspended in H_2O or when heated, giving α -bisthiocarbonylacetone, amorphous, decomp. about 200°; on heating in air, SO_2 is formed. The mixture of Na salts in the above reaction and MeI in MeOH give Me trithiocarbonate, also obtained similarly from COMe_2 , CS_2 , and solid KOH, and from the NH_4 salt of the acid and MeI. s-Methyl isopropyl xanthate has b. p. 65–68°/5 mm., 175–179°/729 mm. C. J. WEST (b).

Photosynthesis of carbohydrates in vitro. J. BELL.—See this vol., 29.

Structure of oses and diholosides. M. BRIDEL (Bull. Soc. Chim. biol., 1931, 13, 1015–1155).—A lecture.

Characterisation of aldehydic and ketonic sugars by oxidation with bromine. F. ZANELLI (Giorn. Chim. Ind. Appl., 1931, 13, 514–515).—In aq. solution containing much AcOH, keto-sugars are not oxidised to an appreciable extent by Br (B., 1909, 919), whereas with aldo-sugars the CHO group undergoes complete oxidation. Exact conditions for the test are given. T. H. POPE.

Action of certain moulds on solutions of aldoses. II. A. ANGELETTI and C. F. CERUTTI (Annali Chim. Appl., 1931, 21, 491–496).—Cultures of *Penicillium luteum purpurogenum* (strain 2A.3) on solutions of l-arabinose do not show any acid products after 20 days' incubation. In solutions of d-xylose, under the same conditions, small amounts of an acid (probably d-xylic acid) are formed. Thus this fungus is able to oxidise to acid products, d-glucose, d-mannose (A., 1930, 1620), and d-xylose, but not d-galactose and d-arabinose. The behaviour is attributed to the arrangement of the atoms or at. groups around the C atoms 3 and 4 in the chain. O. F. LUBATTI.

Molisch's reaction. H. BREDERECK (Ber., 1931, 64, [B], 2856–2859).— α -Naphthol condenses with furfuraldehyde in presence of 10% NaOH to 2-furyl-di-4-hydroxy-1-naphthylmethane (Ac_2 and Bz_2 derivatives), which when covered with conc. H_2SO_4 gives a dark red to bluish-violet solution closely similar to that obtained in the Molisch and von Udransky reaction. Arabinose when treated according to Molisch and then acetylated appears to yield the same Ac_2 derivative. In the case of pentoses, therefore, the Molisch reaction appears to depend on primary conversion of the sugar into furfuraldehyde. H. WREN.

Reactivity of the methylated sugars. V. Action of dilute alkali on trimethyl-l-arabinose. H. T. NEHER [with W. L. LEWIS] (J. Amer. Chem. Soc., 1931, 53, 4411–4423; cf. A., 1931, 1037).—The blocking effect of the Me group on enolisation has been previously demonstrated; these conceptions are now extended to trimethyl-l-arabinose. The sp.

rotation of *l*-arabinose in saturated aq. $\text{Ca}(\text{OH})_2$ at 35° falls from $+100^\circ$ to $+62.6^\circ$ in 195 hr., and shows no further change for 2 months. The aldose content (by I titration) falls from 99.7 to 84.9%, thus showing no intermediate high I-absorbing compound, but indicating the formation of ketose. Trimethyl-*l*-arabinose, m. p. $81-82^\circ$, obtained in 80% yield by careful hydrolysis of its α -methyl derivative (m. p. $46-46.5^\circ$) with 4% HCl , is probably a mixture of the α - and β -forms, since the initial rotation varies with the conditions of crystallisation; all the specimens mutarotate (to a const. val. of $[\alpha]_D^{25} +158^\circ$); the lowest val. observed in CHCl_3 was $[\alpha]_D^{20} +16.4^\circ$, believed to be nearly that of the pure α -form. With aq. $\text{Ca}(\text{OH})_2$ at 35° optical equilibrium was attained in 164 hr. with $[\alpha]_D^{25} +98^\circ$; the % of apparent aldose (by I titration) gradually rose from 100 to 150–155%, as with the other methylated sugars studied. The high I absorption is probably due to the presence of a relatively stable intermediate methylated ene-diol. Treatment of the enolised solution with acid brought the I val. back to 100% aldose, but with more difficulty than with the methylated hexoses. An equilibrated solution of trimethylarabinose (neutral or slightly alkaline) gave no test for furfuraldehyde; distillation of this solution in N_2 gave 0.30 mol. of MeOH (per mol. of sugar) and a trace of furfuraldehyde ($\approx 0.07\%$ of the sugar). Acidification of this solution caused the apparent aldose val. to fall to nearly 100% and the amount of furfuraldehyde present was equiv. to decomp. of 16.7% of the sugar originally present. From the de-enolised and neutralised solution, there was obtained 0.54 mol. of MeOH . The total MeOH obtained (0.84 mol.) would account for a min. val. of 28% of the sugar originally present, assuming that each mol. loses 3 OMe groups. The sugar obtained from the solution gave an aldose val. of 99.3%, $[\alpha]_D^{25} +138^\circ$, amounted to 64.6% of the original sugar, and contained 48.3% of trimethylarabinose. It is believed that the immediate source of furfuraldehyde is the high I-absorbing form (probably the enol) of the methylated sugar, which is produced by the action of the alkali. *l*-Arabinose yields no furfuraldehyde with acid of the concn. used. Trimethyl-*l*-arabinose is not the direct source of furfuraldehyde, as this is not obtained using 6*N*-acid (after 8 hr.) and only in small amounts with 12*N*-acid. A mechanism for the formation of furfuraldehyde is proposed.

C. J. WEST (b).

Aldehyde-*d*-xylose tetra-acetate and the mercaptals of xylose and maltose. M. L. WOLFROM, M. R. NEWLIN, and E. E. STAHL (J. Amer. Chem. Soc., 1931, 53, 4379–4383).—The reaction product from xylose, EtSH , and conc. HCl is freed from HCl with PbCO_3 and Ag_2CO_3 , and the resulting syrup acetylated with Ac_2O in pyridine; the *tetra-acetate* (I), m. p. $46-48^\circ$ (corr.), $[\alpha]_D^{25} +13^\circ$ in CHCl_3 , of *d*-xylose ethylmercaptal (II), m. p. $63-65^\circ$, $[\alpha]_D^{25} -30.8^\circ$ in CHCl_3 , is thereby obtained. (II) may be obtained from the above-mentioned syrup (by seeding) in 70% yields. (I) treated with CdCO_3 and HgCl_2 in COMe_2 gives aldehyde-*d*-xylose tetra-acetate (III), m. p. $87-89^\circ$, $[\alpha]_D^{25} -15.9^\circ$ in CHCl_3 ; in MeOH the initial rotation of $+3.7^\circ$ changes slowly to $+2.5^\circ$ in 2 days.

A cold aq. solution of (III) gives a faint pink colour with Schiff's reagent in 1.5 min.; it reacts immediately with hot Fehling's solution. Maltose and EtSH , followed by acetylation, give *maltose ethylmercaptal octa-acetate*, m. p. $122-122.5^\circ$, $[\alpha]_D^{25} +87.5^\circ$ in CHCl_3 .

C. J. WEST (b).

Novel modification of methyl-*d*-xyloside. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1931, 53, 4454–4455).—Condensation of *d*-xylose with MeOH gives β -methyl-*d*-xyloside and a mol. compound, α -methyl-*d*-xyloside- β -methyl-*d*-xyloside (7:2), m. p. $89-91^\circ$, $[\alpha]_D^{25} +104.4^\circ$ in H_2O . Acetylation in the cold gives a mixture of the tetra-acetates of the known α - and β -methylxylosides, the former predominating; the rate of hydrolysis by 0.05*N*- HCl is $k=0.00121 \pm 2 \times 10^{-5}$ at 99° . An actual mixture of the ordinary α - and β -forms in the ratio of 7:2 has $[\alpha]_D^{25} +105.4^\circ$ and $k=0.00125 \pm 3 \times 10^{-5}$. The mol. compound can be separated (with difficulty) into its components by crystallisation from AeOEt .

C. J. WEST (b).

Reaction of methylpentosides and of α -methylmannoside with triphenylmethyl chloride. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1931, 53, 4456–4457).— α - and β -Methyl-*d*-xyloside, α -methyl-*d*-lyxoside, and β -methyl-*d*-arabinoside react with CPh_3Cl in pyridine, as shown by polarimetric changes in the *l*-direction; reaction is complete in 100–360 hr., and 45–80% of the original sugar reacts. Cryst. products have not been isolated. These results show that CPh_3Cl is not sp. in action towards primary OH groups, or that none of these methylpentosides has a 1:5-ring, or that ring shifts can occur. α -Methyl-*d*-mannoside has yielded a cryst. condensation product, which is being studied.

C. J. WEST (b).

Identity of quinovose with *d*-glucomethylose (isorhodeose). E. VOROČEK and F. RAC (Chem. Listy, 1931, 25, 465–468).—The above sugars are identical.

R. TRUSZKOWSKI.

Optical rotation of rhamnose- and mannose-phenylhydrazones. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1931, 53, 4358–4363).—Mannosephenylhydrazone, m. p. $199-200^\circ$, has $[\alpha]_D^{25} +26.3^\circ$ in pyridine, decreasing to about $+6^\circ$ in 7 hr. and then slowly increasing to $+33.8^\circ$ (67 hr.). In EtOH -pyridine (1:1) the initial val. of $+27.3^\circ$ dropped to -2.6° , and then increased slowly to a const. val. slightly higher than the initial rotation; the rate of change was different in 2 experiments. The sp. rotation of rhamnosephenylhydrazone, m. p. $158-159^\circ$, in H_2O changes from $+57.1^\circ$ (initial) to $+44.3^\circ$ in 41 hr. In EtOH -pyridine (1:1) the initial val. was somewhat below -24° ; this rapidly increased to a max. of $+16^\circ$, and then slowly decreased and became const. at -35° , -100° , and -67.3° (in 3 experiments); the rate of change increased with the age of the sample. No explanation of this behaviour can be offered at present.

C. J. WEST (b).

Optical rotation of the isomeric nitrophenylhydrazones of rhamnose and mannose. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1931, 53, 4363–4367).—Rhamnose-*o*-nitrophenylhydr-

azone, m. p. 152—153°, had $[\alpha]_D -37.5^\circ \rightarrow -33.5^\circ$ (24 hr.) in EtOH-pyridine (1:1); the *m*-isomeride, m. p. 158—159°, changed from -21° to $+18.3^\circ$ in 141.5 hr.; the *p*-isomeride, m. p. 191—192°, changed from -50.3° to -8.5° in 144 hr. Mannose-*o*-nitrophenylhydrazones, m. p. 172—173°, $[\alpha]_D +52^\circ$, and the *p*-isomeride, m. p. 202—203°, $[\alpha]_D +56^\circ$, showed no mutarotation; the *m*-isomeride, m. p. 162—163°, changed from $+26.5^\circ$ to -8.3° in 144 hr. These vals. do not agree with those which might be expected on the basis of rules found to hold for other classes of optically active position isomerides (cf. Cohen, J.C.S., 1910, 97, 1732; 1911, 99, 1058; Frankland, *ibid.*, 1912, 101, 654), but the variations appear less erratic than the variations in the rotations previously recorded. C. J. WEST (b).

Syntheses in the sugar group. III. 1-Phenylglucosone, 1:1-diphenylfructose, and 1:1-dibenzylfructose. H. OHLE and I. BLELL (Annalen, 1931, 492, 1—21; cf. A., 1930, 1274).— α -Ketodisopropylideneglucosonic acid (I) (1 mol.) and MgPhBr (6 mols.) in Et₂O-C₆H₆ give 1-phenyl-2:3:4:5-diisopropylideneglucosone (II), b. p. 166°/0.3 mm., m. p. 134°, $[\alpha]_D -24.75^\circ$ in CHCl₃, and β -1:1-diphenyl-2:3:4:5-diisopropylidenefructose (III), b. p. 213.5°/0.3 mm., m. p. 194.5°, $[\alpha]_D -193.5^\circ$ in CHCl₃, separable by fractional distillation; (III) is obtained almost exclusively when the Me ester of (I) is used. Hydrolysis of (II) with boiling PrOH-N-H₂SO₄ (1:1) affords 1-phenyl-d-glucosone (IV), m. p. 134.5°, $[\alpha]_D -17.72^\circ$ in H₂O, $-7.89^\circ \rightarrow +7.18^\circ$ in pyridine (phenylhydrazone, m. p. 154.5°; tetra-acetate, m. p. 128.5°, $[\alpha]_D +95.72^\circ$ in CHCl₃, which could not be converted into a cryst. Br-derivative, and probably contains a free CO group), and a small amount of a hydrocarbon, (C₁₃H₁₀)₂, m. p. 208.5°. (IV) reduces Fehling's solution and gives an intense reddish-violet coloration with hot conc. KOH (after 10 min. the reducing action disappears). (IV), COMe₂, and anhyd. CuSO₄ afford a 1-phenylisopropylideneglucosone, m. p. 169°, $[\alpha]_D -93.35^\circ$ in CHCl₃, which is also a reducing agent and does not give a coloration with KOH. Hydrolysis of (III) with PrOH-N-H₂SO₄ gives 1:1-diphenyl-2:3-isopropylidene- α -fructofuranose, m. p. 174°, $[\alpha]_D -99.3^\circ$ in COMe₂ (unaffected by COMe₂ and anhyd. CuSO₄), and (mainly) 1:1-diphenyl-2:3-isopropylidene-d-fructopyranose (+0.25CHCl₃), m. p. 104°, $[\alpha]_D -149.6^\circ$ in COMe₂ [reconverted by COMe₂ and CuSO₄ into (III)], both of which are non-reducing agents and are hydrolysed further to 1:1-diphenyl-d-fructose (+H₂O) (V), m. p. 81°, $[\alpha]_D +55.28^\circ \rightarrow +42.28^\circ$ in COMe₂ (tetra-acetate, m. p. 143°, $[\alpha]_D +3.18^\circ$ in COMe₂). The first stage in the hydrolysis of (III) is fission of the oxide ring; the union of the 2:3-isopropylidene group is strengthened (by the electro-negative character of the Ph groups) at C₂, and formation of a 2:5-ring is possible. (V), COMe₂, and anhyd. CuSO₄ give 1:1-diphenyl-d-fructose anhydride, m. p. 149.5°, $[\alpha]_D +76.66^\circ$ in COMe₂; the non-formation of an isopropylidene derivative demonstrates the furoid structure of (V). (I) and CH₃Ph·MgCl give β -1:1-dibenzyl-2:3:4:5-diisopropylidene-d-fructose (VI), m. p. 121.5—122°, $[\alpha]_D -49.25^\circ$ in CHCl₃, hydrolysed by PrOH-N-H₂SO₄

to 1:1-dibenzyl-2:3-isopropylidene-d-fructopyranose, m. p. 127—127.5°, $[\alpha]_D +32.95^\circ$ in CHCl₃ [reconverted by COMe₂ and anhyd. CuSO₄ into (VI)], and 1:1-dibenzyl- α -fructose (VII), m. p. 149°, $[\alpha]_D +5.29^\circ$ in COMe₂ (tetra-acetate, m. p. 94°, $[\alpha]_D +23.6^\circ$ in COMe₂). (VII), COMe₂, and anhyd. CuSO₄ give 1:1-dibenzyl-4:5-isopropylidene-d-fructopyranose, m. p. 107°, $[\alpha]_D +7.29^\circ$ in COMe₂, which is a reducing agent. H. BURTON.

Catalytic oxidation of α -glucose and related sugars by oxygen in presence of iron pyrophosphates. E. F. DEGERING and F. W. URSON (J. Biol. Chem., 1931, 94, 423—431).—The ease of oxidation (measured by the rate of formation of CO₂) of the following substances by O₂ in presence of a Fe pyrophosphate catalyst, prepared essentially by Spoehr's method (A., 1924, i, 836; 1926, 385), is in the order quoted: fructose, mannose, glucose, arabinic acid, arabinose, gluconic acid, α -methylmannoside, α -methylglucoside, mannitol, glycerol, glyceric acid, OH-CH₂-CO₂H, α -methylarabinoside, tetramethylglucose, tetraethyl- α -methylglucoside. CO₂ was not produced from the last two compounds under the experimental conditions, viz., first at 48° (16 days) and then at about 98° (7 days). The activity of the catalyst increases with rise in temp., and the rate of oxidation of the sugars is a function of the rate of enolisation. The probable intermediates in the oxidation processes are discussed. H. BURTON.

Non-fermenting constituents of the product obtained by the action of alkalis on hexoses (glucose). W. COLTOR (Biochem. Z., 1931, 243, 191—224).—The syrups obtained by fermentation of molasses and by Lobry de Bruyn's method are both mixtures and are differently constituted. They give different mixtures of osazones and the reducing substances of the glucose fractions are not identical. Glucose is to be regarded as an unfermentable mixture containing hexose, biose, saccharic acids, protein, etc. P. W. CLUTTERBUCK.

Carbohydrates. XI. α -Glucose. P. BRIGL, H. MUHLSCHEGEL, and R. SCHNLE (Ber., 1931, 64, [B], 2921—2934; cf. A., 1930, 1022; 1931, 71).—Treatment of α -glucose pentabenzozate with NH₃ in MeOH affords glucosidibenzamide, OH-CH₂-[CH(OH)]₄-CH(NHBz)₂, m. p. 202° (decomp.), $[\alpha]_D +1.5^\circ$ in pyridine. Since glucose does not condense with NH₂Bz in MeOH in presence of NH₃, the aldehydic form must be sufficiently stable to permit the separation of the Bz residues and the subsequent condensation. The prep. of less completely benzoylated α -glucose is difficult, since 1 mol. of BzCl and 1 mol. of glucose diethylmercaptal yield the Bz₄ derivative (cf. *loc. cit.*). Treatment of glucofuranose 3:5:6-tribenzozate with NH₃-MeOH affords NH₂Bz, glucose, and a small amount of glucosidibenzamide, indicating the probable presence of the aldehydic form in the initial material. Glucose Na H sulphite is immediately converted by Ac₂O into β -glucose penta-acetate and by MeOH containing NH₃ and NH₂Bz into glucose without a trace of the debenzamide compound. Mannose cyanohydrin is converted by ammoniacal AgNO₃ in presence of NH₂Bz solely into free mannose, whereas its Ac₆ derivative is transformed

into *mannosediacetamide* (+H₂O), m. p. 219° (decomp.), and its *Bz*₆ compound, m. p. 161–162°, $[\alpha]_D^{25} +30.3^\circ$ in CHCl₃, into *mannose-dibenzamide*, m. p. 226° (decomp.), $[\alpha]_D^{25} +3.6^\circ$ in pyridine, and *-monobenzamide*, m. p. (indef.) 254°. The presence of acidic groups therefore stabilises the aldehydic form. Measurements of the rate of addition of HCN to various sugars in H₂O in presence of a little NH₃ at 5.5–6.5° (as a possible means of determining the readiness of formation of the open form from the cyclic form) show the following percentages of nitrile after 1.5 and 5 hr., respectively: glucose, 8.8 and 15.9; maltose, 6.6 and 11.9; lactose, 6.1 and 13.5; mannose, 35.9 and 75.4; galactose, 29.1 and 52.5; fructose, 25.6 and 40.5.

3:4:5:6-Tetrabenzoylglucose diethylmercaptal is transformed by HgCl₂ and BaCO₃ in boiling COMe₂ into *al-glucose* 3:4:5:6-tetrabenzoate, m. p. 220–222°, possibly a polymerised form. It behaves as a true aldehyde, being converted by MeOH-NH₃ into glucosidibenzamide, by NH₂Ph in EtOH into the *anilide*, C₄₀H₃₃O₉N, m. p. 118–120° after softening at 110°, by EtSH under certain conditions into the initial mercaptal, and by diazomethane into the *ketone*, OBz·CH₂·[CH·OBz]₃·CH(OH)·COMe, m. p. 194° (decomp.) after softening at 192°, $[\alpha]_D^{25} +48.9^\circ$ in CHCl₃. *al-Glucose* tetrabenzoate and EtSH in absence of catalyst afford an impure *semimercaptal*; the *methyl-semiacetal* has m. p. 215° (decomp.). EtSH in presence of CHCl₃ saturated with HCl converts *al-glucose* tetrabenzoate into *2-ethylthiolglucose* 1:1-diethylmercaptal 3:4:5:6-tetrabenzoate, OBz·CH₂·[CH·OBz]₃·CH(SET)₂, m. p. 84–85° after softening at 79°, $[\alpha]_D^{25} +57.6^\circ$ in COMe₂, hydrolysed by NaOMe to *2-ethylthiolglucose* 1:1-diethylmercaptal, m. p. 102° after softening at 101°, $[\alpha]_D^{25} +2.27^\circ$ in COMe₂, and transformed by HgCl₂ and BaCO₃ in boiling COMe₂ into *2-ethylthiol-al-glucose* 3:4:5:6-tetrabenzoate, m. p. 65–66°, $[\alpha]_D^{25} -42.7^\circ$ in COMe₂. *2-Ethylthiolmonobenzamide*, m. p. 186–190° (decomp.), is described. H. WREN.

Model experiments based on the theory of alcoholic fermentation. VI. Oxidation of mono- and di-isopropylideneglucose and of isopropylideneglucose 3-sulphuric acid. H. OHLE, G. COUTSICOS, and F. GARCIA Y GONZALEZ (Ber., 1931, 64, [B], 2810–2813; cf. this vol., 144).—Oxidation of isopropylideneglucose at room temp. with KMnO₄ (=4.5O) affords *K isopropylidenexyluronate*, $[\alpha]_D^{25} -52.56^\circ$ in H₂O, similarly obtained from diisopropylideneglucose; it evolves CO₂ when boiled with dil. mineral acids. *K diisopropylideneglucose 3-sulphate* (+2.5H₂O), $[\alpha]_D^{20} -13.17^\circ$ in H₂O (also +0.5H₂O, decomp. 185–195°), is hydrolysed by N·H₂SO₄ at room temp. to *K isopropylideneglucose 3-sulphate*, $[\alpha]_D^{20} -14.56^\circ$ in H₂O, oxidised by KMnO₄ to *K₂ isopropylidenexyluronate-3-sulphate*, $[\alpha]_D^{25} -36.94^\circ$, obtained also from *K isopropylidenexyluronate* and pyridinium-*N*-sulphonic acid in pyridine. The course of the oxidation of diisopropylideneglucose 3-sulphuric acid resembles closely that of the parent compound.

H. WREN.

Mechanism of carbohydrate oxidation. XIV. Alkaline degradation of cellobiose, lactose,

melibiose, and gentiobiose by potassium hydroxide. W. L. EVANS and R. C. HOCKETT (J. Amer. Chem. Soc., 1931, 53, 4384–4400; cf. A., 1930, 1555).—The objectives in the work were: (1) to verify the prediction (based on maltose) that cellobiose and aq. solutions of KOH would give practically the same yields of lactic acid, AcOH, HCO₂H, and pyruvaldehydeosazone as maltose; (2) to verify the prediction that the glucosido-residues of cellobiose and gentiobiose and the galactosido-residues of lactose and melibiose would greatly influence the yields of lactic acid (yields relatively greater in the glucosidoglucoses); (3) to verify the prediction that owing to the hindering action of the hexosido-residue in the 4-hexosidoglucoses (cellobiose, lactose, and maltose, the yields of lactic acid would not be so great in these cases as from gentiobiose and melibiose (compounds in which the hexosido-attachment is on C₆). The reactions were found to be in harmony with these general points of view. Since pyruvaldehyde is regarded as the precursor of lactic acid, the same general relationships were also found in this case. The yields of AcOH from the 6-hexosidoglucoses were greater than those obtained from the 4-hexosidoglucoses, whilst those of HCO₂H show the opposite tendency. The disaccharides show a max. yield of AcOH quite similar to that of the hexoses. A mechanism for the formation of AcOH and HCO₂H from the disaccharides is given. On the enediol theory of action in the disaccharides, the probable oxidation products of gentiobiose and melibiose are given. The interpretation of the max. point in the curve of lactic acid production from gentiobiose and melibiose is based on the assumption that a 6-hexosidoglucose-4:5-enediol must have formed in each case in the regions of higher alkalinity. A mechanism is given to explain the decreasing yield of this acid after the point of max. production has been passed. The results are given in a series of curves. C. J. WEST (b).

Novel modification of lactose. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1931, 53, 4455–4456).—Finely-powdered α -lactose monohydrate, shaken at room temp. with 10 times its wt. of MeOH containing 1–5% of HCl, changes to a needle type of crystal, considered to be a mol. compound, α -lactose- β -lactose (5:3), $[\alpha]_D^{20} +67.9^\circ$ (initial) $\rightarrow +55.2^\circ$ (anhyd. lactose) in H₂O. A mixture of the α - and β -forms of lactose in the ratio of 5:3 would have initial $[\alpha]_D^{20} +67.5^\circ$. The new compound is anhyd., whereas α -lactose has never been obtained anhyd. by crystallisation. C. J. WEST (b).

1-Glucoside of *Asphodeles*. H. COLIN and C. NEYRON (Bull. Soc. chim., 1931, [iv], 49, 1542–1547).—Fresh *Asphodeles* tubercles contain about 8% of laevulose, 1% of sucrose, and 0.5% of reducing sugar. The glucoside obtained by aq. extraction, $[\alpha]_D^{25} -18.6^\circ$, darkens at 170° and decomposes at about 210° and is hydrolysed at *p_H* about 4 in 0.25 hr., yielding mainly fructose together with some glucose. When this mixture is treated with CaO, a sugar, $[\alpha]_D^{25} -86^\circ$, is regenerated from the Ca complex, the sugar obtained from the mother-liquors having $[\alpha]_D^{25} -41^\circ$, indicating the presence of a second glucoside constituent. The latter is slowly oxidised by Br and

I in weak alkaline media, the reducing power of the asphodeloside decreasing about 16% in presence of Br and about 40% in abs. EtOH with the less sol. fractions, indicating the presence of about 1 mol. of glucose to 5–6 mols. of fructose. The glucoside is rapidly hydrolysed by mycelian powder or by *Aspergillus niger*, but is only slowly and partly attacked by yeast-invertase. Living yeast readily ferments both *Asphodeles* sap and the purified glucoside. The latter is probably a glucofructosan or an intimate mixture of fructosan and glucosan.

R. BRIGHTMAN.

[Highly-polymerised compounds. LVI.] K. H. MEYER and H. MARK (Ber., 1931, 64, [B], 2913).—A reply to Staudinger (this vol., 46). H. WREN.

Polymorphism of substances of high mol. wt. II. Amorphous and crystalline inulin. J. R. KATZ and A. WEIDINGER (Rco. trav. chim., 1931, 50, 1133–1137).—X-Ray examination of ordinary inulin and of Berner's form readily sol. in cold H₂O (A., 1931, 716) shows the latter to be a genuine amorphous form slightly contaminated with a cryst. modification. The amorphous form, although stable when dry, rapidly reverts to the ordinary form in moist air. Schlubach and Eisner's β -inulin (A., 1930, 1415) appears to be the same as Berner's prep.

C. W. DAVIES.

Oxidation of cellulose. T. NAKASHIMA (J. Soc. Chem. Ind. Japan, 1931, 34, 414–418B).—On continued oxidation of "biosan acetato" by O₂ in the presence of NaOH, the I val. decreases, whilst the acid val. increases, showing that the CHO groups are oxidised to CO₂H. Determination of residual cellulose by K₂Cr₂O₇ shows that the amount of cellulose decomposed increases with increasing time of oxidation. It is suggested that the reaction proceeds chiefly by oxidation of CHO to CO₂H groups and by decomp. of the terminal glucose residues containing CO₂H to acids of lower mol. wt. When the end glucose residue is decomposed a new CHO group is liberated which is oxidised to CO₂H, and so on. Shortening of the micellar chains must proceed gradually because oxidation takes place mainly at the ends. This is supported by the fact that the viscosity of the material decreases only slowly during the reaction. In the similar oxidation of glucose, the I val. decreases, and the acid val. increases, rapidly. B. P. RIDGE.

X-Ray examination of cellulose derivatives. XI. Additive compounds of cellulose with hydrazine, ethylenediamine, and tetramethylenediamine. C. TROGUS and K. HESS (Z. physikal. Chem., 1931, B, 14, 387–395; cf. A., 1931, 1219).—The existence of additive compounds of cellulose with the above bases has been demonstrated by X-ray examination. The base is directed across the fibre axis of the cellulose crystallite. These compounds are decomposed on treatment with H₂O.

R. CUTHILL.

Least equivalent of β -cellulose, tunicin, and cotton cellulose. E. SCHMIDT, W. SIMSON, and R. SCHNEGG (Naturwiss., 1931, 19, 1006–1007).—The least equiv. of β -cellulose, tunicin, and cotton (Indian and American) cellulose is 96 C₆H₁₀O₅, the same as

for cellulose derived from deciduous and coniferous trees (A., 1931, 827). W. R. ANGUS.

Decomposition of quaternary ammonium hydroxides. VI. J. VON BRAUN and E. ANTON (Ber., 1931, 64, [B], 2865–2869).—Methylation of primary, sec., and tert. bases with Me₂SO₄ affords quaternary salts with the group $\cdot\text{O}\cdot\text{SO}_3\cdot\text{OMe}$ which can be salted out with conc. alkali and purified by dissolution in CHCl₃ and pptn. with Et₂O. With boiling aq. Ba(OH)₂, they gradually yield BaSO₄ and the hydroxide, but hydrolysis is preferably effected with boiling H₂SO₄. Addition of Ba(OH)₂ to the resulting solution ppts. BaSO₄ in a readily filtered form; the filtrate is conc., any BaCO₃ is removed, and after addition of KOH the residual solution is distilled. Thus *n*-hexylamine is converted through the quaternary methosulphate, m. p. 90°, into Δ^8 -hexene (yield 60%) and dimethyl-*n*-hexylamine, b. p. 146° (yield about 20%); piperidine affords "dimethyl-piperidine," b. p. 117–118°, and NEt₃ yields NMeEt₂, b. p. 65° (yield 50%). α,ω -Diaminododecane, b. p. 187°/16 mm., m. p. 66–67°, is transformed through the quaternary salt, m. p. 186°, into $\Delta^{\omega-1}$ -dodecadiene, b. p. 207° (yield 65%), and dimethyl- $\Delta^{\omega-1}$ -dodecenyamine, CH₃·CH·[CH₂]₁₀·NMe₂, b. p. 132–135°/16 mm. (yield 25%) [picrate, m. p. 127°]. The oily naphthenic acid, C₁₅H₂₄O₂, from Galician petroleum (A., 1931, 1396), is converted into the naphthenamine, C₁₇H₃₃·NH₂, b. p. 175–195°/16 mm., which yields a hydrocarbon, C₁₇H₃₂, b. p. 155–175°/16 mm. (yield 63%), and a basic fraction, C₁₇H₃₃NMe₂, b. p. 175–195°/16 mm. (yield 31%). H. WREN.

Existence of molecular compounds between amino-acids in solution and in the solid state. M. FRANKEL (Biochem. Z., 1931, 242, 67–87).—Examination of mixed solutions of the following pairs of substances: *d*-arginine and *l*-aspartic acid; *d*-arginine and *d*-glutamic acid; *d*-arginine and *l*-proline; *d*-arginine and *l*-oxyproline; *l*-histidine and *l*-aspartic acid; *l*-histidine and *d*-glutamic acid; *l*-histidine and *l*-proline; *l*-histidine and *l*-oxyproline, by the cryoscopic and refractometric methods shows that double compounds are present in each case. The isolation of mol. compounds from *d*-arginine with *l*-aspartic acid and *d*-arginine with *d*-glutamic acid is described. P. W. CLUTTERBUCK.

Elimination of halogen by dilute alkali from stereoisomeric halogenoacylamino-acids. Configuration of optically active α -halogeno-fatty acids. V. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1931, 13, 115–125; cf. A., 1931, 1150).—Fractional crystallisation of dl- α -bromoiso-valeryl-dl-leucine, m. p. 105–126°, gave the racemic compounds A, m. p. 164°, and B, m. p. 118–119°. The four optically active forms of α -bromoiso-valeryl-leucine were obtained: *l*-*l*- (I), m. p. 142–143°, [α]_D²⁰ –50.0°; *l*-*d*- (II), m. p. 141–142°, [α]_D²⁰ +5.0°; *d*-*d*- (III), m. p. 145°, [α]_D²⁰ +52.0°; *d*-*l*- (IV), m. p. 143–144°, [α]_D²⁰ –5.0°. (I) and (III) gave compound A, (II) and (IV), B. The four active forms of α -bromoiso-valerylnorleucine were prepared: *l*-*d*- (V), m. p. 113°, [α]_D²⁰ –11.3°; *l*-*l*- (VI), m. p. 111°, [α]_D²⁰ –38.3°; *d*-*l*- (VII), m. p. 104–108°, [α]_D²⁰ +12.7°; *d*-*d*- (VIII), m. p. 111–112°, [α]_D²⁰ +36.0° (all rotations in 99%

EtOH). The racemate *A*, but not *B*, was hydrolysed by trypsin-kinase, *B* was hydrolysed more rapidly than *A* by 0.5*N*-NaOH. Of compounds (I) to (VIII) only (I) and (VI) were hydrolysed by trypsin-kinase.

J. H. BIRKINSHAW.

Neutral salt additive compounds of β -alanine. H. KING and G. V. RUTTERFORD (J.C.S., 1931, 3131—3134).—The following additive compounds are prepared from β -aminopropionic acid (=A) and the appropriate salt in conc. aq. solution: A, LiCl, 1.5H₂O; A, LiBr, 1.5H₂O; A, LiI, 1.5H₂O; A, NaI; A, CaCl₂, 2H₂O; A, CaBr₂, 4H₂O; A, CaBr₂, 3H₂O; A, CaI₂, 4H₂O; A, SrCl₂, 4H₂O; A, SrBr₂, 4H₂O; A, SrI₂, 4H₂O; A, BaBr₂, 2H₂O. Compounds could not be obtained from NaCl, NaBr, KCl, KBr, KI, and BaCl₂.

H. BURTON.

Preparation of crystalline ornithine. Picrates and monosulphates of ornithine. H. B. VICKERY and C. A. COOK (J. Biol. Chem., 1931, 94, 393—399).—Addition of MeCHO-free EtOH and Et₂O to a conc. aq. solution of *d*-ornithine [mono- and dipicrates, both decomp. 208° after darkening at about 200°; monosulphate, decomp. 234° (darkens about 225°)] gives a partly cryst. product, m. p. 140° (softens at 120°), $[\alpha]_D^{25} + 11.5^\circ$ in H₂O, which is not completely stable even in the dark. *dl*-Ornithine monosulphate has m. p. 234° (decomp.) (darkens slightly from 225°) (lit. 213°).

H. BURTON.

Synthesis of glutamic acid. M. S. DUNN, B. W. SMART, C. E. REDEMANN, and K. E. BROWN (J. Biol. Chem., 1931, 94, 599—609).—Et oximinomalonate is reduced by Al-Hg (method of prep. given) using Cerchez's procedure (A., 1931, 205) to Et aminomalonate (I). Et benzamidomalonate, m. p. 62—63°, Et β -bromopropionate, and EtOH-NaOEt give Et α -benzamidopropionate- α - γ -tricarboxylate, decomp. on attempted distillation under 4 mm. pressure, hydrolysed by conc. HCl to *dl*-glutamic acid (II) in 52% yield. (I), Et β -chloropropionate, and EtOH-NaOEt afford Et α -aminopropionate- α - γ -tricarboxylate [probably contaminated with some of the *N*- β -carbethoxyethyl derivative of (I)], also hydrolysed to (II) in 36% yield. Photomicrographs of *d*-glutamic acid and (II) are given.

H. BURTON.

Alkaline deamination of derivatives of cysteine. H. T. CLARKE and J. M. INOUE (J. Biol. Chem., 1931, 94, 541—550).—*S*-Ethylcysteine (I) is obtained in 75% yield when cystine is reduced with Sn and 10% HCl, the mixture basified with aq. EtOH-NaOH, and then treated with Et₂SO₄. *S*-Benzylcysteine (II) is similarly prepared in 62% yield using CH₂PhCl in place of Et₂SO₄, whilst *S*-phenylcysteine (III) is formed in 30% yield when cystine is treated with diazotised NH₂Ph in neutral solution. The reactivity of these compounds towards alkaline deaminating agents is (I) < (II) < (III). Cystine, which is more reactive than cysteine (A., 1931, 76), occupies a position intermediate between (II) and (III). The stability of these compounds towards alkalis is influenced by the degree of unsaturation of the group attached to the S atom. Cysteic acid is deaminated at a much slower rate than cysteine and its derivatives. The deaminating agents used were those previously employed (*loc. cit.*).

H. BURTON.

Alkyl- and dialkyl-ammonium dithiocarbamates and trithiocarbonates and dialkylidene-ammonium alkylidenedithiocarbamates. T. G. LEVI (Gazzetta, 1931, 61, 803—814).—Benzyl- [m. p. 90—93° (decomp.)], camphyl- [m. p. 100—104° (decomp.)], diethyl- [m. p. 98—105° (decomp.)], dipropyl- [m. p. 80—90° (decomp.)], diisobutyl- [m. p. 83—93° (decomp.)], piperidyl- [m. p. 80—90° (decomp.)], dibenzyl- [m. p. 145—155° (decomp.)], and phenylmethyl- (partly melts below 100°) -ammonium dithiocarbamates are obtained from NH₄ dithiocarbamate and the hydrochloride of the corresponding amine. Dimethylammonium pentamethylenedithiocarbamate, m. p. 84—86°, diisobutylammonium dimethyldithiocarbamate, m. p. 84—86°, and dithiocarbamates of *s*- [m. p. 98—100° (decomp.)] and *as*-diphenylguanidine, *s*-ditolylguanidine [m. p. 130—132° (decomp.)], *s*- (m. p. 88—90°), and *as*- (m. p. 103—106°) -triphenylguanidine, quinine (m. p. 107—109°), quinidine (m. p. 202—205°), cinchonine (m. p. 208—209°), strychnine (m. p. above 250°), and brucine (m. p. about 140°), dimethyldithiocarbamates of quinine and strychnine, strychnine pentamethylenedithiocarbamate, and benzyl- and dipropyl-ammonium trithiocarbonates are similarly obtained. Diethyl- (m. p. 82—83°), dipropyl- (m. p. 81—82°), and diisobutyl- (m. p. 101°) -ethylidene-ammonium ethylidenedithiocarbamates are obtained from dialkylammonium dithiocarbamates and MeCHO. With CH₂O there is no reaction. Benzylammonium dithiocarbamate reacts with CH₂O giving a compound, C₁₀H₁₂N₂S₂, m. p. 130°, and with MeCHO giving a compound, C₁₂H₁₆N₂S₂, m. p. 98°. Dimethylammonium propyldithiocarbamate with CH₂O gives a compound, C₇H₁₅N₂S₂, m. p. 52°.

E. E. J. MARLER.

Purification and some physical properties of formamide. G. F. SMITH (J.C.S., 1931, 3257—3263).—Data are recorded for *d*, η , and γ for HCONH₂, which, when purified by freezing in absence of atm. H₂O, has m. p. 2.55°. The parachor is 2% and 0.7% low at 18° and 50°, respectively, possibly owing to association at low temp.

R. S. CAHN.

Constitution of synthetic resins. II. Theoretical basis and quantitative study of carbamide-formaldehyde condensation. G. WALTER and M. GEWING (Kolloid-Beih., 1931, 34, 163—217; cf. A., 1931, 1398).—A quant. study of the resinification of di(hydroxymethyl)carbamide (I) on fusion and subsequent heating in presence of condensing agents, and also of the condensation of (I) or of equiv. amounts of CH₂O and CO(NH₂)₂ in aq. solution, and of fusion of (mono)hydroxymethylcarbamide. The course of resinification is followed by determination of the H₂O and CO₂ evolved and analysis of the final resin, which indicates that the composition of the glass-clear resin is approx. the mean of those of (I) and hydroxymethylmethylenecarbamide (II), whilst those of the turbid resins approach that of (II). Fusion of (I) to a clear liquid can only be carried out either in small quantities by extremely rapid heating or in presence of basic substances, e.g., NaOAc; slow heating, or heating in contact with traces of acid, leads to evolution of CH₂O and formation of an amorphous mass of (II). If a small quantity of acid be added and

heating continued to 150° further condensation occurs with elimination of CH_2O and H_2O and a transparent resin is produced. An optimum p_H exists for this stage, and in aq. solution is approx. 3.0–5.0; within these limits, and close to p_H 5.0, a narrower range exists within which gelatinisation can be controlled. Further condensation of this type does not occur in presence of basic catalysts which cannot bring about elimination of CH_2O .

It is considered that the final resins contain the $>\text{N}\cdot\text{CH}_2\cdot\text{N}<$ and $\cdot\text{CH}_2\cdot\text{OH}$ groups, although the former cannot be detected by a Herzig-Meyer determination. Methylene-carbamide, thiocarbamide, and -bisacetamide, and hexamethylenetetramine also give low results by this method. The structure of the carbamide- CH_2O resins is discussed, and units of a chain structure, probably linked by covalencies into a three-dimensional network, are considered most probable. The peptisation of (II) by aq. CH_2O , and formation of a transparent resin from the product in the usual manner, is regarded as evidence that in this case at least the resin is a solution of $\cdot\text{CH}_2\cdot\text{OH}$ -free substances in $\cdot\text{CH}_2\cdot\text{OH}$ derivatives, an explanation which is also in agreement with the properties of the initial solution.

H. A. PIGGOTT.

Condensation of chloral with carbamide and phenylcarbamide. F. D. CHATTAWAY and E. J. F. JAMES (Proc. Roy. Soc., 1931, A, 134, 372–384).— α -Hydroxy- $\beta\beta\beta$ -trichloroethylcarbamide (I) (modified prep.), m. p. 150° (decomp.), is hydrolysed by hot aq. EtOH or by keeping in aq. NaOH to CHCl_3 , HCO_2H , and carbamide, but is pptd. unchanged on immediate acidification of its solution in aq. NaOH. (I), Ac_2O , and a drop of H_2SO_4 give N -($\beta\beta\beta$ -trichloro- α -acetoxyethyl)- N' -acetylcarbamide, m. p. 160° (decomp.), but (I), Ac_2O , and cold N -NaOH give di -(α -carbamido- $\beta\beta\beta$ -trichloroethyl) ether, $[\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CCl}_3)]_2\text{O}$, m. p. 222° (decomp.) [α - N' -Ac derivative, m. p. 241° (decomp.); α - NN' - Cl_2 derivative (prepared by Cl_2 in AcOH), m. p. 131° (decomp.)], which with Na in EtOH yields CHCl_3 , HCO_2Na , and carbamide [by way of (I)], together with $\beta\beta\beta$ -trichloro- α -ethoxyethylcarbamide (II), m. p. 202° (decomp.) [N -Ac derivative, m. p. 142° (decomp.)]. The following substances were similarly prepared, the group named being the α -substituent: MeO -, m. p. 205° (decomp.) [N -Ac derivative, m. p. 154° (decomp.)]; Pr^o -, m. p. 177° (decomp.); Pr^s -, m. p. 180° (decomp.); Bu^o -, m. p. 165° (decomp.).

Di -(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)carbamide (modified prep.), m. p. 194° (decomp.), is hydrolysed by keeping in aq. NaOH; with Ac_2O and a drop of H_2SO_4 it forms s - di -($\beta\beta\beta$ -trichloro- α -acetoxyethyl)carbamide, m. p. 189° (decomp.), but with Ac_2O and N -NaOH gives $anhydrodichloralcarbamide$, probably $O<\text{CH}(\text{CCl}_3)\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CCl}_3)>\text{O}$ (III), m. p. 137°, which with Na in EtOH forms CHCl_3 , HCO_2Na , carbamide, and s - di -($\beta\beta\beta$ -trichloro- α -ethoxyethyl)carbamide (IV), m. p. 241° (decomp.); the corresponding α - MeO - and α - Pr^o -compounds, m. p. 234° (decomp.) and 224° (decomp.), respectively, were similarly prepared. (II) and chloral at 100° form N -($\beta\beta\beta$ -trichloro- α -ethoxyethyl)- N' -($\beta\beta\beta$ -trichloro- α -hydroxyethyl)carbamide (V), m. p. 147° (decomp.) [N' - α - AcO -derivative, m. p. 187°

(decomp.)]; the corresponding N - α - MeO -compound, m. p. 159° (decomp.) [N' - α - AcO -derivative, m. p. 189° (decomp.)], was similarly prepared. (V) with Ac_2O and N -NaOH gives bis -(α -(N' - $\beta\beta\beta$ -trichloro- α -ethoxyethyl)carbamido)- $\beta\beta\beta$ -trichloroethyl ether, $[\text{CCl}_3\cdot\text{CH}(\text{OEt})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CCl}_3)]_2\text{O}$; this, when kept with Na in EtOH, affords (IV), and with Na in MeOH or PrOH affords N -($\beta\beta\beta$ -trichloro-ethoxyethyl)- N' -($\beta\beta\beta$ -trichloro- α -methoxyethyl)carbamide and the corresponding N' -(α - Pr^o)-compound, m. p. 212° (decomp.) and 228° (decomp.), respectively. Phenylcarbamide, chloral hydrate (2.5 mols.), and HCl, when kept, deposit N -phenyl- N' -($\beta\beta\beta$ -trichloro- α -hydroxyethyl)carbamide, m. p. 142° (decomp.) (decomposes when kept or warmed in aq. NaOH) [Ac_2 derivative, m. p. 104° (decomp.)], which with Ac_2O and N -NaOH gives di -(α -($\beta\beta\beta$ -trichloro- N' -phenylcarbamidoethyl) ether, $[\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CCl}_3)]_2\text{O}$, m. p. 236° (decomp.) after decomp. from 195° [N' - Ac_2 derivative, m. p. 153° (decomp.)]; this with Na in EtOH affords N -phenyl- N' -($\beta\beta\beta$ -trichloro- α -ethoxyethyl)carbamide, m. p. 153° (decomp.) [N -Ac derivative, m. p. 88° (decomp.)]; the corresponding α - MeO -compound, m. p. 189° (decomp.) [N -Ac derivative, m. p. 102° (decomp.)], was similarly obtained.

R. S. CAHN.

Supposed optical activity of ethyl diazo-succinate. A. WEISSBERGER and R. HAASE (Ber., 1931, 64, [B], 2896–2905).—The action of NaNO_2 and HCl on Et_2 aspartate leads in all cases to dextro-rotatory products. Decomp. of the products with dil. acids causes evolution of less than the calc. amount of N_2 and does not affect the sp. rotation. Since the optical activity is unaffected by catalytic hydrogenation of the product in presence of colloidal Pd, it cannot be due to Et diazosuccinate, but is attributed to an impurity. The product contains Cl, but activity cannot be ascribed to Et_2 chlorosuccinate, since diazotisation in presence of H_2SO_4 affords an optically active material. The possible presence of Et_2 d -malate harmonises approx. with the deficit of N_2 and the optical activity of the product and, if this is accepted, the production of d -bromosuccinic acid by treatment of the diazo-ester with HBr in Et_2O loses validity as evidence of the existence of optically active diazo-ester (cf. Levone and Mikeska, A., 1923, i, 25, 663). Since, however, l -aspartic acid is converted by HNO_2 into l -malic acid, the exact nature of the impurity is uncertain. The data with regard to optically active diazosuccinic (and other aliphatic diazo-) esters should be deleted from the literature.

H. WREN.

Action of arsenic chloride on ethyl sodio-malonate. II. Reply to Guglielmelli and Ruiz. E. V. ZAPPI (Anal. Assoc. Quím. Argentina, 1931, 19, 80–81; cf. A., 1930, 899; 1931, 832).—Polemical.

R. K. CALLOW.

Action of fluorine on aromatic compounds and a theory of ring substitution. S. F. WHEARTY, jun. (J. Physical Chem., 1931, 35, 3121–3147).—Very small quantities of impure $\text{C}_6\text{Cl}_4\text{F}_2$, b. p. 230–240°, and of $\text{C}_6\text{Cl}_3\text{F}_3$ have been obtained from F and C_6Cl_6 . From s - $\text{C}_6\text{H}_5\text{Cl}$, some $\text{C}_6\text{H}_5\text{F}_2\text{Cl}$, b. p. 75°/25 mm., was formed. Interaction of F with other C_6H_5 derivatives gave explosions or negative results. The

interpretation of the interaction of a halogen with a C_6H_6 compound is discussed at length.

A. L. HENNE (b).

Thermal vapour-phase chlorination of toluene and benzene. J. MASON, C. A. SMALE, R. N. THOMPSON, and T. S. WHEELER (J.C.S., 1931, 3150—3157).— Cl_2 reacts rapidly (cf. A., 1931, 1267) with PhMe above 250° to give CH_2PhCl and $CHPhCl_2$; in presence of carriers nuclear substitution also occurs. With C_6H_6 above 400° PhCl and $C_6H_4Cl_2$ are formed. The proportions of first- and second-stage products agree well with theory.

C. W. DAVIES.

Compound of nitrobenzene and sulphuric acid. I. MASSON (J.C.S., 1931, 3200—3206).— $PhNO_2$ and H_2SO_4 , m. p. $10-35^\circ$, form the compound $PhNO_2 \cdot H_2SO_4$, m. p. $11-6^\circ$, which is probably $[PhNO_2 \cdot H]^+ [HSO_4]^-$, since it increases the conductance of H_2SO_4 . This compound is unimol. in H_2SO_4 , but bimol. in C_6H_6 . Its influence in substitution reactions is discussed. Pure C_6H_6 and $PhNO_2$ have m. p. $5-58^\circ$ and $5-84^\circ$, respectively. R. S. CAHN.

Action of sodamide on some bromohydrocarbons. (Mlle.) P. AMAQAT (Bull. Soc. chim., 1931, [iv], 49, 1410—1417; cf. A., 1930, 759).— β -Phenylpropyl bromide, β -phenylbutyl bromide, and β -phenylisobutyl bromide are stable towards H_2O and 0.1N- $AgNO_3$ and are not isomerised in ultra-violet light (cf. A., 1928, 255). γ -Phenylpropyl bromide, b. p. $120-122^\circ/16$ mm., is obtained in 85% yield from PBr_3 and γ -phenylpropyl alcohol, but under the same conditions β -phenyl- β -ethylbutyl alcohol is dehydrated, giving a hydrocarbon, b. p. $110-115^\circ/12$ mm. β -Phenyl- β -benzylbutyl alcohol similarly yields an olefine, b. p. $180^\circ/15$ mm. 48% HBr and β -phenyl- β -ethylbutyl alcohol afford only 20% of the bromide, the alcohol being mainly dehydrated to α -phenyl- β -ethyl- Δ -butene, b. p. $114-118^\circ/12$ mm. In xylene-phenylpropyl bromide is unattacked by $NaNH_2$, but in CH_2Ph_2 a mixture of sec. and tert. amines is obtained.

R. BRIGHTMAN.

Diphenyl and its derivatives. VIII. 2:2'-Disubstituted derivatives of diphenyl. L. MASCARELLI and D. GATTI [with M. PIRONA] (Gazzetta, 1931, 61, 782—797).—2-Chloro-, m. p. 71° , 2-bromo-, m. p. $66-67^\circ$, 2-iodo-, m. p. $81-82^\circ$, and 2-acetoxy-, m. p. 102° , 2'-nitrodiphenyl are obtained from 2'-nitro-2-aminodiphenyl. The Sandmeyer reaction with 2'-nitro-2-aminodiphenyl gives mainly products containing a heterocyclic nucleus, e.g., carbazole; diazotisation in presence of Cu halide in a current of CO gives better results. 2-Chloro-, m. p. $56-57^\circ$ (hydrochloride, m. p. $176-177^\circ$), 2-bromo-, m. p. about $46-50^\circ$, b. p. $196-197^\circ/27$ mm., and the Ac derivative of 2-iodo-2'-aminodiphenyl are obtained by reduction of the corresponding halogeno-nitro-compounds. 2-Chloro-2'-bromo-, m. p. 58° , and 2-chloro-2'-iodo-diphenyl, m. p. $63-64^\circ$, are obtained from 2-chloro-2'-aminodiphenyl, and 2'-bromo-2-iodo-diphenyl, m. p. 90° , from 2-bromo-2'-aminodiphenyl. The yields in all cases are small in comparison with the 3:3' and 4:4' series. 2-Chloro- and 2-bromo-2'-nitrodiphenyl are also obtained by the action of

Cu on a mixture of o-iodonitro- and o-chloro- (or bromo-)iodobenzene. E. E. J. MARLER.

Iodo-derivatives of diphenyl obtained by direct action of iodine in presence of nitric acid. I. 4-Iodo-4'-nitrodiphenyl. L. GUGLIAMELLI and M. R. FRANCO (Anal. Assoc. Quim. Argentina, 1931, 19, 5—33).—The following conditions are optimal for the preparation of 4-iodo-4'-nitrodiphenyl, m. p. $202-206^\circ$ (dichloride, m. p. 190°): HNO_3 (d 1.40) (12—24 c.c.) is added dropwise during 30 min. to a mixture of Ph_2 (10 g.) and I (5 g.) at 100° . The product, washed free from acid, is then freed from (?) 2:4'- and 4:2'-compounds by extraction with EtOH. Iodination probably precedes nitration. The substance is identical with the product obtained from 4-nitro-4'-aminodiphenyl by the diazo-reaction, and reduction yields 4-iodo-4'-aminodiphenyl, m. p. 159° , identical with the substance prepared from benzidine and yielding identical derivatives (benzylidene, m. p. $208.5-209.5^\circ$; p-dimethylaminobenzylidene, m. p. 204° , and piperonylidene, m. p. $150-151^\circ$).

R. K. CALLOW.

Ditolyls. III. Derivatives of 2'-nitro-dl-2-aminotolyl. A. ANGELETTI (Gazzetta, 1931, 61, 832—838).—2-Iodo- (m. p. $129-130^\circ$), 2-bromo- (m. p. $122-123^\circ$), and 2-chloro- (m. p. $99-100^\circ$) 2'-nitro-6:6'-dimethyldiphenyls are obtained from 2'-nitro-2-amino-6:6'-dimethyldiphenyl by the Sandmeyer reaction. 2'-Nitro-2-hydroxy-6:6'-dimethyldiphenyl (Ac derivative, m. p. $86-87^\circ$) could not be isolated in a pure state. E. E. J. MARLER.

Conversion of halogenodiphenylenesulphonates into halogenodiphenyl-2-sulphonic acids. C. COURTOT and R. EVAÏN (Bull. Soc. chim., 1931, [iv], 49, 1555—1562; cf. A., 1931, 1281, 1406).—Benzidine-sulphone is converted by diazotisation and decomp. with EtOH into diphenylenesulphone (yield 78%), m. p. 232° . 4:4'-Dichloro-, m. p. $295-296^\circ$, and 4:4'-dibromo-diphenylenesulphone, m. p. 313° , are obtained in 85% yield. On alkaline fusion at $190-200^\circ$, 4:4'-dichlorodiphenylenesulphone affords 4:4'-dichlorodiphenyl-2-sulphonic acid (chloride, m. p. 75° ; amide, m. p. 155°). 4:4'-Dibromodiphenyl-2-sulphonic acid (chloride, m. p. 123° ; amide, m. p. 188°) is similarly obtained at $200-210^\circ$. R. BRIGHTMAN.

Action of scission catalysts in hydrogenative cracking of polynuclear hydrocarbons. A. KLING and D. FLORENTIN (Compt. rend., 1931, 193, 1198—1199).—The decomp. of $C_{10}H_8$ and anthracene in H_2 at $475-492^\circ$ and 225—290 kg. per sq. cm. in presence of hydrogenating catalysts, e.g., NiO, MoS_2 , and Mo oxides, gives small amounts of benzenoid hydrocarbons, the yields of which are improved by addition of S or H_2SeO_3 . Much better results are obtained with $AlCl_3$ in absence of H_2O . H. A. PIGGOTT.

Nitro-derivatives of naphthalene, tetrahydronaphthalene, and dinaphthyl. W. M. CUMMING and G. HOWIE (J.C.S., 1931, 3176—3181).—4-Iodo-2-nitro- (I), m. p. $192-193^\circ$, and 2-iodo-4-nitro- (II), m. p. 234° , α -naphthylamine are prepared by iodinating 2- and 4-nitro- α -naphthylamine, respectively, with ICl in AcOH. 1-Iodo-3-nitro-, m. p. $118-118.5^\circ$, 2-iodo-1-nitro-, m. p. 84° , 2-iodo-3-nitro- (III),

m. p. 76—76.5°, and 3-iodo-1-nitro- (IV), m. p. 64—65°, -ar-tetrahydronaphthalene are prepared by the usual method from the appropriate nitrotetrahydronaphthylamines. Oxidation of (III) and (IV) with Br gives 2-iodo-3-nitro-, m. p. 89—89.5°, and 3-iodo-1-nitro-, m. p. 108°, -naphthalene, respectively; the last-named is also prepared by elimination of NH_2 from (II). Deamination of (I) affords 1-iodo-3-nitro-naphthalene, m. p. 147° (lit. 142—143°). Ullmann's generalisations (A., 1901, i, 586; 1904, i, 725) for the prep. of *s*-diphenyls hold also in the C_{10}H_8 and tetrahydronaphthalene series. Condensation of halogenonitronaphthalenes could not be effected by Na. The following are prepared by Ullmann's method: 1:1', m. p. 187—188°, and 3:3' (V), m. p. 201°, -dinitro-2:2'-ditetrahydronaphthyls; 2:2', m. p. 187° (lit. 179—180°) [Chudozilov's method (A., 1925, i, 903) (modification described) does not give trustworthy results], and 3:3', m. p. 281° (lit. 262—264°), -dinitro-1:1'-dinaphthyls; 1:1'-dinitro-2:2'-dinaphthyl, m. p. 284° (decomp.) (lit. 264—265° and 276°). 3:3'-Dinitro-2:2'-dinaphthyl, m. p. 257—258°, is prepared by oxidation of (V) with Br. 4:4'-Dinitro-1:1'-dinaphthyl, m. p. 246°, obtained by Schoepfle's method (A., 1923, i, 776), could not be prepared from 4-nitronaphthalene-1-diazonium sulphate and Cu. 2:2'-Dinaphthyl and HNO_3 (d 1.42) in AcOH give 1-nitro-2:2'-dinaphthyl, m. p. 179°, nitrated further to a mixture, m. p. 198—208°, of dinitro-isomerides containing the 1:1'-derivative, since reduction with Zn dust and conc. HCl in AcOH affords 1:1'-imino-2:2'-dinaphthyl. The mixture of 1- and 2-nitrotetrahydronaphthalenes obtained from tetrahydronaphthalene, b. p. 95—97°/16 mm. (lit. above 175°/13 mm.), by a modification of Schroeter's method (A., 1922, i, 123), is reduced by Vesely and Chudozilov's method (A., 1925, i, 654); a simple process for the extraction of tetrahydro- β -naphthylamine is described.

H. BURTON.

3-Nitrofluorene. F. E. BARDOUT (Anal. Assoc. Quim. Argentina, 1931, 19, 117—136).—3-Nitro-2-aminofluorene (A., 1902, i, 758; 1928, 521) is converted on deamination (diazo-reaction and Cu_2O) into 3-nitrofluorene, m. p. 105°. Oxidation of the latter with K_2CrO_4 yields 3-nitrofluorenone, m. p. 232° (lit. 210°) [oxime, m. p. 217° (decomp.) (lit. 240°)], which is converted successively into the known 3- NH_2 - and 3-OH-compounds. R. K. CALLOW.

Polycyclic aromatic hydrocarbons. VIII. Chemistry of 1:2:5:6-dibenzanthracene. J. W. COOK (J.C.S., 1931, 3273—3279; cf. A., 1931, 1420).—1:2:5:6-Dibenzanthracene (I) reacts additively with Br, pyridine dibromide, and maleic anhydride (but not with HNO_3 in AcOH), but more reluctantly than anthracene. These and other reactions recorded below show that angular *Bz* rings (in contrast to linear) stabilise the aromatic state of the *meso*-ring. (I) with Br in CS_2 at room temp. gives slowly a little additive compound (not isolated pure). With Br in pyridine (I) gives a salt which with aq. NH_3 gives 1:2:5:6-dibenzanthronyl-9-pyridinium bromide, m. p. indefinite. With HNO_3 (d 1.5) in AcOH (I) affords the 9- NO_2 -compound, m. p. 217—218°, reduced by NHPh-NH_2 (but not by SnCl_2 in AcOH) to 9-amino-1:2:5:6-

dibenzanthracene, m. p. 268—269° (*Ac*₂ derivative, m. p. 215—216.5°; *n*-butyryl derivative, m. p. 300—302°; corresponding succinimide, m. p. 299—300°), which was oxidised by CrO_3 to 1:2:5:6-dibenzanthraquinone (whereby its constitution is proved). (I) and maleic anhydride at 250—260° give a product, hydrolysed by boiling NaOH to 1:2:5:6-dibenzanthracene-9:10-endo- $\alpha\beta$ -succinic acid, m. p. 230° (*Na*₂ salt). 1:2:5:6-Dibenzanthraquinone with Sn and HCl in AcOH gives an insol. substance, but with Al and conc. H_2SO_4 gives 9-hydroxy-1:2:5:6-dibenzanthracene, isolated as *Ac* derivative, m. p. 235°, which led to the *Me* ether, m. p. 178°, unaffected by HCl in boiling AcOH.

R. S. CAHN.

Molecular organic compounds. III. Molecular organic compounds of *o*-, *m*-, and *p*-monosubstituted nitrobenzenes. C. A. BUEHLER, C. R. ALEXANDER, and G. STRATTON (J. Amer. Chem. Soc., 1931, 53, 4094—4096).—The following new mol. compounds (1:1 unless stated otherwise) are described: (a) *p*-nitrophenol and *o*-toluidine, m. p. 53.4° (all m. p. are corr.), benzidine, m. p. 149.9°, NHET_2 , m. p. 109.6°, and pyridine (2:1), m. p. 63.8°; (b) *m*-nitrophenol and *o*-toluidine, m. p. 40.6°, benzidine, m. p. 112.3°, and NHET_2 , m. p. 43°; (c) *o*-nitrophenol and NHET_2 , m. p. 105.1°, and (d) *p*- $\text{C}_6\text{H}_4\text{Cl-NO}_2$ and α -naphthol, m. p. 165.2°. Other mol. compounds previously prepared by Kremann are also described with corr. m. p. The mol. compounds of high m. p. were prepared in EtOH, C_6H_6 , or CHCl_3 , whilst those with low m. p. were obtained by fusion of the components and subsequent heating at a fairly high temp. Differences in the ability of the nitrophenols to form mol. compounds are attributed to the chelate ring in the *o*-derivative. The comparatively high additive power of *m*- and *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-OH}$ and their almost exclusive combination with NH_2 -compounds indicate that in the simpler types union occurs between the OH and NH_2 groups.

C. J. WEST (b).

N-Chlorosulphonamides and N-chlorosulphonylsulphonamides. M. BATTEGAY, L. DENI-VELE, and J. MEYBECK (Compt. rend., 1931, 193, 1195—1198).—N-(Chlorosulphonyl)-formanilide, m. p. 80—81°, -acetanilide, m. p. 75°, -*p*-toluenesulphonanilide, m. p. 139°, -*p*-toluenesulphon-*o*-toluidide, m. p. 108°, -*p*-toluenesulphon-*m*-toluidide, m. p. 126°, and -*p*-toluenesulphon-*p*-toluidide, m. p. 166°, are prepared by action of Na on the appropriate acylamide in dry Et_2O , and interaction of the resulting Na compound with SO_2Cl_2 at -5° to 0°. N-(Chlorosulphonyl)benzanilide, m. p. 109.5—110°, is better prepared by means of the Mg derivative obtained by action of MgPhCl on NHBzPh .

H. A. PIGGOTT.

Chlorination of anilides. VII. Constitutional influence of acyl group on side-chain reactivity. G. WILLIAMS and S. P. HUGHES (J.C.S., 1931, 3125—3131; cf. A., 1928, 668).—The velocities of simultaneous *N*- and *C*-chlorination in 40% AcOH at 18° are measured in the NH_2Ph (CHO, Ac, and CO- C_6H_5 derivatives), *o*-chloroaniline (CHO, Ac, and CO- CH_2Cl derivatives), and *p*-chloroaniline series (CHO, Ac, CO-Et, CO-Pr, CO- Pr^i , CO- CH_2Cl , CO- C_6H_5 , Bz, and PhSO_2 derivatives). Both are reduced by introduc-

tion of Cl or Ph into the acyl group, and the former also by increasing length or branching of the alkyl chain. Nuclear chlorination is favoured by the presence of Me in the acyl radical. The results are discussed in relation to the ionisation const. of the corresponding acids. H. A. PIGGOTT.

Inhibitory effects of substituents in chemical reactions. II. Reactivity of thiocarbimido-group in substituted arylthiocarbimides. D. W. BROWNE and G. M. DYSON (J.C.S., 1931, 3285—3308).—The velocities of interaction of phenylthiocarbimide and a large series of nuclear substituted derivatives with EtOH at its b. p. are measured by determination of unreacted thiocarbimide at definite time intervals by addition of benzidine, which reacts preferentially. In general, the velocity is increased by negative substituents and decreased by alkyl groups in any position; alkoxy groups inhibit the reaction slightly in the *o*- and *p*-positions, and aid it in the *m*-position. The effects are additive in polysubstituted derivatives, and all the Me₃ compounds studied were unreactive. The following thiocarbimides, which appear to be new, are prepared from the appropriate amine and CSCI₂: 4-, m. p. 112°, and 3-nitrophenyl-, m. p. 60°; 3-nitro-*o*-tolyl-, m. p. 70°; 4-fluoro-3-nitrophenyl-, m. p. 55°; 4-ethylphenyl-, b. p. 245°; 4-isopropylphenyl-, b. p. 252°; 3-, b. p. 226—227°, and 4-fluorophenyl-, m. p. 12°, b. p. 228°; 3-, b. p. 269°, 4-, b. p. 268°, 5-, m. p. 36°, and 6-chloro-*o*-tolyl-, b. p. 276°; 4-, b. p. 272°, 5-, m. p. 34°, 2-, b. p. 264°, and 6-chloro-*m*-tolyl-, b. p. 270°; 2-chloro-*p*-tolyl-, b. p. 263°; 6-chloro-*m*-4-xylyl-, b. p. 278°; chloromesityl-, m. p. 44°; 3-chloro-*p*-tolyl-, b. p. 258°; 5-chloro-*ψ*-cumyl-6-, m. p. 36°; 3-chloro-*p*-anisyl-, m. p. 89°; 4-chloro-*m*-anisyl-, m. p. 51°; 5-chloro-*o*-anisyl-, m. p. 61°; 5-chloro-*m*-anisyl-, m. p. 36°; 3:5-dimethoxyphenyl-, m. p. 51°; *p*-xenyl-, m. p. 64°; and 4-, m. p. 71°; and 3-aldehydophenyl-thiocarbimide, m. p. 42°. 4-Ethylphenyl-, m. p. 138°; 4-isopropyl-, m. p. 134°; 3-fluorophenyl-, m. p. 116°; *s*-di-(3-fluorophenyl)-, m. p. 144°; *s*-di-(4-fluorophenyl)-, m. p. 145°; α -(5-chloro-*o*-tolyl)- β -(2-naphthyl)-, m. p. 163°; α -(6-chloro-*m*-tolyl)- β -(2-naphthyl)-, m. p. 154°; α -(6-chloro-*o*-tolyl)- β -(2-naphthyl)-, m. p. 150°; α -5-chloro-*m*-tolyl- β -*p*-tolyl-, m. p. 156°; α -3-chloro-*o*-tolyl- β -*p*-tolyl-, m. p. 180°; 4-chloro-*o*-tolyl-, m. p. 138°; α -(2-chloro-*p*-tolyl)- β -(2-naphthyl)-, m. p. 149°; α -(6-chloro-*m*-4-xylyl)- β -(2-naphthyl)-, m. p. 154°; α -chloromesityl- β -(2-naphthyl)-, m. p. 181°; α -(4-chloro-*m*-tolyl)- β -(2-naphthyl)-, m. p. 158°; α -(2-chloro-*m*-tolyl)- β -(2-naphthyl)-, m. p. 172°; α -3-chloro-*p*-tolyl- β -*p*-tolyl-, m. p. 160°; α -(5-chloro-6-*ψ*-cumyl)- β -(2-naphthyl)-, m. p. 161°; α -(3-chloro-*p*-anisyl)- β -(1-naphthyl)-, m. p. 174°; α -(4-chloro-*m*-anisyl)- β -(1-naphthyl)-, m. p. 155°; 5-chloro-*o*-anisyl-, m. p. 133°; α -(5-chloro-*m*-anisyl)- β -(*p*-tolyl)-, m. p. 136°; and α -3:5-dimethoxyphenyl- β -*p*-tolyl-, m. p. 148°. Thiocarbimides are described. By interaction of the appropriate thiocarbimide with EtOH: *o*-, m. p. 59°, *m*-, m. p. 115°, and *p*-nitrophenyl-, m. p. 175°; 2-nitro-*m*-tolyl-, m. p. 110°; 3-, m. p. 72°, and 2-nitro-*p*-tolyl-, m. p. 89°; 3-, m. p. 109°, 5-, m. p. 116°, and 4-nitro-*o*-tolyl-, m. p. 112°; 4-nitro-*o*-anisyl-, m. p. 76°; 3-nitro-4-fluorophenyl-, m. p.

118°; *m*-, m. p. 82°, and *p*-chlorophenyl-, m. p. 105°; 2:4-, m. p. 79°, 2:5-, m. p. 80°, and 3:5-dichlorophenyl-, m. p. 131°; *m*-, m. p. 84°, and *p*-fluorophenyl-, m. p. 86°; *m*-, m. p. 94°, and *p*-bromophenyl-, m. p. 107°; *m*-, m. p. 107°, and *p*-iodophenyl-, m. p. 98°; *m*-, m. p. 67°, and *p*-tolyl-, m. p. 85°; 3-*o*-xylyl-, m. p. 108°; *p*-xylyl-, m. p. 85°; and *s*-*m*-xylyl-, m. p. 88°; *o*-, m. p. 65°, *m*-, m. p. 85°, and *p*-anisyl-, m. p. 68°; 2:5-, m. p. 72°, 3:4-, m. p. 72°, and 3:5-dimethoxyphenyl-, m. p. 83°; *m*-, m. p. 75°, and *p*-ethoxyphenyl-, m. p. 95°; 2-chloro-*m*-tolyl-, m. p. 77°; 4-chloro-*m*-tolyl-, m. p. 59°; 6-chloro-*o*-tolyl-, m. p. 88°; 2-chloro-*p*-tolyl-, m. p. 88°; 5-chloro-*m*-tolyl-, m. p. 105°; 4-chloro-*o*-tolyl-, m. p. 81°; 5-chloro-*o*-tolyl-, m. p. 79°; 6-chloro-*m*-tolyl-, m. p. 101°; 6-chloro-4-*m*-xylyl-, m. p. 115°; 2-chloro-*p*-anisyl-, m. p. 96°; 5-chloro-*m*-anisyl-, m. p. 86°; 4-chloro-*o*-anisyl-, m. p. 81°; 6-chloro-*m*-anisyl-, m. p. 124°; 3-, m. p. 95°, and 4-cyanophenyl-, m. p. 110°; 3-, m. p. 147°, and 4-aldehydophenyl-, m. p. 135°; 4-acetylphenyl-, m. p. 111°; and 4-xenyl-, m. p. 117°. Thiourethane, NHR·CS·OEt, are prepared.

H. A. PIGGOTT.

Catalytic reduction of nitroanilines and *p*-phenylenediamine in presence of aldehydes and ketones. R. T. MAJOR (J. Amer. Chem. Soc., 1931, 53, 4373—4378; cf. A., 1931, 837).—Catalytic reduction (Adams) of a mixture of *p*-NO₂·C₆H₄·NH₂ or *p*-C₆H₄(NH₂)₂ and COMe₂ at room temp. gives NN'-diisopropyl-*p*-phenylenediamine, m. p. 53° (dihydrochloride, decomp. when heated, obtained from the NN'-dinitroso-derivative, m. p. 110—111°, and conc. HCl; NN'-Bz derivative, m. p. 180—181°; NN'-Ac₂ derivative, m. p. 180°). Similarly, *p*-NO₂·C₆H₄·NH₂ and COMeEt afford some NN'-disec-butylamino-*p*-phenylenediamine (dihydrochloride; dinitroso-derivative, m. p. 62°; Bz₂ derivative, m. p. 159—160°); with COEt₂, NN'-di- α -ethylpropyl-*p*-phenylenediamine (dinitroso-derivative, m. p. 96°; Bz₂ derivative, m. p. 132°) results. In all these reductions some *p*-phenylenediamine is produced. Benzoylation of the reduction product from *m*-NO₂·C₆H₄·NH₂ and COMe₂ gives only NN'-dibenzoyl-*m*-phenylenediamine. *o*-NO₂·C₆H₄·NH₂ and COMe₂ afford (after benzoylation) N-benzoyl-NN'-diisopropyl-, m. p. 147—148°, and N-benzoyl-N'-isopropyl-, m. p. 159—160°, *o*-phenylenediamine (5% yield of each) in addition to NN'-dibenzoyl-*o*-phenylenediamine. Reduction of a mixture of *p*-NO₂·C₆H₄·NH₂ and PhCHO gives 50% of tetrabenzyl-*n*-phenylenediamine.

C. J. WEST (b).

Nitroamines. II. Nitrophenylnitroamines. E. MACCIOTTA (Gazzetta, 1931, 61, 773—777).—3:5-, 2:3-, and 3:4-dinitroanilines with HNO₃ and Ac₂O (J.C.S., 1902, 81, 806) give respectively 3:5-, isolated only as Hg salt, [C₆H₃(NO₂)₂·N(NO₂)₂·Hg], 2:3-, and 3:4-dinitrophenylnitroamines. 2:3- and 3:4-Dinitroanilines with HNO₃ and H₂SO₄ give 2:3:4:6-tetranitrophenylnitroamine, m. p. 105° (decomp.). 3:5-Dinitroaniline gives an unstable compound, probably penta-substituted. E. E. J. MARLER.

Preparation and resolution of α -phenylethylamine. E. ANDRE and C. VERNIER (Compt. rend., 1931, 193, 1192—1194).—dl- α -Phenylethylamine is

obtained in 70% yield by hydrolysis of the cryst. ammonium bromide from α -phenylethyl bromide and hexamethylenetetramine with HCl in EtOH at 95°. It is conveniently resolved into optically active forms by *l*-quinic and *d*-tartaric acids. H. A. PRIGOTT.

Nitroamines. III. *m*-Phenylenedinitroamine. E. MACCIOTTA (Gazzetta, 1931, 61, 777—782).—*m*-Phenylenediamine with EtNO₂ and a solution of K in EtOH and Et₂O or with HNO₃ and Ac₂O gives *m*-phenylenedinitroamine (K₂, Ag₂, Pb salts). *m*-Phenylenediamine nitrate with AlCl₃ (A., 1902, i, 312) gives only *m*-phenylenediamine hydrochloride.

E. E. J. MARLER.

Complex compounds of cobalt with *s*-diphenylethylenediamine. J. V. DUBSKY and A. LANGER (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 145, 1—8).—The products described by Gapon (A., 1930, 765) are not compounds but mixtures of diphenylethylenediamine hydrochloride with CoCl₂ or with the double salt of these two substances.

R. TRUSZKOWSKI.

Reactions of azoxy- and azo-compounds with benzyl alcohol, benzaldehyde, and quinoline. W. M. CUMMING and G. HOWE (J.C.S., 1931, 3181—3185).—Azoxybenzene (I) and *p*-azoxytoluene are reduced by boiling CH₂Ph·OH in CO₂ to azobenzene (II) and *p*-azotoluene, respectively. Similarly, (I) and PhCHO give about 10% of NHBzPh, formed in almost quant. yield from (II) and PhCHO, whilst *p*-azotoluene is converted into benz-*p*-toluidide. Benzoin is not a factor in the second set of reactions, but (II) is reduced by benzoin in absence or presence of CH₂Ph·OH to NH₂Ph. Reaction between (II) and PhCHO may occur thus: 2PhCHO + (NPh)₂ → [Ph·C(OH):NPh]₂ → 2NHBzPh. *s*-1:1'-Azoxy-naphthalene (III) is not reduced by CH₂Ph·OH or PhCHO, but is converted into the *as*-form (IV) (J.C.S., 1923, 123, 2464). 1:1'- and 2:2'-Azonaphthalenes do not react with PhCHO. (III), PhCHO, and quinoline at 170° give (IV) and 33% of 2-hydroxy-1:1'-azonaphthalene (V), m. p. 230°, also prepared by coupling α -naphthylamine and β -naphthol. (V) and not the 4-hydroxyazo-compound [as suggested by Baudisch and Fürst (A., 1913, ii, 38)] is also formed when (III) [or (IV)] is exposed to light; the hydroxyazo-compound, m. p. 224°, of Cumming and Steele (cf. A., 1926, 162) is (V). The reaction between PhCHO and (I) or (II) is inhibited by quinoline. A basic condensation product, m. p. 99—100°, of PhCHO and quinoline is formed when the reactants are heated.

H. BURTON.

Hydrolysis of salts of hydrazo-compounds. B. P. OREKIN, A. T. RYSKALTSCHUK, and M. A. AIZIKOVITSCH (J. Gen. Chem. Russ., 1931, 1, 696—703).—Treatment of hydrazobenzene hydrochloride, prepared in Et₂O solution, with H₂O gives 30% of benzidine, 60% of diphenylene and semidine, and 10% of hydrazobenzene (with some azobenzene); keeping the solution for 24 hr. before hydrolysis increases the benzidine and diphenylene fractions at the expense of the hydrazobenzene. Rapid saturation of ethereal hydrazobenzene with HCl, followed by hydrolysis, gives 46% of benzidine, 14% of diphenylene, and 40% of hydrazobenzene, no semidine

being formed. Solid hydrazobenzene with HCl below -20° forms an emerald-green dihydrochloride, yielding 21% of benzidine, 56% of diphenylene and semidine, and 23% of hydrazobenzene on hydrolysis. The green

salt is formulated as  = NHCl·NHPh·HCl,

and it is assumed that this is hydrolysed to NHPhCl and NH₂Ph, which then combine to form semidine. The formation of NHPhCl cannot take place when 1 mol. of HCl is added to the base, as assumed by Franzen and von Fürst (A., 1917, i, 58), because no semidine is formed unless the reaction product is kept. Hydrolysis of the green salt with aq. NH₃ gives NHPh·NH₂, confirming the formation of intermediate products suggested; the yield of benzidine is reduced. *o*-Hydrazotoluene forms a green dihydrochloride at -50°, yielding *o*-toluidine and *o*-semidine, but no *p*-semidine, on hydrolysis. *p*-Hydrazotoluene forms a brownish-red dihydrochloride, hydrolysed to the appropriate *o*-semidine. *o*- and *p*-Hydrazoanisole form unstable violet dihydrochlorides; violet dihydrochlorides are also obtained from *o*- and *p*-azoanisoles (m. p. 149° and 120°), but these readily lose HCl, re-forming the base.

G. A. R. KON.

Oxidising properties of normal diazonium hydroxides. Z. JOLLES (Atti R. Accad. Lincei, 1931, [vi], 14, 115—119).—A brief summary of published work.

T. H. POPE.

Diazo-compounds sensitive to light. III. *p*-Substituted diazo- and tetrazo-compounds. J. SCHMIDT and W. MAIER (J. pr. Chem., 1931, [ii], 132, 153—162; cf. A., 1931, 752).—Complex salts of the following diazonium chlorides with the components named are described: *p*-diazodimethylaniline + HgCl₂, m. p. 160° (decomp.), + FeCl₃, m. p. 109° (decomp.); *p*-diazodiethylaniline + HgCl₂, m. p. 119° (decomp.); + FeCl₃; *p*-diazodiphenylamine + HgCl₂, m. p. 144° (decomp.), + 0.5ZnCl₂, m. p. 141°, + 0.5CdCl₂; *pp'*-tetrazodiphenyl + 2HgCl₂, + ZnCl₂, + 2CdCl₂. The following substances do not yield similar complex salts: 2:6-dibromodiazobenzene-4-sulphonic acid (I) (dimorphous crystals of the internal betaine), 3:5-dichloro-4-diazophenetole, 3:5-dichloro-4-azophenol, *pp'*-tetrazodiphenylmethane. The above diazo-compounds (except the last-mentioned) are stable in the dark, but sensitive to light. (I) couples with phenols even in acid solution, but not with amines.

R. S. CAHN.

Diazo-compounds. IV. H. T. BUCHERER and G. VON DER RECKE (J. pr. Chem., 1931, [ii], 132, 113—144; cf. A., 1931, 1409—1410).—Previous work (*loc. cit.*) on the action of CO₂ and other weak acids on antidiastates is confirmed, and similar results are obtained with diazotised *o*-nitroaniline, *p*-nitro-anisidine, and *p*-chloro-*o*-nitroaniline. The formation of the diazoamino-compound (the yield of which varies with the experimental conditions) is considered to be due to change of the antidiastate into diazonium hydroxide (? carbonate), which hydrolyses to the amine and HNO₂, the amine subsequently coupling with more diazonium hydroxide. HNO₂ replaces the N₂Cl group in diazonium salts by NO₂ slowly at 0° and more rapidly at temp. up to 50°.

the yields varying according to the amounts of HNO_3 and HCl used; the max. yields of pure NO_2 -compound for the bases named were as follows: *o*-, *m*-, and *p*-nitroaniline, 58, 30, and 50%, respectively; *p*-chloroaniline, 23%; α - and β -naphthylamine, 4 and 5.5%, respectively (together with the naphthols); sulphanilic acid, α -naphthylamine-4- and 5-sulphonic acid, 0%; benzidine, 8%. Diazotised *p*-chloroaniline and HCN give additive compounds, m. p. 178°, 69°, and 103°, and much tar. The compound, m. p. 103°, gives HCN and tar with H_2SO_4 in AcOH , and NH_4Cl with HCl in EtOH ; it condenses with CH_2O , MeCHO , and PhCHO in EtOH or AcOH ; CH_2O leads to a substance, $\text{C}_{17}\text{H}_{10}\text{N}_6\text{Cl}_2$, m. p. 135°, hydrolysed by conc. H_2SO_4 at 125–135° to a substance, m. p. 201°. *p*-Nitroaniline gives a similar compound, m. p. 126°, which with CH_2O , MeCHO , and PhCHO gives substances, m. p. 195°, 144°, and 193°, respectively. Diazotised β -naphthylamine and HCN give naphthalene- β -antidiazocyanide, which does not react with aldehydes. Aq. Na phenylhydrazinesulphonate reacts only after 25–30 min. with PhCHO to form benzaldehydephenylhydrazone, hydrolysis of the sulphonate being slow at first, but later catalysed by the acid formed. CH_2O reacts after 1.5 hr., but the product could not be purified. R. S. CAHN.

Action of hydrogenating and mixed catalysts on the cracking of phenols with hydrogen. A. KLING and D. FLORENTIN (Compt. rend., 1931, 193, 1023–1024).—A study of the action of various catalysts on mixtures of PhOH and H_2 at 470–490° and approx. 300 kg. per sq. cm. The products are identified by determinations of b. p., *d*, and *n*. NiO or Mo_2O_5 with excess of H_2 give mainly C_6H_6 and cyclohexane; with insufficient H_2 the latter catalyst gives heavier hydrocarbons, and conversion is incomplete. Mo_2O_3 activated by heating at 500° induces dehydration rather than hydrogenation even when H_2 is in excess. Dehydrating catalysts, however, activated by heat and addition of 5–10% Mo_2O_5 , cause rapid and complete transformation of PhOH into hydrocarbons rich in C_6H_6 , even with an excess of H_2 .

H. A. PIGGOTT.

Rearrangement of hydroxy-sulphones. I. A. A. LEVY, H. C. RAINS, and S. SMILES (J.C.S., 1931, 3264–3269).—Further examples are given in support of the mechanism assigned to the rearrangement of β -naphthol-1-sulphone (A., 1931, 1153). Interaction of 2-nitrophenylchlorothiols with *p*-cresol in CHCl_3 gives 2-nitrophenyl 4-hydroxy-*m*-tolyl sulphide, m. p. 146–147° (*Ac* derivative, m. p. 106°), which is oxidised by H_2O_2 in AcOH to the corresponding sulphone, m. p. 140–141°; this in presence of alkali (1 mol. or more) rearranges into 2-nitrophenol 3-sulphino-*p*-tolyl ether, m. p. 132–133°, which is reduced by aq. HI in AcOH to 4-*o*-nitrophenoxy-*m*-tolyl disulphide, m. p. 117°, and on oxidation with alkaline KMnO_4 and hydrolysis of the resulting sulphonic acid with 60% H_2SO_4 gives *o*-nitrophenyl *p*-tolyl ether. 2-Nitrophenyl 2-hydroxy-1-naphthyl sulphone, m. p. 181°, obtained by oxidation of the *Ac* derivative of the corresponding sulphide and hydrolysis of the resulting *Ac* derivative, m. p. 152–153°, with 10% H_2SO_4 in EtOH , passes rather more rapidly into

2-nitrophenyl 1-sulphino- β -naphthyl ether, m. p. 118°, in alkaline solution. This sulphonic acid, which is more readily prepared by hydrolysis of the acetyl-sulphone with NaOH in EtOH , gives a *Me* ester, m. p. 141°, with a large excess of Me_2SO_4 and aq. NaOH , and is converted as in the preceding case into 2-*o*-nitrophenoxy-1-naphthyl disulphide, m. p. 207° (identified by further reduction with glucose and NaOH to the sulphide), and *o*-nitrophenyl β -naphthyl ether, m. p. 58°. The last-named is also obtained by interaction of Na β -naphthoxide and *o*-chloronitrobenzene in EtOH . H. A. PIGGOTT.

Simplified preparation of organic compounds. V. 4-Nitropyrocatechol. H. VAN ERP (Ber., 1931, 64, [B], 2813–2815).—2-Chloro-4-nitrophenol, KOH , and H_2O are warmed on the water-bath until a uniform paste of the phenoxide is produced, which is subsequently heated over a free flame until orange and red materials have disappeared and the odour of NH_3 is distinct. The 4-nitropyrocatechol, m. p. 174–174.5° (corr.), is purified through the *Ba* salt (+3 H_2O). The *Ac*, m. p. 78° (corr.) and *Bz*, m. p. 157.5° (corr.), derivatives are described. Substitution of NaOH for KOH leads to complete decomp. of 2-chloro-4-nitrophenol. H. WREN.

Reputed dehydrogenation of quinol by palladium-black. L. J. GILLESPIE and T. H. LIU (J. Amer. Chem. Soc., 1931, 53, 3969–3972).—The dehydrogenation of quinol by Pd reported by Wieland (A., 1912, i, 247) was not observed when precautions were taken to exclude traces of Pd hydroxide.

H. F. JOHNSTONE (b).

Rates of formation of the stereomeric methylcyclohexanols. A. SKITA and W. FAUST (Ber., 1931, 64, [B], 2878–2892).—2-Methylcyclohexanone, when hydrogenated at 70°/3 atm. in AcOH in presence of colloidal Pt , is converted into *cis*-2-methylcyclohexanol, b. p. 165° (corr.)/760 mm., d_4^{25} 0.9356 (3:5-dinitrobenzoyl derivative, m. p. 98–99°; phenylurethane, m. p. 90–91°). When similarly but more slowly reduced, a mixture of about 75% of *cis*- and 25% of *trans*-2-methylcyclohexanol results. Diminution of the rate of hydrogenation by reduction of temp. or pressure of H_2 causes further increase in the proportion of *trans*- to *cis*-alcohol. In almost neutral solution the product contains 35% of the *cis*-modification. In presence of cyclohexylamine reduction proceeds more rapidly than in neutral solution and affords about 50% of *cis*-2-methylcyclohexanol; as by-products, dicyclohexylamine (hydrochloride, m. p. 327°), cyclohexyl-2-methylcyclohexylamine, b. p. 128–129°/17 mm., d_4^{25} 0.9124 (hydrochloride, m. p. 258–259°; picrate, m. p. 149°), and a base, $\text{C}_{13}\text{H}_{25}\text{N}$, b. p. 128–129°/16 mm., d_4^{25} 0.9095 (picrate, m. p. 157–158°), are obtained.

Technical 2-methylcyclohexanol (from *o*-cresol according to Sabatier) is converted into the 3:5-dinitrobenzoate, m. p. 114–115°, which with NaOH in H_2O - MeOH yields homogeneous *trans*-2-methylcyclohexanol, b. p. 166.5° (corr.)/760 mm., d_4^{25} 0.9241 (phenylurethane, m. p. 105–106°). Purification of the technical product through the *H* phthalate, m. p. 123.5–125°, is described. Reduction of 2-methylcyclohexanone by Na in moist Et_2O leads to the

trans-alcohol, whilst slow hydrogenation of *o*-cresol at room temp. in presence of colloidal Pt gives methylcyclohexane and a carbinol mixture containing 60% of the *cis*-isomeride.

Rapid hydrogenation of 3-methylcyclohexanone and treatment of the product with 3:5-dinitrobenzoyl chloride leads to the isolation of *cis*-3-methylcyclohexanol, b. p. 173—174° (corr.)/760 mm., d_4^{20} 0.9173 (3:5-dinitrobenzoate, m. p. 91—92°; phenylurethane, m. p. 87—88°). Reduction of the cyclohexanone with Na in moist Et₂O and subsequent treatment with 3:5-dinitrobenzoyl chloride affords *trans*-3-methylcyclohexanol, b. p. 174—175° (corr.)/762 mm., d_4^{20} 0.9145 (3:5-dinitrobenzoate, m. p. 97—98°; phenylurethane, m. p. 93—94°).

Rapid catalytic reduction of 4-methylcyclohexanone permits the isolation of *cis*-4-methylcyclohexanol, b. p. 173—174° (corr.)/750 mm. (3:5-dinitrobenzoate, m. p. 134°; phenylurethane, m. p. 118—119°), whilst reduction by Na in moist Et₂O leads to *trans*-4-methylcyclohexanol, b. p. 173—174.5° (corr.)/745 mm., d_4^{20} 0.9118 (3:5-dinitrobenzoate, m. p. 139—140°; phenylurethane, m. p. 124—125°). Particularly in the cases of the 3- and 4-methylcyclohexanols the differences in the vals. of d and n for the isomerides are very small and the determination of the heat of combustion is advocated.

It is established that in general the modification richer in energy is formed to a greater extent as the rate of hydrogenation is increased when the possibility exists of converting an unsaturated cyclic compound into stereoisomeric substances by addition of H₂.

H. WREN.

***cis*- and *trans*-2-Methylcyclohexanol.** W. HUCKEL and K. HAGENGUTH (Ber., 1931, 64, [B], 2892—2895).—Technical 2-methylcyclohexanol when purified through the H phthalate, m. p. 124—125°, yields homogeneous *trans*-2-methylcyclohexanol, m. p. —21.2° to —20.5°, b. p. 167.2—167.6°/760.1 mm., d_4^{20} 0.9245 (*p*-nitrobenzoate, m. p. 65°; oxalate, m. p. 61°), oxidised by CrO₃ in AcOH to 2-methylcyclohexanone (oxime, m. p. 43—44°). Hydrogenation of *o*-cresol at 20°/3 atm. in presence of colloidal Pt and aq. HCl affords 30% of methylcyclohexane and 70% of methylcyclohexanol containing a little methylcyclohexanone. The alcohol is purified through the *p*-nitrobenzoate, m. p. 51—52°. *trans*-2-Methylcyclohexyl *p*-toluenesulphonate, m. p. 27—28°, is converted by anhyd. KOAc in EtOH into AcOEt, Δ^1 -methylcyclohexene, Et methylcyclohexyl ether, and methylcyclohexyl acetate, b. p. 64.2—65.4°/10 mm. Hydrolysis of the acetate and purification of the alcohol through the *p*-nitrobenzoate or H phthalate, m. p. 104°, leads to homogeneous *cis*-2-methylcyclohexanol, m. p. —9.5° to —9.2°, b. p. 165.2—165.4°/761.2 mm., d_4^{20} 0.9381 (phenylurethane, m. p. 92°).

H. WREN.

Amino-alcohols. VII. Phenolic arylpropanolamines. W. H. HARTUNG, J. C. MUNCH, E. MILLER, and F. CROSSLEY (J. Amer. Chem. Soc., 1931, 53, 4149—4160; cf. A., 1931, 834).—A study of the physiological activity of the compounds now described shows that the *p*-OH group increases pressor activity and decreases toxicity to rabbits; the *m*-OH group increases activity at least twice as much as does the

p-isomeride and also increases toxicity; the *o*-OH group decreases the activity and probably increases toxicity; the *mp*-(OH)₂ group is the most active and produces an action resembling that of adrenaline. It is not safe to predict the toxicity of a compound obtained by the introduction, simultaneously, of more than 1 group. The following *oximino-ketones*, Ar-CO-CMe:NOH, are prepared in 25—90% yield, where Ar=*p*-OH-C₆H₄, m. p. 184.5° (all m. p. are corr.); *m*-OH-C₆H₄, m. p. 138°; *mp*-Me(OH)C₆H₃, m. p. 188.5—189°; *pm*-Me(OH)C₆H₃, m. p. 158.5°; *mp*-(OH)₂C₆H₃, m. p. 217° (decomp.); *p*-MeO-C₆H₄, m. p. 131°; *o*-MeO-C₆H₄, m. p. 132°; *op*-(MeO)₂C₆H₃, m. p. 110.5°. Catalytic reduction gives the corresponding *amino-ketones*, Ar-CO-CHMe-NH₂, analysed as the *hydrochlorides*, where Ar=*p*-OH-C₆H₄, m. p. 219°; *m*-OH-C₆H₄, m. p. 177°; *mp*-Me(OH)C₆H₃, m. p. 184.5°; *pm*-Me(OH)C₆H₃, m. p. 145°; *mp*-(OH)₂C₆H₃, m. p. 233°; *p*-MeO-C₆H₄, m. p. 226°; *o*-MeO-C₆H₄, m. p. 112°; *op*-(MeO)₂C₆H₃, m. p. 178—180°. Further catalytic reduction gives the *amino-alcohols*, Ar-CH(OH)-CHMe-NH₂, analysed as the *hydrochlorides*, where Ar=*p*-OH-C₆H₄, m. p. 203.5°; *m*-OH-C₆H₄, m. p. 182°; *mp*-Me(OH)C₆H₃, very hygroscopic; *pm*-Me(OH)C₆H₃, m. p. 222°; *mp*-(OH)₂C₆H₃, m. p. 176°; *p*-MeO-C₆H₄, m. p. 216.5°; *o*-MeO-C₆H₄, m. p. 245° (decomp.) (free base, m. p. 75°); *op*-(MeO)₂C₆H₃, m. p. 219°. *o*-Hydroxyphenyl α -aminoethyl ketone, from the MeO derivative and conc. HCl, gives a *hydrochloride*, m. p. 223.5—224°; the reduction product was not obtained pure. 2:4-Di-hydroxyphenyl α -aminoethyl ketone *hydrochloride*, m. p. 176°, 2:4-dihydroxyphenylpropanolamine *hydrochloride*, m. p. 249°, and *o*-propionylphenoloxime, m. p. 94°, are described. Data for the min. lethal dose and relative pressor activity of the amino-alcohol hydrochlorides are given.

C. J. WEST (b).

Reaction between phenylcarbimide and ω -anilinophenyl- β -hydroxynaphthylmethanes. II. A. NERI (Gazzetta, 1931, 61, 815—819).— ω -Anilino-*m*-nitrophenyl-2-hydroxy-1-naphthylmethane reacts with PhNCO to give *diphenyl*-(*m*-nitrophenyl-2-hydroxy-1-naphthylmethyl)carbamide, NHPh-CO-NPh-CH(C₆H₄NO₂)C₁₀H₆OH, m. p. 143°, which when boiled with HCl gives *s*-diphenylcarbamide and *m*-nitrophenyldi-(2-hydroxy-1-naphthyl)methane; *m*-nitrobenzaldehyde is probably present, but was not isolated. ω -Anilinophenyl-1-hydroxy-2-naphthylmethane with PhNCO gives only *s*-diphenylcarbamide, PhCHO, and phenyldi-(1-hydroxy-2-naphthyl)methane.

E. E. J. MARLER.

Condensations by sodium instead of by the Grignard reaction. III. *tert*-Carbinols and acids. A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1931, 53, 4028—4032).—Ph-C₆H₄Cl (0.1 mol.), Et₂CO₃ (0.042 mol.), and Na wire (0.22 g.) in C₆H₆ (100 c.c.) heated for 10 hr. give 23% of (Ph-C₆H₄)₂C(OH), m. p. 207°. Similarly, PhCl affords 66% of CPh₂OH; PhCl, BzCl, and Na give 79% of CPh₂OH, whilst CPh₂ affords 98%; PhCl, BzOEt, and Na in NEt₃Ph yield 62% of CPh₂OH. *p*-C₆H₄Cl-NMe₂, Et₂CO₃, and Na give 22% of crystal-violet (formed in 49% yield using *p*-C₆H₄Br-NMe₂), also obtained in 40% yield using ClCO₂Et for Et₂CO₃.

Malachite-green (69% yield) is prepared from *p*-C₆H₄Br·NMe₂, BzOEt, and Na. Ph·C₆H₄Cl, BzOEt, and Na in absence of solvent give 7.3% of phenyldi-(diphenyl)carbinol; in presence of C₆H₆ the yield is only 1%. 1-C₁₀H₇Cl, Ph diphenyl ketone, and Na in Et₂O afford 7.4% of phenyldiphenylnaphthylcarbinol, whilst (CH₂Ph)₃C·OH is obtained from CH₂PhCl, Et₂CO₃, and Na in C₆H₆. The following acids were prepared from the requisite aryl chloride, CO₂ (30 lb. pressure), and Na in C₆H₆: *m*- (58%) and *p*-toluic (76%), BzOH (45%), *p*-NMe₂·C₆H₄·CO₂H (28%), and *p*-Ph·C₆H₄·CO₂H (12%). Caution is necessary in carrying out these experiments, since the reaction proceeds with explosive violence when it gets beyond control. The formation and methods of removal of a film on the surface of Na are discussed.

C. J. WEST (b).

[Tetraphenyl-*o*-xylylene.] E. DE B. BARNETT and J. W. COOK (Ber., 1931, 64, [B], 2936; cf. Wittig and Leo, A., 1931, 1405).—The identity of 1-hydroxydiphenylmethyl-2-benzhydrylbenzene has been established previously by the authors.

H. WREN.

[Conjugated double linkings. XX. Perkin's synthesis.] P. KALNIN (Ber., 1931, 64, [B], 2935).—A comment on the communication of Kuhn and Ishikawa (A., 1931, 1413).

H. WREN.

Scission of β -hydroxy-substituted acids. Preparation of deoxybenzoins. D. IVANOV and J. POROV (Bull. Soc. chim., 1931, [iv], 49, 1547—1551).—When heated with 10% aq. NaOH for 0.5 hr., triaryl- β -hydroxybutyric acids previously described (A., 1931, 726) are decomposed into phenylacetic acids and deoxybenzoins. When the OH group is attached directly to the ring, e.g., in phenyl-1-hydroxycyclohexylacetic acid, a longer heating is required, e.g., 5½ hr. The following ketones are described: *p*-bromophenyl benzyl ketone, m. p. 113.5—115° (from β -hydroxy- α -diphenyl- β -*p*-bromophenylbutyric acid, m. p. 172.5—173.5°, obtained in 81% yield from CH₂PhCl, CH₂Ph·CO₂·MgCl, and Mg *p*-bromophenyl bromide); *m*-tolyl *p*-chlorobenzyl ketone, m. p. 88—89°; *p*-tolyl *p*-chlorobenzyl ketone, m. p. 112.5—114°; and *p*-bromophenyl *p*-chlorobenzyl ketone, m. p. 126—127°.

R. BRIGHTMAN.

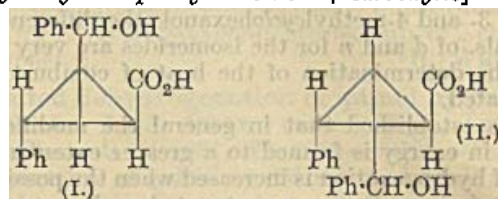
Manufacture of arylamides of aromatic hydroxycarboxylic acids [hydroxydiphenylaminecarboxylic acids]. W. W. GROVES. From I. G. FARBERIND. A. G.—See B., 1932, 57.

Isomeric α -phenyl- β -*p*-tolyl- δ -ketonic acids. S. AVERY and M. J. HALL (J. Amer. Chem. Soc., 1931, 53, 4350—4353; cf. A., 1930, 1433).—Fractional crystallisation of crude γ -trimethylacetyl- α - β -diphenylbutyric acid (cf. loc. cit.) from dil. EtOH gives a form, m. p. 179—180° (ratio to less fusible acid, 1:10); no cryst. alkaloidal salt could be obtained from either form. Condensation of Ph *p*-methylstyryl ketone with derivatives of CH₂Ph·CO₂H using NaOMe or NaOEt gave γ -benzoyl- α -phenyl- β -*p*-tolylbutyric acid, m. p. 250—251° (*Me* ester, m. p. 162°; *Et* ester, m. p. 145—146°; nitrile, m. p. 130°; lactone, m. p. 187—188°); an isomeride of the acid could not be isolated. *p*-Methylstyryl tert.-butyl ketone, m. p. 83.4° (25% yield from *p*-MeC₆H₄·CHO and CMe₃Ac) gave

the following compounds: γ -trimethylacetyl- α -phenyl- β -*p*-tolylbutyric acid, m. p. 215—216° and 198—199° [*Me* ester, m. p. 139—140°; *Et* ester, m. p. 132—133°; nitrile, m. p. 128—129° (corresponds with the more fusible acid)].

C. J. WEST (b).

Degradation of α -truxillic acid. XV. Action of nitrosyl bromide on γ -amino-acids. R. STÖRMER and W. KELLER (Ber., 1931, 64, [B], 2783—2792; cf. A., 1928, 174; 1929, 64).— α -Truxillic chloride is treated with Na truxillato in boiling C₆H₆ or xylene and subsequently with NH₃, thus yielding a mixture of the α -acid, its mono- and di-amide. Treatment of the mixed acids with NaOCl leads to the isolation of " α -truxillamic [3'-amino-2':4'-diphenylcyclobutane-1'-carboxylic] acid (+3H₂O), m. p. 212° (decomp.) [hydrochloride, m. p. 280° (decomp.); *Me* ester, m. p. 73°; *Ac* derivative, m. p. 248°]. It is converted by NOBr in Et₂O into α , δ -diphenylbutadiene, the phenyl- α -hydroxybenzylcyclopropanecarboxylic acids (I), m. p. 168° (decomp.), and (II), m. p. 186°, and α - α' -hydroxybenzyl- β -benzylidenepropionic [α -hydroxy- α , δ -diphenyl- Δ^2 -butene- β -carboxylic] acid,

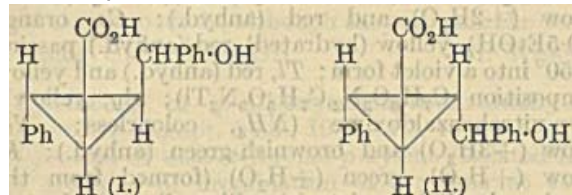


m. p. 148—149°. The last-named acid loses PhCHO when treated with alkali; this property is not shared by the *Me* ester, m. p. 92—93°. It is more conveniently prepared by the action of AcOH and H₂SO₄ on the acid (II) followed by hydrolysis. Acetylation of the acid appears impossible owing to ready loss of H₂O with formation of α , β -dibenzylidenepropionic acid, m. p. 168°. Catalytic hydrogenation (Pd-BaSO₄) gives γ -phenyl- α - α' -hydroxybenzylbutyric acid. α - α' -Hydroxybenzyl- β -benzylidenepropionic acid is converted by Br in CHCl₃ into a compound, m. p. 155—170°, transformed by Ac₂O and NaOAc into γ -phenyl- α -benzylidenesocrotonolactone, m. p. 152°. With HBr in Et₂O the unsaturated acid gives α - α' -bromobenzyl- β -benzylidenepropionic acid, m. p. 167° (decomp.) (*Me* ester, m. p. 118—119°), obtained also from the acids (I) and (II); with AcOH, H₂O, and H₂SO₄ it yields α , δ -diphenylbutadiene and α - α' -hydroxybenzyl- β -benzylidenepropionic acid. With HCl the unsaturated acid does not appear to react, whereas its *Ac* derivative smoothly yields α - α' -chlorobenzyl- β -benzylidenepropionic acid, m. p. 156°. The *Me* ester of the OH-acid is transformed by SOCl₂ and pyridine in Et₂O into *Me* α - α' -chlorobenzyl- β -benzylidenepropionate, m. p. 97°.

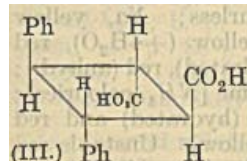
H. WREN.

Degradation of δ -truxinic acid. XVI. R. STÖRMER and E. ASBRAND (Ber., 1931, 64, [B], 2793—2796).— δ -Truxinic acid in C₆H₆ is treated with SOCl₂ (whereby slight isomerisation to the ζ -acid occurs) and subsequently with NH₃. Semi-hydrolysis of the diamide affords δ -truxinamic acid (+3H₂O), m. p. 198° (decomp.) [hydrochloride, m. p. 198°; *Me* ester, m. p. 126° (decomp.)], and its hydrochloride,

m. p. 188°. *Ac* derivative, m. p. 228°, and its *Me* ester, m. p. 105°. The amic acid is converted by

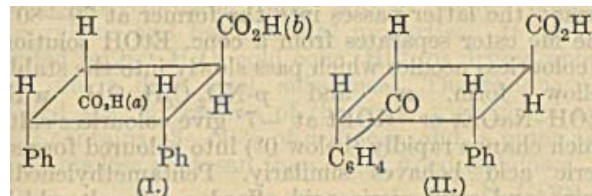


NOBr in Et₂O into αδ-diphenylbutadiene and its tetrabromide, the lactone of the OH-acid (I), the *trans*-OH-acid (II), and an acid, m. p. about 132°, which loses PhCHO when treated with alkali and is identical with or closely related to α-α'-hydroxybenzyl-β-benzylidene-propionic acid. The configuration (III) for δ-truxinic acid is established.



H. WREN.

neoTruxinic acid. XVI. R. STÖRMER and E. ASBRAND (Ber., 1931, 64, [B], 2796—2804).—β-Truxinic acid is treated with H₂O at 215—220°, the product is extracted with 5% EtOH and purified through the NH₂ salt, whereby *neotruxinic* acid is obtained in 25% yield. It is converted by SOCl₂ in C₆H₆ and then by NH₃ into *neotruxindiamide*, m. p. 249°, which yields β-truxinamic acid, m. p. 194.5° (decomp.), when treated with 1 mol. of KOH in EtOH, and a mixture of the β-amic acid and *neotruxin-a-amic acid* (cf. I), m. p. 214°, under the action of 5



moles. of KOH. The last-named acid is conveniently prepared from the β-amic acid and KOH-EtOH, whereby an equilibrium mixture containing 30% of the *neo*-acid is obtained. The *Na* and *NH₄* salts, *Me* ester, m. p. 213.5° (prepared by means of diazo-methane), and *Et* ester, m. p. 139°, are described. Treatment of the esters with HNO₂ and AcOH affords (b) *Me neotruxinate*, m. p. 234° (obtained readily by partial esterification of *neotruxinic* acid with MeOH and HCl), and the (b) *Et* ester, m. p. 123°. The position of the Me group in the (b) MeH ester is established as follows. *neoTruxinic* acid is treated successively with SOCl₂ and AlCl₃, whereby the *keto-acid* (II), m. p. 224° (*oxime*; *Me* ester, m. p. 124°), is obtained. The last-named ester is also obtained when MeH *neotruxinate*, m. p. 234°, is transformed into its chloride and then treated with AlCl₃. (The isomeric ester does not afford a truxinone derivative.) The union of the keto-group to the vicinal and not to the diametrically opposite Ph group in the keto-acid follows from the conversion of the latter by dry distillation into *trans*-cinnamic acid and *indone*, b. p. 69—70°/0.35 mm. (*dibromide*, m. p. 64—65°; *semicarbazone*) (prepared by the action of NaNH₂ and nitrosodimethylaniline on indene and subsequent

hydrolysis with dil. H₂SO₄). Partial hydrolysis of Me₂ and Et₂ *neotruxinates* yields the (a) *Me*, m. p. 139°, and (a) *Et*, m. p. 163—164°, *H truxinates*. Conversion of the *a* esters into the chlorides and amides and cautious hydrolysis of the latter affords β-truxinamic acid. Treatment of *neotruxinic* acid in C₆H₆ with a deficiency of SOCl₂ and then with NH₃ gives a mixture of NH₄ *neotruxinate*, *neotruxindiamide*, m. p. 249°, *neotruxin-a-amic acid*, and *neotruxin-b-amic acid*, m. p. 213° [*Na* salt; *Me* ester, m. p. 153—154°, prepared also from the (a) *Me H* ester by successive action of SOCl₂ and NH₃]. *a-Et neotruxin-b-amic acid* has m. p. 142—143°.

H. WREN.

Bile acids. XXXII. M. SCHENCK (Z. physiol. Chem., 1931, 203, 76—82; cf. A., 1931, 1293).—The nitroso-compound, C₂₄H₃₃O₈N, obtained by the action of HNO₂ on *isobilanic* acid dioxime (A., 1931, 352), with NaOH yields *isobilanic* acid, and with Zn dust and AcOH, and probably also with H₂SO₄, *isobilanic* acid 12-monoxime. J. H. BIRKINSHAW.

Oxidation of toluene by oxides of nitrogen. A. GIACALONE (Gazzetta, 1931, 61, 828—832).—A solution of PhMe in AcOH saturated with N oxides in a sealed tube contains after exposure to light for 1 month or heating at 120° PhCHO, BzOH, and small amounts of nitration products. E. E. J. MARLER.

Condensation of aldehydes with hydrazones. VI. Condensation of cumaldehyde and *p*-amino-benzaldehyde with their respective phenylhydrazones. A. GIACALONE (Gazzetta, 1931, 61, 826—828).—Cumaldehyde condenses with its phenylhydrazone giving *pp'*-dicumylidenedihydrazino-*p''*-isopropyltriphenylmethane, m. p. 198° (decomp.). *p*-Dimethylaminobenzaldehyde similarly gives *pp'*-4:4'-dimethylaminobenzylidenedihydrazino-*p''*-dimethylaminotriphenylmethane, m. p. 220° (decomp.), giving on oxidation with PbO₂ a green colouring matter.

E. E. J. MARLER.

Optical and chemical changes of organic nitro-derivatives and the stereochemical explanation of their isomerisms. A. HANTZSCH (Annalen, 1931, 492, 65—104).—The variations in colour of NO₂-compounds (existing in one form only in the solid state, e.g., nitroquinol Me₂ ether, for which absorption spectra curves in H₂O, CHCl₃, and light petroleum are given) in various solvents is due to the formation of additive compounds of the type R·NO₂-solvent (the phenomenon is termed solvatochromism) and absorption is stronger the more unsaturated is the solvent. The differences in the absorption spectra of 3-nitro-*p*-acet-toluidide [existing in two chromoisomeric forms (cf. A., 1909, i, 331)] in EtOH-CHCl₃, EtOH, and H₂O are due to isomerisation of each form (in solution) to the same equilibrium, the position of which depends on a sp. action of the solvent. Solvatochromism is often an indication of chromoisomerism. The various types of heteropolar and homopolar chromoisomeric NO₂-compounds are reviewed. The structures for the metallic derivatives of *p*-NO₂·C₆H₄·CH₂·CO₂Et suggested by Lifschitz (A., 1916, i, 45) are excluded, since the metal in all aci-NO₂-salts is ionogenically attached to both O atoms of the NO₂-group. The following is a brief summary

of the conclusions regarding the structures of chromo-isomeric salts. Colourless, yellow, and red salts of $\text{CHR}(\text{NO}_2)_2$ [$\text{R}=\text{H}$, Ph, anisyl] are represented as $\text{NO}_2\cdot\text{CR}\cdot\text{NO}_2\cdot\text{M}$, $\text{CR}\begin{smallmatrix} \text{NO}_2 \\ \diagup \diagdown \\ \text{ONO} \end{smallmatrix}\text{M}$, and $\text{CR}\begin{smallmatrix} \text{NO}_2 \\ \diagup \diagdown \\ \text{NO} \end{smallmatrix}\text{M}$, re-

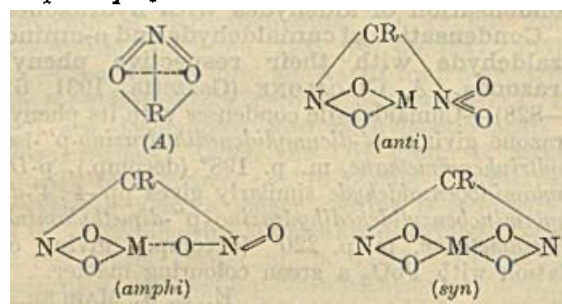
spectively. The corresponding salts of the nitrobenzaldoximes are assigned the constitutions $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NO}\cdot\text{M}$, $\text{ON}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}$, and



$\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}$, respectively; analogous formulæ are $\text{O}_2\cdots\text{M}\cdots\text{O}$

given for the salts of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{OH}$, nitroenols ($\text{NO}_2\cdot\text{CR}\cdot\text{CR}\cdot\text{OH}$), and nitrophenols. The structures assigned to the colourless (probably exist only in solution) and coloured forms of $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$ and related compounds are discussed on the basis of the structures $\text{Ar}\begin{smallmatrix} \text{NR}_2 \\ \diagup \diagdown \\ \text{O}_2\text{N} \end{smallmatrix}$ (colourless), $\text{Ar}\begin{smallmatrix} \text{NR}_2 \\ \diagup \diagdown \\ \text{ONO} \end{smallmatrix}$ (yellow),

and $\text{Ar}\begin{smallmatrix} \text{NR}_2 \\ \diagup \diagdown \\ \text{NO}_2 \end{smallmatrix}$ (red). The existence of homochromoisomerides (cf. A., 1910, i, 474) can be explained by assuming that a nitro-compound ($\text{R}\cdot\text{NO}_2$) possesses a (not regular) tetrahedral configuration (as A). On this basis, the colourless, yellow, and red salts of $\text{CHR}(\text{NO}_2)_2$ (cf. above) are assigned the following *anti*-, *amphi*-, and *syn*-structures, respectively, which are plane-projection formulæ.



Attention is directed to various examples (lit.) of homochromoisomerism, and the cases of 2:4-dinitro-2'-methylidiphenylamine (*loc. cit.*) and *pp'p'*-trinitrotriphenylcarbinol (see below) are discussed.

[With F. HERN.] *pp'p'*-Trinitrotriphenylcarbinol exists in 3 (and possibly 4) unimol. homochromoisomeric forms, having identical absorption spectra in MeOH or CHCl_3 . When dry CO_2 -free air is passed through a solution of *pp'p'*-trinitrotriphenylmethane and EtOH-NaOEt (1+mol.) in C_6H_6 at 0° , the reaction mixture diluted with Et₂O, decomposed with H_2O , evaporated in vac., and the resultant product crystallised from MeOH at room temp., the form of m. p. 167° (*syn-syn-syn*) is obtained. This isomerises only slowly both in the solid state and in solution. Crystallisation of this has given forms of m. p. 175° (*syn-syn-anti*) and $180\text{--}182^\circ$ (*syn-anti-anti*) (obtained in one case only and in very small amount). The stable (*anti-anti-anti*) form has m. p. 189° . The Ti_2 salt of *s*-tetranitroethane has been obtained in yellow and red (unstable) forms.

[With KANASIRSKI.] The following salts are prepared; the anhyd. forms are usually obtained from the hydrated salts at $130\text{--}150^\circ$: *anti-p*-nitrobenzaldoxime [NH_4 , colourless; Na, yellow (+2 H_2O),

green (+2 H_2O), and pale yellow (anhyd.); K, red (+0.2 H_2O), red (+EtOH), yellow (+3 H_2O); Rb, yellow (+2 H_2O) and red (anhyd.); Cs, orange (+0.5EtOH), yellow (hydrated), red (anhyd.), passing at 150° into a violet form; Tl, red (anhyd.) and yellow (composition $\text{C}_7\text{H}_6\text{O}_3\text{N}_2\cdot\text{C}_7\text{H}_5\text{O}_3\text{N}_2\text{Ti}$); Ag, yellow]; *syn-p*-nitrobenzaldoxime (NH_4 , colourless; Na, yellow (+3 H_2O) and brownish-green (anhyd.); K, yellow (+ H_2O), green (+ H_2O) (formed from the anhyd. red salt in moist air); Rb, yellow (hydrated) and red (anhyd.); Cs, yellow (hydrated) and red (anhyd.); Tl, red (anhyd.); Ag, yellow]; *anti-o*-nitrobenzaldoxime [NH_4 , colourless; Na, yellow (+4 H_2O), red (anhyd.); K, yellow (+4 H_2O), red (anhyd.); Rb and Cs, yellow (hydrated), red (anhyd.); Tl, red]; *anti-m*-nitrobenzaldoxime [NH_4 , colourless; Na, K, Rb, and Cs in yellow (hydrated) and red (anhyd.) forms; Tl, red; Ag, yellow]. Unstable red and yellow Na salts of *anti-p*-nitrobenzaldoxime are described also. Yellow (+2 H_2O) and red (anhyd.) K, yellow (+2 H_2O) and almost colourless (anhyd.) Na, and colourless (anhyd.) Ag (compounds with NH_3 and pyridine) salts of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{OH}$ are prepared. A very unstable yellow compound is obtained from colourless trinitroanisole and hexane.

[With E. LESKIEN.] 3-Nitro-4-hydroxybenzoic acid [Na_2 (+ H_2O), K_2 (+4 H_2O), Rb, (+4 H_2O), Cs, (+3 H_2O), all varying shades of red; Li, reddish-yellow (+4.5 H_2O) and red (+5 H_2O), both giving golden-yellow (+2 H_2O) and brick-red (anhyd.) forms, salts described] is isolated in colourless (from H_2O , EtOH, CHCl_3 , C_6H_6) and yellow (from Et₂O) forms; the latter passes into the former at $70\text{--}80^\circ$. The Me ester separates from a conc. EtOH solution in colourless needles which pass slowly into the stable yellow form. *m*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ with EtOH-NaOEt or -KOEt at -7° give colourless salts which change rapidly (below 0°) into coloured forms; picric acid behaves similarly. Pentamethylenediamine and solid picric acid afford a red salt which isomerises slowly to a yellow form. The absorption spectrum of *o*-nitroaniline varies considerably in H_2O , MeOH, and light petroleum, probably owing to the formation of the yellow (unknown) chromoisomeride in solution. 3-Nitro-*p*-toluidine shows the same spectrum in these solvents as does *p*-nitroacetanilide in MeOH and CHCl_3 ; in these cases the second chromoisomeride is apparently incapable of existence, probably because of steric hindrance.

H. BURTON.

Atomic grouping in salicylaldoxime, specific for copper. F. FEIGL and A. BONDI (Ber., 1931, 64, [B], 2819—2823; cf. A., 1930, 1394; 1931, 813).—

The compound $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}=\text{NO} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}\text{Cu}$ is obtained from Fehling's solution and salicylaldoxime or by digestion of Ephraim's salt (*loc. cit.*) with Na_2CO_3 or NaOH and aq. EtOH. It is converted by AcOH into the

salt $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}\cdot\text{N}\cdot\text{OH} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}\text{Cu}$, the constitution of which is supported by the ability of salicylaldoxime Me ether, b. p. $107^\circ/14\text{ mm.}$, m. p. 28° (from salicylaldehyde and *O*-methylhydroxylamine hydrochloride), to give a Cu compound ($\text{C}_8\text{H}_8\text{O}_2\text{N}$)₂Cu, whereas *o*-methoxybenzaldoxime does not react. Ph $\gamma\gamma\gamma$ -trichloro- β -

hydroxy-*n*-propyl ketoxime and *Me* β -hydroxy-*n*-propyl ketoxime, b. p. 123—124°/13 mm., do not yield Cu compounds, although they contain the Cu-sp. grouping OH·C·C·C·N·OH. H. WREN.

Synthesis of *p*-alkoxymethylbenzaldehydes. S. SABETAY (Compt. rend., 1931, 193, 1194—1195).—Interaction of *ωωω*'-tribromo-*p*-xylene (isolated from the products of bromination of *p*-xylene at 140—150°) with NaOEt and EtOH gives *p*-ethoxymethylbenzaldehyde diethylacetal, b. p. 142°/14 mm., which is hydrolysed by aq. H₂SO₄-AcOH to *p*-ethoxymethylbenzaldehyde, b. p. 133—134°/14 mm. (phenylhydrazones, m. p. 86°). *p*-Methoxymethylbenzaldehyde (this vol., 57) and its dimethylacetal, b. p. 122—123°/16 mm., are similarly prepared. H. A. PIGGOTT.

Lignin and related compounds. LXI. Ethers of glycol-lignin. H. HIBBERT and L. MARION (Canad. J. Res., 1931, 5, 302—305; cf. A., 1931, 828).—Glycol-lignin and NaOEt in EtOH give a Na salt, converted by chloro-2:4-dinitrobenzene in PhMe into a dinitrophenyl ether, and by chlorodimethyl ether into a methoxymethyl ether. The dinitrophenyl ether gives a *Me* ether under mild conditions of methylation, whilst a higher temp. and excess of NaOH removes the dinitrophenyl group, the resulting *Me* ether having a lower OMe content than fully methylated glycol-lignin. A. A. LEVI.

Lignin of pinewood. B. RASSOW and H. GABRIEL (Cellulosechem., 1931, 12, 318—320; cf. A., 1931, 1401).—Glycol-lignin (mol. wt. in phenol 569) is amorphous and has colloidal properties. It is converted by hot H₂O, cold conc. HCl, or drying above 90° into a dark insol. substance. The residue obtained after extraction of the wood with glycol and HCl contains 43—50% of cellulose, and is purer and contains less pentosan than other wood celluloses.

R. S. CAHN.

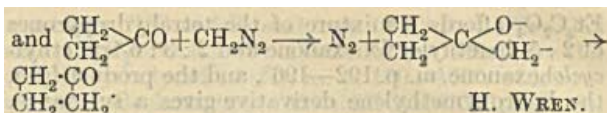
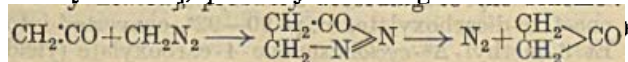
Preparation of syringic aldehyde [4-hydroxy-3:5-dimethoxybenzaldehyde]. W. M. MCCORD (J. Amer. Chem. Soc., 1931, 53, 4181—4183).—Gallic acid Me₃ ether and H₂SO₄ give syringic acid [amide (I), m. p. 192°; anilide (II), m. p. 146°, of Ac derivative]. (I) and PCl₅ in PhMe afford the iminochloride hydrochloride, m. p. 145°, converted by warm pyridine into the Ac derivative (III), m. p. 142°, of syringonitrile, m. p. 129°; (III) is converted by Stephen's method into syringaldehyde. (II) and PCl₅ in PhMe give the corresponding phenyliminochloride, m. p. 136°.

C. J. WEST (b).

Preparation of trimethylgallaldehyde. M. NIERENSTEIN (J. pr. Chem., 1931, [ii], 132, 200).—Details are given for the prep. of trimethylgallaldehyde in 75.5% yield by hydrogenation of galloyl chloride Me₃ ether.

R. S. CAHN.

New route to cyclobutanone. P. LIPP and R. KÖSTER (Ber., 1931, 64, [B], 2823—2825).—Passage of keten into diazomethane in anhyd. Et₂O yields cyclobutanone [semicarbazone, 211—212° (corr.) when slowly heated], probably according to the scheme:



Orientation phenomena among the cyclohexanones. VI. Methylation of inactive 2-methylcyclohexanone. VII. Allylation of inactive 2-methylcyclohexanone and methylation of 1-menthone. R. CORNUBERT and R. HUMEAU. **VIII. Allylation and benzylation of cyclohexanone. Alkylation of cyclohexanones with sodamide. IX. Methylation of 2:3-dimethylcyclohexanone. X. Methylation of 2:4-dimethylcyclohexanone.** R. CORNUBERT and A. MAUREL (Bull. Soc. chim., 1931, [iv], 49, 1468—1487, 1487—1497, 1498—1515, 1515—1523, 1523—1528; cf. A., 1931, 1417).—VI. Methylation of 2-methylcyclohexanone with NaNH₂ and Me₂SO₄ in Et₂O affords a fraction, b. p. 172—176°, containing a mixture of 2:5-dimethylcyclohexanone (oxime, m. p. 108—109°) and pulenone (2:2:5-trimethylcyclohexanone) characterised as oximes, together with a fraction, b. p. 187—191°, *d*₁₅ 0.9097, probably containing 2:5:6-trimethylcyclohexanone (liquid oxime). The intermediate fraction, b. p. 180—190°, after extraction with NaHSO₃ with PhCHO in presence of HCl affords (1) a fraction b. p. 180—210°/14 mm., containing benzylidenepulenone, m. p. 89—90°, and substances of m. p. 109—109.5° and m. p. 73°, and (2) fractions b. p. 210—240°/14 mm. and 240—262°/14 mm., containing the tetrahydropyrones, m. p. 133—137° and 190—195°, of 2:5-dimethyl- and 2:5:6-trimethylcyclohexanone. The original fraction, b. p. 187—191°, with PhCHO in presence of HCl similarly affords benzylidenepulenone and the tetrahydropyrone of 2:3:6-trimethylcyclohexanone. The monomethylation products, b. p. 178—185°, with PhCHO and HCl similarly yield a fraction, b. p. 150—215°/20 mm., containing benzylidene compounds, affording a semicarbazone, m. p. 220—221°, possibly a mixture of the semicarbazones of benzylidene-2:5-dimethyl- and -2:2:5-trimethylcyclohexanone, and fractions, b. p. 215—245°/20 mm., 245—270°/20 mm., containing the tetrahydropyrones of -2:5-di- and 2:2:5-trimethylcyclohexanones. The yield of 2:5-dimethylcyclohexanone amounts to about 55%. Obtained by condensation of 2-methylcyclohexanone with Et₂C₂O₄ in presence of NaOEt, alkylation with MeI and elimination of H₂C₂O₄, and separation with HCl, 2:5-dimethylcyclohexanone has b. p. 76—77°/27 mm., *d*₁₅ 0.906 (semicarbazone, m. p. 168—168.5°), and gives a mixture of tetrahydropyrones, m. p. 103—107° and 133—137°. Pulenone, b. p. 182—184°, *d*₁₅ 0.8871 (oxime, m. p. 94°; semicarbazone, m. p. 169—170°), with PhCHO in presence of HCl at -15° yields benzylidenepulenone, m. p. 90° (hydrochloride, m. p. 106°; semicarbazone, m. p. 158.5—159°). 2:3:6-Trimethylcyclohexanone, b. p. 79—80°/20 mm., *d*₁₅ 0.9053, obtained in low yield by condensation of Et₂C₂O₄ and 2:5-dimethylcyclohexanone, is better prepared from 2:5-dimethylcyclohexanone and amyl formate in presence of NaNH₂ and hydrogenation of the hydroxymethylene derivative in presence of Pd. The product from

$\text{Et}_2\text{C}_2\text{O}_4$ affords a mixture of the tetrahydropyrones of 2:5-dimethylcyclohexanone and 2:3:6-trimethylcyclohexanone, m. p. 192—196°, and the product from the hydroxymethylene derivative gives a substance, $\text{C}_{23}\text{H}_{26}\text{O}_2$, m. p. 183—185°. The substance, m. p. 73°, obtained from the methylation product is not 5-hydroxybenzyl-2-methylcyclohexanone, the latter, obtained, together with a little 5:5-dihydroxybenzyl-2-methylcyclohexanone, by Vorländer and Kunze's method, having m. p. 106.5—107°. The benzylidene derivative of 2-methylcyclohexanone has m. p. 42—43°, the dibenzylidene derivative, m. p. 118—118.5°. Methylation of 2:5-dimethylcyclohexanone with NaNH_2 and Me_2SO_4 in Et_2O affords only pulenone. In the disodiation of 3-methylcyclohexanone, 2:3:6-trimethylcyclohexanone is formed as well as pulenone and 2:5-dimethylcyclohexanone.

VII. The 3-methyl-6:6-diallylcyclohexanone obtained on allylation of 3-methylcyclohexanone with H_2 in presence of Ni formate at 60—70° affords 3-methyl-6:6-dipropylcyclohexanone, b. p. 130—131°/23 mm., d^{16}_4 0.8970 (benzylidene derivative, m. p. 83.5—84°). 3-Methyl-2:6-diallylcyclohexanone, b. p. 118—125°/12 mm., obtained by allylating in a dry tube at 140° for 12 hr. the product obtained by condensation of 3-methyl-2-propylcyclohexanone and ethyl oxalate in presence of NaOMe, when hydrogenated in presence of Ni formate affords 3-methyl-2:6-dipropylcyclohexanone, yielding a tetrahydropyrone compound, m. p. 156—157°. 5-Methyl-2-propylcyclohexanone with PhCHO in presence of HCl yields a fraction, b. p. 204—206°/18 mm., and crystals, m. p. 124—126°, but no benzylidene derivative; with 2 mols. of PhCHO fractions b. p. 185—245°/12 mm. and 245—270°/12 mm. were obtained, the latter yielding two tetrahydropyrone compounds, m. p. 88—90° and 127—128°. 2:3-Dimethyl-6-isopropylcyclohexanone, b. p. 95—97°/12.5 mm., d^{15}_4 0.905, obtained by hydrogenation in presence of Pd of hydroxymethylmenthone, b. p. 124—125°/16 mm. (yield 50% from menthone), yields a tetrahydropyrone, m. p. 99—100°. The chloromenthone, b. p. 113—120°/16 mm., obtained by chlorination of menthone in presence of CaCO_3 , with MgMeI yields a methylmenthone, b. p. 104—110°/21 mm., which still contains 2.7% Cl; a dichloromenthone, m. p. 64.5—65°, is simultaneously obtained. Methylation of menthone by the NaNH_2 process yields a methylmenthone, b. p. 100°/17 mm., $d^{13.5}_4$ 0.9124 (semicarbazone, m. p. 193—195°), yielding a benzylidene derivative, b. p. 192—194°/16 mm., probably a mixture of isomerides. The benzylidene derivative obtained directly from the methylation product contains a small amount of substance, b. p. 185—195°/12 mm. and 225—260°, from which, however, no tetrahydropyrone was deposited.

VIII. In the allylation of cyclohexanone with allyl bromide, the yield of allylcyclohexanone, b. p. 97—98°/20 mm., is increased from 20% to 50% by using double the vol. of Et_2O , the yield of diallylcyclohexanone increasing simultaneously. Allylation of allylcyclohexanone affords a mixture, b. p. 114—123°/16 mm., of diallylcyclohexanones, hydrogenated to about 87% of 2:2-dipropylcyclohexanone, b. p. 123—126°/20 mm. (benzylidene derivative, m. p.

48°), and 13% of 2:6-dipropylcyclohexanone (tetrahydropyrone, m. p. 127—127.5°). The direct diallylation of cyclohexanone yields a mixture of diallylcyclohexanones, b. p. 114—123°/14 mm., converted on hydrogenation into a mixture of dipropylcyclohexanones, b. p. 120—123°/20 mm., containing 91% of 2:2- and 9% of 2:6-derivative. In presence of the Na derivative of cyclohexanone, allylcyclohexanone and allyl bromide gave three times the normal yield of diallylcyclohexanone, in which the 2:2-isomeride predominated, but the difference is possibly due in part to differences in concn. Benzylcyclohexanone under similar conditions with the Na derivative of allylcyclohexanone yields a benzylallylcyclohexanone, b. p. 178—190°/16 mm., hydrogenated to 2-benzyl-2-propylcyclohexanone, b. p. 176—179°/13 mm. (semicarbazone, m. p. 203°; benzylidene derivative, b. p. 257—260°/14 mm.). 2:6-Dipropylcyclohexanone, b. p. 115—115.5°, d^{14}_4 0.8955 (tetrahydropyrone, m. p. 128°), is also obtained by hydrogenation of 2-allyl-6-propylcyclohexanone, b. p. 108—109°/12 mm., d^{15}_4 0.9122, prepared from 2-propylcyclohexanone, ethyl oxalate, and NaOMe at -15°, followed by allylation with allyl bromide at 145—150° for 9 hr. 2':2-Dipropylcyclohexanone, b. p. 120—121°/18 mm., $d^{15.5}_4$ 0.9086, is obtained in 19% yield by regeneration from the benzylidene derivative. Hydrogenation of 2:2-diallylcyclohexanone in presence of Ni formate is very sensitive to temp. and does not occur at 60—68°. Above 70° it is very rapid and the range 68—70° must be strictly maintained. Use of MeOH , Bu^nOH , or isoamyl alcohol in place of EtOH in regenerating the ketone from the benzylidene derivative is less effective, amyl alcohol affording a liquid, b. p. 105—112°/22 mm. Similarly with amylalcoholic KOH the benzylidene derivative of 2-methylcyclohexanone affords a liquid, $\text{C}_{17}\text{H}_{20}\text{O}_2$, b. p. 107—109°/20 mm., d^{11}_4 0.9201, representing a condensation of 1 mol. of 2-methylcyclohexanone and 2 mols. of isovaleraldehyde. Allyl bromide was obtained in only 37% yield by Merlin and Jacobi's method. By passing HBr into allyl alcohol below 0° until about 5% more than the theoretical increase in wt. occurs and leaving 12—15 hr. a yield of 80—85% is obtained. Benzylation of cyclohexanone in Et_2O with NaNH_2 and CH_2PhBr affords 2-benzylcyclohexanone, b. p. 167—168°/20 mm., m. p. 30°, d^{23}_4 1.0298 (semicarbazone, m. p. 170—171°; benzylidene derivative, m. p. 75—76°, b. p. 267°/25 mm.), together with a fraction, b. p. 224—225°/13 mm., containing benzylcyclohexylidene-cyclohexanone (oxime, m. p. 198—199°), and a residue, containing 2:2-dibenzylcyclohexanone, m. p. 53—54° (oxime, m. p. 121°; benzylidene derivative, m. p. 105—106°, yielding tribenzylcyclohexanone, m. p. 57—58°, on hydrogenation), also obtained together with 2:6-dibenzylcyclohexanone, m. p. 103°, by benzylation of 2-benzylcyclohexanone.

IX. 2:3-Dimethylcyclohexanone, b. p. 78°/24 mm., d^{20}_4 0.9159 (semicarbazone, b. p. 202—203°), has been obtained as follows: Et acetoacetate is condensed with trioxymethylene in presence of piperidine, the reduction product of Et 3-methylcyclohexan-3-ol-1-one-4:6-dicarboxylate, m. p. 90—92°, converted into Et 3-methyl- Δ^2 -cyclohexenone-4-carboxylate (yield

20%), b. p. 135—136°/9 mm., d_{20}^{20} 1.0702, which on successive methylation, hydrolysis, and hydrogenation gives Et 2:3-dimethyl- Δ^2 -cyclohexenone-4-carboxylate, b. p. 138—139°/10 mm., d_{20}^{20} 1.0659, 2:3-dimethyl- Δ^2 -cyclohexenone, b. p. 86°/13 mm., d_{15}^{15} 0.9725 (semicarbazone, m. p. 218—220°), and 2:3-dimethylcyclohexanone. Methylation of the last with MeI and NaNH₂ in Et₂O affords 67% of 2:2:3-trimethylcyclohexanone (benzylidene derivative, m. p. 85—86°) and 33% of 2:3:6-trimethylcyclohexanone (tetrahydropyrone compounds, m. p. 168—169° and 190—192°) calc. from the wts. of crude benzylidene and tetrahydropyrone formed or 77% and 23%, respectively, calc. on the cryst. products.

X. 2:4-Dimethylcyclohexanone, b. p. 70—71°/16 mm., d_{15}^{15} 0.91 (oxime, m. p. 98—99°), obtained from 4-methylcyclohexanone, NaNH₂, and Me₂SO₄ in Et₂O, from Et₂C₂O₄ and 4-methylcyclohexanone in presence of NaOMe or NaOEt, and heating with MeI, or from the hydroxymethylene derivative of 4-methylcyclohexanone, b. p. 106—109°/27 mm., by hydrogenation in presence of Pd, similarly affords a mixture, b. p. 74—76°/16 mm., of about 95% of 2:2:4-trimethylcyclohexanone (benzylidene derivative, m. p. 91—92°) and about 5% of 2:4:6-trimethylcyclohexanone, b. p. 85—87°/23 mm., d_{15}^{15} 0.902 (semicarbazone, m. p. 222°; tetrahydropyrone, m. p. 203°), also obtained by hydrogenation in presence of Pd of the hydroxymethylene derivative, b. p. 102.5—104°/17 mm., prepared from 2:4-dimethylcyclohexanone, NaNH₂, and amyl formate.

R. BRIGHTMAN.

Preparation of ketochloroimines. C. R. HAUSER, G. J. HAUS, and H. HUMBLE (J. Amer. Chem. Soc., 1931, 53, 4225—4226).—CPh₂N·MgBr and an equiv. of Cl₂ in the cold give a product containing about 60% of benzophenonechloroimine. The Mg compound from *p*-C₆H₄Cl·CN similarly affords a chloroimine, m. p. 103—104°; a bromoimine can be prepared. Details are to be published later.

C. J. WEST (b).

Oximes of $\alpha\beta$ -unsaturated ketones and the Beckmann rearrangement. II. A. H. BLATT and J. F. STONE, jun. (J. Amer. Chem. Soc., 1931, 53, 4134—4149; cf. A., 1931, 621).—The previously described oxime of *p*-C₆H₄Br·CO·CH·CHPh is a mixture of the *syn* (I) and *anti* (II) isomerides, since hydrolysis of its Beckmann rearrangement product gives NH₃ and *p*-C₆H₄Br·CO₂H. Separation of (I) and (II) by fractional crystallisation was unsuccessful, but acetylation and fractional crystallisation from AcOEt gives the *syn*-acetate (III), m. p. 145°, and the *anti*-acetate (IV), possibly not entirely free from (III), m. p. 105—106°. (III) gives a Br₂-derivative (V), m. p. 146—147°, also obtained by acetylating (VII). (V) and KI in COMe₂ give (III). Hydrolysis of (III) with EtOH·KOH gives 80% of (I), m. p. 145—158° according to rate of heating, partly converted into (II) by prolonged boiling with EtOH·KOH, heating with HCO₂H, and reaction with MgEtBr. The Beckmann rearrangement of (I) gives cinnam-*p*-bromoanilide (VI), whilst the Br₂-derivative (VII), m. p. 173°, from (III) and Br affords $\alpha\beta$ -dibromo- β -phenylpropion-*p*-bromoanilide, m. p. 195—196°; also synthe-

sised from (VI) and Br and from CHPhBr·CHBr·COCl and *p*-C₆H₄Br·NH₂. (VII) and KI in COMe₂ give (I). (IV) is hydrolysed to (II), m. p. 150—163°, which rearranges (Beckmann) to CHPh·CH·NH·CO·C₆H₄Br (?), m. p. 204°, hydrolysed to NH₃ and *p*-C₆H₄Br·CO₂H. (II) and Br give (VII); it is not possible to say whether this shift in configuration is due to the saturation of the double linking or to a sp. isomerising action of the reagent. Since it has been suggested by von Auwers that thermal decomp. of (VII) to the isooxazole (cf. *loc. cit.*) might proceed through the α -bromo-oxime (VIII), CHPh·CBr·C(NO·H)·C₆H₄Br, m. p. 163—164°, this was prepared from the reaction product of the Br₂-ketone and EtOH·KOAc (with out isolating the α -Br-ketone) and NH₂OH·HCl. Hydrolysis of the Beckmann rearrangement product of (VIII) gives NH₃ and *p*-C₆H₄Br·CO₂H, but when (VIII) is heated the isooxazole is not produced; (VIII), therefore, probably has the *anti*-configuration. (VIII) is unaffected by dissolution in conc. H₂SO₄, as is the oxime of α -bromobenzylideneacetophenone. Benzylidenedeoxybenzoinoxime, m. p. 208° (cf. Knoevenagel and Weissgerber, A., 1893, i, 353), undergoes the Beckmann rearrangement, forming BzOH and deoxybenzoin, whilst treatment with H₂SO₄ gives a red oil, from which neither of the two known forms of 3:4:5-triphenylisooxazoline could be isolated. The oxime, m. p. 149—153°, of Ph β -phenylstyryl ketone undergoes the Beckmann rearrangement, yielding β -phenylcinnamanilide, m. p. 130—131°, whilst treatment with H₂SO₄ gives 3:4:5-triphenylisooxazoline, m. p. 139°. The formation of isooxazolines from $\alpha\beta$ -unsaturated ketones does not proceed through an oxime as an intermediary but through a complex bimol. 1:4-additive process. The work of von Auwers and Seyfried (A., 1931, 223) is discussed; the divergent conclusions reached by these authors are due to the different emphasis and interpretation placed on the reaction of the bromo-oximes and alkali.

C. J. WEST (b).

Reduction product of benzylidenepinacolone (styryl *tert*-butyl ketone). G. A. HILL and S. SUSSELMAN (J. Amer. Chem. Soc., 1931, 53, 4424—4428).—The compound, m. p. 142°, previously thought (A., 1923, i, 789) to be β -phenylethyl-*tert*-butylcarbinol (cf. A., 1930, 343) is probably a stereoisomeride (I) (m. p. 147°) of $\epsilon\zeta$ -diphenyl- $\beta\beta\alpha\alpha$ -tetramethyldecane- $\gamma\delta$ -dione, m. p. 208° (cf. *loc. cit.*). The homogeneity of (I) is shown by crystallisation experiments, cooling curves, analysis, and mol. wt.; its structure is established by the action of MgMeI. C. J. WEST (b).

Nitration in the fluorene series. E. LANGECKER (J. pr. Chem., 1931, [ii], 132, 145—152).—Attempts to prepare 1- or 1:8-substituted fluorenone derivatives were unsuccessful. 9-Acetamidofluorenone (modified prep. from fluorenoneoxime) gives, when nitrated by Kuhn's method (A., 1925, i, 1260), 2-nitrofluorenone and other products, whilst with conc. HNO₃ in Ac₂O 2:7-dinitrofluorenone is formed together with an isomeride, m. p. 236—237°, giving a diamino-compound, m. p. 196° (Ac₂ derivative, m. p. above 290°). Fluorenoneoxime and conc. HNO₃ in Ac₂O give an unstable substance, probably of the 9-oximinofluorene type, which with H₂SO₄ in boiling AcOH gives a

dinitrofluorenone, m. p. above 300° (reduced to a *nitroaminofluorenone*, m. p. $243-244^{\circ}$, by Na_2S), and 2-nitrofluorenone; cold, fuming HNO_3 gives a similar unstable substance, which forms 2:7-dinitrofluorenone on oxidation. *O*-Acetylfluorenoneoxime and conc. HNO_3 in Ac_2O at $30-40^{\circ}$ give the 2-nitro-compound, m. p. 228° , hydrolysed by KOH or conc. H_2SO_4 to 2-nitrofluorenoneoxime, m. p. 249° (decomp.), which was prepared also from 2-nitrofluorenone, which it yields on oxidation by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH .

R. S. CAHN.

Haloform reaction. IV. Influence of *o*-methoxy-groups. R. C. FUSON, M. W. FARLOW, and C. J. STERMAN (J. Amer. Chem. Soc., 1931, 53, 4097-4103).—In no case has it been found possible to isolate the trihalogenomethyl intermediate using acetophenones with only one *o*-substituent. 2:4:6-Trimethoxyacetophenone and NaOBr in dil. or conc. alkali give *alpha*-tribromo-2:4:6-trimethoxyacetophenone, m. p. $102.5-103^{\circ}$ (corr.), in 67% and 58% yields, respectively; reaction is about 6 times as fast in dil. alkali. The *Cl*-derivative, m. p. $119-120^{\circ}$ (corr.), results in 68% yield. Both halogeno-compounds are oxidised to 2:4:6-trimethoxybenzoic acid by alkali. 2-Methoxyacetophenone and NaOBr in H_2O or in 20% EtOH give 51 or 64% of 2-methoxy-1-tribromoacetylphenylene, m. p. $136.5-137^{\circ}$ (corr.) (the 1-trichloroacetyl derivative has m. p. $131-131.5^{\circ}$), converted by alkali into 2-methoxy- α -naphthoic acid. The retardation of the haloform reaction is of the same order of magnitude in both cases. Since the effect observed with 2:1- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\text{Ac}$ is to be ascribed to the combined influences of the *OMe* and the benzo-groups, it is evident that the separate effect of the benzo-group is similar to that of the *OMe* group.

C. J. WEST (b).

Action of Grignard solutions on 10-methoxy-anthrones. E. DE B. BARNETT (J.C.S., 1931, 3340-3341).—10-Methoxyanthrone (prep. improved) interacts with $\text{CH}_3\text{Ph}\cdot\text{MgCl}$ in the cold to form anthraquinone, 10:10'-dimethoxy-10:10'-dianthrone, and 10-methoxy-9-benzyl-9:10-dihydroanthranol, m. p. 129° , which with HCl and AcOH gives 10-chloro-9-benzylanthracene. 10-Methoxy-1:4-dimethylanthrone with MgMeI (3 mols.) gives 10-methoxy-1:4:9-trimethyl-9:10-dihydroanthranol, m. p. 148° , but this did not give a definite product with $\text{HCl}\cdot\text{AcOH}$. A poor yield of 10-phenyl-1:4-dimethylanthrone was obtained with PhMgBr , and $\text{CH}_3\text{Ph}\cdot\text{MgCl}$ and Mg *o*-tolyl bromide gave only resinous products.

H. A. PIGGOTT.

Chemical participation of water in the oxidising action of *p*-benzoquinone; theory of oxidative processes. A. BACH and K. NIKOLAEV (Ber., 1931, 64, [B], 2769-2772).—In absence of H_2O there is no reaction between *p*-benzoquinone and EtOH when irradiated; reaction increases with increasing amounts of H_2O , although there is no direct proportionality. The presence of H_2O is essential for the oxidation by *p*-benzoquinone of pyrogallol in EtOH , COMe_2 , or Et_2O or of *p*-phenylenediamine in Et_2O . It is considered that H_2O has a somewhat stabilising effect on the peroxide form of *p*-benzoquinone owing to the formation of *p*-hydroxyphenyl

H peroxide, which imparts its active *O* to the substrate and is therefore deoxidised to quinol. H. WREN.

Complex salts of hydroxyquinones. I. A. MANGANI (Gazzetta, 1931, 61, 820-826).—The *Na* salt of 2-hydroxy- α -naphthaquinone, *Co*, *Mg*, and *Zn* salts of 5-hydroxy- α -naphthaquinone, and *Co* and *Zn* salts of naphthazarin, which are probably additive compounds with *Co* and *Zn* acetates, are described. Chrysazin (1:8-dihydroxyanthraquinone) forms hydrogen *Co*, *Mg*, *Zn*, and *Cu* salts, the last being a very sensitive test, and a neutral *Co* salt.

E. E. J. MARLER.

Hydroxyanthraquinones. I. Synthesis of purpurin. P. G. MARSHALL (J.C.S., 1931, 3206-3208).—Quinizarin heated with Na_2SO_3 and CuO in H_2O gives an almost quant. yield of the 2-sulphonic acid (I); the *Na* salt when heated with Ca(OH)_2 and H_2O at 250° affords purpurin (84% yield). Zimmermann's method (A., 1930, 941) of prep. of (I) does not give exclusively the 2-sulphonic acid. H. BURTON.

Anthrone series. III. Synthesis of 3-methoxyphthalaldehydic acid and a new synthesis of chrysazin. IV. Synthesis of the anthrones derived from chrysophanic acid. C. A. NAYLOR, jun. [with J. H. GARDNER] (J. Amer. Chem. Soc., 1931, 53, 4109-4113, 4114-4119).—III. Oxidation of 1:5-dimethoxynaphthalene with alkaline KMnO_4 gives 11-16% of 3-methoxyphthalaldehydic acid (I), m. p. $121-122^{\circ}$ to a turbid liquid, which then partly solidifies and re-melts at 144.8° ; all m. p. are corr. $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$ and (I) with 85% H_2SO_4 afford 55% of 3-methoxy-2-(*o*-bromo-2-hydroxyphenyl)phthalide, m. p. $198-200^{\circ}$, reduced by *Zn* and 10% NaOH to 3-methoxy-2-*o*-hydroxybenzylbenzoic acid, m. p. $185-186^{\circ}$, which is converted by conc. H_2SO_4 at room temp. into 1-hydroxy-8-methoxy-10-anthrone, m. p. $170-171^{\circ}$. This is oxidised by CrO_3 in AcOH to 1-hydroxy-8-methoxyanthraquinone (chrysazin Me ether), demethylated to chrysazin (11% yield) (Ac. derivative, m. p. $231-232^{\circ}$).

IV. 6-Bromo-*m*-cresol and (I) with 85% H_2SO_4 give 3-methoxy-2-(5-bromo-2-hydroxy-4-methylphenyl)phthalide, m. p. $243-244.6^{\circ}$, convertible (as above) into 3-methoxy-2-(2'-hydroxy-4'-methylbenzyl)benzoic acid, m. p. $164-164.6^{\circ}$, and 1-hydroxy-8-methoxy-3-methyl-10-anthrone (II), m. p. $173.8-175^{\circ}$. Demethylation of 1-hydroxy-8-methoxy-3-methylantraquinone, m. p. $202-204^{\circ}$, gives chrysophanic acid (III), identical with the acid prepared by Eder and Widmer's method (A., 1922, i, 260; 1923, i, 688). Reduction of (III) with *Sn* and conc. HCl in AcOH affords 1:8-dihydroxy-3-methyl-9-anthrone, m. p. $203.4-204^{\circ}$ (corresponding anthranil acetate, m. p. $236-237^{\circ}$, identical with a product obtained by successive demethylation and acetylation of chrysarobin). Demethylation of (II) gives 1:8-dihydroxy-3-methyl-10-anthrone, m. p. $179-180^{\circ}$ (corresponding anthranil acetate, m. p. $209-210^{\circ}$), also obtained from 3-hydroxy-2-(2'-hydroxy-4'-methylbenzyl)benzoic acid, m. p. $157-158^{\circ}$, which is prepared by reducing the corresponding benzoylbenzoic acid with *Zn* and aq. NH_3 .

C. J. WEST (b).

Hydroxy-derivatives of retene. L. F. FIESER and M. N. YOUNG (J. Amer. Chem. Soc., 1931, 53,

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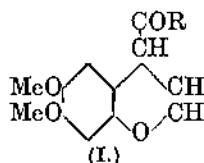
[With H. D. NEWMAN.] The following compounds are described: 2-allyloxyphenanthrene, m. p. 92°; 1-allyl-2-phenanthrol, m. p. 125.5° (acetate, m. p. 105°; coumaran derivative, m. p. 155°; allyl ether, m. p. 91.5°); 4-allyl-3-phenanthrol, m. p. 91° (acetate, m. p. 56°; coumaran derivative, m. p. 89°).

C. J. WEST (b).

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F. B. LAFORGE (J. Amer. Chem. Soc., 1931, 53, 4400—4408, 4450—4451, 4460—4462).—XVI. The reactions involving the formation of derritol, rotenol, dehydrorotenone, and derric acid are explained on the basis of their oxidation products.



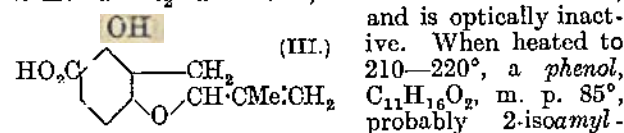
All these reactions are concerned with the MeO-containing part of the rotenone mol., which is best expressed as (I), where R represents that part of the mol. yielding tubaia acid. The original must be con-

sulted for the arguments advanced.

Dihydorreritol and CH₂Br.CO₂Et with NaOEt give the Et ester, m. p. 128°, of dihydorreritic acid. Similarly, isoderritol affords the Et ester, m. p. 128°, of isoderric acid (esterified to the same ester), whilst derritol gives dehydrorotenone and Et derric acid.

XVII. Dihydorreritenone exists in dimorphic forms, m. p. 164° and 216°; the former changes into the latter on keeping.

XVIII. A small amount of tetrahydrotubaia acid (II), C₁₂H₁₈O₄, m. p. 206° (decomp.), is formed in addition to the dihydro-acid when tubaia acid is reduced catalytically. (II) gives a violet colour with FeCl₃, forms a Ac₂ derivative, a Me ester Me ether, and is optically inactive.



When heated to 210—220°, a phenol, C₁₁H₁₆O₂, m. p. 85°, probably 2-isoamyl-resorcinol, is formed. Tubaia acid is represented as (III), and (II) as 2:4-dihydroxy-3-isoamylbenzoic acid.

C. J. WEST (b).

α -Terpenyl acetate. I. H. PAILLARD and P. TEMPIA (Helv. Chim. Acta, 1931, 14, 1314—1317).— α -Terpenyl acetate (I) is best obtained pure by Houben's method (A., 1906, i, 440). Boulecz's method (A., 1907, ii, 306) also gives good results; the *m*-xylene can be replaced by turpentine. (I) is not obtained from α -pinene and AcOH in presence of H₂SO₄ (G.P. 67,255) or PhSO₃H (Barbier and Grignard, A., 1908, i, 94).

H. BURTON.

Reducing action of magnesium bornylchloride.

I. R. SHERWOOD and W. F. SHORT (J.C.S., 1931, 3340).—Ethereal Mg bornyl chloride reduces isovaleraldehyde, citral, and piperitone to isoamyl alcohol, geraniol, and phellandrene, respectively, together with small amounts of borneol (3:5-dinitrobenzoate, m. p. 154.5°) in each case.

J. W. BAKER.

Catalytic production of camphor from borneol. P. P. SCHORIGIN and Y. MAKAROV-SEMLIANSKI (J. Appl. Chem., Russia, 1931, 4, 69—75).—Borneol, C₁₅H₂₆, H₂O, and air react at 300° in presence of active V₂O₅; the yield is 80% of the theoretical, 50% of the borneol being recovered. Camphane is formed if the optimal conditions are not observed. When borneol and C₆H₆ are passed over finely-divided Cu or bronze at 255°, H₂ is eliminated and 86—88% of camphor is obtained, 12—13% of the borneol being recovered.

CHEMICAL ABSTRACTS.

Isomerisation of linalool into camphor. (MLLE.) I. K. VINOGRADOVA (J. Gen. Chem. Russ., 1931, 1, 660—667).—*l*-Linalool, when heated with 10—15% of Al and a trace of HgCl₂ for 8 hr., gives

dinitrofluorenone, m. p. above 300° (reduced to a *nitroaminofluorenone*, m. p. $243-244^{\circ}$, by Na_2S), and *2-nitrofluorenone*; cold, fuming HNO_3 gives a similar unstable substance, which forms 2 : 7-dinitrofluorenone on oxidation. *O*-Acetylfluorenoneoxime and conc. HNO_3 in Ac_2O at $30-40^{\circ}$ give the 2-nitro-compound, m. p. 228° , hydrolysed by KOH or conc. H_2SO_4 to 2-nitrofluorenoneoxime, m. p. 249° (decomp.), which was prepared also from 2-nitrofluorenone, which it yields on oxidation by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH .

R. S. CAHN.

Haloform reaction. IV. Influence of *o*-methoxy-groups. R. C. FUSON, M. W. FARLOW, and C. J. STEHMAN (J. Amer. Chem. Soc., 1931, 53, 4097-4103).—In no case has it been found possible to isolate the trihalogenomethyl intermediate using acetophenones with only one *o*-substituent. 2 : 4 : 6-Trimethoxyacetophenone and NaOBr in dil. or conc. alkali give $\alpha\alpha\alpha$ -tribromo-2 : 4 : 6-trimethoxyacetophenone, m. p. $102.5-103^{\circ}$ (corr.), in 67% and 58% yields, respectively; reaction is about 6 times as fast in dil. alkali. The *Cl*-derivative, m. p. $119-120^{\circ}$ (corr.), results in 68% yield. Both halogeno-compounds are oxidised to 2 : 4 : 6-trimethoxybenzoic acid by alkali. 2-Methoxyacetophenone and NaOBr in H_2O or in 20% EtOH give 51 or 64% of 2-methoxy-1-tribromoacetylnaphthalene, m. p. $136.5-137^{\circ}$ (corr.) (the 1-trichloroacetyl derivative has m. p. $131-131.5^{\circ}$), converted by alkali into 2-methoxy- α -naphthoic acid. The retardation of the haloform reaction is of the same order of magnitude in both cases. Since the effect observed with 2 : 1- $\text{OMe} \cdot \text{C}_{10}\text{H}_6\text{Ac}$ is to be ascribed to the combined influences of the OMe and the benzo-groups, it is evident that the separate effect of the benzo-group is similar to that of the OMe group.

C. J. WEST (b).

Action of Grignard solutions on 10-methoxy-anthrone. E. DE B. BARNETT (J.C.S., 1931, 3340-3341).—10-Methoxyanthrone (prep. improved) interacts with $\text{CH}_3\text{Ph} \cdot \text{MgCl}$ in the cold to form anthraquinone, 10 : 10'-dimethoxy-10 : 10'-dianthrone, and 10-methoxy-9-benzyl-9 : 10-dihydroanthranol, m. p. 129° , which with HCl and AcOH gives 10-chloro-9-benzylanthracene. 10-Methoxy-1 : 4-dimethylanthrone with MgMeI (3 mols.) gives 10-methoxy-1 : 4 : 9-trimethyl-9 : 10-dihydroanthranol, m. p. 148° , but this did not give a definite product with $\text{HCl} \cdot \text{AcOH}$. A poor yield of 10-phenyl-1 : 4-dimethylanthrone was obtained with PhMgBr , and $\text{CH}_3\text{Ph} \cdot \text{MgCl}$ and Mg *o*-tolyl bromide gave only resinous products.

H. A. PIGGOTT.

Chemical participation of water in the oxidising action of *p*-benzoquinone; theory of oxidative processes. A. BACH and K. NIKOLAEV (Ber., 1931, 64, [B], 2769-2772).—In absence of H_2O there is no reaction between *p*-benzoquinone and EtOH when irradiated; reaction increases with increasing amounts of H_2O , although there is no direct proportionality. The presence of H_2O is essential for the oxidation by *p*-benzoquinone of pyrogallol in EtOH , COMe_2 , or Et_2O or of *p*-phenylenediamine in Et_2O . It is considered that H_2O has a somewhat stabilising effect on the peroxide form of *p*-benzoquinone owing to the formation of *p*-hydroxyphenyl

H peroxide, which imparts its active O to the substrate and is therefore deoxidised to quinol. H. WREN.

Complex salts of hydroxyquinones. I. A. MANGANI (Gazzetta, 1931, 61, 820-826).—The Na salt of 2-hydroxy- α -naphthaquinone, *Co*, *Mg*, and *Zn* salts of 5-hydroxy- α -naphthaquinone, and *Co* and *Zn* salts of naphthazarin, which are probably additive compounds with *Co* and *Zn* acetates, are described. Chrysazin (1 : 8-dihydroxyanthraquinone) forms hydrogens *Co*, *Mg*, *Zn*, and *Cu* salts, the last being a very sensitive test, and a neutral *Co* salt.

E. E. J. MARLER.

Hydroxyanthraquinones. I. Synthesis of purpurin. P. G. MARSHALL (J.C.S., 1931, 3206-3208).—Quinizarin heated with Na_2SO_3 and CuO in H_2O gives an almost quant. yield of the 2-sulphonic acid (I); the Na salt when heated with Ca(OH)_2 and H_2O at 250° affords purpurin (84% yield). Zimmermann's method (A., 1930, 941) of prep. of (I) does not give exclusively the 2-sulphonic acid. H. BURTON.

Anthrone series. III. Synthesis of 3-methoxyphthalaldehydic acid and a new synthesis of chrysazin. IV. Synthesis of the anthrones derived from chrysophanic acid. C. A. NAYLOR, jun. [with J. H. GARDNER] (J. Amer. Chem. Soc., 1931, 53, 4109-4113, 4114-4119).—III. Oxidation of 1 : 5-dimethoxynaphthalene with alkaline KMnO_4 gives 11-16% of 3-methoxyphthalaldehydic acid (I), m. p. $121-122^{\circ}$ to a turbid liquid, which then partly solidifies and re-melts at 144.8° ; all m. p. are corr. $p\text{-C}_6\text{H}_4\text{Br} \cdot \text{OH}$ and (I) with 85% H_2SO_4 afford 55% of 3-methoxy-2-(5-bromo-2-hydroxyphenyl)phthalide, m. p. $198-200^{\circ}$, reduced by Zn and 10% NaOH to 3-methoxy-2-*o*-hydroxybenzylbenzoic acid, m. p. $185-186^{\circ}$, which is converted by conc. H_2SO_4 at room temp. into 1-hydroxy-8-methoxy-10-anthrone, m. p. $170-171^{\circ}$. This is oxidised by CrO_3 in AcOH to 1-hydroxy-8-methoxyanthraquinone (chrysazin Me ether), demethylated to chrysazin (11% yield) (Ac_2 derivative, m. p. $231-232^{\circ}$).

IV. 6-Bromo-*m*-cresol and (I) with 85% H_2SO_4 give 3-methoxy-2-(5-bromo-2-hydroxy-4-methylphenyl)phthalide, m. p. $243-244.6^{\circ}$, convertible (as above) into 3-methoxy-2-(2'-hydroxy-4'-methylbenzyl)benzoic acid, m. p. $164-164.6^{\circ}$, and 1-hydroxy-8-methoxy-3-methyl-10-anthrone (II), m. p. $173.8-175^{\circ}$. Demethylation of 1-hydroxy-8-methoxy-3-methylanthraquinone, m. p. $202-204^{\circ}$, gives ehrysophanic acid (III), identical with the acid prepared by Eder and Widmer's method (A., 1922, i, 260; 1923, i, 688). Reduction of (III) with Sn and conc. HCl in AcOH affords 1 : 8-dihydroxy-3-methyl-9-anthrone, m. p. $203.4-204^{\circ}$ (corresponding anthranil acetate, m. p. $236-237^{\circ}$, identical with a product obtained by successive demethylation and acetylation of chrysarobin). Demethylation of (II) gives 1 : 8-dihydroxy-3-methyl-10-anthrone, m. p. $179-180^{\circ}$ (corresponding anthranil acetate, m. p. $209-210^{\circ}$), also obtained from 3-hydroxy-2-(2'-hydroxy-4'-methylbenzyl)benzoic acid, m. p. $157-158^{\circ}$, which is prepared by reducing the corresponding benzoylbenzoic acid with Zn and aq. NH_3 .

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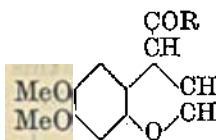
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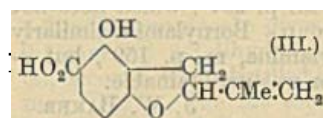
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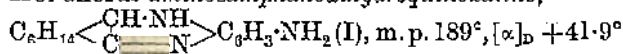
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30% of dipentene, traces of myrcene or linaloolene, 2% of camphor, 0.8% of borneol, 22% of dimyrcene, 8.5% of H_2O , and 15% of tar; all these products are inactive or dextrorotatory. Geraniol on similar treatment gives only dipentene and dimyrcene. The formation of borneol and camphor is explained by assuming the intermediate production of camphene; this was not isolated.

G. A. R. KON.

Derivatives of phenylaminocamphor. F. L. ROSE (J.C.S., 1931, 3337—3339).—Aminocamphor (best prepared by electrolytic reduction of oximinocamphor) and 2:4-dinitrochlorobenzene yield 2:4-dinitroanilino-camphor, m. p. 204°, $[\alpha]_D -120.3^\circ$ in $CHCl_3$, in which attempts to reduce only one NO_2 -group were unsuccessful, but which with $SnCl_2$ and HCl affords *aminocamphanodihydroquinoxaline*,



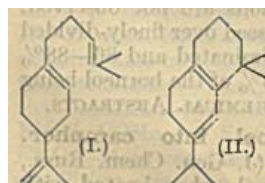
in $EtOH$ (Ac_2 , m. p. 220°, Bz , m. p. 227°, derivatives), the $(NH_2)_2$ -compound being formed intermediately. With MeI at 100° (I) affords a mixture of the yellow *methiodide* (insol. in $CHCl_3$) and the red *hydriodide* of *methylaminocamphanodihydroquinoxaline* (*nitrosoamine*). With 2:4-dinitrochlorobenzene (I) gives a *dinitrophenyl* derivative, m. p. 237°, which does not contain a primary NH_2 -group. Bornylamine similarly gives *dinitrophenylbornylamine*, m. p. 159°, but *o*-nitrophenylaminocamphor was unobtainable.

J. W. BAKER.

Identification of hydroxyphenylhomocampholic acid. L. PALFRAY (Bull. Soc. chim., 1931, [iv], 49, 1529—1540; cf. A., 1924, i, 854).—With 1 mol. of $BzCl$, sodiocamphor gives only dibenzoylcamphor and not the monobenzoyl derivative. By using 2 mols. of $NaNH_2$ in $PhMe$, heating for 6 hr. to eliminate NH_3 , and adding 1 mol. of $BzCl$ the yield of dibenzoylcamphor is appreciably raised; with a further mol. of $BzCl$ at 110°, tribenzamide, m. p. 202°, is also formed and a smaller amount of dibenzoylcamphor. The latter is converted into 1-hydroxy-2-benzoylcamphene by boiling aq. alcoholic alkali. With $NaOEt$ at 160—170° dibenzoylcamphor affords 92% of 1-hydroxy-2-benzoylcamphene and $BzOH$ with some benzoylcampholic acid, m. p. 163°; at 200—220° a 72% yield of (impure) benzoylcampholic acid is obtained. Hydroxybenzoylcamphene is only partly hydrolysed by alcoholic $NaOH$, yielding 60% of benzoylcampholic acid at 200—220°, and is not attacked by fused Na *p*-tolylxide at 200—220°. Phenylhydroxyhomocampholic acid, m. p. 202—203°, $[\alpha]_D^{25} +73.22^\circ$ (Me ester, m. p. 104—105°), and $BzCl$ give benzylidene-camphor, m. p. 96°.

R. BRIGHTMAN.

Polyterpenes and polyterpenoids. LXII. Constitution of cycloisoprenemyrcene. L. RUTICKA and W. BOSCH (Helv. Chim. Acta, 1931, 14, 1336—1339).—*cycloisoprenemyrcene* (Semmler and Jonas, A., 1913, i, 742), b. p. 136—139°/14 mm., when regenerated from its trihydrochloride, m. p. 81° (cf. *loc. cit.*), is considered to be



(I), since it is cyclised by 85% HCO_2H to *dicyclopentenemyrcene* (II), b. p.

130—134°/13 mm., which is dehydrogenated by Se at 320° to eudalene.

H. BURTON.

3-Methylfuran. I. J. RINKES (Rec. trav. chim., 1931, 50, 1127—1132).—*Et* 3-carbethoxy-4-methyl-2-furylacetate (A., 1899, i, 675) is converted by $NaOEt$ and amyl nitrite in $EtOH$ into the *oximino*-derivative, m. p. 82°, which when heated with aq. H_2SO_4 gives 2-cyano-4-methylfuran-3-carboxylic acid, m. p. 203—204°, decarboxylated by quinoline and Cu-bronze at 210—220° to 2-cyano-4-methylfuran; this is hydrolysed by KOH in aq. $MeOH$ to 4-methylfuran-2-carboxylic acid, m. p. 129°, which is partly decomposed at 200° into CO_2 and 3-methylfuran, b. p. 65—66°.

3:6-*Endoxo*-4-methyl-, m. p. 82°, and 3-methyl- Δ^4 -tetrahydrophthalic anhydride, m. p. 80°, are obtained by interaction of 3- and 2-methylfuran, respectively, with maleic anhydride.

H. A. PIGGOTT.

Synthesis of 3-methylfuran. T. REICHSTEIN and H. ZSCHOKKE (Helv. Chim. Acta, 1931, 14, 1270—1276).—*Et* 3-carbethoxy-4-methyl-2-furylacetate, b. p. 109—110°/0.5 mm., produced with the corresponding pyrrole from *Et* acetonedicarboxylate, chloroacetone, and NH_3 in Et_2O , is converted by *Et* nitrite in presence of dry $NaOEt$ and Et_2O into *Et* 3-carbethoxy-4-methyl-2-furyloximinoacetate, m. p. 83—84° (all m. p. are corr.). The free *oximino*-dicarboxylic acid, m. p. 187—191° (decomp.), and Ac_2O give 2-cyano-4-methylfuran-3-carboxylic acid (I), m. p. 195—199°, which with quinoline and Cu-bronze at 220° affords 2-cyano-4-methylfuran, b. p. 57—58°/12 mm., hydrolysed to 4-methylfuroic acid, m. p. 131—132°. The *oximino*-acid and $NH_2OH \cdot HCl$ give (I) and 3-carboxy-4-methylfuran-2-carboxylamide, m. p. 228—230°, hydrolysed to 4-methylfuran-2:3-dicarboxylic acid, m. p. 233° (decomp.), which when heated alone passes into 4-methylfuran-3-carboxylic acid, m. p. 138—139°. The dicarboxylic acid with quinoline and Cu-bronze at 270—290° gives 3-methylfuran.

H. BURTON.

Derivatives in the tetrahydrofuran series. R. PAUL (Compt. rend., 1931, 193, 1428—1430).—The action of powdered K in Et_2O on δ -dibromopentanol affords some δ -bromo- Δ^3 -pentenol and chiefly 2-bromo-methyltetrahydrofuran, b. p. 67°/18 mm., which can be converted through the acetate, b. p. 93—94°/22 mm., into 2-tetrahydrofurfuryl alcohol. It is suggested that a positive charge on the δ -C atom causes 5-ring formation.

F. R. SHAW.

Aldehyde syntheses in the furan series. II. Synthesis of elsholtzic [3-methylfuroic] acid and elsholtzia [3-methyl-2-furyl isobutyl] ketone. T. REICHSTEIN, H. ZSCHOKKE, and A. GOERG (Helv. Chim. Acta, 1931, 14, 1277—1283; cf. Asahina *et al.*, A., 1924, i, 976).—2:4-Dimethylfuran is converted by the method previously described (A., 1930, 783) into 3:5-dimethylfurfuraldehyde, b. p. about 78°/13 mm. [*semicarbazone*, m. p. 220—221° (decomp.)], oxidised by Ag_2O in aq. $EtOH$ - $NaOH$ to 3:5-dimethylfuroic acid, m. p. 146—147° (corr.). 3-Methylfuran is similarly converted into 3-methylfurfuraldehyde, b. p. 60—61°/12 mm. [*semicarbazone*, m. p. 216—218° (decomp.)], and thence into 3-methylfuroic acid [*amide*, m. p. 90—90.5° (lit. 85—86°)]. 3-Methylfurfuraldehyde-*oxime*, m. p. 73—76°, and Ac_2O give 2-cyano-3-methyl-

furan, b. p. 54.5—55°/12 mm., m. p. about 19°, which with MgBu^{Br} affords 3-methyl-2-furyl Bu^{Br} ketone.

H. BURTON.

Exhaustive O-methylation of quercetin. A. S. GOMM and M. NIERENSTEIN (J. Amer. Chem. Soc., 1931, 53, 4408—4411).—Quercetin and diazomethane in dioxan give 3:7:3':4'-tetramethylquercetin, m. p. 159—160° (Ac derivative, m. p. 169—170°), previously supposed to be the 7:3':4'- Me_3 derivative (Waliaschko, A., 1909, i, 248; cf. Wunderlich, A., 1908, i, 559), converted by Me_2SO_4 and solid KOH into the Me-derivative, m. p. 151—152°. C. J. WEST (b).

Ring closure studies in the piperidine series. G. R. CLEMO, J. ORNSTON, and G. R. RAMAGE (J.C.S., 1931, 3185—3190).—Et piperidine-3-carboxylate (I), $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, and anhyd. K_2CO_3 at 100° (bath) give Et 3-carbethoxypiperidinoacetate (II), b. p. 125°/0.1 mm. (dihydrazide, m. p. 162°; diamide, m. p. 213°, distills unchanged), hydrolysed by dil. HCl to 3-carboxypiperidinoacetic acid, m. p. 270° (Cu salt). Piperidine and β -cyanoethyl *p*-toluenesulphonate (III) at 130° afford β -piperidinopropionitrile, b. p. 116°/18 mm. (methiodide, m. p. 155°), whilst (I) and (III) give β -3-carbethoxypiperidinopropionitrile, b. p. 133°/0.1 mm., converted by EtOH-HCl into Et β -3-carbethoxypiperidinopropionate, b. p. 130°/0.1 mm. (free acid, m. p. 195—196°; dihydrazide, m. p. 152°), also prepared from (I), $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and NaOAc. The last-named ester and (II) do not undergo the Dieckmann reaction and ring closure could not be effected by distillation of the Th salts of the corresponding acids. γ -3-Carbethoxypiperidinobutyronitrile, b. p. 135°/0.1 mm., from (I), $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$, and K_2CO_3 , is converted by EtOH-HCl into Et γ -3-carbethoxypiperidinobutyrate (IV), b. p. 133°/0.1 mm. (dihydrazide, m. p. 165°); distillation of the Th salt of the free acid gives a basic, non-ketonic oil, b. p. 105—110°/20 mm. Ring closure of 3-carbethoxypiperidinoacetone, b. p. 110°/0.1 mm., from (I), bromoacetone, and K_2CO_3 , could not be effected. The quaternary salt, m. p. 139°, from (IV) and Me *p*-toluenesulphonate when treated with Na in boiling PhMe, and then hydrolysed with HCl, gives a little basic, non-ketonic oil, b. p. 70°/0.3 mm.

H. BURTON.

Electron-sharing ability of organic radicals. Nitrogen heterocycles. L. C. CRAIG and R. M. HIXON (J. Amer. Chem. Soc., 1931, 53, 4367—4732).—The relationship previously demonstrated (A., 1927, 814; 1930, 1525, 1526) between the electron-sharing ability of the org. radicals and the affinities of the polar groups in the series $\text{R}\cdot\text{NH}_2$, $\text{R}\cdot\text{CO}_2\text{H}$, $\text{R}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$, and $\text{R}\cdot\text{HgX}$ has been shown to hold for both the 2- and *N*-substituted pyrrolidines. 2-Aminomethylpyridine (I), b. p. 91°/15 mm. [oxalate, m. p. 167°; chloroaurate, m. p. 204° (decomp.); chloroplatinate], and 3-aminomethylpyridine (II), b. p. 112°/18 mm. (chloroplatinate, not melted at 320°; picrate, m. p. 211°), are prepared by reduction of the corresponding pyridylformaldoximes with Zn dust and AcOH. The following dissociation consts. are reported: pyrrolidine, 1.3×10^{-3} ; *N*-cyclohexyl-, 5.0×10^{-4} ; *N*-butyl-, 2.3×10^{-4} ; *N*-methyl-, 1.5×10^{-4} ; *N*-benzyl-, 3.2×10^{-5} ; *N*-*p*-tolyl-, 5×10^{-10} ; *N*-phenyl-, 2×10^{-10} ; 2-ethyl-, 2.7×10^{-1} ; 2-phenyl-, 4×10^{-5} ; β -pyridyl- α -*N*-methyl-

pyrrolidines, 9×10^{-7} ; metanicotine, 9×10^{-5} ; 2-ethylpyrrolidine, 2.7×10^{-7} ; 2-pyrrolmethylamine, 9×10^{-6} ; (II), 1.1×10^{-6} ; (I), 1×10^{-6} . The 2-pyrrol radical is more negative than Ph, but is less negative than pyridyl.

C. J. WEST (b).

Action of aldehydes on 2-amino- and 2-dimethylaminopyridine. A. E. TSCHITSCHIBABIN and I. L. KNUNJANZ (Ber., 1931, 64, [B], 2839—2842; cf. A., 1930, 221).—2-Aminopyridine is converted by PhCHO, anisaldehyde, and piperonal in boiling HCO_2H , respectively, into 2-benzylamino-, m. p. 94°, 2-*p*-methoxybenzylamino-, m. p. 128°, and 2:3':4'-methylenedioxybenzylamino-, m. p. 99—100°, -pyridine. 2-Formamidopyridine has m. p. 71°. 2-Dimethylaminopyridine, PhCHO, and anhyd. ZnCl_2 at 230—240° afford phenyldi-2-dimethylamino-5-pyridylmethane, m. p. 130—131°, readily oxidised by PbO_2 to the corresponding carbinol, m. p. 123—124°, which does not yield true dyes with acids. *o*-Nitrobenz- and salicyl-aldehydes do not react with 2-amino-pyridine.

H. WREN.

Strychnine and brucine. XIII. Dihydroindolylpropionic and dihydroindolylbutyric acids. B. K. BLOUNT and R. ROBINSON (J.C.S., 1931, 3158—3160).—Catalytic reduction (PtO_2) of Et β -3-indolylpropionate gives the Et ester, b. p. 145°/0.1 mm., of β -3-dihydroindolylpropionic acid (I), an oil, decomp. when distilled in high vac. (Bz derivative, m. p. 152°). The Me ester, b. p. 160°/0.1 mm., of γ -3-dihydroindolylbutyric acid (II), a resin (1-*p*-nitrobenzoyl derivative, m. p. 163—164°), is prepared similarly from Me γ -3-indolylbutyrate. (I) and (II) show no tendency to form cyclic amides. Strychnine acid is not regarded as a substituted derivative of (I) or (II) (cf. Leuchs, A., 1931, 242). H. BURTON.

Attempts to find new antimalarials. VI. Derivatives of 2- β -aminoethylquinoline. W. O. KERMACK and W. MUIR. VII. Quinoline compounds having in the 4-position a side-chain containing two or more nitrogen atoms. W. O. KERMACK and J. F. SMITH (J.C.S., 1931, 3089—3096, 3096—3104).—VI. Et β -2-quinolylpropionate and N_2H_4 hydrate at 140° give β -2-quinolylpropionhydrazide, m. p. 165°, converted by HNO_2 into *s*-di-(β -2-quinolylpropion)hydrazide, m. p. 265°. 2-Methylquinoline hydrochloride (1 mol.), 40% CH_2O (2 mols.), and piperidine (2 mols.) at 100° (bath) afford 2- β -piperidinoethylquinoline, decomp. on attempted distillation (isolated in 72% yield as the picrate, m. p. 155°). 2- β -Diethylamino- [picrate, m. p. 123—124° (33% yield)] and 2- β -phenylmethylamino-ethylquinoline [picrate, m. p. 175° (decomp.) (poor yield)] are prepared similarly, using NH_2Et and NHPhMe , respectively, instead of piperidine. Unsuccessful attempts were made to substitute MeCHO for CH_2O in these reactions. α -Piperidino- β -methylbutan- γ -one (I) (A., 1928, 299) and *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (II) in aq. EtOH-NaOH give 2- β -piperidinoisopropylquinoline [picrate, m. p. 167—168°; dipicrate (?), m. p. 201°] and 2:3-dimethylquinoline; the last-named is probably formed from (II) and COMeEt, which arises by hydrolysis of (I). Similarly, 2-piperidinomethylcyclohexanone and (II) afford 1-piperidinomethyl-1:2:3:4-tetrahydroacridine (picrate, m. p. 206°), whilst 2-di-

ethylaminomethylcyclohexanone and (II) give an amorphous compound, $C_{11}H_{17}O_2N$, m. p. 65–75°.

VII (cf. A., 1930, 1048). Piperidine, *N*-β-bromoethylphthalimide (III), and anhyd. K_2CO_3 in boiling PhMe give *N*-β-piperidinoethylphthalimide, m. p. 91°, hydrolysed (N_2H_4 , hydrate method) to β-piperidinoethylamine (IV), decomp. when heated in vac. [picrate, m. p. 225° (decomp.)]. (IV), 4-chloro-6-methoxy-2-methylquinoline (V), and a trace of Cu-bronze at 100–120° afford 4-β-piperidinoethylamino-6-methoxy-2-methylquinoline (+2H₂O), m. p. 73°, m. p. (anhyd.) 140–141°, which has no antimalarial action. The oxime, m. p. 91–92°, of α-piperidinobutan-γ-one is reduced by Zn dust and EtOH–AcOH to γ-amino-α-piperidinobutane (poor yield), b. p. 106–110°/12 mm. [hydrochloride, m. p. 210°; dihydrochloride, m. p. 241°; dipicrate, m. p. 241–242° (decomp.)], which could not be condensed with (V) or 4-bromo-6-methoxy-2-methylquinoline (VI). Piperazine hexahydrate and (III) at 140–150° give *N*-β-piperazinoethylphthalimide [dihydrobromide, m. p. 243° (decomp.)] and 1:4-di-(β-phthalimidoethyl)piperazine, m. p. 240° [dihydrobromide, m. p. 300°], hydrolysed to β-piperazinoethylamine (dipicrate, m. p. 290°) and 1:4-di-(β-aminoethyl)piperazine (VII) [tetrahydrochloride, m. p. 295° (decomp.)], respectively. Extraction of a strongly alkaline EtOH solution of (VII) with $CHCl_3$ [during a prep. by a modification of Franchimont and Kramer's method (A., 1912, i, 391)] resulted in the formation of 1:4-di-(β-isocyanoethyl)piperazine, m. p. 280° [dihydrochloride, m. p. 277° (decomp.)]. (VI) and (VII) at 170° give 4-(4'-β-aminoethylpiperazinoethylamino)-6-methoxy-2-methylquinoline [picrate (+3H₂O), m. p. 175°] and 1:4-di-(β-6'-methoxy-2'-methyl-4'-quinolylaminoethyl)piperazine [tetrahydrochloride (+5H₂O), m. p. above 310°]; the last-named is obtained in better yield when an excess of (VI) is used. The Cl atom in 4-(4'-chloroacetyl)piperazino-6-methoxy-2-methylquinoline [hydrochloride, m. p. 256° (decomp.)]; unstable picrate, m. p. 155–160°, prepared from the 4-piperazino-derivative (*loc. cit.*) and $CH_2Cl-COCl$, is relatively inactive. α-Piperidinobutan-γ-one hydrochloride is apparently dehydrated by $CH_2Cl-COCl$ (not by $AcCl$) in $CHCl_3$ to the dihydrochloride, m. p. 182°, of α-dipiperidino-γ-keto-ε-methyl-Δ⁸-heptene or α-dipiperidino-β-acetyl-γ-methyl-Δ⁸-pentene.

H. BURTON.

Phthalone-imides and their derivatives. A. MEYER and R. VITTENET (Compt. rend., 1931, 193, 1095–1098).—By hydrolysis of azomethines of the type $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ C(NR) \quad CO \end{smallmatrix}$ (A., 1931, 1414) with dil. HCl at 100° the following α-ketohomophthalimides, $C_6H_4 \begin{smallmatrix} CO \cdot NR \\ \diagup \quad \diagdown \\ CO \cdot CO \end{smallmatrix}$, have been obtained: imide, m. p. 228–229° [lit., m. p. 220–224°; phenylhydrazone, m. p. 269–263° (?); phenylmethylhydrazone, m. p. 242–5°; oxime, m. p. 242–243°]; phenyl-, m. p. 220–221° (phenylhydrazone, m. p. 246–247°; phenylmethylhydrazone, m. p. 204°; oxime, m. p. 224–236°; semicarbazone, m. p. 230–231°); p-tolyl-, m. p. 238° (phenylhydrazone, m. p. 258–259°; phenylmethylhydrazone, m. p. 199°; oxime, m. p. 241–242°; semicarbazone, m. p. 236–237°); α-, m. p. 239–240°

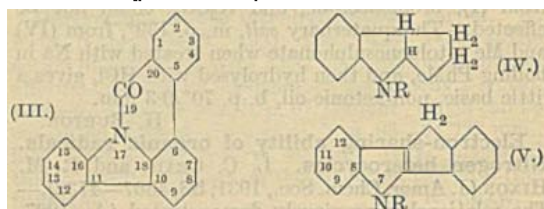
(phenylhydrazone, m. p. 283–284°; phenylmethylhydrazone, m. p. 212°); and β-, m. p. 268–269° (phenylhydrazone, m. p. 262–263°; phenylmethylhydrazone, m. p. 199–200°), -naphthyl-imide.

J. W. BAKER.

Nitration of carbazole. G. T. MORGAN, J. G. MITCHELL, and (in part) J. R. DOLPHIN (J.C.S., 1931, 3283–3285).—Nitration of carbazole with 60% HNO_3 at 40° raised to 80–90°, or with $BzNO_2$ in dry petroleum at –15° affords mainly 3-nitrocarbazole and the yellow compound, m. p. 164°, which is the main product when Ziersch's conditions (HNO_3 and $AcOH$; A., 1909, i, 961) are used. This compound is a mol. complex of the 1- and 3- NO_2 -derivatives and is separated into its components by fractional sublimation or by addition of EtOH to its solution in NH_3 Ph or pyridine, when the 1- NO_2 -compound, m. p. 186.5–187.5°, crystallises. This is reduced to 1-amino-carbazole, from which no internal diazoimine could be obtained.

J. W. BAKER.

Action of halogens on polycyclic indole derivatives. I. Reaction between bromine and acyl derivatives of tetrahydrocarbazole and benzopentindole. S. G. P. PLANT and M. L. TOMLINSON (J.C.S., 1931, 3324–3337).—9-Acetyltetrahydrocarbazole and Br in CS_2 give an unstable 10:11-additive dibromide, m. p. 60° (decomp.), converted by H_2O into 10:11-dihydroxy-9-acetylhexahydrocarbazole, m. p. 203°, which is the sole product of bromination in $AcOH$. Similar bromination of the 9-benzoyl compound affords the 9-Bz derivative (I), m. p. 144–146°, of 11-hydroxy-2:3:4:11-tetrahydrocarbazole (II), m. p. 115°, which is obtained on hydrolysis with KOH in aq. EtOH and which, with $BzCl$ and KOH , gives, not (I), but the 11-benzoyloxy-derivative, m. p. 128°. (I) is formed by elimination of 1 mol. of HBr from the additive dibromide and subsequent hydrolysis of Br to OH, since it is not identical with the 6-Bz derivative, m. p. 107° (by action of $BzCl$ and KOH) of



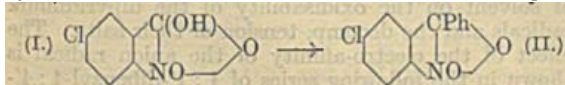
ψ-indoxylspirocyclopentane. When boiled with Ac_2O , (I) affords 19-ketophenanthrindoline (III), m. p. 225° (parent substance has H_2 in place of O). Similar treatment of (II) affords 2:3-dihydrocarbazole, m. p. 293–295°. Bromination of 9-phenylacetyl- and 9-cinnamoyl- (improved prep. described) tetrahydrocarbazole affords 10:11-dihydroxy-9-phenylacetylhexahydro- (J.C.S., 1923, 123, 676), and 9-cinnamoyl-2:3:4:11-tetrahydro-, m. p. 102–106°, carbazole, respectively. Hydrolysis of the latter gives (II), whilst distillation under reduced pressure affords $CHPh:CH \cdot CO_2H$ and carbazole. Bromination of dihydropentindole and of its 8-Ac-, -Bz-, $-CO_2Et$, and -phenylacetyl, m. p. 116°, derivatives causes development of intense colour, but no definite reaction products could be isolated, but with 8-acetyltetrahydro-

pentindole (IV; R=Ac) substitution occurs, giving the 5-*Br*-derivative, m. p. 114°, identical with a specimen prepared from 5-bromodihydropentindole, m. p. 140° (by the Fischer indole synthesis from cyclopentanone-*p*-bromophenylhydrazine), by electrolytic reduction to the tetrahydro-compound, m. p. 73°, and subsequent acetylation. Bromination of tetrahydropentindole (IV; R=H) occurs so readily that, even with 1 mol. of Br, the main product, after acetylation, is 5:7-dibromo-8-acetyltetrahydropentindole, m. p. 145°, only a small amount of the 5-*Br*-compound being obtained. Bromination of 7-acetylbenzopentindole (V; R=Ac) gives a mixture (5: I) of the 10 (or 12)- (VI), m. p. 150°, and 12 (or 10)- (VII), m. p. 168°, -*Br*-derivatives (separated by fractional crystallisation from EtOH-COMe₂), identical with specimens synthesised by acetylation of the product of the Fischer reaction from α -hydrindone-*m*-bromophenylhydrazine, m. p. 118–120°. The corresponding -*p*-bromophenylhydrazine, m. p. 153–159°, similarly affords 11-bromobenzopentindole, m. p. 230° (Ac derivative, m. p. 174°), but attempts to obtain the 9-bromo-compound from the *o*-bromophenylhydrazine (dimorphous), m. p. 136° (colourless needles, unstable) and m. p. 134° (red prisms), were unsuccessful. Bromination of 7-benzoylbenzopentindole gives only the 10 (or 12)-*Br*-derivative, m. p. 193° (converted into the Ac derivative described above), but *Et* benzopentindole-7-carboxylate, m. p. 116° (ClCO₂Et and aq. KOH on benzopentindole in COMe₂), gives a mixture of *Et* 10 (or 12)-, m. p. 166° [converted by hydrolysis and acetylation into (IV)], and 12 (or 10)-, m. p. 127° [synthesised by hydrolysis of (VII) and treatment with ClCO₂Et], -bromobenzopentindole-7-carboxylate. J. W. BAKER.

ψ -Bases. III. The so-called methylphenyl-acridol. Activity coefficients of 5-phenyl-10-methylacridinium hydroxide from solubility measurements. J. G. ASTON and C. W. MONTGOMERY (J. Amer. Chem. Soc., 1931, 53, 4298–4305; cf. A., 1931, 742).—Hantzsch and Kalb (A., 1900, i, 113) found that the conductivity of a mixture of 5-phenyl-10-methylacridinium sulphate and NaOH fell rapidly with time, and concluded that the change was due to the slow establishment of the equilibrium which, they concluded, was greatly in favour of the ψ -base, phenylmethylacridol. The activity coeffs. of the 5-phenyl-10-methylacridinium hydroxide ψ -basic system have been determined by solubility measurements in dil. solutions of KCl and BaCl₂. The vals. are those of a typical strong electrolyte. The solubilities in NH₄Cl and NaOH also show that the base is a strong electrolyte. The interpretation placed on their results by Hantzsch and Kalb appears to be erroneous.

C. J. WEST (b).

Mechanism of the formation of acridones by condensation of *o*-nitrobenzaldehydes with aromatic hydrocarbons. I. TANASESCU and (Mme.) M. MACAROVICI (Bull. Soc. chim., 1931, [iv], 49, 1295–1303).—Unlike *o*-nitro- and 2:4-dinitrobenzaldehyde,



5-chloro-2-nitrobenzaldehyde yields no acridone with H₂SO₄ and C₆H₆, but only 2-chloro-*N*-oxyphenylanthr-

anil (II), m. p. 360–362°, the aldehyde reacting in its tautomeric form (I). With Zn, aq. NH₄Cl, and 95% EtOH the anthranil gives 3-chloroacridone, which, like 2-chlorophenylanthranil *N*-oxide, is converted by dimethylaniline and POCl₃ into 3-chloro-5-dimethylanilinoacridine, m. p. 230–232°, and a substance, C₈H₉O₂N, m. p. 261°. The same products are obtained from the 3-chloroacridine from 4-chlorodiphenylamine-2-carboxylic acid. The substance, m. p. 168–169°, obtained with 2-nitroacridone in the condensation of 2:4-dinitrobenzaldehyde with C₆H₆ is 2:4-dinitrobenzophenone. R. BRIGHTMAN.

New hypnotic, ethyl- β -ethylbutylbarbituric acid and some derivatives of β -ethylbutyl alcohol. E. FOURNEAU and J. MATTI.—See this vol., 142.

Influence of nitration and amination on the physical and physiological properties of phenylmethylmalonylcarbamide (rutonal) and of phenylethylmalonylcarbamide (gardinal or luminal). A. LEULIER and F. POSTIC (Compt. rend., 1931, 193, 1476–1478).—Nitro-, m. p. 278°, and amino-phenylethyl-, m. p. 213°, nitro-, m. p. 218°, and amino-phenylmethyl-malonylcarbamide, m. p. 226°, have lower partition coeffs. between H₂O and olive oil than the unsubstituted compounds, and have no hypnotic action. F. R. SHAW.

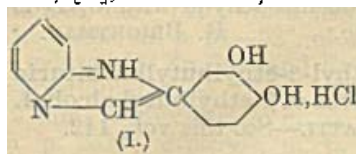
Pyrazole series. Diazotisation of amino-phenylpyrazoles. J. REILLY, B. DALY, and P. J. DRUMM (Proc. Roy. Irish Acad., 1931, 40, B, 94–101).—Benzoylacetone and *p*-nitrophenylhydrazine give 5-phenyl-1-*p*-nitrophenyl-3-methylpyrazole, m. p. 100–101°, reduced to the NH₂-derivative, m. p. 150° [dihydrochloride, m. p. 245° (decomp.); Bz derivative, m. p. 170°; benzylidene derivative, m. p. 145°; chloroplatinate; chloroaurate], which gives a diazonium chloride (chloroplatinate; chloroaurate; dichromate hydrochloride). This by coupling with suitable substances gives β -naphtholazo-, m. p. 177°, β -naphthylaminoazo-, m. p. 182°, chromotropic acid azo-, carbethoxyacetoneazo-, and acetylacetoneazo-diphenylmethylpyrazole, m. p. 159°. The stability of the above diazonium chloride was measured. A. A. LEVI.

Constitution of Fischer and Bulow's pyrazole. P. J. DRUMM (Proc. Roy. Irish Acad., 1931, 40, B, 106–108).—Condensation of benzoylacetone with NHPh-NH₂ (A., 1885, 1237) gives a pyrazole, m. p. 63°, purified through the picrate, m. p. 124°, and shown to be identical with 1:5-diphenyl-3-methylpyrazole (A., 1926, 624). It is converted by MeI into 1:5-diphenyl-3-methylpyrazolemethyllummonium iodide, m. p. 186°, and by Br in CHCl₃ into 4-bromo-1:5-diphenyl-3-methylpyrazole, m. p. 76°, identical with the product of bromination of the diphenylmethylpyrazole obtained from benzoylacetone and NHPh-NH₂ (A., 1885, 555). A. A. LEVI.

Condensation of chloroisatins with dioxindole and oxindole. G. FERICEAN (Bull. Soc. Chim. Romania, 1931, 13, 27–31).—5- and 7-Chloroisatin condense with dioxindole in the presence of piperidine to give, respectively, 5-, m. p. 255°, and 7-, m. p. 238°, -chloroisatide, similar condensation with oxindole giving 5-, m. p. 207°, and 7-, m. p. 182° (decomp.),

-chloroisatin, $\text{NH} \begin{array}{c} \text{C}_6\text{H}_3\text{Cl} \\ \text{CO} \end{array} \text{C(OH)} \cdot \text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \text{NH}$. When condensation with oxindole is effected in the presence of AcOH-HCl the products are, respectively, 5- [reduced by Zn and AcOH to the leuco-compound, m. p. 251° (decomp.)] and 7- (leuco-compound), -chloroisindigotin. J. W. BAKER.

2-3':4'-Dihydroxyphenylpyrimidazole. A. E. TSCHITSCHIBABIN and M. PLASCHENKOVA (Ber., 1931, 64, [B], 2842—2844).—2-Aminopyridine and chloro-

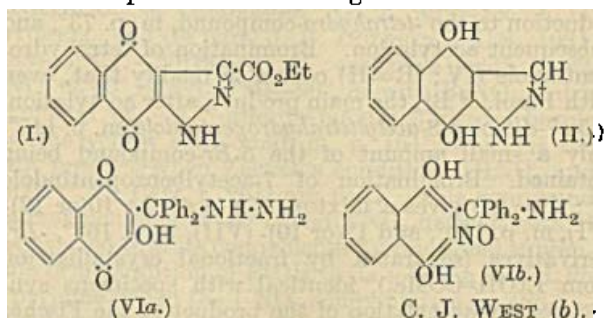


acetypyrocatechol at 120° yield 2-3':4'-dihydroxyphenylpyrimidazole hydrochloride (I), not molten below 285°.

The base, m. p. 255° (decomp.), and its *picrate*, m. p. 137° (decomp.) (also + EtOH), are described. H. WREN.

Comparison of heterocyclic systems with benzene. III. Addition of diazomethane and its derivatives to α -naphthaquinone. L. F. FIESER and M. A. PETERS (J. Amer. Chem. Soc., 1931, 53, 4080—4093; cf. A., 1927, 1198).— α -Naphthaquinone and $\text{N}_2\text{CH}\cdot\text{CO}_2\text{Et}$ in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ give 48% of α -naphthahydroquinone and 47% of 3-carbethoxylin-naphthindazole-4:9-quinone (I), m. p. 186.5°, which forms a red vat with $\text{Na}_2\text{S}_2\text{O}_4$. The reaction apparently consists in the slow addition of $\text{N}_2\text{CH}\cdot\text{CO}_2\text{Et}$ to the quinone, isomerisation of an azo- to a pyrazole ring, enolisation, and subsequent oxidation of the dienol by unreacted quinone. Reductive acetylation of (I) gives the *quinol triacetate*, m. p. 179°. Hydrolysis of (I) gives the free acid, m. p. 281°; the vat is red. Diazomethane gives 93% of lin-naphthindazole-4:9-hydroquinone (II), which changes on crystallisation to lin-naphthindazole-4:9-quinone, m. p. 349° (block) (cf. von Pechmann and Seel, A., 1899, i, 947); analysis indicates the formula $\text{C}_{11}\text{H}_6\text{O}_4\text{N}_2$, instead of $\text{C}_{11}\text{H}_8\text{O}_2\text{N}_2$ (cf. loc. cit.). The quinone also results when the above acid is heated at 281° with a trace of Cu powder. The quinone and Me_2SO_4 give the 1-Me derivative, m. p. 312°. Diazodiphenylmethane and α -naphthaquinone react vigorously, giving 44% of 2:3-(3:3-diphenyl- ψ -pyrazolo-4:5)-1:4-naphthahydroquinone (III), m. p. 203° [diacetate, m. p. 259° (slow decomp.); monobenzoate (+H₂O), decomp. about 144°; dibenzoate, m. p. 215° (decomp.); Me, ether, m. p. 192° (decomp.)]. Oxidation of (III) with HgO in C_6H_6 or with NaNO_2 in AcOH gives 2:3-(3:3-diphenyl- ψ -pyrazolo-4:5)-1:4-naphthaquinone (IV), m. p. 231°, whilst reduction with Zn and AcOH gives 3-amino-1:4-dihydroxy-2-(α -amino- α -diphenylmethyl)naphthalene, m. p. 255° (decomp.) [diacetate, m. p. 142° (decomp.)]. Alkaline oxidation of (III) gives 3-hydroxy-2-benzhydryl-1:4-naphthaquinone, m. p. 188°. Thermal decomp. of (III) at 205—210° for 5—10 min. gives (IV), 2-benzhydryl-1:4-naphthaquinone, (V), m. p. 189°, and 1-hydroxy-4-keto-2:3-(diphenylmethylene)-3:4-dihydronaphthalene, m. p. 274° (acetate, m. p. 245°) [reduced to (V)]. Hydrolysis of the diacetate of (II) gives the compound (VIa or VIb), orange (unstable) and red (stable) forms, m. p. 268—269° (decomp.), converted by and Ac_2O into the original diacetate. *p*-Benzoquinone and

diazodiphenylmethane give 93% of 2:3-(3:3-diphenyl- ψ -pyrazolo-4:5)-hydroquinone, m. p. 210° (decomp.) [diacetate, m. p. 181° (decomp.); monobenzoate, m. p. 192° (decomp.); Me, ether, m. p. 196.5°]. A table of reduction potentials at 25° is given.



Reduction of ethyl oximinoacetoacetate. V. CERCHEZ and (MLLE.) C. COLESIU (Bull. Soc. chim., 1931, [iv], 49, 1291—1295).—Reduction (Al-Hg; Et₂O) of Et oximinoacetoacetate affords 35% of Et 3:6-dimethylpyrazine-2:5-dicarboxylate, m. p. 86°, via the aminoacetoacetate; in presence of Et acetoacetate, Et dimethylpyrroledicarboxylate, m. p. 134—135°, is obtained. Reduction with Zn in HCO₂H gave 25% of dimethylpyrazinedicarboxylate and not the expected formylaminoacetoacetate.

R. BRIGHTMAN.

Synthesis of 3-keto-1-ethyl-1:2:3:4-tetrahydroquinoxaline. P. VAN ROMBROGH and W. B. DEYS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1004—1006).—The constitution of 6-nitro-3-keto-1-ethyl-1:2:3:4-tetrahydroquinoxaline (A., 1928, 428) is confirmed by reduction with Fe and HCl, and subsequent elimination of the NH₂-group by diazotisation in EtOH and heating, which gives 3-keto-1-ethyl-1:2:3:4-tetrahydroquinoxaline, m. p. 98—99°, identical with the product obtained from EtI and 3-keto-tetrahydroquinoxaline (cf. A., 1886, 351). Me phenylethylaminoacetate, b. p. 145—146°/18 mm., prepared from CH₂Cl-CO₂Me and NHPhEt at 130°, is converted by HNO₃ (d 1.4) in AcOH into the 2:4-(NO₂)₂-derivative, m. p. 119° (identified by oxidation by CrO₃ in aq. AcOH to 2:4-dinitroaniline); attempted partial reduction of this with NH₄SH gave indefinite products.

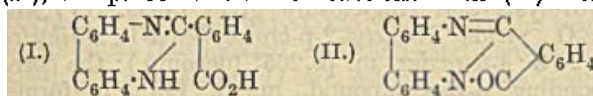
H. A. PIGGOTT.

Coloured salts of the dipyrindyl series. Theory of quinhydrones. E. WEITZ and E. MEITZNER (Ber., 1931, 64, [B], 2909—2913).—In analogy with the quinhydrones, the colour of onium salts is attributed to the incomplete heteropolarity of their components. The cyclic, unsaturated onium radicals are shown by the readiness of their chemical or electrochemical reduction to be comparatively "noble," much more so than the alkali-like, tetra-alkylammonium radicals. The intensity of the colour of onium salts increases in solution in the order H₂O, EtOH, COMe₂, CHCl₃, and this sequence is maintained for the influence of solvent on the oxidisability of the dipyrindium radicals and the decomp. tension of their salts. The effect of the electro-affinity of the anion radical is shown in the following series of 1:1'-dibenzyl-4:4'-dipyrindinium salts, generally prepared by double decomp. from the chloride: dithiocyanate, decomp.

about 180°, orange-yellow; *diselenocyanide*, dark red; *thiosulphate*, anhyd. black, *tetrahydrate*, red; unstable *dinitrile*, pale yellow; *diazide*, yellow; *sulphite*, orange-red; *cyanide* and normal *sulphite* are yellow in H₂O; *fluoride*, *cyanide*, *acetate*, and *oxalate* are colourless; *picrate* and *chromate* are yellow, corresponding with the colour proper to the anion. Complete parallelism exists between the depth of colour of the salts and the "nobility" of the anion radical according to Birckenbach and Kellermann. Towards solvents, the salts show the same behaviour as the known onium salts, being darker in org. media, paler in H₂O, or colourless if the solution is sufficiently dil.

H. WREN.

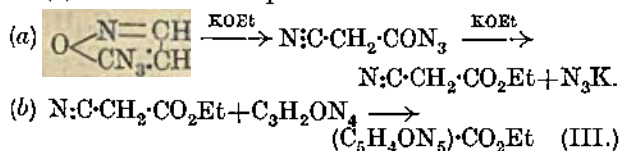
Condensation products of anhydrides of dibasic acids with aromatic diamines. L. GUGLI-ALMELLI, P. CHANUSSOT, and C. L. RUIZ (Anal. Assoc. Quim. Argentina, 1930, 18, 257—273).—The interaction of phthalic anhydride with benzidine is considered to be analogous to that with *o*-phenylenediamine. Condensation in H₂O at 100°, or in cold C₆H₆, treatment of the product with warm 1% NaOH, and acidification yields a substance regarded as (I), m. p. indef., which loses 1H₂O at 120°/10 mm. to give (II), m. p. 309°. Amine reactions with (II) were



obtained only under conditions in which decomp. occurs. It could be diazotised only in 50% HCl, and addition of H₂O to the solution in H₂SO₄ yielded a diazotisable sulphate of monophthalylbenzidine, which is converted by NaOH into the Na salt of (I), or by NaCO₃ into (II). Benzylidenemonophthalylbenzidine (A., 1926, 1131) has m. p. 333°.

R. K. CALLOW.

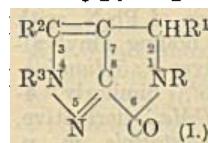
Action of nitric acid on acetylene. VI. A. QUILICO (Gazzetta, 1931, 61, 759—772).—The compound C₃H₂ON₄ (cf. A., 1931, 1169) condenses with C₂H₂, giving a *triazole*, m. p. 126°, and with CH₃CPh, giving a *C-phenyltriazole*, m. p. 154°, showing that it is a diazoimide, (C₃H₂ON₃)N₃ (I). With KOH-EtOH (I) gives N₃H and a dibasic acid, (C₃H₄ON₅)CO₂H (II), m. p. 163—165° (decomp.) [Ac derivative, m. p. 205° (decomp.) + 2H₂O; + 0.5H₂O; Ag salt], giving with diazomethane a Me₂ derivative, m. p. 120°, Me(C₃H₂ON₅)CO₂Me, converted by KOH into the Me derivative, Me(C₃H₂ON₅)CO₂H, m. p. 190° (decomp.). Adopting the α -isooxazolidiazoid formula for (I) the reaction is explained thus:



This is confirmed by the fact that Et cyanoacetate condenses with (I), giving the Et ester (III), m. p. 230° (decomp.) (Ac derivative, m. p. 148°), of (II), for which the formula $\text{N} \begin{array}{c} \diagup \text{C}(\text{CO}_2\text{H}) \\ \diagdown \text{NH} \end{array} \gg \text{C}\cdot\text{NH}\cdot\text{C}_3\text{H}_2\text{ON}$ is suggested. The compounds C₃H₂ON₃ and C₃H₄ON₂ are probably α -isooxazolyldiazine and α -isooxazolyldiazine.

E. E. J. MARLER.

Pyrazopyrrolidones. M. DOHRN and A. THIELE (Ber., 1931, 64, [B], 2863—2865).—Acetylpyruvic ester, PhCHO and NH₃, in C₆H₆-EtOH give 4:5-diketo-3-acetyl-2-phenylpyrrolidine, m. p. 195—196°, the phenylhydrazone, m. p. 217°, of which passes in boiling EtOH containing H₂SO₄ into 2:4-diphenyl-3-methylpyrazopyrrolid-6-one, m. p. 214—215° (cf. I).



The following substances are similarly derived: 4:5-diketo-3-acetyl-2-phenyl-1-methylpyrrolidine, m. p. 215—216° after softening (from acetylpyruvic ester, NH₂Me and PhCHO), its methylhydrazone, m. p. 204—205°, and 2-phenyl-1:3:4-trimethylpyrazopyrrolid-6-one, m. p. 250—255° after softening; 4:5-diketo-3-acetyl-2-piperonylpyrrolidine, m. p. 158—159°, its phenylhydrazone and 4-phenyl-2-piperonyl-3-methylpyrazopyrrolid-6-one, m. p. 216—217°; 4:5-diketo-3-acetyl-1:2-diphenylpyrrolidine, m. p. 229—231° (decomp.), its phenylhydrazone and 1:2:4-triphenyl-3-methylpyrazopyrrolid-6-one, m. p. 174—175°; 4:5-diketo-3-acetyl-1:2-diphenylpyrrolidine-*p*-tolylhydrazone, m. p. 218° (decomp.), and 1:2-diphenyl-4-*p*-tolyl-3-methylpyrazopyrrolid-6-one, m. p. 158—159°; 4:5-diketo-3-acetyl-1-*m*-tolyl-2-*p*-methoxyphenylpyrrolidine, m. p. 186—188° (from *m*-toluidine, anisaldehyde, and Et acetylpyruvate in C₆H₆), its phenylhydrazone and 4-phenyl-1-*m*-tolyl-2-*p*-methoxyphenyl-3-methylpyrazopyrrolid-6-one, m. p. 167—169°; 4:5-diketo-3-acetyl-1-*o*-methoxyphenyl-2-*p*-methoxyphenylpyrrolidine, m. p. 218—220° after darkening at 210°, its phenylhydrazone and 4-phenyl-1-*o*-methoxyphenyl-2-*p*-methoxyphenyl-3-methylpyrazopyrrolid-6-one, m. p. 161—163°; 4:5-diketo-3-acetyl-1:2-di-*p*-methoxyphenylpyrrolidine, m. p. 163—164°, its phenylhydrazone and 4-phenyl-1:2-di-*p*-methoxyphenyl-3-methylpyrazopyrrolid-6-one, m. p. 162—164°; 1:2:3:4-tetraphenylpyrazopyrrolid-6-one, m. p. 195—197°.

H. WREN.

Optically active *spiro*-5:5-dihydantoin. (SIR) W. J. PORE and J. B. WHITWORTH (Proc. Roy. Soc., 1931, A, 134, 357—371).—When *dl*-*spiro*-5:5-dihydantoin [Ac₂ derivative (modified prep.), + H₂O, m. p. 248—249°; 1:9-Bz₂ derivative, m. p. 295° (decomp.) after darkening at 290°] (1 mol.) is boiled with brucine (2 mols.) in EtOH and cooled, the brucine salt, + H₂O (lost at 125—135° in vac.), m. p. 259—260°, of 1-*spiro*-5:5-*o*-dihydantoin, + H₂O, darkens at 240°, m. p. above 320° [1:9-Ac₂ derivative, m. p. 262—264°; 1:9-Bz₂-derivative, m. p. 307—308° (decomp.) after darkening at 280°], separates; when the mother-liquor is kept, the dibrucine salt, + 2H₂O (1.5 mols. lost at 120—130° in vac.), m. p. 205—206° (decomp.), of the *d*-isomeride crystallises. The rotatory dispersions of the *d*-base in EtOH, pyridine, H₂O, and 1, 2, and 4 mols. of aq. NaOH indicate the existence of the substance in diketonic, mono- and di-enolic forms. Optical data, crystal form, and X-ray structure are recorded for the *dl*- and *l*-forms. The crystal of the *dl*-base contains alternate layers of *d*- and *l*-mols., has a higher *d*, and is more closely packed than that of the active forms; the high *d* is possibly connected with the high m. p. and low solubility.

R. S. CAHN.

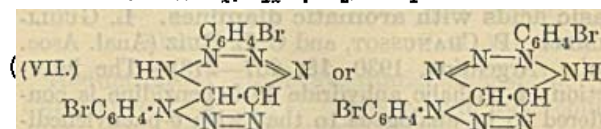
1:5-Diamino- and 1-amino-5-hydrazino-tetrazoles. R. STOLLÉ and E. GAERTNER (J. pr. Chem., 1931, [ii], 132, 209—226).—Interaction of thiosemicarbazide with PbO and NaN_3 in boiling EtOH in a stream of CO_2 , followed by acidification with aq. HCl and shaking with PhCHO , gives 1-benzylidene-amino-5-aminotetrazole, m. p. 210° (decomp.), also obtained in poor yield by interaction of Pb_2N_6 with benzaldehydethiosemicarbazone in boiling amyl alcohol; hydrolysis with 10% HCl gives 1:5-diamino-tetrazole hydrochloride, m. p. 176°. Similarly, 4-phenylthiosemicarbazide and its CMe_2 derivative, m. p. 130°, give 1-amino-5-anilinetetrazole, m. p. 210° (decomp.) [1-N- CMe_2 derivative, m. p. 136° (action of COMe_2 at 100°)], but benzaldehyde-4-phenylthiosemicarbazone gives the CHPh derivative, m. p. 216°. The first method gives as by-product 3:6-dianilino-1:2-dihydro-1:2:4:5-tetrazine, m. p. 275° (decomp.) [hydrochloride, m. p. 172° (decomp., sinters at 150°)], also obtained by action of PbO alone on 4-phenylthiosemicarbazide. 1-Benzylidene-amino-5-allylamino-, m. p. 117°, and 1-amino-5-allylamino-tetrazole, m. p. 94°, are similarly prepared, the latter being accompanied by 3:6-diallylamino-1:2:4:5-tetrazine, m. p. 118°.

Thiocarbohydrazide (prop. improved) with NaN_3 and PbO gives 1-amino-5-hydrazinotetrazole [hydrochloride, m. p. 171° (decomp.); (CHPh), derivative, m. p. 225° (decomp.)]; this appears to be converted by diazotisation into Thiele's tetrazyl azide (A., 1896, i, 107). From 1-benzoyl-4-phenylthiosemicarbazide is obtained, not the tetrazole, but 2-anilino-5-phenyl-1:3:4-furodiazole, $\frac{\text{N} \cdot \text{C}(\text{NHPh})}{\text{N}=\text{CPh}} > \text{O}$, m. p. 217° (+xAgNO₃, decomp. 200°), also obtained by action of PbO, CO₂, and EtOH alone. This is converted by NaNO_2 and AcOH into two NO₂-compounds, m. p. 278° and 168°, by N_2O_3 in AcOH into an (NO_2)₂-derivative, m. p. 231°, and by HNO_3 - H_2SO_4 into a substance, m. p. 207°. From hydrazine dithiocarbazinate ($\text{NH}_2\text{-NH-CS-S-N}_2\text{H}_4$) is obtained 1-amino-5-hydrazinotetrazole, carbohydrazide, thiocarbohydrazide (CHPh derivative, m. p. 193°), and, as its CHPh derivative, m. p. 173° (decomp.), the compound $\text{NH}_2\text{-NH-CS-N}_3$. The yields of tetrazoles obtained in these reactions are considerably reduced if the CO₂ be replaced by H₂. H. A. PIGGOTT.

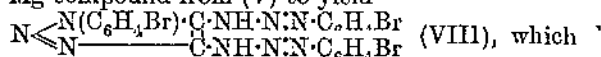
Reaction between magnesium acetylenyl bromide and azides. H. KLEINFELLER and G. BONE (J. pr. Chem., 1931, [ii], 132, 175—199).—Mg acetylenyl bromide and PhN_3 give partly $[\text{NPh} \cdot \text{N} \cdot \text{N}(\text{MgBr}) \cdot \text{C}]_2$, which on decomp. affords bis-phenyltriazenoacetylene (I), m. p. 174° (A., 1928, 630, m. p. 170°), and partly $[\text{NPh} \cdot \text{N} \cdot \text{N} \cdot \text{C}(\text{MgBr})]_2$, which affords the substance $(\text{NPh} \cdot \text{N} \cdot \text{N} \cdot \text{CH})_2$ (II), m. p. 170°, on decomp. The substance, m. p. 166° (loc. cit.), is a mixture of (II) and the substance, $\text{C}_8\text{H}_8\text{N}_4$, m. p. 172° (III). The constitutions assigned (loc. cit.) to (I) and 2-phenyl-1:2-dihydro-1:2:3:4-tetrazine (IV) are confirmed. (I) and boiling AcOH give the N-Ac derivative of (IV), m. p. 219°, this and the N-formyl derivative (similarly obtained), m. p. 172°, being converted by NaOH in hot EtOH into (IV) (hydrochloride, m. p. 185°; NO-derivative, explosive,

giving with NaOH a violet additive compound, $\text{C}_8\text{H}_8\text{N}_4\text{O}_2\text{Na}$, decomp. 175°; o-Br-derivative, m. p. 135°). (II) with cold H_2SO_4 gives (III) [does not form acyl derivatives; hydrochloride, hydrolysed by H_2O or EtOH; o-Br-derivative, m. p. 150° (decomp.)], considered to be 2-phenyl-2:5-dihydro-1:2:3:4-tetrazine.

Mg acetylenyl bromide and p-bromophenyl azide give a little bis-p-bromophenyltriazenoacetylene (V), m. p. 198° (by normal reaction), much 1-p-bromophenyl-4-p-bromophenyltriazene-1:2:3-triazole (VI), m. p. 215° [by addition to the half-reaction product $\text{C}(\text{MgBr}) \cdot \text{C} \cdot \text{NH} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$] [previously (loc. cit.) assigned the constitution now given to (V)], and the substance (VII), $\text{C}_{14}\text{H}_{11}\text{N}_7\text{Br}_2$, m. p. 203°. The last



compound is formed by addition of the azide to the Mg compound from (V) to yield



hydrolysis and ring-closure gives (VII). (V) with Ac_2O yields N-acetyl-2-p-bromophenyl-1:2-dihydro-1:2:3:4-tetrazine, m. p. 265° (decomp.); the corresponding o-Br-compound, m. p. 148°, is formed by bromination of the Ac derivative of (IV). When shaken in alcoholic KOH with palladised CaCO_3 in presence of H₂ at 4 atm., (V) gives (I), whereby its constitution is proved. With conc. acids (VI) [Ac derivative, m. p. 172° (decomp.)] forms diacidic salts [dinitrate, m. p. 153° (decomp.); (?) disulphate, m. p. 143° (decomp.); $4\text{C}_{14}\text{H}_{10}\text{N}_6\text{Br}_2 \cdot 3\text{H}_2\text{SO}_4$, m. p. 195°], hydrolysed by H_2O to monoacidic salts [nitrate, m. p. 174° (decomp.)], from which the former are regenerated by conc. acids. (VII) is unaffected by most reducing agents, but with Zn dust and AcOH gives a dihydro-derivative, m. p. 224° (decomp.), and with H₂ at 4 atm. in presence of palladised CaCO_3 in alcoholic KOH affords 1-phenyl-4-phenyltriazene-1:2:3-triazole, m. p. 108° (Br-derivative, m. p. 206°), which with hot dil. HCl gives 4-amino-1-phenyl-1:2:3-triazole, m. p. 110° [Br-derivative, m. p. 172°; Ac derivative, m. p. 143° (Br-derivative, m. p. 178°)]; the aminotriazole and HNO_2 give N₂ and 4-hydroxy-1-phenyl-1:2:3-triazole, m. p. 160°. (VII) [Ac derivative, m. p. 149° (decomp.); NO derivative, m. p. 103° (decomp.)] [nitrate, m. p. 162° (decomp.)] on catalytic dehalogenation yields the substance, $\text{C}_{14}\text{H}_{13}\text{N}_7$ [corresponding with (VII)], m. p. 176° (decomp.) [Ac derivative, m. p. 149° (decomp.)]. The relative stability of the Br-compounds to acids is considered to be due to steric influences. R. S. CAHN.

Oxidation of uric acid by hydrogen peroxide under physiological conditions. H. WIELAND and T. F. MACRAE (Z. physiol. Chem., 1931, 203, 83—86).—Uric acid, buffered to p_H 8, is oxidised by H_2O_2 to allantoin (main product), carbonyldicarbamide, and cyanuric acid. J. H. BIRKINSHAW.

Porphyrin syntheses. XLI. Synthesis of haemin III. H. FISCHER and L. NUSSLER (Annalen,

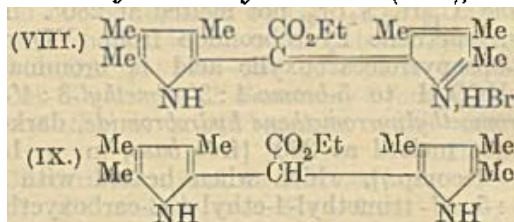
1931, 491, 162—188).—2:3-Dimethylpyrrole (I), obtained from its 4-carboxylic acid and glycerol at 210°, is converted by the Gattermann method into 2:3-dimethylpyrrole-5-aldehyde (II), m. p. 126° [oxime, m. p. 121°; semicarbazone, m. p. 202° (corr.); azine, m. p. 180° (corr.)]. (I) and (II) condensed with 48% HBr in EtOH give 4:5:4':5'-tetramethylpyrromethene hydrobromide (III), m. p. 213° (corr.). 5:5'-Dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethene hydrobromide heated with the Br₂-derivative of (III) and succinic acid at 190°, gives, after esterification (MeOH-HCl), 7% of the Me₂ ester, m. p. 290° (corr.) [Br₂-derivative, m. p. 306° (corr.); Cu salt, m. p. 288° (corr.); haemin, m. p. 285° (corr.)], of deuteroporphyrin III [hydrochloride; haemin (IV)]. (IV) and Ac₂O in presence of SnCl₄ give, after removal of Fe with HBr in AcOH, diacetyldeuteroporphyrin III {Me₂ ester, m. p. 311° (corr.) [dioxime; Cu salt, m. p. 259° (corr.); haemin, m. p. 298° (corr.)], converted by EtOH-KOH into haematoporphyrin III (30% yield). Prolonged treatment of this with HBr in AcOH, removal of volatile products, dissolution of the residue in MeOH, and subsequent addition of MeOH-KOH gives tetramethylhaematoporphyrin III, decomp. 178° (corr.) with elimination of MeOH. When haematoporphyrin III is heated at 125°/high vac., the resulting product fractionated, and then esterified (MeOH-HCl), protoporphyrin III Me₂ ester, m. p. 284° (corr.), is obtained; this with Fe(OAc)₂, AcOH, and NaCl gives haemin III, m. p. 269° (corr.), which depresses the m. p. of natural haemin.

Re-investigation (cf. A., 1926, 1256) of the mixture of porphyrins (24% yield) formed when opsopyrrole and its carboxylic acid are heated with HCO₂H shows the presence of aetiopyrporphyrin (12.3%), tetramethyltriethylporphyrinpropionic acids (40%) [a Me ester, m. p. 223° (corr.), is described], mesoporphyrins (27.3%) [Me₂ ester, m. p. 189° (corr.), described], a mixture of tricarboxylic acids (15.3%) [the mixture of Me₂ esters has m. p. 187—229° (corr.) (sinters at 167°)], and coproporphyrin [Me₄ ester, m. p. 176° (corr.)]. The imine obtained from opsopyrrolecarboxylic acid, anhyd. HCN, and HCl is converted by NaOEt and N₂H₄.H₂O at 160° into haemopyrrolecarboxylic acid. 3:3'-Dicarbethoxy-4:5:4':5'-tetramethylpyrromethene (Cu salt) has m. p. 166° (corr.). H. BURTON.

Porphyrin syntheses. XLII. Heptamethyl-β-carboxyethylporphyrin, a pyrromethene carbethoxylated on the connecting carbon, and pyrroles. H. FISCHER and J. HIRNEIS (Annalen, 1931, 492, 21—35).—5-Aldehydo-2:3:4-trimethylpyrrole condensed with hamo-, crypto-, and opso-pyrrolecarboxylic acids in EtOH-HBr gives 3:4:5:4':5'-pentamethyl-3' (I), m. p. 235°, 3:4:5:3':5'-pentamethyl-4' (II), m. p. 207°, and 3:4:5:3':5'-tetramethyl-4' (III), m. p. 228°, -β-carboxyethylpyrromethene hydrobromides, respectively, brominated in AcOH to 3:4:4'-trimethyl-5:5'-di(bromomethyl)-3', 3:4:3'-trimethyl-5:5'-di(bromomethyl)-4', and 5'-bromo-3:4:3'-trimethyl-5-bromomethyl-4'-β-carboxyethylpyrromethene hydrobromides, respectively. Fusion of (I) or (II) with 5:5'-dibromo-3:4:3':4'-tetramethylpyrromethene hydrobromide (IV) (A., 1926, 1256) and succinic acid gives heptamethyl-β-carb-

oxyethylporphyrin [Me ester, m. p. above 420° (Cu salt; haemin)], also obtained unexpectedly from (III) and (IV).

Et 2:3:4-trimethylpyrrole-5-carboxylate and SO₂Cl₂ in Et₂O afford (after hydrolysis) Et 2-aldehydo- (V), m. p. 108° (azine, m. p. 260°), and Et 2-carboxy- (VI), m. p. 243°, -3:4-dimethylpyrrole-5-carboxylates. 2:3:4-Trimethylpyrrole (VII) and (V) give 5-carbethoxy-3:4:3':4':5'-pentamethylpyrromethene (as hydrobromide, m. p. 202°). Hydrolysis of (VI) with 10% NaOH affords 3:4-dimethylpyrrole-2:5-dicarboxylic acid; hydrolysis with 30% KOH and subsequent treatment with superheated steam gives 3:4-dimethylpyrrole. Et 3:4:5-trimethyl-2-pyrrolyglyoxylate and (VII) with HBr (d 1.49) in EtOH or COMe₂ afford 3:4:5:3':4':5'-hexamethylpyrrocarbethoxymethene hydrobromide (VIII), m. p. 141°,

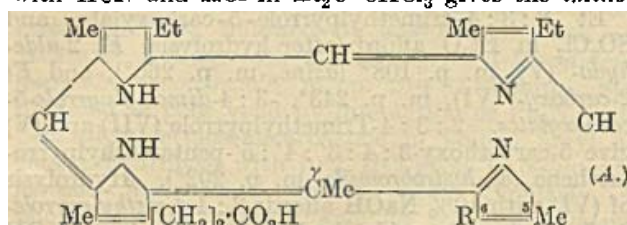


whilst (VII), Et glyoxylate, and HBr (d 1.49) give 3:4:5:3':4':5'-hexamethylpyrrocarbethoxymethene (IX), m. p. 167°, and the hexamethylpyrromethene hydrobromide. Fusion of (VIII), 5:5'-dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethene hydrobromide, and succinic acid yields 1:2:3:4:5:8-hexamethyl-6:7-di-β-carboxyethylporphyrin (A., 1930, 1449). (VII) and 2-aldehydo-3:4-dimethylpyrrole-5-carboxylic acid, m. p. 229° [by hydrolysis of (V)], give 5-carboxy-3:4:3':4':5'-pentamethylpyrromethene [as hydrobromide, m. p. 247° (decomp.)], whilst cryptopyrrole and Et 2-cryptopyrrolyglyoxylate afford 3:5:3':5'-tetramethyl-4:4'-dioethylpyrromethene.

H. BURTON.

Porphyrin syntheses. XLIII. Syntheses of 6-ethylphylloporphyrin and γ-methylmesoporphyrin. Chloroporphyrin c₄ (phylloporphyrin-6-carboxylic acid). H. FISCHER and H. K. WEICKMANN (Annalen, 1931, 492, 35—65).—Xanthopyrrolecarboxylic acid, HCN, and HCl in Et₂O-CHCl₃ give β-(2-aldehydo-3-methyl-5-ethyl-4-pyrrolyl)propionic acid, m. p. 170° (corr.; all m. p. are corr. unless stated otherwise) (semicarbazone, m. p. 239°), which with opsopyrrole and 48% HBr in MeOH affords 3:3'-dimethyl-4:5'-diethyl-4'-β-carboxyethylpyrromethene hydrobromide (I), m. p. 187°. The 5-Br-derivative, chars gradually about 195°, of this, formed by bromination in AcOH, is brominated further in 90% HCO₂H to 5-bromo-3:3'-dimethyl-4-ethyl-5'-bromoethyl-4'-β-carboxyethylpyrromethene hydrobromide (II), not melted at 280°. Fusion of (I), 5-bromo-3:4'-dimethyl-4:3'-diethyl-5'-bromomethylpyrromethene hydrobromide (III), and methylsuccinic acid at 135—160° gives aetiopyrporphyrin, tetramethyltriethylporphyrinmonopropionic acid III (IV), and about 1% of 6-ethylphylloporphyrin (V) (A, where R=Et) (Me ester, m. p. 275°) [also obtained from (II) and (III)]. Et opsopyrrolecarboxylate, AcCl, and AlCl₃ in CS₂ afford Et 5-acetyl-3-methyl-4-ethylpyrrole-2-carboxylate, m. p. 96°,

reduced by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and NaOEt at 160° to 4-methyl-2:3-diethylpyrrole (VI), b. p. $95^\circ/14$ mm., which with HCN and HCl in $\text{Et}_2\text{O}-\text{CHCl}_3$ gives the imine



hydrochloride, m. p. 183° , of 5-aldehyde-4-methyl-2:3-diethylpyrrole, m. p. 70° . (VI), anhyd. HCO_2H , and 48% HBr furnish 3:3'-dimethyl-4:5:4':5'-tetraethylpyrromethene hydrobromide, decomp. 180° (free base, m. p. 116°), converted by Br in (sun)light into a compound, $\text{C}_{19}\text{H}_{27}\text{N}_2\text{Br}_2$, not melted at 280° . The crude pyrromethene hydrobromide from (VI) and aldehyde-opsopyrrolecarboxylic acid is brominated in 95% HCO_2H to 5-bromo-4:3'-dimethyl-3:4'-diethyl-5'-bromoethylpyrromethene hydrobromide, darkens at 220° , not melted at 280° [free base, m. p. 150° (uncorr.; decomp.)], which when heated with 5'-bromo-3:5:3'-trimethyl-4-ethyl-4'- β -carboxyethylpyrromethene hydrobromide and succinic and methylsuccinic acids (1:2) at $135\text{--}170^\circ$ affords (V) and mesoporphyrin V. (V) is converted by 30% MeOH-KOH in pyridine at $190\text{--}200^\circ$ into (IV).

5'-Bromo-4:5:3'-trimethyl-3-ethyl-4'- β -carboxyethyl- and 5-bromo-3:3'-dimethyl-4:5'-diethyl-4'- β -carboxyethylpyrromethene hydrobromides (VII) fused with methylsuccinic acid give mesoporphyrin II and γ -methylmesoporphyrin (mesophylloporphyrin) (VIII) (A, where $\text{R}=[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$) [Me ester, m. p. 245° , converted (about $\frac{1}{2}$) by boiling with 18% HCl in O_2 for 3 hr. into mesoporphyrin].

The 5-Br-derivative, decomp. 228° , of 4-carbethoxy-3:4':5'-trimethyl-3'-ethylpyrromethene hydrobromide, m. p. 208° (from haemopyrrole and Et 2-aldehyde-3-methylpyrrole-4-carboxylate), fused with (VII) and methylsuccinic acid gives small amounts of phyllopyrro-, and (mainly) rhodo-porphyrins; phylloporphyrin-6-carboxylic acid (chloroporphyrin e_4) is not isolated. Chloroporphyrin e_4 (IX) is unaffected by heating with succinic or methylsuccinic acid at 300° for 45 sec., or with methylsuccinic acid at 170° for 2 hr., whilst the Me esters of (V) and (VIII) are similarly converted into 1:3:5:8-tetramethyl-2:4:6-triethyl-7- β -carbomethoxyethylporphyrin and mesoporphyrin, respectively. (IX) is not affected by boiling 20% HCl in N_2 during 4 hr., whilst in O_2 it is oxidised to chloroporphyrin e_5 (formylrhodoporphyrin) (X) (the Me_2 ester, prepared by esterification with MeOH-HCl , had m. p. 310° and not 284°). (X) is converted by 18% HCl in O_2 into rhodoporphyrin- γ -carboxylic acid. The $\text{C}(\gamma)\text{Me}$ group (as in A) is termed the phyllo-principle.

Haemopyrrolealdehyde and SO_2Cl_2 in Et_2O give, after hydrolysis with H_2O , opsopyrrolealdehyde; when the reaction proceeds energetically (no cooling), a compound, m. p. 159° , containing Cl and unaffected by NaOH , results. The metheno from aldehyde-opsopyrrolecarboxylic acid and opsopyrrole is brominated in AcOH to 5'-bromo-3:5:3'-trimethyl-

4'-ethyl-4- β -carboxyethylpyrromethene hydrobromide, m. p. about 240° (uncorr.) with darkening and sintering. An improved method of prep. of 2:3'-dimethyl-4:4'-diethylpyrromethene hydrobromide is given. The Me, m. p. 140° , and Et, m. p. 86° , esters of 5-carbethoxy-4-methyl-2-ethyl-3-pyrrolylmethylmalonic acid (XI) are prepared by the action of HCl on Et 4-methyl-2-ethylpyrrole-5-carboxylate and Me and Et methoxy-methylmalonate, respectively. (XI), HCO_2H , and 48% HBr give a mixture, m. p. 171° , of 3:3'-dimethyl-5:5'-diethyl-4:4'-di- β -carboxyethyl- and -4:4'-di- β -dicarboxyethylpyrromethene hydrobromides.

H. BURTON.

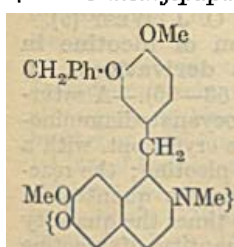
Chlorophyll series. VIII. Structure of chlorophyll b. J. B. CONANT, E. M. DIETZ, and T. H. WERNER (J. Amer. Chem. Soc., 1931, 53, 4436—4448; cf. A., 1931, 1310).—The methods developed for the elucidation of the structure of chlorophyll a have been applied to a study of chlorophyll b (I). The transformations in the b series closely parallel those in the a series and two simple rhodins have been obtained from which certain functional groups have been removed. The formation of senicarbazonones shows that a CO group is present in the modified porphyrin ring in these rhodins and also throughout the b series. The explanation of allomerisation and the "phase test" reaction applies to the b as well as the a series. A variety of evidence thus leads to the conclusion that (I) is a keto-derivative of chlorophyll a in which a CO group connects two of the pyrrole rings in a modified porphyrin nucleus. Pure rhodin g (II) is best prepared by hot rapid saponification of pure methylphæophorbide b (III) (semicarbazone); pyrolysis of (II) in presence of talc and boiling Ph_2 gives pyrrohodin g (IV) (acid val. 12.5—13) and pyrrohodin g-porphyrin (V) (acid val. 3); two other compounds with acid vals. of about 1 and 8 are found in very small quantities. (IV) and (V) were not isolated as free acids, but as the corresponding Me esters, m. p. (block) 235° (semicarbazone) and $228\text{--}230^\circ$, respectively. Rhodin g Me_2 ester yields a semicarbazone. (II) and $\text{K}_3\text{Mo}(\text{CN})_6$ give a rhodin n (Me ester, acid val. 18), which is being studied. Dehydrogenation of (III) with $\text{K}_3\text{Mo}(\text{CN})_6$ gives a methyldehydrophæophorbide b, which was not isolated in a crystalline form and on rapid saponification, gives an unstable rhodin i; diazomethane converts this into the Me_3 ester, m. p. $250\text{--}252^\circ$, of rhodin k, hydrolysed by 25% KOH in $\text{MeOH-Et}_2\text{O}$ to the Me ester, m. p. 206° . Pyrolysis of the Me ester gives rhodin l Me ester, m. p. 187° , and porphyrin 11 Me ester, which gives a Me_2 ester, m. p. $185\text{--}187^\circ$. Hot saponification of rhodin k Me ester gives rhodin 1 (VI), and $(\text{CO}_2\text{K})_2$; rhodin 1 Me_2 ester yields a semicarbazone. Hot oxidative saponification of (III) gives the Me ester of (VI) and at least two other rhodins. Reduction of (VI) with N_2H_4 and NaOEt gives a small quantity of pyrroporphyrin and possibly rhodoporphyrin. Pyrolysis of (III) gives methylpyrophæophorbide b. Formulæ are proposed for (I), (II), (IV), and (VI).

C. J. WEST (b).

Synthetical experiments in the morphine group. I. R. ROBINSON and S. SUGASAWA (J.C.S., 1931, 3163—3172).—The blocked hydroaromatic struc-

ture of the morphine-thebaine-sinomenine group of alkaloids may have its biogenesis in a union of the two aromatic nuclei of a base of the landanosine type. If the union occurs in such a position that loss of H with re-formation of a true aromatic nucleus is feasible, then an aporphine alkaloid results. If addition of one nucleus to the other occurs at a position already bearing a substituent, then loss of H is impossible without migration and a member of the morphine group is obtained. The phytosynthesis of thebaine from a protothebaine [8-hydroxy-7-methoxy-1-(3'-hydroxy-4'-methoxy)benzyl-1:2:3:4-tetrahydroisoquinoline] (A) by union of the nuclei, migration of H, oxide ring formation, and subsequent transposition of substituents, is discussed. Sinomenine can result from a protosinomenine [6-hydroxy-7-methoxy-1-(3'-hydroxy-4'-methoxy)benzyl-1:2:3:4-tetrahydroisoquinoline] (B). A and B could both arise from 2 mols. of 3-hydroxy-4-methoxyphenylalanine. Preliminary work on the synthesis of B is now described.

O-Benzylisovanillin (I) (improved prep.; cf. A., 1930, 785), hippuric acid, Ac_2O , and NaOAc at 100° give 2-phenyl-4-(3'-benzyloxy-4'-methoxybenzylidene)-oxazolone, m. p. 155° , hydrolysed by 10% NaOH to 3-benzyloxy-4-methoxyphenylpyruvic acid, m. p. $160-161^\circ$, which is oxidised by H_2O_2 in 2% KOH to 3-benzyloxy-4-methoxyphenylacetic acid ($-\text{H}_2\text{O}$), m. p. (anhyd.) 125° . (I), MeNO_2 , Na_2CO_3 , and NH_2Me , HCl in EtOH afford ω -nitro-3-benzyloxy-4-methoxystyrene, m. p. $127-128^\circ$, reduced electrolytically to β -3-benzyloxy-4-methoxyphenylethylamine (II) [*H* oxalate, m. p. 161° ; hydrochloride, m. p. 166° (softens at 162°)]. (I) and $\text{CH}_2(\text{CO}_2\text{H})_2$ in pyridine and piperidine give O-benzylhesperetic (3-benzyloxy-4-methoxycinnamic) acid, m. p. $179-180^\circ$ (accompanied by the corresponding styrene), reduced to O-benzylidihydrohesperetic acid, m. p. $121-122^\circ$ (the Me ester, m. p. 64° , is best prepared by benzylating Me dihydrohesperate); the amide, m. p. 142° , could not be converted into (II) by the Hofmann method. O-Benzylhomoisovanillyl chloride and (II) give O-benzylhomoisovanillo- β -3-benzyloxy-4-methoxyphenylethylamide, m. p. 118° , which could not be cyclised. O-Benzylhomoisovanillo- β -methoxy- β -veratrylethylamide, m. p. 124° , obtained from the above chloride and methoxyaminoethylveratrole (prep. from ω -nitro-3:4-dimethoxystyrene by addition of MeOH and subsequent reduction given), is cyclised by POCl_3 in PhMe to 6:7-dimethoxy-1-(3'-benzyloxy-4'-methoxy)benzylisoquinoline (III), m. p. $112-113^\circ$ (picrate, m. p. 192° ; methiodide, m. p. $230-231^\circ$), and some of the 3'-hydroxy-derivative (3'-de-O-methylpapaverine), m. p. $181-182^\circ$. The



methosulphate of (III) is hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to anhydro-6-hydroxy-7-methoxy-1-(3'-benzyloxy-4'-methoxy)benzylisoquinoline methohydroxide (annexed formula), m. p. $239-240^\circ$, which with HCl gives a methochloride, m. p. 242° , reduced catalytically (PtO_2) in 90% EtOH to a product which is debenzylated to protosinomenine (not yet obtained cryst.).

H. BURTON.

Synthetic experiments in the morphine group.

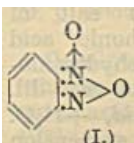
II. Derivatives of diphenyl ether. R. ROBINSON and S. SUGASAWA (J.C.S., 1931, 3173-3176).—Possible intermediates in the synthesis of 3:3'-oxido-di-(*p*-methoxyphenylalanine) are described. 2:2'-Dimethoxydiphenyl ether (I) (improved prep.; cf. A., 1906, i, 258) is converted by the Gattermann method into 2:2'-dimethoxy-5:5'-diformyldiphenyl ether (II), m. p. 136° (dioxime, m. p. 192°), also prepared from isovanillin, 2-bromoanisaldehyde, Cu-bronze, K_2CO_3 , and pyridine at 190° . The yields of (II) are poor. (II), hippuric acid, Ac_2O , and NaOAc at 100° (bath) give dianhydro-(2:2'-dimethoxy-5:5'-diformyldiphenyl ether) bis-2-phenyloxazolone, m. p. $223-225^\circ$. (I) and HNO_3 (d 1.42) in AcOH afford some 5:5'-dinitro-2:2'-dimethoxydiphenyl ether, m. p. 174° ; the NH_2 groups in the corresponding diamine could not be replaced by CN. The K salt of Et isovanillate heated with 2-bromoanisaldehyde, Cu-bronze, and $\text{Cu}(\text{OAc})_2$ at $170-180^\circ$ gives, after hydrolysis with EtOH-KOH, 2:2'-dimethoxy-5-formyl-5'-carboxydiphenyl ether, m. p. 212° (sinters at $208-209^\circ$).

H. BURTON.

Chromanquinoline derivatives. J. ALGAR and T. A. M'CULLAGH (Proc. Roy. Irish Acad., 1931, 40, B, 84-89; cf. A., 1929, 349).—*o*-Hydroxybenzylideneacetophenone, *o*-nitrobenzaldehyde, and HCl in EtOH give *o*-nitrobenzylidene flavanone, m. p. $155-156.5^\circ$, reduced in AcOH with SnCl_2 and HCl to 2:5-(2-phenylchromano-3:4)-quinoline, m. p. $178-179^\circ$ (yield 40%). Similarly, *o*-hydroxyanisylideneacetophenone gives *o*-nitrobenzylidene-4'-methoxyflavanone, m. p. $149-150^\circ$, and 2:3-(2-anisylchromano-3:4)-quinoline, m. p. $165-166^\circ$ (yield 50%), whilst *o*-hydroxypiperonylideneacetophenone gives *o*-nitrobenzylidene-3':4'-methylenedioxyflavanone, m. p. $179.5-180.5^\circ$ (yield 70%), and 2:3-(2-piperonylchromano-3:4)-quinoline, m. p. $177-178^\circ$ (small yield).

A. A. LEVI.

Constitution of benzfurazan and benzfurazan oxide. D. L. HAMMICK, W. A. M. EDWARDS, and E. R. STEINER (J.C.S., 1931, 3308-3313).—Benz-



furazan oxide (I) with Br in CS_2 gives two isomeric forms, m. p. 170° and m. p. 117° of tetrabromotetrahydrobenzfurazan oxide, both converted by aq. KOH into the same dibromofurazan oxide, m. p. 132° (II). Similarly, benzfurazan [by reduction of (I) with 4% KOH in MeOH] affords tetrabromotetrahydrobenzfurazan, m. p. 147° , converted into dibromobenzfurazan, m. p. 113° , identical with a specimen obtained by reduction of (II) with NH_2OH . These results indicate a quinonoid structure (I) for benzfurazan and its oxide as originally suggested by Green and Rowe (J.C.S., 1912, 101, 2452), a view which is confirmed by determinations of the parachor of benzfurazan, 252.2, its oxide, 274.3, and toluofurazan oxide, 311.4. The formation of the same furazan oxide from *o*-nitroazoisimide or *o*-nitroaniline substituted in the 4- or 5-positions may be due to the conversion of an unstable oxide into a stable isomeride through the *s-o*-dinitroso-form in the liquid state.

J. W. BAKER.

Isatogens. VIII. Isatogens from 4:6-dinitro-*m*-xylene. P. RUGGLI and R. THOUVAY

(*Helv. Chim. Acta*, 1931, 14, 1256—1265).—The *di-chloride* (I), m. p. 181°, and *tetrachloride* (II), m. p. 158°, of 4:6-dinitro-1:3-distyrylbenzene (III) (this vol., 56) are converted by boiling pyridine into 4:6-dinitro-3-styryl-1- α -chlorostyryl-, m. p. 181°, and 4:6-dinitro-1:3-di- α -chlorostyryl-benzene (IV), m. p. 145°, respectively. When a solution of (II) in cold pyridine is exposed to sunlight or ultra-violet light, 6-nitro-2-phenyl-5- α -chlorostyrylisatogen (V), m. p. 243°, is produced after 3—10 days; a trace of (V) is also formed during the prep. of (IV). (V) is converted by NH_2NHP in EtOH into 6-nitro-2-phenyl-5- α -chlorostyrylindoxyl, m. p. 203°. (I) is converted [as (II)] into 6-nitro-2-phenyl-5-styrylisatogen (VI), m. p. 233—234°, chlorinated in $\text{C}_2\text{H}_2\text{Cl}_4$ to (probably) the 5- β -chlorostyryl derivative, m. p. 247°. The *tetrabromide*, m. p. 206°, of (III) and boiling pyridine give 4:6-dinitro-3-styryl-1- α -bromostyrylbenzene, m. p. 173°, convertible [as (II)] into (VI). (IV) is stable to light when dissolved in pyridine. H. BURTON.

Monoarylguanidines. III. **Benzthiazolyl-guanidine.** G. B. L. SMITH, C. W. MASON, and R. H. CARROLL (*J. Amer. Chem. Soc.*, 1931, 53, 4103—4109; cf. A., 1929, 1186).— $\text{o-NH}_2\text{-C}_6\text{H}_4\text{-SH}$ (Zn salt) and dicyanodiamidine in 95% EtOH and conc. HCl give the *hydrochloride*, m. p. 239—241°, of *benzothiazolylguanidine* (I), m. p. 175—176° (Ac_2 derivative; *sulphate*, m. p. 294—295°; *nitrate*, m. p. 236—239°; *picrate*, m. p. 280—289°). Crystallisation of (I) from H_2O by cooling rapidly gives an anhyd. (plates) form, m. p. 175—176°, whilst slow crystallisation gives a *monohydrate*, m. p. 175—176°; crystallographic data are given for the several forms of (I). Potentiometric titration shows that (I) is a very weak base. The third crvst. modification, obtained when the molten base is supercooled, is believed to be a tautomeric form of (I). C. J. WEST (b).

Search for trypanocidal activity. Derivatives of dehydrothio-*p*-toluidinesulphonic acid and of 3-aminocarbazoledisulphonic acid. G. T. MORGAN and J. G. MITCHELL (*J.C.S.*, 1931, 3279—3283).—Reduction of the $\text{Na} + 3\text{H}_2\text{O}$ salt of 3-nitrobenzoyldehydrothio-*p*-toluidinesulphonic acid [by $\text{m-NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ and NaOH on dehydrothio-*p*-toluidinesulphonic acid (I)] with Fe and very dil. HCl gives the corresponding 3-amino-acid, $+\text{H}_2\text{O}$. This is converted by COCl_2 in aq. Na_2CO_3 suspension into the *ureido*-derivative, purified as its $\text{Na} + 5\text{H}_2\text{O}$ salt. (I) similarly gives *ureidodehydrothio-p-toluidinesulphonic acid* ($\text{Na} + 6\text{H}_2\text{O}$ salt), whilst *sulphodehydrothiotoluene-p-arsinic acid* (Na salt) is obtained by the Bart reaction. Reduction of the *Ca* salt of 3-nitrocarbazoledisulphonic acid (best obtained by sulphonation of 3-nitrocarbazole with conc. H_2SO_4 at 70—75°) with Fe and very dil. HCl gives the 3-amino-acid (II) in poor yield; therefore the reduction product was treated directly with 2-nitro-*p*-toluoyl chloride and NaOH to give 3-(3'-nitro-4'-methylbenzamido)carbazoledisulphonic acid (III) (Na salt), similarly reduced and converted by $\text{m-NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ into 3-(3'-3''-nitrobenzamido-4'-methylbenzamido)carbazoledisulphonic acid (IV) (Na salt). Reduction of III with FeCl_2 and NaOH and of (IV) with Fe and very dil. HCl, and subsequent

phosgenation gives, respectively, *ureido*-3-(3'-amino-4'-methylbenzamido)- (Na salt) and -3-(3'-3''-amino-benzamido-4'-methylbenzamido)- (Na salt) carbazoledisulphonic acid; *ureido*-3-aminocarbazoledisulphonic acid (Na salt) is similarly prepared from COCl_2 and (II). None of these derivatives exhibits trypanocidal activity. J. W. BAKER.

Thiazines. I. **Syntheses in the perinaphtho-m-thiazine group.** M. T. BOGERT and J. H. BARTLETT (*J. Amer. Chem. Soc.*, 1931, 53, 4046—4057).—Reduction of 1:8- $\text{ClO}_2\text{S-C}_{10}\text{H}_6\text{-NO}_2$ by SnCl_2 and HCl in AcOH gives 79% of 8-thiol- α -naphthylamine chlorostannate (I); if the reaction product is refluxed for 6—7 min., the product is the additive compound of SnCl_4 and 8-thiolacet- α -naphthalide (II), which is more stable than (I). (II) in EtOH-NaOH, or, better, in AcOH-NaOAc with Ac_2O , gives 2-methyl-perinaphthothiazine (III), m. p. 96.5—97.5° (all m. p. are corr.), in yields of 15 and 93%, respectively. (II) and PhCHO in EtOH-NaOH give 45% of the 2-styryl derivative, m. p. 132—133°. (III), $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$, and ZnCl_2 give 27% of the *phthalone*, amorphous, m. p. 173.5—174.5°, which with conc. H_2SO_4 affords a pale brown analogue of quinoline-yellow; this dyes wool a bright yellow and resembles its analogue in fastness to light, laundering, and bleeding. (I), decomposed with AcOH and NaOAc and treated with $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-COCl}$, gives a mixture of the NS-di-*o*-nitrobenzoyl (IV), m. p. 185.5—186.5° (decomp.), and the N(?) -*o*-nitrobenzoyl derivatives, amorphous, m. p. about 225° (decomp.), of 8-thiol- α -naphthylamine; either derivative with AcOH and NaOAc gives 2-*o*-nitrophenylperinaphthothiazine, m. p. 166—168°, reduced by SnCl_2 and HCl in EtOH to the *o*-amino-derivative, m. p. 154—154.5° [also formed by reduction of (IV)]. The NS-di-*m*-nitrobenzoyl (V), m. p. 185.5—186.5° (decomp.), and -di-*p*-nitrobenzoyl derivatives, m. p. 248—249° (decomp.), of 8-thiol- α -naphthylamine are prepared similarly from (I), or, better, from (II). (I), AcOH, NaOAc, and $\text{m-NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ at 60° give 55% of 2-*m*-nitrophenylperinaphthothiazine, m. p. 182.5—183°, also formed from (V), NaOAc, and AcOH, reduced to the 2-*m*-aminophenyl derivative, m. p. 148—149°. 2-*p*-Nitro-, m. p. 208.5—209°, and 2-*p*-amino-phenylperinaphthothiazines, m. p. 143—143.5°, are also prepared. 2-*m*-, m. p. 186°, and 2-*p*-, m. p. 217—219°, -hydroxyphenylperinaphthothiazines are prepared by the diazo-reaction. Chloramine-yellow dyes are prepared from the *m*- and *p*- NH_2 -derivatives and their dyeing properties tested. In method of synthesis, structure, and properties, these new products resemble the benzthiazoles.

C. J. WEST (b).

Microchemical determination of nicotine in presence of pyridine and its derivatives. R. HOFMANN (*Mikrochem.*, 1931, 10, 53—56).—A saturated solution of hydroxotriethiocyanatodiamminochromic acid gives a characteristic cryst. ppt. with a neutral or slightly acid solution of nicotine; the reaction is sp. in presence of 3 times the quantity of pyridine, lutidine, or picoline, or 9 times the quantity of collidine, and the smallest quantity of nicotine which can be detected is 0.157 microg. Na silicotungstate normally yields amorphous ppts. with

alkaloids, but if a solution of the salt is added to a nicotine solution of such concn. that slight turbidity only is produced, and a crystal of NaCl is then introduced, a characteristic cryst. ppt. separates within 5–10 min.; the limit of sensitivity is 0.4 microg. Pyridine yields similar crystals, which, however, may be differentiated by using polarised light. The methylpyridines do not form characteristic ppts.

H. F. GILLBE.

Alkaloids of tobacco. M. EHERNSTEIN (Arch. Pharm., 1931, 269, 627–659).—"Nicotine" (A., 1901, i, 339), from extracts of Kentucky tobacco, is a mixture of *normicotine* (I) and *l*-2-(β -pyridyl)piperidine (II), separated by distillation, and fractionation of the picrates. Previous specimens of (I) (A., 1930, 1444) were partly racemised or impure. (II) is possibly identical with anabasine (A., 1931, 498). (I), b. p. 130.5–131.3°/11 mm., miscible with H₂O, $[\alpha]_D^{25}$ –17.7° (base), +9.19° (in *N*-HCl) [*dipicrate*, m. p. 191–192°; *dipicolonate*, m. p. 250–252° (decomp.); *-carbamide*, m. p. 167–170°; *-phenylthiocarbamide*, m. p. 176–177.5°], gives nicotine methiodide on exhaustive methylation, nicotinic acid when oxidised with HNO₃, and 2-(β -pyridyl)pyrrole, m. p. 100–102° (*picrate*, m. p. 202–203°), when dehydrogenated by Pt-asbestos at 320–330°. (II), b. p. 137–138.5°, $[\alpha]_D^{25}$ –72.59° (base), –14.69° (in *N*-HCl) [*dipicrate*, m. p. 201–204.5°; *dipicolonate*, m. p. 233–235° (decomp.); *-carbamide*, m. p. 182–185°; *-phenylthiocarbamide*, m. p. 162–164°], with hot conc. HNO₃ gives 2-nitro-2':3'-dipyridyl, m. p. 154.5–155°, and nicotinic acid; with KOH and MeI in MeOH it yields *l*-2-(β -pyridyl)-*N*-methylpiperidine methiodide, m. p. 212–214° after decomp. from 209°, and when dehydrogenated 2:3'-dipyridyl, b. p. 158–160°/19 mm., insol. in H₂O [*picrate*, m. p. 168–170° (once obtained with m. p. 148–151°; lit. 149°); *picrolonate*, m. p. 243–244.5° (decomp.)]. 3:3'-Dipyridyl is sol. in H₂O and has b. p. 173–175°/70 mm. (*picrate*, new m. p. 235–236°). When kept with MeI in MeOH, (II) gives the impure *N*-Me derivative (III), b. p. 135–138°/18 mm. [*dipicrate*, m. p. 213–214°; *dipicolonate*, amorphous, m. p. 230–231° (decomp.)], and an oil, from which by treatment with KOH and distillation a little (III) was obtained.

R. S. CAHN.

Berberubine, palmatrubine, and similar compounds. IV. Alkaloids of columba root. K. FEIST and W. AWE (Arch. Pharm., 1931, 269, 660–678; cf. A., 1925, i, 830).—Even when washed with alkali, palmatine contains jatrorrhizine and a phenolic base, C₂₀H₁₉O₃N (*hydriodide*, m. p. 228°), reduced by Zn and H₂SO₄ to an amorphous, phenolic, tertiary base, m. p. 135–137°. Palmatine gives a *thiocyanate*, m. p. 210° (decomp.), and *perchlorate*, m. p. 262° (decomp.). Palmatine chloride, when heated alone or in petroleum (b. p. above 200°) at 190°, gives *palmatrubine* (I), m. p. about 300°, converted by MeI at 100° into palmatine iodide, and by HCl and III into 9-hydroxy-2:3:10-trimethoxyprotoberberinium chloride and iodide (m. p. of the latter 224–228°), respectively. With Zn, dil. H₂SO₄, and AcOH (I) gives the 7:8:13:14-tetrahydro-base, m. p. 150° (lit. 148–149°), and with EtI or NaOH and Me₂SO₄ affords 2:3:10-trimethoxy-9-ethoxyprotoberberinium

iodide, m. p. 227–230° (decomp.), which after conversion into the nitrate is reduced by Zn, dil. H₂SO₄, and AcOH to the 7:8:13:14-tetrahydro-base, m. p. 116° (lit. 115°). Jatrorrhizine chloride when heated at 190° in an atm. of CO₂ gives *jatrorrhizrubine*, reduced as usual to 3:9-dihydroxy-2:10-dimethoxy-7:8:13:14-tetrahydroprotoberberine, m. p. 164°. 8-Phenyldihydroberberine, m. p. 196° (lit. 195°) (modified prep.), when oxidised by Hg(OAc)₂ in AcOH and treated with HCl, affords 8-phenylberberine chloride, m. p. about 270° (decomp.) [*iodide*, m. p. 276° (decomp.)], reduced to 8-phenyltetrahydroberberine, m. p. 222°, and converted by heating at 250° in an atm. of CO₂ into MeCl and 8-phenylberberubine, m. p. 173° (*hydrochloride*). Palmatine chloride and hot aq. NaOH give dihydropalmatine and oxypalmatine, and the following substances were similarly obtained: oxy- and dihydroberberine; 10-methoxy-9-ethoxy-2:3-methylenedioxy-7:8-dihydroprotoberberine, m. p. 151–153°, and its 8-keto-derivative (II), m. p. 170°. Oxyberberine, when heated with HCl and AcOH for 10 min., yields 9-hydroxy-8-keto-10-methoxy-2:3-methylenedioxy-7:8-dihydroprotoberberine [9-EtO derivative of (II)], m. p. 248°. 10-Methoxy-9-ethoxy-2:3-methylenedioxyprotoberberinium chloride gives the corresponding rubine when heated at 200°, but "ruboxyberberine Et ether" and HCl-AcOH give a substance, m. p. 320°. 2-Ethoxy-*m*-cresol, prepared from 3-nitro-*o*-cresol by way of 3-nitro-2-ethoxytoluene and 2-ethoxy-*m*-toluidine (modified preps.), with Me₂SO₄ and 10% aq. KOH gives 3-methoxy-2-ethoxytoluene, b. p. 98–103°/20 mm., which with AcCl and AlCl₃ in CS₂ at 50–60° affords 7-aceto-3-methoxy-2-ethoxytoluene [*methoxyethoxyacetophenone*] (III), b. p. 170–180°/20 mm. (*oxime*, m. p. 123°; *semicarbazone*, m. p. 149°, solidifying on further heating and remelting at 231°), oxidised by NaOI to a *methoxyethoxytoluic acid*, m. p. 115°, further oxidised by alkaline KMnO₄ to 4-methoxy-3-ethoxyphthalic acid and two acids, m. p. 246° and 183°. The same three acids were obtained when (III) was treated with alkaline KMnO₄, and the resulting *keto-acid*, C₁₅H₁₄O₅, m. p. about 130°, was further oxidised with KMnO₄.

R. S. CAHN.

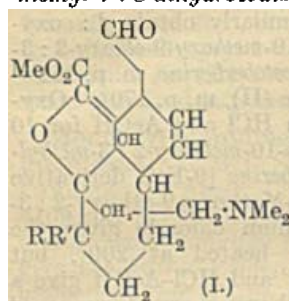
Configuration of optically active α -phenylethylamine and of bases of the type of laudan- osine and tetrahydroberberine. W. LEITHE (Ber., 1931, 64, [B], 2827–2832; cf. A., 1930, 1049).—Successive nitration, reduction, diazotisation, and treatment with boiling H₂O of *l*-*N*-benzoyl- α -phenylethylamine followed by oxidation with CrO₃ in AcOH leads to alanine, isolated as *l*(+)-benzoylalanine, identical with that prepared from natural *l*(+)-alanine. (–)- α -Phenylethylamine has therefore the *l*-configuration. Determination of the configuration of bases of laudan- osine and canadine type with respect to *l*(+)-alanine is justifiable, since the asymmetric centres in the compounds are similarly constructed, all including a H atom, a C₆H₅ nucleus, an amine-like N, and a Me residue. Direct degradation is impossible and comparison is made of the effect of salt formation and neighbouring mols. (solvent) on optical activity. The sp. rotations of *l*-phenylethylamine, *l*-*N*-ethylphenylamine, *l*-1-methyltetrahydro- isoquinoline, *l*-protolaudanosine, and *l*-tetrahydro-

protoberberine in substance, in *cyclohexane*, CHCl_3 , and EtOH , and as salt in H_2O are recorded. The following configurations are assigned in the sense of the Wohl-Freudenberg system; the opium bases *l* (in CHCl_3)-laudanosine, *l* (+)-codamine, *d* (-)-laudanidine; *l* (-)-canadine from *Hydrastis canadensis*; the *Corydalis* alkaloids *d* (+)-tetrahydropalmatine, *d* (+)-corypalmine, *d* (+)-canadine, and *a* (+)-tetrahydrocoptisine; *l* (-)-sinactine from *Sinomenium acutum*.

H. WREN.

Action of ozone on de-N-methyldihydrocodeine.

I. E. SPEYER and K. KOULEN (Ber., 1931, 64, [B], 2815—2819).—*De-N-methyldihydrocodeine hydrochloride* in H_2O is transformed by O_3 into "*de-N-methyl-7:8-dihydrocodizal-3-methyl ester*" (I; $\text{R}=\text{H}$, $\text{R}'=\text{OH}$), m. p. 205—206°.



[α] -101.4° in dil. AcOH (oxime, decomp. 220°; hydriodide, slow decomp. 250°; methiodide, decomp. above 290°; Ac derivative and its hydriodide, m. p. 234—235°). In presence of colloidal Pd and 2% AcOH the ester is hydrogenated to *de-N-methyl-4:5:7:8-tetrahydrocodizal-3-methyl ester*, m. p. 175—176°.

[α] -56.8° in dil. AcOH . The dihydro-ester is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ and 5% AcOH to *de-N-methyl-7:8-dihydrocodizal-3-methyl ester* (I; $\text{R}+\text{R}'=\text{O}$), m. p. 172°.

[α] -18.0° in dil. AcOH (hydrochloride, slow decomp. above 268°).

H. WREN.

Lupin alkaloids. V. G. R. CLEMO, G. R. RAMAGE, and R. RAPER (J.C.S., 1931, 3190—3200).—Prolonged interaction of Me lupinine and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 100° gives *lupininhydrazide*, m. p. 118—119°, converted by amyl nitrite in EtOH-HCl into the *hydrochloride*, m. p. 277—278° (decomp.), of *methylnorlupinanylturethane*, b. p. 125—128°/1 mm., which with cone. HCl affords *aminonorlupinane* (I), b. p. 73—75°/1 mm. (I) and HNO_2 give (mainly) *d-norlupinene* (II), b. p. 40—43°/1 mm., [α] $+33.7^\circ$ in COMe_2 [picrate, m. p. 175°; methiodide, m. p. 308—310° (decomp.)], some *hydroxynorlupinane*, b. p. 68—72°/1 mm., and other bases, b. p. 100—120°/1 mm. [α picrate, $\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}_3\cdot\text{C}_6\text{H}_5\text{O}_7\text{N}_3$, m. p. 207—208° (decomp.), is isolated]. Catalytic reduction (Pd-charcoal) of (II) in AcOH affords *norlupinane*, b. p. 43—45°/1 mm. ($\alpha=0$), identical with the base obtained (A., 1931, 499) by distilling lupinic acid with soda-lime. 1-Keto-octahydropyridocoline, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, and NaNH_2 in Et_2O give *Et β -1-octahydropyridocolylglycidate*, b. p. 152°/0.1 mm.; the free acid (or the corresponding aldehyde by loss of CO_2) could not be isolated. *Et piperidine-2:3-dicarboxylate*, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$, and K_2CO_3 at 100° (bath) afford, after treatment with EtOH-HCl , *Et γ -2:3-dicarbethoxypiperidinobutyrate*, b. p. 160—166°/0.1 mm. This undergoes the Dieckmann reaction; the resulting product after hydrolysis with HCl (loss of CO_2), Clemmensen reduction, and esterification (MeOH) gives *Me octahydropyridocolinc-1-carboxylate* (III), b. p. 102—105°/0.5 mm. [picrate, m. p. 187°]. If the above product is hydro-

lysed and then esterified a considerable amount of 1-keto-octahydropyridocoline (IV) [semicarbazone, m. p. 230° (lit. 215°)] is obtained in addition to Me 9-keto-octahydropyridocoline-1-carboxylate. Octahydropyridocoline does not occur in *cis*- and *trans*-forms, since the same product is produced by reduction of (IV) (occurring as a by-product) irrespective of the configuration of the starting materials. Me lupinate heated with aq. NH_3 *d*-bromocamphorsulphonate furnishes the cryst. *Me lupinate d*-bromocamphorsulphonate, m. p. 171—173°, whilst (III) does not react. Reduction (Bouveault) of (III) gives an oil which affords a non-cryst. tartrate, whilst lupinine furnishes a *d*-tartrate, m. p. 171°. These results show that lupinine does not possess the structure assigned by Karrer *et al.* (A., 1929, 200).

Oxidation of oxylupanine with aq. KMnO_4 at 40—50° gives a substance "*A*," $\text{C}_{15}\text{H}_{25}\text{O}_3\text{N}_2$, m. p. 212°, hydrolysed by aq. Ba(OH)_2 at 270° to glutaric acid, a compound (V), $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_2$, a substance (VI) (picrate, m. p. 231°), and a trace of a compound (picrate, decomp. 290°). Glutaric acid, (V), and (VI) are also formed from oxylupanine and aq. Ba(OH)_2 at 270°. The substance recovered when "*A*" is treated with SO_2 in H_2O , the solution boiled, and then evaporated, has the same composition as "*A*," but shows a variable m. p. (144—157°). A small amount of compound "*B*," m. p. 233°, isomeric with "*A*," is produced as a by-product in the oxidation of lupinine (cf. A., 1928, 1030). A partial structure is suggested which explains the introduction of O without loss of H (as in the formation of "*A*").

H. BURTON.

New Aconitum alkaloid. R. MAJIMA and S. MORIO (Proc. Imp. Acad. Tokyo, 1931, 7, 351—352).—A new alkaloid, *lucidusculine*, $\text{C}_{22}\text{H}_{37}\text{O}_4\text{N}$, has been isolated from *A. lucidusculum*. The base and most of its salts, in contrast to the known *Aconitum* alkaloids, is cryst. and has greater optical activity. It combines with MeI , forms a picrate, and with KOH-EtOH loses an Ac group, forming *luciculine*, $\text{C}_{22}\text{H}_{35}\text{O}_3\text{N}\cdot\text{H}_2\text{O}$, from which the H_2O cannot be abstracted. *Lucidusculine* has no OMe-group, but probably 2 OH and a NMe groups. It is suggested that the compound, $\text{C}_{22}\text{H}_{31}\text{O}_3\text{N}\cdot\text{H}_2\text{O}$ obtained from atisine by Jowett (J.C.S., 1896, 69, 1518) is probably related to *luciculine*.

F. R. SNOW.

Formulae of three opium derivatives. D. B. DORR (Pharm. J., 1931, 127, 520—521).—Cryst. codeine sulphate does not ordinarily effloresce and the anhyd. salt gains $3\text{H}_2\text{O}$ in air, whereas the corresponding ethylmorphine salt gains $5\text{H}_2\text{O}$. Ethylmorphine may be distinguished from codeine by the cryst. ppt. which is formed when 0.1 g is dissolved in H_2O , 8 c.c., and shaken with 4 drops of conc. aq. KOH (codeine: no ppt.). Cryst. cotarnine hydrochloride, $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$, becomes anhyd. at 98°. The m. p. (130°) of cotarnine should be determined quickly, as the alkaloid melts slowly at temp. lower than 100°, possibly due to oxidation.

E. H. SHARPLES.

Strychnine and hucine. XIV. Oxidation of hexahydrostrychnine. L. H. BRIGGS and R. ROBINSON (J.C.S., 1931, 3160—3163).—Oxidation of hexahydrostrychnine (improved prep.; cf. A., 1927,

1208) with CrO_3 in dil. H_2SO_4 at $16-80^\circ$ gives 22% of an acid (I), $\text{C}_{21}\text{H}_{22}\text{O}_4\text{N}_2$ ($+2\text{H}_2\text{O}$), m. p. $281-282^\circ$ (decomp.), $[\alpha]_D^{20} +10.73^\circ$ in 1% HCl [methosulphate, not melted at 318° ; methiodide, m. p. $280-287^\circ$ (decomp.); methochloride, darkens at 280° and begins to melt at 320°], which may result from the change $\text{C}_{17}\text{H}_{19}\text{ON}(\text{CH}\cdot\text{CH})(\text{CH}_2\cdot\text{OH}\cdot\text{NH})(\text{Me}) \rightarrow \text{C}_{17}\text{H}_{19}\text{ON}(\text{CH}\cdot\text{CH})(\text{CO}\cdot\text{N})(\text{CO}_2\text{H})$. The changes involved may be more complex, since (I) does not exhibit the usual strychnine colour reaction with H_2SO_4 and a dichromate. (I) probably contains the original $\text{N(a)}\cdot\text{CO}\cdot\text{CH}_2\cdot$ group of strychnine, since it gives a benzylidene derivative (picrate). The acid, $\text{C}_{21}\text{H}_{22}\text{O}_4\text{N}_2$, described by Leuchs (A., 1931, 242) is probably $\text{C}_{21}\text{H}_{20}\text{O}_4\text{N}_2$; it is reduced catalytically (Pd-charcoal) to (I), which is identical with the acid, $\text{C}_{21}\text{H}_{24}\text{O}_4\text{N}_2$, prepared by Leuchs and Beyer (A., 1931, 1312). H. BURTON.

Strychnos alkaloids. VI. Typical colour reactions. H. WIELAND, F. CALVET, and W. W. MOYER (Annalen, 1931, 491, 107-110).—All derivatives of vomicine in which the original lactam ring has been opened (except bromo- and bromodihydrovomycinic acids) are oxidised by CrO_3 in dil. acid to dyes, which are postulated as diphenquinonedi-imonium dicarboxylates; the failure of the above Br derivatives to undergo this change is due to the *p*-configuration of the Br atom and $\cdot\text{NH}\cdot$ group. The above also applies to the analogous strychnine derivatives but not to the brucine compounds (OMe group *para* to $\cdot\text{NH}\cdot$). The dyes are reduced to colourless intermediates which, when warmed (lactamisation) with the dil. acid, afford lactams (when possible) of the corresponding benzidine dicarboxylates. The original mol. is doubled during the process. Thus, vomycinic acid and CrO_3 (~ 20) in cold *N*-HCl give a violet dye (not isolated), reduced by SO_2 or Zn dust to *didehydrovomicine* (*divomicyl*) (I), $\text{C}_{44}\text{H}_{46}\text{O}_8\text{N}_4$, not melted at 320° (darkens at 250°); FeCl_3 , $\text{Br}\cdot\text{H}_2\text{O}$, and H_2O_2 can be used instead of CrO_3 . (I) is not re-oxidised to the violet dye, but the solution obtained by hydrolysis with $\text{EtOH}\cdot\text{KOH}$ is readily autoxidised (blue coloration). Strychnidine is converted through a red dye into *didehydrostrychnidine* (*distrychnidyl*), $\text{C}_{42}\text{H}_{46}\text{O}_8\text{N}_4$, not melted at 320° , re-oxidised to the dye. Tetrahydrostrychnine gives a brownish-red dye convertible into *didehydrodihydrostrychnine* (*dihydrostrychnyl*), $\text{C}_{42}\text{H}_{50}\text{O}_8\text{N}_4$, not melted at 300° (darkens above 260°), whilst *ON*-dimethylvomycinic acid affords a bluish-violet dye reduced to an acid, $\text{C}_{48}\text{H}_{58}\text{O}_{10}\text{N}_4$ ($+8\text{H}_2\text{O}$), decomp. above 300° (*Me*, ester, m. p. $214-220^\circ$). Most of the above compounds separate from pyridine with solvent of crystallisation which is lost at $150-180^\circ/\text{vac}$.

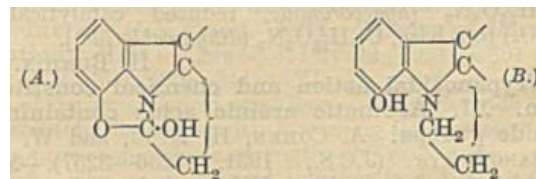
The formula $\text{C}_{42}\text{H}_{46}\text{O}_8\text{N}_4$ is suggested for the acid, $\text{C}_{21}\text{H}_{22}\text{O}_4\text{N}_2$, obtained by Leuchs (A., 1931, 242) by CrO_3 oxidation of tetrahydrostrychnine. Partial formulae are suggested. H. BURTON.

Strychnos alkaloids. VII. Methylation of vomycinic acid and derivatives of vomicine. H. WIELAND and F. CALVET. VIII. Vomycinic acid. H. WIELAND and W. W. MOYER. IX. Oxidation of vomicine and dihydrovomicine with chromic acid. H. WIELAND, F. HOLSCHER, and F. CORTESI.

X. Nitrations in the vomicine group. H. WIELAND and F. HOLSCHER (Annalen, 1931, 491, 117-129, 129-133, 133-148, 149-161).—VII. Vomycinic acid and MeI in $\text{MeOH}\cdot\text{KOH}$ and H_2 at room temp. give *ON*-methylvomycinic acid (I), $\text{C}_{24}\text{H}_{30}\text{O}_5\text{N}_2$ ($+2\text{H}_2\text{O}$), m. p. $242-244^\circ$ after loss of H_2O at 170° , its *Me* ester (II), m. p. $214-216^\circ$, $[\alpha]_D^{20} +61.7^\circ$ in EtOH , and *N*-methylvomycinic acid (III); (I) is identical with the substance previously described as vomycinic acid betaine (A., 1929, 708), and is usually isolated as its *hydriodide*, m. p. $185-200^\circ$ (with loss of H_2O). When the methylation is carried out first at room temp. and then in the hot, (I), (II), and the *Me* ester, m. p. $262-266^\circ$ (decomp.), $[\alpha]_D^{20} +38.6^\circ$ in EtOH , of (III) are produced. In one experiment an alkali-insol. methylvomicine, m. p. $286-290^\circ$ (decomp.), $[\alpha]_D^{20} +16.4^\circ$ in EtOH (demethylated by conc. HCl to vomicine), was produced. The methiodide, m. p. 210° (decomp.), of (II) is converted by AgOH into the quaternary hydroxide; evaporation of a solution causes elimination of MeOH and a betaine, $\text{C}_{25}\text{H}_{32}\text{O}_5\text{N}_2$, m. p. $195-198^\circ$ [methiodide, m. p. $245-250^\circ$ (decomp.)], of (I) results. (II) is reduced catalytically (PtO_2) in AcOH to a dihydro-derivative, m. p. $183-185^\circ$. Successive treatment of dihydrovomicine with $\text{MeOH}\cdot\text{KOH}$ and MeI in H_2 gives the *Me* ester (*dihydrochloride*, not melted at 320°) of an acid, $\text{C}_{48}\text{H}_{52}\text{O}_{10}\text{N}_4$, decomp. about 290° .

The compound previously described (*loc. cit.*) as the Bz derivative hydrochloride of vomicine [benzylidene derivative, m. p. 280° (decomp.)] is probably an additive compound, since it is hydrolysed immediately by dil. alkali to *BzOH* and vomicine. A similar compound, decomp. 185° , is obtained from *BzCl* and dihydrovomicine. Vomycinic acid contains an $\cdot\text{NH}\cdot$ group, since it gives a *N*-nitroso-derivative, decomp. about 190° .

VIII. Electrolytic reduction of vomicine affords vomycinic acid, $\text{C}_{27}\text{H}_{26}\text{O}_3\text{N}_2$, m. p. $283-284^\circ$ (decomp.), which is sol. in alkali hydroxides (not in Na_2CO_3); the *Bz* derivative, m. p. $208-209^\circ$, is insol. in alkalis. The results so far obtained indicate that vomicine contains the (partial) structure (A); vomycinic acid is



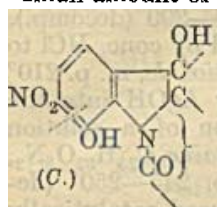
represented by (B). The formation of *O*-Me derivatives (Part VII) involves fission of the oxazoline ring also.

IX. The acid, $\text{C}_{17}\text{H}_{22}\text{O}_5\text{N}_2$ ($+3\text{H}_2\text{O}$), $[\alpha]_D^{20} -90.6^\circ$ in H_2O , previously obtained (*loc. cit.*) by oxidising vomicine, decomposes at $307-310^\circ$ forming a base (IV), $\text{C}_{16}\text{H}_{22}\text{O}_3\text{N}_2$ ($+ \text{EtOH}$), m. p. $302-310^\circ$ (decomp.) according to the rate of heating, $[\alpha]_D^{20} -86.2^\circ$ in H_2O , and is reduced catalytically (PtO_2) in H_2O to a mixture of an acid (V), $\text{C}_{17}\text{H}_{24}\text{O}_5\text{N}_2$ ($+4\text{H}_2\text{O}$), m. p. 264° (decomp.), and a base (VI), $\text{C}_{16}\text{H}_{26}\text{O}_2\text{N}_2$, m. p. $201-202^\circ$, $[\alpha]_D^{20}$ about $+18^\circ$ in EtOH (*Bz* derivative, m. p. 158° becoming red; methiodide, decomp. 295° after sintering at 124° and partial decomp. at $240-$

250°). Similar reduction of (IV) gives (VI) and a small amount of a base, $C_{16}H_{24}O_3N_2$, m. p. 272° (decomp.) after sintering, also formed when (V) is heated. The acid, $C_{17}H_{22}O_3N_2$, previously described (*loc. cit.*), is probably $C_{18}H_{24}O_3N_2$, m. p. 266–268° (decomp.).

Oxidation of dihydrovomisine with CrO_3 in dil. H_2SO_4 at 0°–room temp. gives (V) and an acid, $C_{18}H_{26}O_7N_2$ (+ H_2O), m. p. 315° (decomp.) (darkens at 270°), which could not be reduced and is stable to acid $KMnO_4$. Partial formulæ are given for the above acids and their mode of formation is discussed in conjunction with the corresponding acids from strychnine.

X. Vomisine and 20% HNO_3 at room temp. give a small amount of the nitrate (+ $2H_2O$), darkens gradually above 200°, of nitrovomisine (as C), m. p. 253° (decomp.); the nitration conditions are difficult to reproduce. More dil. HNO_3 converts vomisine, after some months, into a substance, $C_{16}H_{20}O_3N_2$. Nitration with HNO_3 (d 1.4) and conc. H_2SO_4 gives a compound



(VII), $C_{22}H_{23}O_9N_3$, red and orange-yellow forms, oxidised by Br in 48% HBr to a base, $C_{18}H_{22}O_3N_2Br_2$ [hydrobromide, reduced (Pd– $BaSO_4$) to a hydrobromide, $C_{18}H_{23}O_4N_2Br.HBr$]. (VII) probably results by further nitration of nitrovomisine and subsequent fission of the ring (with loss of NO_2) at the dotted line (in C). Dihydrovomisine and dil. HNO_3 give the nitrate (+ $2H_2O$) of a dinitrodihydrovomisine (VIII), reduced by $SnCl_2$ and conc. HCl to an aminohydroxydihydrovomisine [dihydrochloride, not melted at 300° (darkens at 200°)]. The replacement of NO_2 by OH probably occurs by hydrolysis of an intermediate quinonoid oxime or imine. (VIII) is oxidised by Br in aq. HBr to the compound, $C_{15}H_{18}O_3N_2.HBr$ (+ $3H_2O$). Nitration of dihydrovomisine with HNO_3 + H_2SO_4 gives a compound (IX), $C_{22}H_{23}O_{10}N_4$ (+ H_2O), not melted at 300° (darkens from 200°), which is probably formed by fission of the ring (as above) and conversion of the $tert.-OH$ into $\cdot O\cdot NO$. (IX) is oxidised by Br in aq. HBr to the substance, $C_{19}H_{25}O_8N_3$ [hydrobromide, reduced catalytically (PtO_3) to a base, $C_{19}H_{25}O_5N_3$ (dihydrochloride)].

H. BURTON.

Trypanocidal action and chemical constitution. XI. Aromatic arsinic acids containing amide groups. A. COHEN, H. KING, and W. I. STRANGEWAYS (J.C.S., 1931, 3236–3257).—Me 4-arsinophthalate and aq. NH_3 at below 0°–room temp. give usually 5-arsinophthalamic acid (I), shrinks 220–225° [NH_4 salt (+ $0.5H_2O$)], but in two cases phthalamide-4-arsinic acid (II) (+ $1.5H_2O$), decomp. 147°, was obtained. (I) passes at 230°/vac. into phthalimide-4-arsinic acid, not melted at 300°, converted by aq. NH_3 at 50° into (I) and (II) and at 150° into (I). (I) and alkaline $NaOBr$ give an acid K salt, $C_8H_7O_5As.C_8H_6O_5AsK$, of 3-hydroxy-5-arsinophthalic acid, probably formed through an intermediate Br-acid. *p*-Xylylarsinic acid, m. p. 191–192° (decomp.) (lit. 223°), from *p*-xylidine, is oxidised by alkaline $KMnO_4$ to 2-arsinoterephthalic acid (III), reduced (SO_2) to terephthalic acid 2-arsenoxide and converted by successive treatment with PCl_5 and

2*N*- NH_3 into a mixture of chloroterephthalamide, 3:4-dichlorobenzamide, and 2-arsinoterephthalamide acid (IV), not melted at 300°. Successive treatment of (III) with $MeOH-HCl$ and $NaHCO_3$ gives Me arsinoterephthalate, oxidised by H_2O_2 in aq. $NaHCO_3$ to Me arsinoterephthalate (V) and some 4-Me 1-*H* ester [converted by aq. NH_3 into (IV)]. (V) and aq. NH_3 afford 80% of terephthalamidearsinic acid and 20% of (IV). The 2- NO_2 -derivative of *p*-tolylarsinic acid (convenient prep. given) is oxidised by $KMnO_4$ to 3-nitro-4-benzarsinic acid (acid K salt, $C_7H_5O_7NaAs.C_7H_5O_7NaK$), reduced by $FeCl_2$ and alkali to 4-arsinoanthranilic acid (VI). (VI) is reduced by H_3PO_2 to 4-arsenoanthranilic acid and converted by Ac_2O in *N*- $NaOH$ into acetic 4-arsino-*N*-acetanthranilic anhydride, hydrolysed by short treatment with boiling 2*N*- $NaOH$ to 4-arsino-*N*-acetanthranilic acid hydrate. Acetantranilic acid 4-arsenoxide and 4-arsenoacetanthranilic acid are prepared by the usual methods. Successive treatment of anthranilic acid 4-dichloroarsine hydrochloride with $MeOH-HCl$ and $NaHCO_3$ gives Me anthranilate 4-arsenoxide, oxidised by alkaline H_2O_2 to Me 4-arsinoanthranilate, converted by aq. NH_3 into anthranilamide-4-arsinic acid (*N*-Ac derivative). (VI) is converted through its diazonium H sulphate into 4-arsinosalicylic acid; the Me ester and aq. NH_3 give salicylamide-4-arsinic acid.

5-Nitroacetanthranilic acid (obtained with the 3- NO_2 -isomeride from acetanthranilic acid and fuming HNO_3) is reduced by $FeSO_4$ and aq. NH_3 to 5-aminoacetanthranilic acid (sulphate; hydrochloride), convertible (Bart reaction) into 5-arsinoacetanthranilic acid (+ H_2O) (VII), m. p. 236–237° (decomp.) (lit. 230°). (VII) and 5-arsinoanthranilic acid (VIII) are reduced by H_3PO_2 to 5:5'-arsenoacet-, not melted at 300°, and 5:5'-arsenoanthranilic acids, darkens and shrinks at about 280°, respectively. Attempted esterification of (VIII) or anthranilic acid *o*-dichloroarsine hydrochloride (IX) with $MeOH-HCl$ gives Me anthranilate, whilst successive treatment of (IX) with $SOCl_2$ and aq. NH_3 affords 5-chloroanthranilamide. The Me ester, not melted at 300°, of (VII), prepared by the Ag salt method, is convertible by aq. NH_3 into acetanthranilamide-5-arsinic acid. Hippuric acid *p*-arsenoxide (corresponding dichloride) is converted through Me *p*-arsinohippurate into hippuramide-*p*-arsinic acid, which is inferior in its therapeutic activity to the corresponding ethylamide.

The therapeutic activities of the above compounds are recorded and it is again found (cf. A., 1930, 796) that only the amides (or imides) possess curative action; several of the arseno-derivatives show some activity. In the last case, the solubilising action of the CO_2H group is more than counterbalanced by the physical properties of the As:As linking. The view that trypanocidal action is favoured when an arsenoxide is retained by the body is supported by the observations that the liver and spleen of mice contain more As 14 days after injection of salvarsan than they do 24 hr. after injection of 3-amino-4-hydroxyphenylarsinic acid.

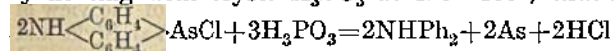
H. BURTON.

Absorption spectra of organic compounds of the salvarsan group. J. EISENBRAND (Arch. Pharm., 1931, 269, 683–689).—The absorption of

4-hydroxy-3-aminophenylarsin oxide, arsenobenzene, and salvarsan in the ultra-violet region is recorded. There is no relation between this absorption and the toxicity of the substances. Any relation would be expected in the visible region. R. S. CAHN.

10-Chloro-5:10-dihydrophenarsazine and its derivatives. XVII. Constitution of the nitro-derivatives produced from 3-nitrodiphenylamine-6'-arsinic acid and its homologues. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1931, 3270—3273).—2-Bromo-4-nitrophenylarsinic acid (I) (from 2-bromo-4-nitroaniline) has decomp. 240—242° (Na salt). With NH_2Ph (K_2CO_3 ; Cu; EtOH) it gives 3-nitrodiphenylamine-6'-arsinic acid, decomp. 193° (shrinks at 135°), converted by SO_2 in aq. EtOH-HCl into orange 10-chloro-3-nitro-5:10-dihydrophenarsazine, decomp. 268—271°, not identical with the red compound obtained by reducing 3-nitrodiphenylamine-6'-arsinic acid, which must therefore be the 1- NO_2 -compound as previously suggested (A., 1927, 1210). Condensation of (I) with the appropriate amine affords 3'-nitro-4-, decomp. 194°, -3-, decomp. 116°, and -2-, decomp. 127—132°, -methyl-diphenylamine-6'-arsinic acid, similarly converted into 10-chloro-7-nitro-2-, decomp. 263° (converted by H_2O_2 in AcOH into 7-nitro-2-methylphenarsazinic acid, not melting at 285°), -1(or 3)-, decomp. 292—294°, and -4-, decomp. 305—307°, -methyl-5:10-dihydrophenarsazine. J. W. BAKER.

Fission of the heterocyclic ring of dihydrophenarsazine derivatives with separation of arsenic. G. A. RAZUBAIEV (Ber., 1931, 64, [B], 2860—2863).—Separation of As from derivatives of 5:10-dihydrophenarsazine (with the exception of 10-aryl or -alkyl compounds) usually is smoothly effected by heating with cryst. H_3PO_3 at 120—180°, thus:



+ 3HPO_3 and $2\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_3 \end{smallmatrix} \text{AsO} \cdot \text{OH} + 5\text{H}_3\text{PO}_3 = 2\text{NHPh}_2 + 2\text{As} + 4\text{H}_2\text{O} + 5\text{HPO}_3$. Examples cited are 10-chloro-, 10-chloro-2:8-dinitro-, 10-chloro-5-aceto-, 5:4-benzo-10-chloro-5:10-dihydrophenarsazine, and phenarsazinic acid. With 10-alkyl (aryl) compounds at 200°, complicated decomp. results in the evolution of spontaneously inflammable derivatives of As and P. Diphenylchloroarsine, chlorophenoxazine, and 3:10-dichloro-5:10-dihydroarsanthrene do not behave similarly. With aq. HI fission of the 10-alkyl derivatives is easier, but that of 10-chloro-5:10-dihydrophenarsazine more difficult in accordance with the scheme $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{AsCl} + 2\text{HI} = \text{NHPh}_2 + \text{AsClH}_2$. Examples cited are 10-ethyl-, 10-phenyl-, and 10-chloro-5:10-dihydrophenarsazine.

H. WREN.

[Path to optically active germanium compounds.] E. KRAUSE (Ber., 1931, 64, [B], 2935).—The probable analogy between compounds of Ge and Pb is indicated (cf. Schwarz and Lewinsohn, A., 1931, 1435).

H. WREN.

Salts of the tolyl- and mixed phenyltolyl-selenonium hydroxides. H. M. LEICESTER and F. W.

BERGSTROM (J. Amer. Chem. Soc., 1931, 53, 4428—4436; cf. A., 1930, 231).—Diphenyl-p-tolylselenonium chloride (I), hygroscopic glass, resulted from SePh_2Cl_2 , PhMe, and AlCl_3 from $\text{Ph}(p\text{-MeC}_6\text{H}_4)\text{SeCl}_2$, C_6H_5 , and AlCl_3 , and also from SePh_2Cl_2 and $(p\text{-MeC}_6\text{H}_4)_2\text{Hg}$ by heating until fusion begins. (I) and NaI give the corresponding iodide, decomp. 199—200° (all m. p. are corr.), which, when distilled, affords PhI and $p\text{-MeC}_6\text{H}_4\text{SePh}$, the dibromide of which has m. p. 128—129°; $p\text{-IC}_6\text{H}_4\text{Me}$ and SePh_2 could not be identified. $\text{Se}(p\text{-MeC}_6\text{H}_4)_2$ is best prepared from $p\text{-MeC}_6\text{H}_4\text{N}_2\text{Cl}$ and SeK_2 ; its dichloride decomp. 188—189°, with C_6H_6 and AlCl_3 yields phenyldi-p-tolylselenonium chloride (+ $2\text{H}_2\text{O}$), m. p. about 130°, (+ H_2O), decomp. 189—190°; the corresponding iodide, decomp. 189—191°, when heated, gives PhI and $\text{Se}(p\text{-MeC}_6\text{H}_4)_2$; the picrate has m. p. 158—159°. $(p\text{-MeC}_6\text{H}_4)_2\text{SeCl}_2$ and HgPh_2 , on fusion, give $(p\text{-MeC}_6\text{H}_4)_2\text{PhSeCl}$ as the main product, but some SePh_2Cl also results; this result indicates that the p-tolyl group is more negative than the Ph. $(p\text{-MeC}_6\text{H}_4)_2\text{SeCl}_2$ with PhMe and AlCl_3 or with $(p\text{-MeC}_6\text{H}_4)_2\text{Hg}$ gives tri-p-tolylselenonium chloride (+ H_2O), decomp. 158—160°; the iodide (+ H_2O), decomp. 202—203°, on dry distillation gives $p\text{-IC}_6\text{H}_4\text{Me}$ and $\text{Se}(p\text{-MeC}_6\text{H}_4)_2$. The dichloride, decomp. 149—150°, of di-m-tolyl selenide, b. p. 187—188°/16 mm., and Hg di-m-tolyl give the compound, $\text{C}_{21}\text{H}_{21}\text{SeCl}_2\text{HgCl}_2$, m. p. 145°; removal of Hg from this with H_2S or NaOH and reaction with NaI gives tri-m-tolylselenonium iodide, decomp. 156—157°. SePh_2OH was prepared in dil. solution; on concn. it decomposes to C_6H_6 (?) and SePh_2O . Preliminary conductivity measurements indicate that the triaryl-selenonium iodides are weak electrolytes and approach the max. conductivity only at very high dilutions. The corresponding hydroxides are much better conductors. C. J. WEST (b).

Denaturation of proteins. XI. Effect of hydrogen-ion concentration on rate of denaturation of egg-albumin by carbamide. H. WU and E. F. YANG. XII. Effect of denaturation and coagulation on titration curve of egg-albumin. H. WU, S. C. LIU, and C. Y. CHOU. XIII. Theory of denaturation. H. WU (Chinese J. Physiol., 1931, 5, 301—308, 309—320, 321—344).—XI. At const. p_H , the rate of denaturation of egg-albumin by carbamide in aq. solution decreases with increasing ionic strength. At approx. const. ionic strength, the rate is min. at p_H 7.6. The p_H of neutral solution is displaced to 7.5 ± 0.1 , and the isoelectric point of egg-albumin from p_H 4.8 to 5.2 by carbamide. The rate of denaturation is therefore at a min. at the neutral point.

XII. Quinhydrone and hydrogen electrode titration curves of egg-albumin denatured in aq. solution at 70° are displaced to the alkaline side of neutrality as compared with curves for the natural protein. The change in acid- and base-binding power is confirmed by the increase in p_H of egg-albumin solution denatured by carbamide to exclude coagulation. Contrary to Booth (A., 1931, 316), the p_H of haemoglobin solution increases on denaturation by EtOH.

XIII. A hypothesis is advanced to account for the above results. A. COHEN.

Determination of polypeptides in protein solutions. N. FIESSINGER and M. HERBAIN (Compt. rend. Soc. Biol., 1930, 103, 1211—1212; Chem. Zentr., 1931, ii, 95).—Polypeptides are determined from the difference between the N content of the filtrate from $\text{CCl}_3\text{CO}_2\text{H}$ and that of the filtrate from tungstate. In dil. solutions high vals. are obtained, particularly with serum.

A. A. ELDRIDGE.

Electrometric titration of proteins. J. ERREIRA (Compt. rend., 1931, 193, 1347—1350).—Titration curves (Sb electrode) for NaCl solutions of peanut globulin against 0.01*N*- and 0.02*N*-HCl are given. The isoelectric point is approx. p_H 4.7, whilst $K_a = 7.1 \times 10^{-8}$ and $K_b = 1.6 \times 10^{-10}$. Titrations of serum and of egg-white with different concns. of HCl confirm the stoichiometric combination of protein with acids. Treatment of egg-white with NaOH at p_H 10.25—11.3 effects partial hydrolysis.

F. O. HOWITT.

Composition of soya-bean protein. 1. Butyl alcohol extraction method. 2. Ester method. M. MASHINO (J. Soc. Chem. Ind. Japan, 1931, 34, 433B, 433—434B).—(1) [With S. NISHIMURA.] Fat-free soya-bean, purified with MeOH, was decomposed by 25% H_2SO_4 ; tyrosine crystallised from the neutralised conc. product. Extraction of the filtrate by BuOH yielded arginine, histidine, and lysine; leucine and phenylalanine were separated from the sol. part,

and proline from the insol. part of the BuOH extract. Dibasic NH_2 -acids were not extracted by BuOH. Omission of the MeOH purification prevented the extraction and crystallisation of the components.

(2) [With T. SHIMIZU.] On evaporation of the Et_2O solution of the Me esters of the NH_2 -acids from purified soya-bean protein a cryst. (monoclinic) substance, $\text{C}_{10}\text{H}_{16}\text{O}_8$, m. p. 78° (sol. in H_2O , Et_2O , MeOH, C_6H_6 ; insol. in light petroleum), was obtained. The glutamic acid isolated had $[\alpha]_D^{25} +12.4^\circ$. Valine, leucine, proline, and phenylalanine were isolated by the ester method.

E. LEWKOWITSCH.

Sensitive reaction of bivalent Fe, Co, Ni, and Cu. Determination of phenanthrene in commercial anthracene. T. PAVOLINI (Ind. Chim., 1930, 5, 862—864; Chem. Zentr., 1931, ii, 283).— Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} give coloured ppts. (bluish-green, scarlet, ochre-yellow, chestnut-brown) with phenanthrenequinoneoxime. The trivalent cations do not react in this way. For the determination excess of the precipitant must be avoided and the ppt. must be washed on the filter with 40% EtOH.

A. A. ELDRIDGE.

Determination of cysteine in proteins. S. L. TOMPSETT.—See this vol., 206.

Naphtharesorcinol reaction of alduronic acids. C. NEUBERG and M. KOBEL.—See this vol., 206.

Biochemistry.

Catalase as an agent for economising oxygen consumption. A. STAFFE (Biochem. Z., 1931, 243, 380—385).—Since blood is richer in catalase at high altitudes than at low and since the catalase content of cows' milk increases when they are taken to such altitudes, when they climb, or when they are exposed to the cold, it is concluded that catalase acts as an agent for economising O_2 consumption.

W. MCCARTNEY.

Segloff's method for the detection of blood. P. SCHUGT (Pharm. Presse, 1930, 166—167; Chem. Zentr., 1931, ii, 283).—The material (faecal extract or urine, 1 c.c.) is preferably treated with 8 drops of AcOH and an equal quantity of H_2O_2 and then (without mixing) with a 5% solution of pyrimidone in abs. EtOH. A violet ring indicates the presence of blood.

A. A. ELDRIDGE.

Pipette for the handling of whole blood samples, for use with the Van Slyke gasometric apparatus. G. M. GUEST (J. Biol. Chem., 1931, 94, 507—509).—A pipette made from a 2-way stop-cock and fitted with one bulb to contain and another to deliver the sample (1 c.c.) is described.

F. O. HOWITT.

Clinical hæmoglobinometry. H. E. HARVEY, V. H. TRAXLER, and R. L. WRIGHT (J. Lab. Clin. Med., 1931, 16, 1012—1016).—The Sahli double-standard hæmoglobinometer is preferred. Normal blood contains 14 mg. of hæmoglobin per 100 c.c.

CHEMICAL ABSTRACTS.

State of carbon dioxide in blood. O. M. HENRIQUES (Biochem. Z., 1931, 243, 241—255; cf. A., 1931, 1174).—Although evidence in support of the view of Stadie and O'Brien has been given by Van Slyke and Hawkins (A., 1930, 1053) and by Brinkman and Margaria (J. Physiol., 1931, 72, 6r), this evidence is not satisfactory and evidence against the view has been adduced by the author and by others. On the other hand, whilst there is no evidence against the author's view, there is much to support it. W. MCCARTNEY.

Conversion of carbon monoxide into dioxide by green and mixed hæmins. E. NEGELEIN (Biochem. Z., 1931, 243, 386—395).—Provided that the amount of O_2 present is insufficient to oxidise all the Fe-CO compound, the conversion of CO into CO_2 by unreduced green or mixed hæmin in alkaline solution is catalysed by Fe. The hæmins react, not directly with the CO, but only with CO which is combined with Fe. Hence the reaction begins with the production of a little Fe-CO compound, a small amount of Fe^{3+} of the hæmin being reduced. During the process the one Fe compound activates the O_2 , the other the CO. It is not impossible that Fe-CO compound is also directly oxidised.

W. MCCARTNEY.

Decomposition of glucose in the blood. E. SATO (Nagoya J. Med. Sci., 1931, 5, 167—174).—The decomp. of sugar in human blood is greatest in the first 3 hr., and decreases gradually up to 48 hr. No

differences were observed at room temp. and 37°. The rates of decomp. by human blood-corpuscles in physiological salt solution and in blood-serum are almost the same, but decomp. is more rapid in phosphate solution. The decomp. decreases in proportion to hæmolysis.

CHEMICAL ABSTRACTS.

Determination of galactose in blood and urine. V. J. HARDING and G. A. GRANT (J. Biol. Chem., 1931, 94, 529—539).—Ordinary baker's yeast grown in a medium containing galactose provides a strain capable of quantitatively removing galactose from aq. solutions or suitably treated physiological fluids. Galactose is not detectable by such yeast in fasting blood or urine either in normal subjects, in cases of late pregnancy, or 3 days *post partum*. The non-fermentable sugar of fasting urine in late pregnancy or the puerperium yields on hydrolysis "fermentable sugar" and "galactose sugar" in a ratio of approx. 2:1, a result inconsistent with the lactosuria of pregnancy or of lactation being produced by simple excretion of lactose in the urine. F. O. HOWITT.

Fœtal blood. II. Lactic acid content of umbilical cord blood under various conditions. N. J. EASTMAN and C. M. McLANE (Bull. Johns Hopkins Hosp., 1931, 48, 261—268).—The fœtal blood-lactic acid is normal, but in infants at birth it is high (35 mg. per 100 c.c.); in asphyxiated infants it reaches 90 mg.

CHEMICAL ABSTRACTS.

Colloidal chemical differences between paraglobulins of normal and antitoxic sera. P. VON MUTZENBECHER (Biochem. Z., 1931, 243, 100—112).—Using an improved method of electrodialysis, the paraglobulins of serum in diphtheria, tetanus, dysentery, and scarlet fever are found to sensitise Fe_2O_3 sol more feebly than the corresponding paraglobulin of normal serum. On the other hand, by fractional pptn. of diphtheritic serum, a paraglobulin is obtained which sensitises the sol much more strongly than the corresponding normal paraglobulin. The so-called paraglobulin fraction cannot therefore represent a well-defined substance of uniform composition.

P. W. CLUTTERBUCK.

Influence of hydrogen-ion concentration on sensitisation and protective action. P. VON MUTZENBECHER (Biochem. Z., 1931, 243, 113—124).—Electrodialysed paraglobulin coagulates Fe_2O_3 sol, and addition of acid, alkali, or neutral salts stabilises it. The action of HCl on the coagulation val. is followed, p_H measurements being given. Both the concn. and the protein charge as determined by the p_H affect the coagulation val. of protein- Fe_2O_3 sol mixtures.

P. W. CLUTTERBUCK.

Clinical determination of serum-proteins. E. H. FISHBERG and B. T. DOLIN (J. Lab. Clin. Med., 1931, 16, 1107—1112).—The protein content of blood sera or exudates is determined by colorimetric or electrometric measurement of the buffering power.

CHEMICAL ABSTRACTS.

Determination of fibrin, globulin, and albumin in blood-plasma. H. THEORELL and G. WIDSTRÖM (Z. ges. exp. Med., 1931, 75, 692—698; Chem. Zentr., 1931, i, 3706).—For 0.5 or 1 c.c. of plasma, N is determined micro-chemically in citrated plasma after combustion with H_2SO_4 , in fibrin after recalcification and

expression of the coagulum, in albumin after salting out the globulin with MgSO_4 ; globulin is determined by difference.

A. A. ELDRIDGE.

Determination of amino-acids in blood-serum. K. L. ZIRM and J. BENEDICT (Biochem. Z., 1931, 243, 312—315).—The method of Linderström-Lang (A., 1928, 536, 551) has been applied to the determination of NH_2 -acids in blood-serum and can be used for other body-fluids also. The insolubility of pentamethoxytriphenylcarbinol is a disadvantage and α -naphthol-red gives equally good results. W. MCCARTNEY.

Effect of intravenous administration of pancreatic lipase on the blood-lipase. J. BALÓ and E. BACH (Z. ges. exp. Med., 1931, 75, 583—589; Chem. Zentr., 1931, ii, 69).—After a single administration (5 units) the blood-lipase is sharply increased, but becomes normal after 1 hr. After 25 injections in 32 days no effect on the blood-lipase was observed.

A. A. ELDRIDGE.

Calcium content of the blood of sea fish. M. FONTAINE and P. PORTER (Compt. rend., 1931, 193, 1218—1220).—Ca is distributed between the corpuscles and the serum of fish-blood in the same order and ratio as in men. No difference was discernible between the blood-Ca of Selachii and Teleostei or between male and female specimens.

C. C. N. VASS.

Two factors influencing serum-calcium and inorganic phosphate of the rabbit. I. Influence of diet. II. Diurnal variation. E. F. DUPRÉ and E. SEMENOFF (J. Biol. Chem., 1931, 94, 341—351).—Dietary factors are mainly responsible for the wide variations in the serum-Ca and inorg. P of normal rabbits. High vals. of the former are accompanied by low vals. for the latter, and *vice versa*. The high Ca and low P resulting from a diet of cabbage are respectively lowered and raised when cabbage is replaced by bran and oats. Normal vals. are established by fasting 12—24 hr. The normal serum-Ca increases by 1.0—1.5 mg. per 100 c.c. from morning to evening, whilst the inorg. P decreases by a similar amount.

A. COHEN.

Copper content of blood. L. SCHINDEL (Klin. Woch., 1931, 10, 743—744; Chem. Zentr., 1931, ii, 76).—The Cu content of the corpuscles is always less than that of the plasma except for newly-born infants, for which the reverse holds.

A. A. ELDRIDGE.

Specificity of hæmoglobin precipitins. L. HEKTOEN and A. K. BOOR (J. Infect. Dis., 1931, 49, 29—36).—Extraspecific action of anti-hæmoglobin precipitin may be overcome by diluting the serum.

CHEMICAL ABSTRACTS.

Specificity of serological reactions with simple chemical compounds (inhibition reactions). K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1931, 54, 295—305).—The specificity of inhibitory reactions involving substituted aromatic acids is influenced by the position of the substituent. Results of differentiation are given for antigens from 93 org. acids with immune sera.

CHEMICAL ABSTRACTS.

Antigenic properties of fibrinogens. P. KYES and R. T. PORTER (J. Immunol., 1931, 20, 85—88).—Fowl, sheep, and horse fibrinogens, when injected into

rabbits, produce antibodies sp. for the fibrinogen injected.

CHEMICAL ABSTRACTS.

Cold hæmotoxin in heated serum. I. K. TOSHIMA (J. Biochem., Japan, 1931, 13, 291—308).—When heated for 30 min. at 75—90° the serum from rabbits immunised against human or chicken erythrocytes hæmolyses the erythrocytes at low temp. but does not affect them at 37°, and no complement is necessary for this purpose. The factor is present in the albumin fraction.

CHEMICAL ABSTRACTS.

Specific combination in immunity reactions. J. R. MARRACK and F. C. SMITH (Nature, 1931, 128, 1077).—The sp. combination of hapten, i.e., a compound of known composition, with antibody has been demonstrated.

L. S. THEOBALD.

Factors influencing the concentration of complement in the blood. T. W. B. OSBORN (Biochem. J., 1931, 25, 2136—2149).—Young weaned rats tend to have a lower complement than adult animals. The ingestion of food may cause a variation in the blood-complement of rats. Irradiation of rats with a Hg-vapour lamp sometimes causes a rise in complement. Complement tends to be lower when the animals are fed on a diet deficient in vitamin-A than in the blood of controls receiving cod-liver oil.

S. S. ZILVA.

Absorption spectrum of cytochrome. H. KATAGIRI and K. MASUDA (Mem. Coll. Agric. Kyoto, 1931, No. 15, 19 pp.).—Cytochrome from the thoracic muscle of the honey bee and other sources shows absorption bands at 605 (I), 566 (II), 550 (III), 539 (IV), 532 (V), 522 (VI), and 509 m μ (VII). When heated to 65° (I) is replaced by an asymmetrical band at 590 m μ . Heating to 45° in the presence of KCN destroys (II) and part of (V), new bands appearing at 575 and 539 m μ . The latter two bands are given by a substance (A) which is changed to B with absorption at 560 and 528 m μ by reduction at p_H 9.0. The change is reversed by neutralisation to p_H 5.5. Cytochrome b shows characteristic bands at 566 and 532 m μ . The c component, extracted from muscles or yeast by NaCl solution, shows seven bands at 667, 550, 539.5, 529.7, 521.8, 509, and 405—410 m μ , which on oxidation give place to bands at 563.7, 519—535, and 485 m μ .

A. COHEN.

Suprarenal gland. E. C. KENDALL (Proc. Staff Meetings Mayo Clinic, 1931, 6, 296).—Separation of cryst. hexuronic acid, cryst. adrenaline, and the active agent of the cortex has been accomplished.

CHEMICAL ABSTRACTS.

Structure of glutathione and the behaviour of the free compound and of derivatives towards enzymes. E. ABDERHALDEN and W. GEIDEL (Fermentforsch., 1931, 13, 97—114).—Glutathione (I) forms the following derivatives: phenylcarbamido- (II), m. p. 210° (decomp.) (giving glutamic acid phenylhydantoin, m. p. 143°, on acid hydrolysis); α -naphthylcarbamido- (giving glutamic acid α -naphthylhydantoin on acid hydrolysis); dl-leucyl- (oxidised form) [from dl- α -bromoisohexoyl- (III), m. p. about 90° (decomp.)]; dl-leucyl- (cystine compound); glycyl-dl-leucyl- (from chloroacetyl-dl-leucyl-). Boiling (I) with H₂O gives cysteinylglycine, isolated as the phenylcarbamido-

derivative (IV), m. p. about 150° (decomp.). dl-Leucyl-dl-leucylglycine ester hydrochloride with CH₂Ph.NH₂ yields the benzylamine, which when coupled with a carbimide gives phenylcarbamido-dl-leucyl-dl-leucylglycylbenzylamine. Hydrolysis with HCl gives leucine phenylhydantoin, m. p. 126°. Glycylbenzylamine was isolated as the phenylcarbamido-derivative, m. p. 202°. The benzylamine compound of glutathione could not be obtained. Cysteine Me ester hydrochloride, m. p. 131° (1 mol.), and COMe₂ (1 mol.) give an additive compound, m. p. 162°. Some polypeptides containing cysteine were synthesised: dl- α -bromoisohexoylcysteine Me ester, hippurylcysteine Me ester, S-benzyl-n-hippurylcysteine Me ester (V).

Erepsin attacked neither (I) nor its derivatives. At 7.8, HBr was eliminated from (III). Trypsin-knase hydrolysed the oxidised (I), yielding glycine, but not the reduced form. It also attacked (II), (III), and (IV), but not (V). Cathepsin had no action on (I) or its derivatives, but (I) accelerates its action on gelatin. (I) was not hydrolysed by pancreas powder or yeast maceration juice.

J. H. BIRKINSHAW.

Spermine in human tissues. G. A. HARRISON (Biochem. J., 1931, 25, 1885—1892).—The distribution of the base in human tissues is virtually the same as that found by Dudley and Rosenheim (A., 1926, 194). It occurs in human faeces. The spermine content of the human prostate is remarkably high. The absence of spermine from bull's semen is possibly due to the absence of a true functional prostate in that animal. A modification has been introduced in the steam-distillation method (A., 1924, i, 294) to obtain the base as phosphate more readily in a relatively pure state.

S. S. ZILVA.

Histological detection of uric acid and urates. A. SCHULTZ and W. SCHMIDT (Arch. path. Anat. Physiol., 1931, 280, 529—533; Chem. Zentr., 1931, ii, 96).—Uric acid (but not urate) is detected by means of hæmatoxylin-carmin or methylene-blue and picric acid. By a modification of technique Na urate may be detected.

A. A. ELDRIDGE.

Basic amino-acids of wool. A. M. STEWART and C. REMINGTON (Biochem. J., 1931, 25, 2189—2192).—Australian wool contained 0.55% of histidine, 6% of arginine, and 2.2% of lysine (cf. A., 1929, 632; 1930, 1328).

S. S. ZILVA.

Constitution of the keratin molecule. J. B. SPEAKMAN and M. C. HIRST (Nature, 1931, 128, 1073—1074).—From a study of the action of acids on wool it is concluded that one of the linkings between the peptide chains in the keratin mol. is a salt of glutamic acid and arginine; the former may be replaced occasionally by aspartic acid and the latter by lysine.

L. S. THEOBALD.

Fatty acids from oil of cantharis (Mylabris pustulata, Fb., India). B. H. IYER and P. R. AYYAR (J. Indian Inst. Sci., 1931, 14A, 40—45).—From the EtOAc extract of the dried beetles, 12.5% of crude fat was obtained by extraction with (40—60°) petrol. It consisted of 5% of unsaponifiable matter, 11% of palmitic acid, 27% of stearic acid, 46% of oleic acid and isomeride, 1% of arachidic acid, with 10% of dissolved cantharidin.

C. C. N. VASS.

Fatty acids and cholesterol in the seminal vesicles of the guinea-pig. S. COMHAIRE (Arch. Biol., 1931, 41, 485—490).—The cholesterol content of the epithelium of the seminal vesicles of the guinea-pig is approx. const.; the fatty acid content increases and the unsaponifiable matter decreases with advancing stages of sexual development.

A. G. POLLARD.

Determination of the iodine value of lipins. M. YASUDA (J. Biol. Chem., 1931, 94, 401—409).—The Hanus method gives very high results for the I val. of cholesterol and its esters. For lipins generally, the Rosenmund-Kuhnheim method, employing pyridine dibromide as halogenator, is preferable. Details are given for the adaptation of this method to the micro-determination of the I val. of tissue extracts, in conjunction with Bloor's micro-determination of lipins.

A. COHEN.

Histochemistry of phenols and their derivatives. L. LISON (Arch. Biol., 1931, 41, 343—436).—Diazo-reactions are utilised in technique developed for the examination of phenols and derivatives in animal tissues.

A. G. POLLARD.

Calcium salts of bone. L. J. BOGERT and A. B. HASTINGS (J. Biol. Chem., 1931, 94, 473—481).—The inner and outer portions of bone and also the cortex were analysed before and after treatment by various methods for removal of org. matter. The inner and outer parts do not differ materially in inorg. constituents, which are more conc. in the cortex. Normal methods of ashing result in loss of carbonates. The chief constituent is probably a cryst. salt, $\text{CaCO}_3 \cdot 2\text{Ca}_3(\text{PO}_4)_2$.

F. O. HOWITT.

Dehydrating agents for paraffin embedding. L. A. MAROLENA (Stain Tech., 1932, 7, 25).— BuOH is recommended.

H. W. DUDLEY.

Determination of total protein in cerebrospinal fluid. J. B. McNAUGHT (J. Lab. Clin. Med., 1931, 16, 999—1012).—Tsuchiya's reagent is employed, the ppt. being measured volumetrically, after centrifuging, in a calibrated tube. Normal vals. are 17—40 (average 29) mg. per 100 c.c.

CHEMICAL ABSTRACTS.

Determination of total precipitable protein in cerebrospinal fluid. A. R. BAUER and P. H. SCHENCK (J. Lab. Clin. Med., 1931, 16, 1090—1100).—The ppt. produced by a reagent containing 1.5% of picric acid and 3.0% of citric acid is centrifuged in a calibrated tube.

CHEMICAL ABSTRACTS.

Indoxyl (indican) in the milk of the cow and the goat. C. HERVIEUX (Compt. rend., 1931, 193, 1480—1482).—Small amounts of indican were present in all normal milks examined.

W. O. KERNACK.

Influence of environmental temperature on the percentage of butter-fat in cow's milk. H. J. BROOKS (J. Dairy Sci., 1931, 14, 483—493).—The % of fat in butter is inversely related to environmental temp. The latter factor exerts a greater influence on the fat content of milk than does the stage of lactation.

A. G. POLLARD.

Colorimetric determination of the thiocyanate content of gastric juice. G. LOCKEMANN and W.

ULRICH (Biochem. Z., 1931, 243, 150—159).—A method is described for the colorimetric determination of CNS^- in gastric juice with the help of the FeCl_3 reaction which permits the detection of CNS^- in dilutions of 1 in 10^6 corresponding with a content of 0.1 mg. per 100 c.c.

P. W. CLUTTERBUCK.

Stimulating effect of amino-acid hydrochlorides on gastric secretion. I. Experiments on men. II. Experiments on dogs with gastric pouches. III. Experiments on men in whom the substances are introduced into the duodenum. J. TAGAWA (Biochem. Z., 1931, 243, 330—343, 344—354, 355—368).—I. Although neither NH_2 -acids (glycine, *L*-leucine, *L*-phenylalanine, *L*-tyrosine, *L*-asparagine, *D*-glutamic acid, *D*- and *L*-histidine, *L*-cystine, *D*-alanine, *L*-tryptophan) nor HCl have appreciable effect on gastric secretion the hydrochlorides of the acids stimulate secretion to varying extents and at various rates. Of the acids tested glutamic is the most active. It is probable that the stimulating effect produced by proteins takes place only after degradation to NH_2 -acids and combination of these with HCl .

II. In dogs with gastric pouches the administration of the NH_2 -acid hydrochlorides has effects very similar to those produced in man. The effect produced by glutamic acid hydrochloride is not influenced by administration of atropine, is inhibited by administration of adrenaline, and slightly increased by administration of pilocarpine.

III. When the acids are introduced into the human duodenum they have no effect on the gastric secretion, but introduction of HCl or of the hydrochlorides of the acids has stimulating effects similar to those produced by introduction of the hydrochlorides into the stomach. In all cases glutamic acid hydrochloride is the most active compound. No connexion can be traced between the extent of the stimulating effect and the $[\text{H}^+]$ of the solutions given. It is concluded that the NH_2 -acid hydrochlorides exert their stimulating action after resorption below the duodenum.

W. MCCARTNEY.

Variations in pancreatic secretion during hyperglycæmia resulting from intravenous injection of glucose. J. LA BARRE and P. DESTREE (Compt. rend. Soc. Biol., 1930, 105, 35—36; Chem. Zentr., 1931, ii, 76).—Hyperglycæmia stimulates the higher nervous system, leading to vigorous pancreatic secretion.

A. A. ELDRIDGE.

Fluorescence of pigments of urobilin group. Fluorescence spectra. C. DNÉRE and J. ROCHE (Bull. Soc. Chim. biol., 1931, 13, 987—1014).—The fluorescence of mesobiliviolin, mesobilirubinogen, and preps. of urobilin and hydrobilirubin in EtOH solution alone and in presence of Zn and Hg salts is described. The absorption and fluorescence spectra under these conditions are depicted.

H. A. PIGGOTT.

Relation between endogenous and enterotropic uric acid. H. ROTHMANN (Ver. deut. Ges. inn. Med., 1930, 42, 159 pp.; Chem. Zentr., 1931, ii, 78).—Adenosinephosphoric acid is excreted with the bile into the intestine, and is therefore a source of enterotropic uric acid.

A. A. ELDRIDGE.

Detection of formaldehyde in urine. E. CHERICI (L'Ateneo Parm., 1930, 2, No. 1; Chem. Zentr., 1931, ii, 95—96).—Labat's reaction is employed. A. A. ELDRIDGE.

Colour reaction for carbohydrates. Detection of hexoses and pentoses in urine. E. CHERICI (L'Ateneo Parm., 1930, No. 2, 8 pp.; Chem. Zentr., 1931, ii, 96).—Urine (0.2 c.c.) is added without mixing to H_2SO_4 (4 c.c.); after careful mixing 5% alcoholic gallic acid (0.2 c.c.) is added. In the cold or on gentle warming (H_2O -bath) a green coloration indicates hexoses or carbohydrates yielding hexoses with H_2SO_4 . If the reaction is not given, but the deproteinised urine reduces Fehling's solution, pentose is present. A. A. ELDRIDGE.

Occurrence of phenol derivatives in urine. Determination by means of the Millon reaction. O. FURTH and R. SCHOLL (Biochem. Z., 1931, 243, 274—291).—The phenolic compounds in urine not volatile in steam can be separated into an Et_2O -sol. (substances derived from tyrosine) and an Et_2O -insol. fraction. The amount of phenolic substances in urine cannot be determined by direct application of the Millon reaction, but the amount of these fractions can be colorimetrically determined with the Millon reagent if the urine is treated in the manner described. The usual methods for the determination of the indican content of urine are very inaccurate, but by using Na indigotinsulphonate for colorimetric comparison estimates of this content can be made. Normal human urine contains traces only of Et_2O -sol. phenolic substances, but has an average of 4.7 mg. per 100 c.c. of the Et_2O -sol. (as tyrosine) and 0.8—1.3 mg. per 100 c.c. of indigo (from indican). No relationship can be found between the indican (derived from putrefaction of protein) content of urine and its content of Et_2O -sol. phenolic compounds. In diseases in which the function of the liver is seriously affected, in advanced tuberculosis, and to some extent in other diseases also, the content of Et_2O -insol. phenolic compounds increases greatly, although the content of the Et_2O -sol. fraction does not alter. In dementia praecox and in amentia increase in the amount of phenolic compounds in the urine occurs only exceptionally. In the rabbit, dog, and guinea-pig poisoning with P leads to great increase in the amount of Et_2O -insol. phenolic compounds in the urine. W. MCCARTNEY.

Urinary proteases. I. B. H. E. CADNESS and C. G. L. WOLF (Fermentforsch., 1931, 13, 1—21).—Ninhydrin-positive, dialysable substances are present in most pregnancy and pathological urines, but absent from normal urines. Certain pathological urines contained enzymes which digested placental tissue slightly. The enzyme of pregnancy urine was not sp. for placenta, but digested other substrates. The COMe_2 ppt. of all urines examined hydrolysed fibrin. Boiling the COMe_2 ppt. for 2 min. prevented the attack on placenta, and autoclaving for 30 min. the attack on fibrin. J. H. BIRKINSHAW.

Pigment metabolism and destruction of blood in pernicious anaemia. R. F. FARQUHARSON, H. BORSOOK, and A. M. GOULDING (Arch. Int. Med., 1931,

48, 1156—1185).—In severe relapses and, to a smaller extent, in patients without much anaemia the faecal excretion of urobilinogen increases to several times the normal val. Serum-bilirubin also increases, and in some cases urobilin is found in the urine. Normal vals. are rapidly restored during the reticulocyte response following effective treatment with liver or liver extract. The pigment excretion is attributed to early destruction of the abnormal red blood-cells of anaemia. Liver therapy favours the production of red cells which are less readily destroyed, and the blood returns to normal. A. COHEN.

Relationship between oxygen consumption and nitrogen metabolism. I. Pernicious anaemia. C. W. BALDRIDGE and A. BAKER (J. Clin. Invest., 1931, 10, 529—543).—There is a direct causal relationship between the increase in N catabolism and increased O consumption and also between N storage and decrease in O requirement.

CHEMICAL ABSTRACTS.

Crystalline derivative of an acid present in liver. Correction. R. WEST and M. HOWE (J. Biol. Chem., 1931, 94, 611).—The statement that the cryst. quinine salt previously described (A., 1930, 1309) is clinically active is now withdrawn. Contrary to previous findings (*loc. cit.*), an appreciable amount of active material is removed by BuOH from liver extract saturated with picric acid. The active material is recovered from the BuOH extract by shaking with dil. mineral acid. H. BURTON.

Iron and carbon of visceral pigments. J. PAVIOT, R. CHEVALLIER, and A. BADINAND (Compt. rend. Soc. Biol., 1930, 105, 18—19; Chem. Zentr., 1931, i, 3708).—Anthracotic lungs contain an Fe-bearing pigment, generally in quantity exceeding that of C. The intensity of the colour depends on the condition of the Fe and not on its quantity. Pb could not be found in the lungs of a worker in a lead mine. The Fe content of the spleen is lower than that of the lungs or liver. A. A. ELDRIDGE.

Potassium content of bone marrow in carcinoma. T. HOFFMANN (Biochem. Z., 1931, 243, 145—149).—Human bone marrow has during growth a high K content, but in adults decreases to $\frac{1}{4}$ — $\frac{1}{6}$ of this val. In presence of carcinoma, K enrichment of bone marrow again occurs, the vals. being at least double those of normal adults. The Na content showed similar but not such regular variations, whilst the Ca content was irregular and could not be correlated with growth. P. W. CLUTTERBUCK.

Lipins of human tumours, especially the sulphophospholipins of the tumours. A. BOLAFFI (Atti R. Accad. Lincei, 1931, [vi], 14, 62—64).—Various neoplastic tissues, human and otherwise, all exhibit distinct analogies as regards their lipoidal constitution. Each contains a complex sulphophospholipin extractable by hydrated COMe_2 (d 0.850), but, if pure, insol. in anhyd. COMe_2 . This lipin, which is moderately conc. in the tumours, appears to have a constitutional character sp. for each tumour and is characteristic if not absolutely sp. for neoplastic tissue. In human tumours it is probably identical with jecorin. T. H. POPE.

Determination of small amounts of phosphatides and cholesterol in tissues. M. JOWETT and E. W. LAWSON (Biochem. J., 1931, 25, 1981—1990).—The phosphatides are pptd. with $MgCl_2$ and the P not pptd. is subtracted from the total P. The cholesterol is pptd. with digitonin and determined gravimetrically. S. S. ZILVA.

Phosphatide and cholesterol contents of normal and malignant human tissues. M. JOWETT (Biochem. J., 1931, 25, 1991—1998).—Pure malignant tissues have a higher phosphatide and cholesterol content and tend to show a higher phosphatide:cholesterol ratio than do malignant tissues admixed with normal tissue. Malignant tissues show a high proportion of bound cholesterol. Malignant and benign tumours show a higher phosphatide:cholesterol ratio than do the neighbouring tissues from which they may have arisen. S. S. ZILVA.

Kidney threshold for glucose in diabetic and non-diabetic persons. B. V. GLASSBERG (J. Lab. Clin. Med., 1931, 16, 948—952).—The kidney threshold varies greatly. Neither glycosuria nor the presence of both glycosuria and a high blood-sugar level necessarily indicates a disturbance in carbohydrate metabolism. CHEMICAL ABSTRACTS.

Mineral metabolism during involution of simple goitre. E. J. BAUMANN, S. KURLAND, and N. METZGER (J. Biol. Chem., 1931, 94, 383—391).—Rabbits suffering from thyroid deficiency caused by a diet of cabbage retain Ca, Mg, and P, whilst the metabolism of Na, K, Cl, and S is unaffected. Administration of I to such rabbits increases the excretion and restores the balance of Ca, Mg, and P. A. COHEN.

Change in the isoelectric point of the haemoglobin and of the chlorine distribution in the blood in exophthalmic goitre. J. GLASS (Z. klin. Med., 1931, 116, 478—509; Chem. Zentr., 1931, ii, 260).—Normally the isoelectric point of the oxyhaemoglobin is between 5.95 and 6.40 (average 6.20); in exophthalmic goitre it is usually higher. In exophthalmic goitre and on administration of thyroxine the Cl distribution in the blood is acidotic in character. A. A. ELDRIDGE.

Acid-base equilibrium in pathological conditions. II. Alkalosis observed in hypertensive states. E. MUNTWYLER, C. T. WAX, and D. BRUNS (J. Clin. Invest., 1931, 10, 489—506).—In 6 of 12 cases of persistent hypertension with slight N retention a plasma- HCO_3^- val. above 0.031 equiv. was found; in 11 cases the plasma pH exceeded 7.48. Two cases with vomiting showed loss of Cl^- and total base and a rise in HCO_3^- . CHEMICAL ABSTRACTS.

Thiosulphate treatment of pellagra. I. SABRY (J. Egypt. Med. Assoc., 1931, 14, 603—610).—Intravenous injection of 10 c.c. of 10% $Na_2S_2O_3$, repeated 20—60 times according to the severity of the disease, supplemented by a milk diet, is an effective treatment for pellagra. A. LAWSON.

Iron in normal and pathological tissues and its biological interpretation. IV. Iron content of various organs of white rats during pregnancy and under normal conditions. V.

Rice pigeons. VI. Starvation rabbits. VII. Rachitic rabbits. K. KOJIMA (Nagoya J. Med. Sci., 1931, 5, 78—82, 83—93, 94—102, 103—109).—IV. In all organs studied, except the uterus, where it was increased, the Fe content of pregnant rats was less than that of normal females.

V. Pigeons fed on polished rice showed increase in the Fe content of the liver and spleen, and the Fe content of the brain and peripheral nerve was greater than in starvation pigeons. The Fe content of various grains, and of polished and unpolished rice, is parallel with the vitamin-B content. All preps. of vitamin-B examined contained Fe, although in small amount. Vitamin-A preps. contained only traces or none.

VI. The Fe content of the liver increased with duration of the starvation period, but the spleen-Fe decreased.

VII. In rachitic rabbits the spleen- and liver-Fe decreases, but the blood- and bone marrow-Fe increases. In the bones there is no difference between rachitic and normal rabbits.

CHEMICAL ABSTRACTS.

Nitrogen, calcium, and phosphorus balances in late gestation under a specified dietary regime. I. G. MACY, E. DONELSON, M. L. LONG, A. GRAHAM, M. E. SWEENEY, and M. M. SHAW (J. Amer. Dietet. Assoc., 1931, 6, 314—320).—During the 7th and 8th months of pregnancy, N, Ca, and P were stored on an adequate diet.

CHEMICAL ABSTRACTS.

Healing of rickets coincident with low serum-inorganic phosphorus. G. STEARNS and J. D. BOYD (J. Clin. Invest., 1931, 10, 591—602).—In two children with a persistent low level of serum-inorg. P clinical healing was observed with sufficient retention of Ca and P for building bone.

CHEMICAL ABSTRACTS.

Viscosity of the blood-serum in syphilis. Serum-albumin and -globulin content. M. C. MCINTYRE (J. Lab. Clin. Med., 1931, 16, 952—956).—Increased viscosity (1.82, 1.99) does not appear to be due only to an increase in serum-globulin.

CHEMICAL ABSTRACTS.

Enzymes and immunity. M. GHIRON (Atti R. Accad. Lincei, 1931, [vi], 14, 48—52).—Addition of an active, atoxic, sterile suspension in glycerol of a lipase from pig's liver to a broth culture of the tubercle bacillus results in an attenuated strain of the organism. When inoculated systematically into an animal during the development of the tubercular process, the enzymic suspension arrests the disease at the first phase of the inflammatory process, which may be followed by a cure. T. H. POPE.

Variations in the content of reduced glutathione in toxic and infected conditions. R. A. C. GHERZI (Anal. Asoc. Quim. Argentina, 1931, 19, 173—197).—The liver of the guinea-pig contains more reduced glutathione than the heart and kidneys. The amounts in each organ are normally const., but poisoning by KCN, $HgCl_2$, As_2O_3 , $CHCl_3$, $H_2C_2O_4$, strychnine, morphine, atropine, or snake-venom causes characteristic variations in the amounts present in different organs, generally independent of the size of the dose, but dependent in some cases on the mode

of administration. Subcutaneous injections of carbuncle, tetanus, or Koch's bacilli, or of tetanus toxin, all cause a decrease in the reduced glutathione content of the liver and kidneys and an increase in that of the heart, but diphtheria toxin increases the amount in the liver. In anaemia produced by bleeding the ratio (red corpuscles)/(reduced glutathione content of blood) is decreased. Injection of thyroid extract increases the amount of reduced glutathione in the organs.

R. K. CALLOW.

Energy changes in the anaerobic phosphagen synthesis in muscle extract. O. MEYERHOF and K. LOHMANN (Naturwiss., 1931, 19, 575—576).—The energy required for phosphagen synthesis is covered approx. by the sum of the energies of decomp. of glycogen to lactic acid and of adenylypyrophosphate to inosic acid, NH_3 , and phosphate. This explanation holds especially for cold-blooded muscles. With rabbit muscle complications arose through the secondary action of the adenylic acid compound, and agreement is not so good.

J. W. SMITH.

Behaviour of lactacidogen in fatigue induced by stimulation of isolated frog's gastrocnemius. D. WILHELM (Z. physiol. Chem., 1931, 203, 34—47).—Fatigue of frog's gastrocnemius by isolated stimuli was studied in relation to lactacidogen content. The change in lactacidogen content depends on the season; in autumn, fatigue always causes an increase. During the last third of August, *R. esculenta* regularly and *R. temporaria* to some extent show a decrease. In the transition period the effect on lactacidogen content is variable even with *R. esculenta*. The seasonal change is about a month earlier for *R. temporaria* than for *R. esculenta*.

J. H. BIRKINSHAW.

Fission of lactacidogen in muscular contraction. II. G. EMBDEN and H. JOST (Z. physiol. Chem., 1931, 203, 48—57; cf. Arch. Soz. Biol. de Montevideo, Suppl., Fasc. II, 1931).—Frog's gastrocnemii were electrically fatigued until immersion in liquid air produced no contraction. A muscle so fatigued and electrically stimulated to contraction at the moment of immersion usually contained much less lactacidogen than a fatigued muscle immersed without such treatment.

J. H. BIRKINSHAW.

Heat production of skeletal muscle in arrested lactic acid formation. E. FISCHER (Pflüger's Archiv, 1931, 226, 500—517; Chem. Zentr., 1931, i, 3698—3699).—The quotient initial heat/(tension \times length of muscle) is unchanged by poisoning with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$. The poisoned muscle shows under aerobic conditions the same heat production as a normal muscle under anaerobic conditions.

A. A. ELDRIDGE.

Oxidation of lactic acid by brain-tissue. C. A. ASHFORD and E. G. HOLMES (Biochem. J., 1931, 25, 2028—2049; cf. A., 1930, 1312).—A Meyerhof quotient can be obtained, but no carbohydrate synthesis takes place when brain-tissue is shaken with lactate in the presence of a hydrogen carbonate buffer in an $\text{O}_2\text{-CO}_2$ atm. The O_2 uptake is greater in the presence of a CO_2 -hydrogen carbonate buffer than in the presence of phosphate and increases with increased O_2 tension in both cases. The R.Q. both of the brain-

tissue alone and of the "extra O_2 " are close to unity even in the case of animals rendered hypoglycemic by insulin injection. Glucose, lactate, succinate, and glycerophosphate act with brain-tissue as H_2 donors to methylene-blue. Glycerol and dihydroxyacetone are without effect on the reduction time; formate, acetate, and mandelate prolong it. "Extra O_2 " gives a true measure of lactic acid oxidised. Volatile acid or any substance capable of binding hydrogen sulphite is not formed from lactic acid in presence of brain-tissue. There is a small increase in inorg. and in total P at the expense of org. P both in presence and in absence of lactate. There is no synthesis of any P compound from the fraction of lactic acid which disappears and is not accounted for by oxidation.

S. S. ZILVA.

Importance of bile acids in carbohydrate metabolism. X. Influence of bile acids and phosphates on sugar assimilation. S. FUJITA (J. Biochem., Japan, 1931, 13, 219—236).—The formation of glycogen in the rabbit's liver is stimulated by oral administration of Na_2HPO_4 (0.5 g. per kg.) or cholic acid. Glycogen formation from glucose, mannose, and galactose is, however, thereby diminished (except with glucose and very small quantities of Na_2HPO_4).

CHEMICAL ABSTRACTS.

Action of adrenaline and the mechanism of glycogen mobilisation in the isolated frog's liver. E. GEIGER (Biochem. Z., 1931, 243, 160—174).—Perfusion of frog's liver with isotonic Ringer's solution is accompanied with absorption of H_2O by the liver. Addition of adrenaline to the perfusion fluid inhibits absorption of H_2O and leads to a loss of it by the liver. Adrenaline does not constrict the vessels of the perfused frog's liver and the loss cannot be explained in terms of vaso-constriction. The loss of H_2O is also obtained in glycogen-free livers of hibernating frogs and cannot be the result of decomp. of glycogen. It does not appear to be caused by alteration in permeability, but is most probably the result of contraction of cell-colloids, which can be inhibited by ergotamine. Histamine, which brings about mobilisation of glycogen, also leads to a loss of H_2O by the liver, a loss inhibited by ergotamine. CaCl_2 and Na_2SO_4 added to the Ringer's solution cause a mobilisation of glycogen and a loss of H_2O by the liver. A causal relationship exists between contraction of cell-colloids and glycogen mobilisation, the cell-enzyme system being brought into action by contraction.

P. W. CLUTTERBUCK.

Relationship of fat and carbohydrate degradation in the liver. Biological oxidation-reduction potentials. J. KÜHNAU (Biochem. Z., 1931, 243, 14—50).—The oxidation-reduction potential and the glutathione content of the liver is followed with normal rabbits and rabbits in experimental ketosis. Both in phloridzin and P ketosis, the potential with max. excretion of ketone substances is considerably displaced to the positive side, the reduced and total glutathione contents are decreased, and the oxidised glutathione content is increased. After injection of dihydroxyacetone, the potential of the liver in phloridzin ketosis returns rapidly to negative vals., the total and reduced glutathione contents increase,

but the abs. amount of oxidised glutathione decreases only slightly. The liver is therefore able to form reduced glutathione from an unknown precursor. In P ketosis, the potential and the total glutathione content of the liver are not affected by injection of dihydroxyacetone. The bearing of the results on fat and carbohydrate metabolism is discussed.

P. W. CLUTTERBUCK.

Body-fats of the pig. I. Influence of ingested fat on the component fatty acids. R. BHATTACHARYA and T. P. HILDITCH (Biochem. J., 1931, 25, 1954—1964).—There is a general relationship of the various fatty acids of the pig body-fats to those of tallows (A., 1931, 757). The composition of the outer layer of back fat which is most unsaturated differs from that of the inner layer, the latter being intermediate in type between the former and the perinephric fat, which it resembles more closely. The differences are much reduced when the diet of the animals includes arachis oil. Body-fats from pigs which consume the relatively saturated shea butter are not greatly different from those of the animal fed on the control ration. The consumption of arachis oil leads to an increase of unsaturation in the stored fat and also increases the proportion of linoleic acid in the unsaturated acids. Much of the normal fat of the pig must be derived from carbohydrate or other non-fatty part of the ration. S. S. ZILVA.

Do peanut- or arachis nut-fed hogs yield lards containing arachidic acid? A. H. GILL and G. T. VAALA (Science, 1931, 74, 548).—Saponification followed by methylation of lard obtained from hogs fed on peanuts gave no evidence of Me arachidate; palmitic and stearic acids only were indicated.

L. S. THEOBALD.

New contributions in sterol metabolism. R. SCHOENHEIMER (Science, 1931, 74, 579—584).—A lecture.

L. S. THEOBALD.

Animal ergosterol synthesis. G. BISCHOFF (Klin. Woch., 1931, 10, 455; Chem. Zentr., 1931, i, 2497).—During the hatching of hen's eggs the hydrogenated sterol constituent (dihydrocholesterol) increases from 3.2 to 9.1%. Contrary to Schonheimer, a simultaneous dehydrogenation of other sterol constituents was not observed. The ergosterol content in hen's eggs amounts to approx. 0.17% of the substances pptd. by digitonin. During hatching the total sterol increases to approx. 5%.

L. S. THEOBALD.

Urinary excretion of ketonic substances during starvation in various species of animals. E. F. TERROINE and H. TRIMBACH (Compt. rend., 1931, 193, 1345—1347).—A diminution in ketonuria occurs during starvation following a milk diet in the pig, rabbit, dog, cat, and rat. In the pig alone there is an increase in $\text{COMe}_2 + \text{CH}_2\text{Ac} \cdot \text{CO}_2\text{H}$ during inanition, but this is more than compensated by the decrease in β -hydroxybutyric acid. No parallelism exists between the N-excretion and the ketonuria during the period of starvation. F. O. HOWITT.

Parenteral denaturation of foreign proteins. V. Effect of starvation. T. H. BOONE (J. Immunol., 1931, 21, 139—140).

CHEMICAL ABSTRACTS.

Nutritive value for growing swine of the proteins of linseed meal and of cottonseed meal both alone and in combination with the proteins of maize. H. H. MITCHELL (J. Agric. Res., 1931, 43, 743—748).—The true digestibility of cottonseed proteins is 83%, that of linseed proteins 94%, and that of maize proteins 91%. The combinations of cottonseed and maize proteins and of linseed and maize proteins give average coeffs. of 86% and 92%, respectively. The biological vals. of all three proteins are almost identical at 61—63%. The pig appears to utilise maize proteins as efficiently as the rat, but cottonseed and linseed proteins less efficiently.

W. G. EGGLETON.

Nitrogen balance in the white rat on a diet of ovalbumin and fat or of ovalbumin and carbohydrate. F. MAIGNON and M. A. CHAHINE (Compt. rend., 1931, 193, 1474—1476).—White rats fed on a diet of ovalbumin supplemented by either fat or carbohydrate of approx. equal calorific val. show the smaller loss of N and better utilisation of the protein with the fat than with the carbohydrate when these are administered in relatively small quantities. With larger relative amounts of fat or carbohydrate, these may exert approx. equal effects or the carbohydrate may even be more active than the fat.

W. O. KERMACK.

Role of non-essential amino-acids in partly covering the specific endogenous nitrogen loss. MEZINCESCO (Compt. rend., 1931, 193, 1469—1471).—The administration of non-essential NH_2 -acids (glycine, alanine, aspartic or glutamic acid) to pigs on a purely carbohydrate diet decreases the negative N balance, the extent of the decrease (25—30%) being of the same order as that obtained with NH_4 citrate. The effect of the acids appears therefore to depend solely on the NH_2 -group as such. The administration of these acids is without definite effect on the excretion of total and neutral S or of creatinine.

W. O. KERMACK.

Amino-acid metabolism. I. Relative rates of amino-acid disappearance and urea formation. V. C. KIECH and J. M. LUCK (J. Biol. Chem., 1931, 94, 433—449).— NH_2 -acid metabolism has been studied by analysis of whole bodies and excreta of rats. The high NH_2 -N content of rats immediately after injection of *DL*-alanine soon decreases to the normal val., but only about 50% of the N is recovered as urea. Following injection of glycine and *L*-aspartic acid a 6—8 hr. lag in formation of urea is observed, which is followed by a period in which urea formation exceeds that possible from deamination. 3—4 hr. after injection of *L*-aspartic acid the decrease in NH_2 -N is replaced by an increase, due to protein hydrolysis stimulated by the NH_2 -acid. Glycine administered *per os* is metabolised without lag in urea formation, and no endogenous-protein hydrolysis occurs. The results are explained by the formation of intermediate N compounds.

A. COHEN.

Behaviour of heterocyclic compounds in the frog. K. KUSUI (J. Biochem., Japan, 1931, 13, 343—350).—The frog excretes nicotinic acid partly unchanged. It converts to a slight extent ingested quinoline and isoquinoline into Me compounds, and

oxidises a small amount of 2-methylquinoline to quinaldinic acid. Quinoline-2-carboxylic acid behaves differently from picolinic acid in not being conjugated with glycine, but appearing in the urine largely unchanged. Although 2-dihydroxypropylquinoline is readily oxidised *in vitro* to quinaldinic acid, this transformation does not occur in the frog.

CHEMICAL ABSTRACTS.

Acid-base balance in animal nutrition. IV. Effect of long-continued ingestion of acid on reproduction in swine, rats, and rabbits. A. R. LAMB and J. M. EVVARD (J. Biol. Chem., 1931, 94, 415—422).—Three generations of swine were reared in 3·5 years on a normal diet to which were added 200—300 c.c. of $N\text{-H}_2\text{SO}_4$ daily without impairing growth, health, or reproductive ability. No abnormal composition of bone resulted. Similar results were obtained with rats receiving acid salts equiv. to 1·5—2·0 c.c. of $N\text{-acid}$ daily. Rabbits reproduce successfully if the daily balance of acid received is not greater than 5 c.c. (N). Higher doses are fatal. The acid is mainly excreted as acid phosphate, the rabbit showing less ability than swine or rats to neutralise acid with NH_3 .

A. COHEN.

Magnesium absorption in dogs and its effect on the metabolism of calcium. H. G. BARBOUR and J. E. WINTER (J. Pharm. Exp. Ther., 1931, 43, 607—620).—The administration to dogs of equal quantities of Mg oxide, lactate, or gluconate produces apparently equal increases in the Mg content of the serum and has practically no effect on the Ca content. When account is taken of the Mg content of the three compounds, it follows that Mg gluconate is most readily absorbed and MgO least. When large doses of Mg lactate or gluconate are administered over a long period no loss of Ca occurs provided that the P_2O_5 intake is adequate. If the P_2O_5 intake exceeds 4 millimol. per kg. per day, extra Ca is retained.

W. O. KERMACK.

Calcium and phosphorus metabolism. XII. Effect of ingestion of acid-producing substances. R. F. FARQUHARSON, W. T. SALTER, D. M. TIBBETTS, and J. C. AUB. **XIII. Effect of ingestion of phosphates on the excretion of calcium.** R. F. FARQUHARSON, W. T. SALTER, and J. C. AUB. **XVIII. Temporary fluctuations in the level of calcium and inorganic phosphorus in blood-serum of normal individuals.** R. F. FARQUHARSON and D. M. TIBBETTS (J. Clin. Invest., 1931, 10, 221—249, 251—269, 271—286).—**XII.** Excretion of Ca varied with the total excess acid eliminated and especially with the output of NH_3 . The quant. increase in Ca excretion from acid ingestion was influenced by the basal level of Ca excretion as well as by the amount of excess acid ingested. Alkali has little effect on Ca excretion. Faecal Ca remained const. even with great changes in the acidity of the diet.

XIII. Great variation in P did not appreciably affect urinary or faecal Ca. A high-protein diet, the acidosis being controlled by NaHCO_3 , was without effect. NaH_2PO_4 produced a rise in urinary acidity, but had no effect on excretion of NH_3 or Ca.

XVIII. The normal fasting vals. of serum-Ca and

-P change little over long periods. Large amounts of carbohydrates cause a fall in serum-inorg. P, and sometimes an increase in Ca.

CHEMICAL ABSTRACTS.

Effect of iodoprotein decomposition products on processes of development and regeneration. W. BRANDT, H. MATTIS, and E. NOLTE (Biochem. Z., 1931, 243, 369—379; cf. A., 1931, 1463).—Six fractions obtained by hydrolysis of the iodoprotein accelerate development of tadpoles and newts. The most active fraction produces metamorphosis in tadpoles in 8 days and in newts in 12—14 days, and in its action is exactly similar to active thyroid preps. The growth before metamorphosis and the intensity with which amputated parts are regenerated are not accelerated to the same extent as is metamorphosis itself.

W. MCCARTNEY.

Contraction of rectus abdominis muscle of frogs caused by acetylcholine. R. MIURA (Arch. exp. Path. Pharm., 1931, 163, 553—561).—Acetylcholine (1:50,000—100,000) induces a strong and persistent contraction in the rectus muscle, but has only a weak action in the sartorius; in no instance was there an increase in the lactic acid level. Higher concns. (1:1000) impair the excitability and increase the lactic acid content in both muscles to the same extent as occurs with tetanising stimulation, which also causes a marked decrease in phosphagen content, a phenomenon not exhibited by acetylcholine (1:50,000). Hence fundamental differences exist between contraction due to acetylcholine and that due to tetanisation.

F. O. HOWITT.

Reflex-hyperlipæmia. Y. D. KOSKOFF and J. G. D. DE BARENNE (Science, 1931, 74, 550).—Reflex-hyperlipæmia generally occurs when the sciatic nerve of cats is electrically stimulated; the increase in blood-fat is abrupt, since it is present in the blood drawn immediately after afferent stimulation.

L. S. THEOBALD.

Influence of denervation on sympathomimetic action. T. MASAYAMA (Arch. exp. Path. Pharm., 1931, 163, 562—582).—The changes in glycogen and phosphagen levels in the tibialis muscle of the rabbit were investigated during (a) denervation by section of the corresponding ischiadicus, (b) curarisation, (c) treatment with adrenaline, caffeine, and tetrahydro- β -naphthylamine before and after denervation, (d) treatment with adrenaline and caffeine in curarised muscle, and (e) administration of picrotoxin, ergotamine, and insulin in normal muscle. The results are discussed with reference to the nervous control of the "chemical tonus" of muscle. Thus the correlation existing between glycogen and phosphagen metabolism is dependent on that between the sympathetic and central motor nervous control.

F. O. HOWITT.

Effect of naphthalene on the tissue oxidation of the lens [of the eye]. D. MICHAEL and P. VANCEA (Compt. rend. Soc. Biol., 1930, 105, 59—60; Chem. Zentr., 1931, ii, 83).

Appearance of a reducing substance in the urine after administration of ethyl urethane. E. ZUNZ (Arch. Int. Pharmacodyn. Ther., 1930, 38,

359—362; Chem. Zentr., 1931, ii, 261).—Different animal species react differently as regards the appearance of a reducing substance of unknown composition; also different samples of Et urethane differ in their power to generate the substance.

A. A. ELDRIDGE.

Effect of narcosis on the blood-lactic acid. I. H. SCHMIDT and E. SCHMUTZLER (Schmerz, Narkose, Anæsth., 1930, 3, 309—325; Chem. Zentr., 1931, ii, 82).—With frog's muscle, Et₂O or CHCl₃ does not inhibit the resynthesis of lactic acid to hexosephosphoric acid, but rather promotes it. Clinical increase in blood-lactic acid is attributed to liver injury. After N₂O the increase in blood-lactic acid is less than after Et₂O.

A. A. ELDRIDGE.

Lactic acid metabolism. I. Blood-lactic acid in narcosis. Pharmacology of "pernocton." F. MATAKAS (Arch. exp. Path. Pharm., 1931, 163, 493—504).—"Pernocton" injected into various species of animals results in unchanged levels of blood-lactic acid and -sugar, whilst Et₂O or urethane produces a rise. The increase in blood-lactic acid due to Et₂O narcosis is a secondary action due to inhibition of oxidation and increase in lactic acid formation by striated muscle and not to any influence on the respiratory centres.

F. O. HOWITT.

Influence of narcotics on sugar-excretion threshold. Y. IWANAGA (J. Biochem., Japan, 1931, 13, 351—368).—Morphine produces hyperglycæmia and glycosuria in the dog, lowering the sugar excretion threshold, but only when large doses are given. When the threshold is raised by adrenaline the effect of morphine is very marked. CHCl₃ and Et₂O narcosis produce hyperglycæmia and lower the sugar-excretion threshold, especially in dogs treated with adrenaline. EtOH does not affect the blood-sugar level, and lowers the sugar threshold less than other narcotics. Morphine, CHCl₃, and Et₂O markedly reduce the sugar threshold abnormally increased by acetylcholine.

CHEMICAL ABSTRACTS.

Action of some hypnotics on methylene-blue decolorisation. K. BEHNECKE (Arch. exp. Path. Pharm., 1931, 163, 594—601).—Urethane, "voluntal," and "adaline" inhibit, whilst veronal accelerates the decolorisation of methylene-blue by muscle incubated in PO₄ buffer with hexose- or glycerophosphoric or succinic acid as donator. Veronal, however, inhibits the O₂-consumption by such a system and hence behaves in a manner similar to that of PhMe or HCN.

F. O. HOWITT.

New hypnotic, ethyl-β-ethylbutylbarbituric acid, and some derivatives of β-ethylbutyl alcohol. E. FOURNEAU and J. MATIL.—See this vol., 142.

Hypnotic action of ethyl-β-ethylbutylbarbituric acid ("Fourneau 769") on the rat. D. BOVER (J. Pharm. Chim., 1931, [viii], 14, 523—527).—The compound is 8.2 times as active as veronal on the rat, and dos. tol./dos. cur.=72/28; it is 3 times as active as veronal on mice.

R. S. CAHN.

Metabolic action of cutaneously applied camphor and related substances. M. TENNENBAUM (Arch. exp. Path. Pharm., 1931, 163, 505—516).—

A decrease in blood-sugar level is produced in rabbits by injection of olive oil solutions of camphor, turpentine oil, and to a smaller extent of borneol or menthol. The effect commences ½ hr. after treatment, reaches a max. in 5 hr., and then decreases. No correlation between chemical constitution of the compounds and hypoglycæmic action could be deduced.

F. O. HOWITT.

Animal calorimetry. XLI. Influence of phloridzin glycosuria on the metabolism of dogs after thyroidectomy. M. DANN, W. H. CHAMBERS, and G. LUSK [with J. EVENDEN] (J. Biol. Chem., 1931, 94, 511—527).—Thyroidectomy in dogs tends to inhibit the increase in heat production and also in protein metabolism following administration of phloridzin. With one prep. of phloridzin the "extra sugar," which could be accounted for by the glycogen reserves and did not arise from metabolism of fat as indicated by the R.Q., was only gradually eliminated. In this instance the D:N ratios were high, whereas with another prep. of phloridzin the ratios were lower and the delayed elimination of extra glucose was not apparent.

F. O. HOWITT.

Effect of cholic acid on excretion of creatinine under the influence of vegetative nervous system poisons. A. TAKU (J. Biochem., Japan, 1931, 13, 237—254).—Tetrahydro-β-naphthylamine, caffeine, atropine, and CaCl₂, but not pilocarpine, increase the creatinine excretion of the rabbit. The action is inhibited by simultaneous administration of cholic acid.

CHEMICAL ABSTRACTS.

Distribution of quinine in the organism. A. A. KIRSTNER and M. M. PANTSCHENKOV (Arch. Schiffs- u. Tropen-Hyg., 1931, 35, 286—297; Chem. Zentr., 1931, ii, 266).—In rabbits treated with quinine the highest concn. was present in the brain, followed by the lungs; moderate quantities were found in the liver, but relatively little in the blood and spleen. The quantity in human blood after 6 hr. was 1% of the dose. The max. quinine concn. is found after 3 hr.; the red corpuscles contain three times as much as the plasma.

A. A. ELDRIDGE.

Colloid chemistry of the nervous systems. III. Histamine. W. D. BANCROFT and J. E. RUTZLER, jun. (J. Physical Chem., 1931, 35, 3189—3206; cf. A., 1931, 1454).—The superior cervical ganglia of rabbits are peptised by NaCNS and reversibly agglomerated by histamine. In presence of lipins, histamine may appear to cause swelling of the nervous tissue, but is more probably being dissolved by the lipins. CHCl₃ dissolves in the lipins of the cerebral cortex, but does not peptise the proteins. *In vivo* ephedrine and NaCNS antagonise histamine. Pre-treatment with NaCNS counteracts skin reactions to histamine and giant ragweed pollen extract. Reversible agglomeration of protein colloids is probably responsible for skin reactions, since histamine, CaCl₂, lactic acid, and morphine behave similarly.

C. T. SNELL (c).

Reversible coagulation in living tissue. VIII. W. D. BANCROFT and J. E. RUTZLER, jun. (Proc. Nat. Acad. Sci., 1931, 17, 597—601; cf. A., 1931, 1328).—Bulbocapnine is an agglomerating agent, as shown

by an improvement after its administration in a case of human dementia præcox, and by its induction of catatonia and catalepsy in rabbits. In rabbits NaCNS and ephedrine sulphate relieve bulboapnine catatonia on account of their peptising action, whilst Na amytal aggravates this condition on account of its agglomerating action.

N. H. HARTSHORNE.

Reversible coagulation in living tissue. IX. W. D. BANCROFT, R. S. GUTSELL, and J. E. RUTZLER, jun. (Proc. Nat. Acad. Sci., 1931, 17, 637—642; cf. A., 1931, 513, 649, 872, 1088).—NaCNS by its peptising action of the tissue colloids coagulated by morphine addiction removes or alleviates the withdrawal symptoms when the drug is suddenly withdrawn from addicted dogs. The use of NaCNS for human addicts is advocated.

F. O. HOWITT.

Taste deficiency for creatine. R. J. WILLIAMS (Science, 1931, 74, 597—598).—Creatine is tasteless to certain individuals.

L. S. THEOBALD.

Curariform action of quaternary ammonium salts. H. R. ING and W. M. WRIGHT (Proc. Roy. Soc., 1931, B, 109, 337—353).—The time of diffusion of quaternary NH_4 salts into isolated frogs' gastrocnemii is appreciable in comparison with the time of poisoning. In isolated sartorii the diffusion period is negligible. Methyl-, *n*-amyl-, hexyl-, heptyl-, and octyl-trimethylammonium iodides are equal in curariform action on the isolated sartorius. *n*-Propyl-, ethyl-, and dodecyl-trimethylammonium iodides are progressively less active. The Ph Me_3 , $\text{Ph CH}_2\text{Ph Me}_2$, and Me_4 derivatives are equally active. Replacement of Me by Et in the last-named lowers the activity rapidly, the MeEt_3 and Et_4 derivatives causing initial increases in the response of sartorii to indirect stimulation. Slight activity is shown by NMe_3 and NPhMeEt oxides. Paralyzed sartorii recover slowly in NMe_3I solution. For the latter drug a temp. coeff. of 1.5 per 10° at 23.5 — 13.5° and 13.5 — 3.5° is found for the rate of poisoning. Curariform action may be due to ionic exchange of the permittit type between the drug and the affected muscle system.

A. COHEN.

Effects on albino rats of nutrition solely with seeds of *Lathyrus sativus*, L. V. ZAGAMI (Atti R. Accad. Lincei, 1931, [vi], 14, 218—221).—These seeds form an incomplete or qualitatively deficient food for growing rats. Although nervous or motor phenomena related to those described as lathyrism are not observed, young rats fed solely on these seeds show diminished resistance, torpor, and slow growth, especially of the genital organs and skeleton.

T. H. POPE.

Assimilation of aluminium by the human system. S. J. LEWIS (Biochem. J., 1931, 25, 2162—2167).—Normal blood usually contains no Al and when it does the proportion is very small. A considerable quantity of Al is found in the blood after one meal of food containing Al. Similar observations apply to milk.

S. S. ZILVA.

[Physiological] action of calcium. I. Effect of intravenous injections of calcium salts on the heart in cattle having diseased mineral metabolism. Dependence of action of calcium on the

heart on mineral composition of the blood-serum. L. SEEKLES, B. SJOLLEMA, and F. C. VAN DER KAAAY (Biochem. Z., 1931, 243, 316—329; A., 1931, 383).—In parturient paresis and grass staggers in cattle injections of CaCl_2 produce fundamentally the same effects on the heart, viz., alterations in the frequency, which is sometimes greatly increased, with blocking, during and soon after the injection. The effect on the heart in parturient paresis is dependent on the mineral composition of the blood before injection; if the serum is low in Ca and high in P there is predisposition to dangerous changes in frequency, whilst, on the other hand, high Ca and low P lead to harmless changes. In grass staggers there is no connexion between the mineral composition of the blood and the effect of the injection; the effect of this composition on the heart in this disease is due to other influences and to greatly increased sensitivity. It is concluded that the occurrence of heart block and systolic arrest in parturient paresis could be prevented by injections of mixtures, in suitable proportion, of CaCl_2 and MgCl_2 .

W. MCCARTNEY.

Blood-calcium following intravenous injection of calcium salts. G. D. GREVILLE (Biochem. J., 1931, 25, 1931—1942).—The rate of fall of serum-Ca at any time greater than 5 min. after the intravenous injection of CaCl_2 and of Ca laevulate into cabbage-fed rabbits is approx. proportional to the excess at that time of the serum-Ca above the final const. level. There is a large disappearance of serum-Ca during the first 5 min. not accounted for by this relationship. Serum-Ca as determined by direct pptn. gives an accurate measure of the Ca content of the blood following the intravenous injection of Ca laevulate.

S. S. ZILVA.

Bismuth derivative of sodium β -hydroxy- γ -thiolpropanesulphonate. A. LEULIER and M. JUVIN (J. Pharm. Chim., 1931, [viii], 14, 527—531).—The Bi salt of Na β -hydroxy- γ -thiolpropanesulphonate, injected into guinea-pigs, is excreted in the urine and faeces, but some is deposited in various organs, notably the liver and kidney.

R. S. CAHN.

Toxicological practice. W. AUSTEN (Pharm. Zentr., 1931, 72, 385—388).—In a case of Hg poisoning Hg was determined as HgS . On addition of Br water to the steam-distillate of portions of the intestine from a case of lysol poisoning a turbidity was obtained; none was obtained in the distillates from the kidney, urine, or liver. It was not possible to demonstrate the individuality of the Br ppt. In a case of As poisoning As was conc. in the stomach, but was present also in the intestines and the liver.

C. C. N. VASS.

Hydrases. Mechanism of the action of and the specificity of fumarase. K. P. JACOBSON (Biochem. Z., 1931, 243, 1—13).—Fumarase does not add the elements of H_2O to methylfumaric acid. This is not due to toxicity, since when mixtures of methylfumaric and fumaric acids are used, the former is unaffected, whereas the latter is converted into *l*-malic acid. The mechanism of fumarase action is discussed.

P. W. CLUTTERBUCK.

Activation of oxido-reductions by cozymase. H. VON EULER and R. NILSSON (Biochem. J., 1931,

25, 2168—2171).—Phosphate is not required for aldehyde transformation when catalysed by dialysed liver-juice and purified cozymase. The transformation in dialysed liver-juice is increased by the addition of hexosediphosphate or of phosphate. Both in the presence and in the absence of hexosediphosphate cozymase is indispensable for the transformation of MeCHO by liver-juice. S. S. ZILVA.

Enzymic amylolysis. I. Capability for enzymic fission of amylo- and erythro-substances from starch. M. SAMEC and E. WALDSCHMIDT-LEITZ (Z. physiol. Chem., 1931, 203, 16—33).—The action of pancreatic, malt-, and barley-amylases on amylo- and erythro-amyloses from potato-starch was compared. Amylo-amyloses are completely hydrolysed by all the enzymes, which differ, however, in their rate and manner of action as shown by the I colour reaction. In pancreatic fission of the erythro-amyloses a partial breakdown product remains which is resistant to further hydrolysis.

J. H. BIRKINSHAW.

Influence of proteins and protein derivatives on the enzymic hydrolysis of starch by malt-diaxase. B. FILIPOWICZ (Biochem. J., 1931, 25, 1874—1884).—EtOH retards at p_H 5.6 hydrolysis of starch or dextrin by malt-diaxase to an extent proportional to the concn. of EtOH. The percentage of retardation is greater the more the p_H of the system exceeds 4.5, the optimal p_H in the presence or absence of EtOH. The activity of 20% EtOH amylose solutions is greater than that of similar solutions not containing EtOH after keeping up to 48 hr. Ovalbumin, gelatin, peptone, glycine, and aspartic acid retard at p_H below and accelerate at p_H higher than 4.5 to an extent increasing with the alkalinity of the medium. In the case of glycine the relative acceleration is greater the higher is the temp. Carboxylic acids and amines retard the reaction.

S. S. ZILVA.

Hydrolysis of concentrated sugar solutions by invertase. H. A. AUDEN and E. R. DAWSON (Biochem. J., 1931, 25, 1909—1916).—The rate of hydrolysis by invertase of solutions containing 40% or more of sucrose decreases as the substrate concn. increases, the relation between substrate concn. and invertase activity being linear. The optimum temp. for the hydrolysis of 70% sucrose in the presence of invertase is 65—70°. The relation between the crit. increment in g.-cal. per mol. and the temp. for the hydrolysis of 70% sucrose by invertase can be expressed by $E=20,500-168t$. S. S. ZILVA.

Relationships between structure of saturated aliphatic alcohols and their inhibiting effect on liver-esterase. D. GLICK and C. G. KING (J. Biol. Chem., 1931, 94, 497—505).—The inhibitions of sheep liver-esterase acting on Et butyrate by n -primary alcohols increase rapidly as the series is ascended. Those of the 7 isomerides of amyl alcohol decrease as the steric hindrance about the OH group increases. With secondary alcohols the effect of steric hindrance is eclipsed by that of the length of the hydrocarbon chain. Other aspects of the inhibitory power of these alcohols are discussed. F. O. HOWITT.

Distribution of phosphatase in the tissues of teleosts and elasmobranchs. O. BODANSKY, R. M. BAKWIN, and H. BAKWIN (J. Biol. Chem., 1931, 94, 551—560).—Phosphatase occurs both in the cartilaginous skeleton of the elasmobranch and, to a greater extent, in the bony skeleton of the teleost. Hence an assumption of a necessary association between presence of the enzyme and the occurrence of ossification (cf. A., 1923, i, 730; 1925, i, 201; 1929, 1197; 1931, 258) is not justified.

F. O. HOWITT.

Does bodily effort give rise to defence enzymes specific for substrates prepared from incretion organs? S. BUADZE (Fermentforsch., 1931, 13, 126—127).—Severe exercise produced no effect.

J. H. BIRKINSHAW.

Latent period in autolysis. A. NEUBERGER and H. REINWEIN (Biochem. Z., 1931, 243, 225—235).—By addition of phosphate, pyrophosphate, hexosediphosphate, and lactate to rats' liver-pulp, autolysis sets in immediately, hexosediphosphate having the strongest action. NaCl, KCl, NaF, and Na_2SO_4 have no effect on the latent period. Acetate, citrate, and glycerophosphate have slight and irregular accelerating action. Adjusting the p_H of the autolysate to 5 also causes autolysis to set in immediately.

P. W. CLUTTERBUCK.

Latent period of autolysis with [tissues of] fasting animals. A. NEUBERGER (Biochem. Z., 1931, 243, 236—240).—With liver of fasting animals, the latent period is usually shorter, and addition of acetate and citrate accelerates the autolytic process more strongly than with normal tissue. Phosphate addition accelerates autolysis as in the experiments with normal animals.

P. W. CLUTTERBUCK.

Enzymic synthesis of proteins with special reference to the action of pepsin. D. P. CUTHBERTSON and S. L. TOMSETT (Biochem. J., 1931, 25, 2004—2013).—The optimum $[H^+]$ for the synthesis of plastein from conc. digests of egg- and serum-albumin and from caseinogen incubated at 37° is p_H 4. The formation from the first two sources increases with rise of temp., reaching a max. at 70°. Increase in the concn. of enzyme increases plastein formation in conc. peptic digests of egg- and serum-albumin. The ratio of the decrease in the NH_2 and CO_2H groups in the process of formation from egg- and serum-albumin and caseinogen is 1:1. There is no appreciable liberation of NH_3 . The longer a protein is allowed to digest the less is the yield. Better yields are obtained from egg- and serum-albumin than from caseinogen. Plastein is not obtained from the products of digestion of gelatin.

S. S. ZILVA.

Nature of proteases. X. Determination of the optimum temperature for the digestion of egg-albumin by frog-pepsin at p_H 1.6—1.9. N. P. PLATNITZKI (Z. physiol. Chem., 1931, 203, 10—15; cf. A., 1931, 1191).—The activity of frog's gastric juice increases with rising temp. to a max. at 45—50°; it is destroyed when the juice is heated to 65° for $\frac{1}{2}$ hr. Frog and human pepsins show no substantial differences in behaviour.

J. H. BIRKINSHAW.

Nature of proteases. X. Relations between activity of pepsin preparations and viscosity of the digestion mixtures. I. A. SMORONINCEV and A. N. ADOVA (Fermentforsch., 1931, 13, 36—46; cf. A., 1931, 1191).—The changes in viscosity of gelatin solutions under the action of pepsin at 38° reach a limit in 3 hr. The fall in viscosity indicates the strength of the prep. In digestion of caseinogen, active preps. are distinguished by the fact that the viscosity rises gradually to a max. in 3 hr. The viscosity of 1% enzyme solutions is independent of the activity.

J. H. BIRKINSHAW.

Homogeneity of trypsin solutions prepared by the method of Waldschmidt-Leitz. II. E. ABDERHALDEN and E. VON EHRENEWALL (Fermentforsch., 1931, 13, 47—51; cf. A., 1931, 766).—A trypsin solution originally inactive to *dl*-leucylglycine developed ereptic power after contact with glycerol at 37°. After removal of erepsin by adsorption on $\text{Al}(\text{OH})_3$, ereptic power again developed. After repeating the adsorption, no ereptic action was observed on keeping, but it was evoked by the addition of glycine.

J. H. BIRKINSHAW.

Behaviour of polypeptides composed of *l*(+)-alanine towards dilute alkali and enzymes. E. ABDERHALDEN and W. GOHDES (Fermentforsch., 1931, 13, 52—63).—The following polypeptides (and precursors) were obtained from *l*(+)-alanine etc. and *d*(+)- α -bromopropionyl chloride [from *d*(-)-alanine, $[\alpha]_D^{20} -14.1^\circ$ (*d*-methylencampor-*d*-alanine *Et* ester, m. p. 108—109°, $[\alpha]_D^{20} +250^\circ$); *l*-alanyl-*l*-alanine, m. p. 297° (decomp.), $[\alpha]_D^{20} -21.6^\circ$; *di*-*l*-alanyl-*l*-alanine (+ $\frac{1}{2}\text{H}_2\text{O}$), decomp. 250—253°, $[\alpha]_D^{20} -72.2^\circ$ (*Br*-precursor, decomp. 193—195°, $[\alpha]_D^{20} -47.2^\circ$ in *N*-NaOH); *tri*-*l*-alanyl-*l*-alanine (+ H_2O), decomp. 269—272°, $[\alpha]_D^{20} -120.5^\circ$ (*Br*-precursor, decomp. 243—245°); *tetra*-*l*-alanyl-*l*-alanine (+ H_2O), decomp. above 275°, $[\alpha]_D^{20} -136.4^\circ$ (*Br*-precursor, decomp. 260—261°); *penta*-*l*-alanyl-*l*-alanine (+ H_2O), colloidal, decomp. above 278° (*Br*-precursor, decomp. 269—272°). *N*-NaOH hydrolysed the polypeptides more rapidly as mol. wt. increased. Gastric juice did not attack any of the polypeptides, trypsin-kinase hydrolysed the tetrapeptide most readily, and also attacked the penta- but not the di-peptide. Erepsin attacked all the polypeptides.

J. H. BIRKINSHAW.

Behaviour of hydroxyacylamino-acids or polypeptides towards enzymes. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1931, 13, 128—136).—By boiling the corresponding *Br*-compounds with H_2O and pyridine the following were prepared: *dl*- α -hydroxyisohexoylglycine, m. p. 108—109°, *dl*- α -hydroxyisohexoylglycylglycine, *dl*- α -hydroxyisohexoyl-*dl*-leucylglycylglycine, m. p. about 140°. α -Bromoacetyl-*dl*-leucine gave the betaine anhydride of acetyl-*dl*-leucylpyridonium hydroxide, m. p. 223—224°, and with NMe_3 the corresponding trimethylammonium hydroxide derivative, m. p. 236—237° [additive compound with acetyl-*dl*-leucinotrimethylammonium bromide (1 mol.), m. p. 222°]. *dl*- α -Bromoisohexoylglycyl-*dl*-leucine gave the betaine anhydride of isohexoylglycyl-*dl*-leucinepyridonium hydroxide, m. p. 206° (decomp.).

J. H. BIRKINSHAW.

Alcoholic fermentation. S. VEIBEL (Dansk Tidsskr. Farm., 1931, 5, 201—218; cf. A., 1931, 1332).—Neuberg's theory of the production of EtOH by fermentation from hexoses is discussed. A mixture of sugar, NaH_2PO_4 , and NaHCO_3 in H_2O was fermented for periods of 4, 8, and 32 hr. After 4 hr. the salt produced is nearly pure hexosemonophosphate, whilst the 8-hr. salt contains 35% and the 32-hr. salt contains 45% of trehalosemonophosphate. The ratio of diphosphate to glucosephosphate increased continuously during the experiment, reaching a val. of 8.7 after 32 hr. The percentages of P present at the close of the 4-, 8-, and 32-hr. periods in combination as inorg. P, trehalosemonophosphate, glucose- and fructose-mono- and -di-phosphate have been determined, and the bearing of the results on the mechanism of phosphorylation is discussed.

H. F. HARWOOD.

Acetoacetic acid and yeast. E. FRIEDMANN (Biochem. Z., 1931, 243, 125—144).—The material extracted by Et_2O from a solution obtained in yeast fermentations in presence of $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$, on methylation with diazomethane and fractionation of the esters, consists of a small fraction, b. p. 40—44°/9 mm., comprising a mixture of the esters of *dl*- and *d*(-)-lactic acid together with a chief fraction, b. p. 64—68.5°/11 mm., which is Me *d*(+)- β -hydroxybutyrate. The same products are obtained with yeast and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ in the absence of sugar. The two samples of Me β -hydroxybutyrate had $[\alpha]_D^{20} +25.48^\circ$ and $+17.12^\circ$, respectively, differing amounts of the *dl*-ester being also present. In fermentations in presence of sugar, the yield of β -hydroxybutyric acid from the rotation is 38% and of ester isolated from 86 to 100% of the $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ added, the difference representing the *dl*-variety. In absence of sugar, the yield of β -hydroxybutyric acid from the rotation is 13 to 17% and from isolation 95% of the $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ added.

P. W. CLUTTERBUCK.

Production of equimolecular amounts of glycerol and pyruvic acid in the cell-free fermentation of glucose. M. LOBEL (Biochem. Z., 1931, 243, 406—415; cf. A., 1931, 393).—In order to cause the decomp. of glucose by cell-free yeast-maceration juice to assume the fourth form of fermentation it is sufficient to add Na_2HPO_4 until the p_H is 6.9 and, when the juice is very active, to delay the start of the experiment. At first the inorg. phosphate of the juice is almost quantitatively converted into org. P compounds. Then hydrolysis of the esters sets in and accumulation of pyruvic acid takes place. Even when the experiment is prolonged about half of the combined PO_4''' remains as such. Glycerol and pyruvic acid are produced in equimol. amounts and at the same time normal conversion of the sugar into CO_2 and EtOH occurs.

W. MCCARTNEY.

Decarboxylation of α -keto-*n*-valeric acid. E. HOFMANN (Biochem. Z., 1931, 243, 429—434).— α -Keto-*n*-valeric acid is rapidly (3 hr.) decarboxylated to the extent of 80% by yeast under the same conditions as is pyruvic acid and the amount of butaldehyde which can be recovered after 7 hr. is 73% of the calc. quantity. Thereafter the amount decreases,

but there is no production of butyrolin. The sulphite compound of the acid is decarboxylated in the same way to the extent of 75% (cf. Dirscherl, A., 1931, 1457). W. McCARTNEY.

Yeast fat. I. G. WEISS (Biochem. Z., 1931, 243, 269—273).—Yeast fat contains *d*-valeric acid (probably a mixture of optically active and inactive acids), a fatty acid, m. p. 88.5°, mol. wt. 379 (probably a C_{24} acid), and (probably) an unsaturated oxidised acid of mol. wt. about 346. Unsaturated OH-acids of high mol. wt. are also present. W. McCARTNEY.

Chemistry of the white rots of wood. II. Effect on wood substance of *Armillaria mellea* (Vahl), Fr., *Polyporus hispidus* (Bull.), Fr., and *Stereum hirsutum*, Fr. W. G. CAMPBELL (Biochem. J., 1931, 25, 2023—2027).—Analytical data of original and of decayed wood are given. In every case there is no marked increase in the total alkali-solubility of the major components of wood substance. In the case of *A. mellea* it is due to the fact that the pentosans not in the cellulose become less sol. in 1% NaOH as decay proceeds. S. S. ZILVA.

Biological decomposition of plant materials. III. Physiological studies of some cellulose-decomposing fungi. A. G. NORMAN (Ann. Appl. Biol., 1930, 17, 575—613; cf. A., 1930, 261; this vol., 93).—The optimum temp. of development of cellulose-decomposing fungi is higher than that usual for fungal growth. The availability of various N and C compounds to the various species is recorded. Pentoses, although readily utilised, are less suitable sources of C than hexoses. CO_2 formation and heat evolution during fermentation are closely parallel. The period of max. heat production corresponds with that of rapid destruction of hemicellulose.

A. G. POLLARD.

Soluble enzymes secreted by *Hymenomyces*. Alcoholic constituents of essential oils and anti-oxidogenic function. L. LUTZ (Compt. rend., 1931, 193, 1220—1221).—The changes produced in a medium containing the alcoholic constituent and methylene-blue on the growth of *Corioliolus versicolor*, *Stereum hirsutum*, and *S. purpureum* are recorded.

C. C. N. VASS.

Biochemistry of micro-organisms. J. J. VAN DE VELDE and A. VERBELEN (Bull. Acad. roy. Belg., 1931, [v], 17, 1262—1273).—The p_H vals. (given in parentheses, the first being that of the original medium) resulting when *Penicillium glaucum*, *Phycomyces nitens*, *Aspergillus niger*, and *Oidium lactis* are grown on carrot (5.30, 7.27, 5.93, 5.80, 7.80), potato (6.46, 7.43, 6.08, 4.48, 7.23), pork (6.58, 8.62, 8.85, 6.68, 7.78), and fish (6.86, 8.42, 7.74, 6.52, 8.44) for 2 months at 25°, have been determined. The proteins, fats, and ash in the dried H_2O -insol. products and the sugars and ash in the dried H_2O -sol. products have been determined in each case. The results indicate that the quant. metabolism of micro-organisms is influenced more by the properties of the medium than by any specificity. J. W. BAKER.

Production of oxalic acid from uronic acids by *Aspergillus niger*. E. HOFMANN (Biochem. Z., 1931, 243, 423—428).—The K salts of *d*-glycuronic,

α -*d*-galacturonic, and tetragalacturonic acids are completely decomposed in 5 weeks by *A. niger*. The only org. acid produced is $H_2C_2O_4$, of which large amounts (up to 20% of the theoretical in the case of galacturonic acid) are obtained. W. McCARTNEY.

Adsorption of potassium by *Penicillium glaucum* in Raulin's solution with increasing quantities of potassium nitrate. BRETIN, P. MANCEAU, and REY (Compt. rend. Soc. Biol., 1931, 106, 197—198; Chem. Zentr., 1931, ii, 257).

Metabolism of sugar, phytosterol, and lecithin in *Penicillium glaucum* grown in Raulin's solution with increasing quantities of potassium nitrate. BRETIN, P. MANCEAU, and COCHET (Compt. rend. Soc. Biol., 1931, 106, 195—196; Chem. Zentr., 1931, ii, 257).—In a medium containing sucrose, tartaric acid, NH_4NO_3 , $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, K_2CO_3 , $MgCO_3$, $MnCO_3$, and $ZnSO_4$, the sugar assimilation and the production of lecithin are retarded, whilst the formation of phytosterol is accelerated, by addition of KNO_3 . When larger quantities of KNO_3 are added the formation of both phytosterol and lecithin is retarded. A. A. ELDRIDGE.

Biochemistry of micro-organisms. XXII. Isolation and characterisation of ergosterol from *Penicillium puberulum*, Bainier, grown on synthetic medium with dextrose as sole source of carbon. J. H. BIRKINSHAW, R. K. CALLOW, and C. F. FISCHMANN (Biochem. J., 1931, 25, 1977—1980).—Ergosterol was isolated. S. S. ZILVA.

Action of certain moulds on solutions of aldoses. II. A. ANGELETTI and C. F. CERUTTI.—See this vol., 145.

Specificity in fermentation. M. SCHOEN (Ann. Inst. Pasteur, 1931, 47, 690—742).—A general discussion of the chemical reactions which take place in the degradation of glucose by micro-organisms.

W. O. KERMACK.

Decomposition of sugars by Lindner's *Thermobacterium mobile*. C. NEUBERG and M. KOBEL (Biochem. Z., 1931, 243, 451—460; cf. Lindner, B., 1931, 776).—The bacterium decarboxylates pyruvic acid, at least 60% of it being converted into $McCHO$ and CO_2 . From glucose by the action of the bacterium 24.4% of the theoretical amount of $McCHO$ is obtained. In the presence of phosphate the dried micro-organism causes phosphorylation of glucose. Mg hexosediphosphate is decomposed with elimination of H_3PO_4 , and fermentation and Ba hexosemonophosphate are dephosphorylated by the bacterium, but glucose is not fermented unless cozymase from yeast is first added. W. McCARTNEY.

Mechanism of the primary attack on hexoses by lactic acid bacteria. I. C. FROMAGEOT and J. ROUX (Biochem. Z., 1931, 243, 175—190).—The early stages of the fermentation of sugars by *B. bulgaricus* are followed in terms of the manometrically determined CO_2 liberated by reaction of the formed lactic acid with $NaHCO_3$. Curves show the rate of fermentation of glucose, mannose, fructose, galactose, and lactose. For all these sugars, the curves show an induction period followed by a period of vigorous fermentation and finally by a period in which the

reaction almost ceases. The ordinates for this third stage are different for the different sugars, but always below the theoretical. The fermentation velocities are in the following order: fructose>mannose>glucose>galactose. Lactose shows a greater induction period, the curve then rising more quickly than with galactose. Fructose has the shortest induction period. In comparing the kinetics of the lactic acid fermentation of glucose and mannose, the same bacterial wt. under the same conditions did not give analogous results. The longer the culture was kept on milk or bouillon, the more did the fermenting power decrease. The smaller was the fermenting power, the less was the power to multiply in bouillon, whereas the power to grow in milk remained normal. The decrease of activity is accompanied with an increase of induction period. Phosphate causes an activation and a decrease of induction period only with bacteria showing decreased activity.

P. W. CLUTTERBUCK.

Bacterial decomposition of glucose ureide. E. HOFMANN (Biochem. Z., 1931, 243, 416—422).—Although many bacteria have no effect on the ureide, manure from hen-runs contains one or two organisms which completely decompose the substance and its constituents. These organisms have not yet been fully characterised. When the decomp. is complete almost all the N of the ureide, about half of it as NH_3 , is found in the culture fluid.

W. MCCARTNEY.

Dismutation of aldehyde and acetic fermentation. E. SIMON (Biochem. Z., 1931, 243, 401—405; cf. Bertho and Basu, A., 1931, 394).—Confirmation of the view that the dismutation can proceed aerobically has been obtained by the author and by Tanaka (this vol., 94).

W. MCCARTNEY.

Relation of urea fermentation to oxidation-reduction potential of the medium. S. I. KUZNETZOV (Trans. Sci. Inst. Fertilisers, Moscow, 1930, No. 76, 128—131).—The fermentation of urea may take place at p_{H} 2.8—0.8, i.e., under aerobic and anaerobic conditions. When N_2 is used instead of H_2 the methods accepted for determining anaerobic conditions gave entirely different results.

CHEMICAL ABSTRACTS.

Liberation of elementary nitrogen by bacteria. N. W. BARRITT (Biochem. J., 1931, 25, 1965—1972).—It is confirmed that N_2 is liberated by soil bacteria during denitrification and that there is no evolution of N_2 from org. compounds under anaerobic conditions in absence of oxidised N nor from oxidised N in absence of oxidisable org. compounds. The reduction of NO_3^- to NO_2^- is effected most rapidly in presence of compounds of low C/N ratio and the formation of N_2 is strictly confined to the reduction of oxidised N provided the reaction of the medium does not fall below p_{H} 6.5. The production of N_2 from org. compounds does not occur by bacterial action, but only indirectly by the interaction between free HNO_2 and NH_2 -compounds, both of which may be produced simultaneously by bacteria. Free HNO_2 is liberated from nitrites by org. acids and H_2CO_3 , but does not effect the decomp. of NH_2 -acids unless the p_{H} of the medium is less than 6.0. The presence

in a culture of readily available carbohydrates may result in a loss of N_2 from org. matter by the indirect process mentioned above. In Kjeldahl determinations of solutions of org. N the presence of NO_2^- results in a loss of $\text{NH}_4\text{-N}$ during the acid digestion. There is no liberation of N_2 by the decomp. of NH_4NO_2 in culture solution at room temp.

S. S. ZILVA.

Effect of certain soil bacteria on the growth of root nodule bacteria. K. KONISHI (Mem. Coll. Agric. Kyoto, 1931, No. 16, 17 pp.).—In soil cultures the development of the root-nodule bacteria associated with lucerne is not inhibited by *B. subtilis*, *B. mycoides*, *B. prodigiosus*, *B. fluorescens*, *B. coli*, *B. megatherium*, and *B. aerogenes*. In liquid cultures *B. coli* and *B. subtilis* exert an inhibitory influence, the last-named not only towards the lucerne bacteria, but also towards those associated with pea and soya bean. The inhibitory influence was less in liquid cultures containing CaCO_3 .

W. G. EGGLETON.

Biological degradation of arginine to citrulline. D. ACKERMANN (Z. physiol. Chem., 1931, 203, 66—69).—Citrulline, m. p. 220—222° (cf. A., 1930, 1224), is formed by the action of putrefactive bacteria on arginine.

J. H. BIRKINSHAW.

Phosphorus distribution in bacterial cultures. II. J. GORDON and K. E. COOPER (Brit. J. Exp. Path., 1931, 12, 234—238).—The org. P present in *B. coli* grown in media free from org. P consists of approx. 86% of org. P other than lipin and 14% of lipin-P. The bacteria appear to be capable of synthesising lipin-P from inorg. sources.

CHEMICAL ABSTRACTS.

Multiplication of micro-organisms. Modification brought about in the composition of various liquid media by the growth of micro-organisms (*B. pyocyaneus*). J. RÉGNIER and R. DAVID (Compt. rend., 1931, 193, 1487—1490).—*B. pyocyaneus*, grown in various media, causes a rise in surface tension, an increase in alkalinity due to formation of NH_3 , and a decrease in C, total N, $\text{NH}_2\text{-N}$, and total P. The cessation of growth which occurs about the 11th day does not depend on the exhaustion of any of the nutritive factors so far investigated.

W. O. KERMACK.

Distribution of electrolytes in serum during immunisation. K. C. BERTHELSEN and P. P. MURDICK (J. Immunol., 1931, 21, 69—84).—The diffusible Ca in the serum of horses undergoing immunisation with diphtheria toxin decreased after injection of large amounts. The total Ca and total base behaved somewhat similarly. Considerable fluctuation in total and diffusible P was observed.

CHEMICAL ABSTRACTS.

Diphtheria toxin produced in synthetic media. M. E. MAVER (J. Infect. Dis., 1931, 49, 1—8).—Diphtheria bacilli, grown on a modified Braun-Hofmeier synthetic medium, synthesise a protein simultaneously with the production of toxin; in an electric field both migrate to the anode at p_{H} 4.05 and to the cathode at p_{H} 3.75, and they are simultaneously destroyed by trypsin and pepsin. The toxin fraction of the filtrate is identical with, or closely associated with, a protein.

CHEMICAL ABSTRACTS.

Acid precipitation of diphtheria toxin. W. E. BUNNEY, J. CIANCARULO, and M. KIAMIL (J. Immunol., 1931, 20, 417—431).—The toxin is purified by adding dil. HCl (1 : 10) to max. pptn., centrifuging, washing, and dissolving the ppt.

CHEMICAL ABSTRACTS.

Purification of diphtheria toxin. S. OHYAMA (J. Biochem., Japan, 1931, 13, 255—272).—Toxin conc. by adsorption on $Zn(OH)_2$, $Zn_3(PO_4)_2$, or Ca, Sr, or Ba hydroxides or phosphates gives no reaction for protein or sugar, although trypsin destroys it. Probably the toxin is constitutionally related to protein.

CHEMICAL ABSTRACTS.

Speed of flocculation of diphtheria toxin. W. E. BUNNEY and M. KIAMIL (J. Immunol., 1931, 20, 433—445).—A toxin which on acidification yields a slight ppt. (flocculating slowly in the Ramon test), when treated with the toxin of a foreign protein pptg. at the same p_H , yields a rapidly flocculating ppt. Hence the toxin is probably merely adsorbed on pptd. protein.

CHEMICAL ABSTRACTS.

Flocculation-reaction time in course of immunisation and quantitative and qualitative changes in the proteins. K. C. BERTHELSEN (J. Immunol., 1931, 21, 43—67).—The increase in flocculation-reaction time during immunisation of horses for production of diphtheria antitoxin was not related to quant. changes in the protein fractions. Qual. differentiation of the protein complexes could not be demonstrated.

CHEMICAL ABSTRACTS.

Relationship of surface phenomena to the reaction of toxin and antitoxin, with toxin produced in an infusion-free peptone medium. K. C. BERTHELSEN (J. Immunol., 1931, 21, 21—41).—Toxin-antitoxin flocculation first takes place at the liquid-air surface, where the surface energy is minimal. The shorter is the flocculation-reaction time the higher is the surface tension. An antitoxic serum in which the protein particles had been denatured by heat showed parallelism between flocculation-reaction time and surface tension.

CHEMICAL ABSTRACTS.

Oxidation-reduction potentials of *Staphylococcus* cultures. II. Effect of bacteriophage. L. F. HEWITT (Biochem. J., 1931, 25, 2068—2071).—The potential of these cultures falls initially even in the presence of bacteriophage despite the delay in the proliferation of the bacteria. When bacteriophage is present the potential soon ceases to fall and commences to rise, but a further fall in potential occurs at the time when growth first becomes apparent in the cultures.

S. S. ZILVA.

Protein fractions of a scarlatinal strain of *Streptococcus hemolyticus*. M. HEIDELBERGER and F. E. KENDALL (J. Exp. Med., 1931, 54, 515—531).—The extraction of a labile nucleoprotein is described. The product differs from the fractions prepared by subsequent alkaline extraction of the cell residues and from "nucleoprotein" obtained in the usual way. It is sensitive to weak alkalis, readily losing nucleic acid. The protein degradation products resemble the alkali-extracted protein fractions of the cell residues.

CHEMICAL ABSTRACTS.

Formation of bacterial proteases, especially in synthetic media. R. B. HAINES (Biochem. J., 1931, 25, 1851—1859).—Sterile filtrates of broth cultures of *B. mesentericus* and a *Pseudomonas* attack commercial caseinogen or gelatin readily, but have little action on native ovalbumin. Mixtures of salts of Ca and Mg or Mg salts alone, but not Ca salts alone, stimulate the growth of micro-organisms in simple synthetic media. Proteases are formed in simple synthetic media with NH_4Cl as the source of N if Ca and Mg salts are present. Little or no protease formation occurs in presence of Mg salts alone despite good growth. Protease formation is stimulated by these salts in a medium containing NH_4 lactate and asparagine. The influence of Ca and Mg salts on protease formation cannot be explained on the basis of stimulation of growth only.

S. S. ZILVA.

Chemo-immunological studies on conjugated carbohydrate proteins. IV. Synthesis of the *p*-aminobenzyl ether of the soluble specific substance of type III pneumococcus and its coupling with protein. W. F. GOEBEL and O. T. AVERY. V. Immunological specificity of an antigen prepared by combining the capsular polysaccharide of type III pneumococcus with foreign protein. O. T. AVERY and W. F. GOEBEL (J. Exp. Med., 1931, 54, 431—436, 437—447).—IV. The *p*-nitrobenzyl ether (2.99% N) has $[\alpha] -26.5^\circ$, acid equiv. 480. Reduction with $Na_2S_2O_4$ in nearly neutral solution gives the *p*-aminobenzyl ether, $[\alpha] -28.5^\circ$, acid equiv. 453.

V. Type sp. antipneumococcus immunity has been induced in rabbits with the antigen.

CHEMICAL ABSTRACTS.

Lipins of tubercle bacilli. XXIV. Acetone-soluble fat of bovine tubercle bacillus. M. L. BURT and R. J. ANDERSON. XXV. Phosphatide fraction of timothy bacillus. M. C. PANGBORN and R. J. ANDERSON (J. Biol. Chem., 1931, 94, 451—463, 465—472).—XXIV. The fat consists mainly of free fatty acids. After hydrolysis by alcoholic KOH and removal of fatty acids, the aq. solution contains an unidentified polyhydric alcohol and a trace of volatile (butyric) acid. The unsaponifiable matter (10%) is unsaturated, but gives no definite sterol reactions. The fatty acids have been separated into (a) a solid fraction consisting of palmitic, cerotic, and hexacosic acids, fractionated as Me esters, (b) a liquid unsaturated fraction, probably a mixture of linoleic and linolenic acids, and (c) a liquid saturated fraction containing tuberculostearic acid and an optically inactive acid of higher mol. wt. than stearic acid.

XXV. Timothy phosphatide yields, on acid hydrolysis, 60% of Et_2O -sol. and 40% of H_2O -sol. material. The former fraction comprises palmitic acid (20% of whole phosphatide), a liquid saturated optically inactive acid (18%), and unsaturated acids (5.6%), which yield a mixture of stearic and palmitic acids on reduction. The H_2O -sol. fraction contains glycerophosphoric acid (10%), mannose (9%), inositol (2%), and a residue of unidentified reducing sugar and glycerol.

A. COHEN.

Composition of the active principle of tuberculin. XIII. Anaphylactogenic action of the

protein from filtrates of acid-fast bacteria. J. H. LEWIS and F. B. SEIBERT (J. Immunol., 1931, 20, 201—220).—The proteins isolated from filtrates of acid-fast bacterial cultures on a synthetic medium are actively anaphylactogenic. A definite antigenic relationship exists between human, bovine, and avian tubercle bacillus proteins, but none exists between those of tubercle bacillus and timothy bacillus. CHEMICAL ABSTRACTS.

Stability of solutions of tuberculin. E. FERNBACH (Compt. rend., 1931, 193, 1486—1487).—A dil. solution of tuberculin in saline containing PhOH retained its activity without significant loss for 25 years, having been preserved in sealed tubes at 20°.

W. O. KERMAK.

Specific cytotoxic action of tuberculin in tissue culture. J. D. ARONSON (J. Exp. Med., 1931, 54, 387—397). CHEMICAL ABSTRACTS.

Anaphylactic and tuberculin types of hypersensitiveness. II. Influence of the nature of the antigen on the development of different types of hypersensitiveness. L. DIENES (J. Immunol., 1931, 20, 333—345).—Differences between cryst. ovalbumin and ovoglobulin are described.

CHEMICAL ABSTRACTS.

Differential stain for acid-fast bacteria and spores. V. BURKE, R. DICKSON, and S. PHILLIPS (Stain Tech., 1932, 7, 21—24).—After staining with carbol-fuchsin the slide is immediately covered with a saturated solution of malachite-green in COMe₂ for 3—5 min. It is then washed and examined. If the smear is too dense it is dried for 3 min. and decolorised in NH₃ vapour. On exposure to air the green colour returns; this can be prevented by making the smear alkaline with Na₂CO₃. In order to detect tubercle bacilli in thick sputum smears the slide is stained with carbol-fuchsin, decolorised with 30% aq. phenol-disulphonic acid, washed, and examined at once. The organisms appear red on a colourless background.

H. W. DUDLEY.

Bacterial fluorescence in various media. I. Inorganic substances necessary for bacterial fluorescence. F. R. GEORGIA and C. F. POE (J. Bact., 1931, 22, 349—361).—Mg, phosphates, and sulphates are essential for pigment production by bacteria. Sufficient Mg may be dissolved from soft glass tubes and may occur even in highly purified reagents. The production of fluorescence may be utilised as a very delicate test for Mg⁺⁺, PO₄⁻⁻⁻, and SO₄⁻⁻⁻.

A. G. POLLARD.

"Resting" bacteria. B. R. SANDIFORD and W. R. WOOLDRIDGE (Biochem. J., 1931, 25, 2172—2180).—Thick suspensions of bacterial cells which have previously been well shaken in physiological saline or Ringer's solution ("resting bacteria") consist in part of cells which will proliferate when inoculated on suitable media. The total no. of cells remains practically const. throughout long periods of anaerobic incubation at 45° in presence of various substrates with or without methylene-blue. In absence of the dye the no. of viable organisms steadily decreases, whereas in presence of methylene-blue the viable count first shows a fall, followed by a temporary

rise, subsequently falling more slowly. The enzymic activity of these preps. towards the various substrates remains practically const. throughout incubation. Both viable and dead cells are enzymically active. The no. of living cells may sometimes increase under conditions thought to inhibit growth.

S. S. ZILVA.

Effect of sodium ricinoleate on the *Gonococcus*. C. P. MILLER, jun., and R. CASTLE (J. Bact., 1931, 22, 339—348).—Na ricinoleate solutions (1:20,000) inhibited the growth of *Gonococcus*, which was almost completely dissolved by 0.1 and 1.0% solutions of the soap. Na ricinoleate increases the lethal action of the organism to mice.

A. G. POLLARD.

Biochemical action of arsenic. J. PASKUJ (Magyar Chem. Fol., 1930, 36, 111—118; Chem. Zentr., 1931, ii, 73).—As was adsorbed only from H₃AsO₄ and salvarsan by the spores used; the As did not kill the spores, but hindered their germination.

A. A. ELDRIDGE.

Behaviour of Gram-negative and -positive bacteria towards distilled water and the action of very small quantities of salts of heavy metals. K. TAUCHERT (Z. Desinfekt., 1931, 23, 213—232; Chem. Zentr., 1931, ii, 257—258).—In oligodynamic experiments the dilution water must be completely free from nutrients and metallic impurities. The highly toxic action of salts of heavy metals is regarded as an oligodynamic action. Only with salts of tervalent metals was there a difference between Gram-positive and -negative bacteria, the former being somewhat more resistant.

A. A. ELDRIDGE.

Bactericidal water by filtration and sterilisation. G. LAKHOVSKY (Compt. rend., 1932, 194, 137—139).—H₂O unfit for drinking, passed through a candle which had been previously treated with AgCl at 1200° for 24 hr., is rendered non-toxic and sterile and possesses bactericidal activity. Analysis of the H₂O shows no Ag, and its bactericidal action is believed to be due to ionisation produced by contact of the dissolved matter with the Ag during filtration, since after filtration the *pH* increases. On boiling, the bactericidal action is lost.

A. LAWSON.

Blood corpuscles and absorption of certain nutrients and hormones, especially adrenaline. M. GEDROYC and W. KOSKOWSKI (Compt. rend. Soc. Biol., 1930, 105, 409—412; Chem. Zentr., 1931, i, 2492).—When solutions of adrenaline or histamine are allowed to act on blood-corpuscles for approx. 30 min. a part of the hormone is absorbed, and after the corpuscles are washed the biological action of the hormone can readily be detected. This absorption must be important in transporting hormones and partly explains the rapid disappearance from the plasma of adrenaline injected into the blood-vessels.

L. S. THEOBALD.

[Pharmacology of] sparteine and adrenaline. R. HAZARD (Compt. rend., 1932, 194, 130—132).—Sparteine increases and prolongs the hypertensive action of adrenaline by its action on the vagus nerve-endings and by potentiating the action of adrenaline on the cardiac and vascular sympathetic nerve-endings.

A. LAWSON.

Determination of hexosemonophosphate in muscle. G. T. CORI and C. F. CORI (J. Biol. Chem., 1931, 94, 561—579).—Rat muscle is treated with aq. $\text{CCl}_3\text{CO}_2\text{H}$ and the reaction of the extract adjusted to p_H 8.2 by $\text{Ba}(\text{OH})_2$, whereby PO_4''' , adenosinetriphosphate, and the fraction containing undetermined P are pptd. Decomp. of the ppt. by H_2SO_4 and reppn. at p_H 8.2 removes some hexosephosphate included in the Ba ppt. The combined liquids are then pptd. by 80% EtOH in presence of aq. NH_3 and the reducing power and P content of this ppt. determined. Incubation of the muscle in NaHCO_3 solution at 37° results in formation of PO_4''' from 92.4% of the adenosinetriphosphate and undetermined P fraction, whilst only 15—30% of the hexosephosphate is converted, accounting for 7% of the inorg. P liberated. Thus, whilst decomp. of added Embden's ester is quant., the liberated inorg. P other than that due to "pyrophosphate" is not formed by total decomp. of hexosephosphate present in the muscle, but mainly from adenylic acid derived from adenosinetriphosphate (cf. A., 1929, 347). F. O. HOWITT.

Influence of adrenaline and insulin injections on hexosephosphate content of muscle. C. F. CORI and G. T. CORI (J. Biol. Chem., 1931, 94, 581—591).—The average hexosephosphate content of muscle removed from rats under amytal anaesthesia is 0.0533% (as hexose). This val. rises as high as 0.20% immediately after death by stunning, bleeding, etc. Subcutaneous administration of adrenaline is followed 15 min. later by a rise in the hexosephosphate level, attaining a max. of 0.109% after 1 hr. and returning to normal within 4 hr. A similar phenomenon occurs with insulin injection, but is inhibited by simultaneous glucose administration or by adrenalectomy. Hence the secondary liberation of adrenaline is responsible for the increase attending insulin hypoglycaemia. In no instance is there an accumulation of hexosediphosphate or fission of P from adenosinetriphosphate. Glucose-feeding does not change the hexosephosphate content of muscle, hence the decrease in urinary P following ingestion of glucose is not explained on these grounds as it is when adrenaline or insulin is injected. The intermediary metabolism of the glycogen-lactic acid transformation is discussed. F. O. HOWITT.

Metabolism of animals on carbohydrate-free diet. III. Effect of alkali on the sensitivity towards insulin of albino rats. A. HYND and D. L. ROTTER (Biochem. J., 1931, 25, 1893—1901; cf. A., 1931, 771).—Rats previously rendered resistant to insulin by a cheese diet soon become responsive after the addition of NaHCO_3 , but not of an equiv. of KHCO_3 . NaHCO_3 is also more efficient in this respect when a carbohydrate-free diet is used. The difference in behaviour of the two salts bears no relationship to the carbohydrate stores of the animal. Administration of NaHCO_3 does not reduce the liver- or muscle-glycogen of carbohydrate-fed rats, and it favours rather than inhibits the action of insulin. An NH_4Cl acidosis is accompanied by marked resistance to insulin, which readily disappears after the addition of either NaHCO_3 or KHCO_3 to the diet.

S. S. ZILVA.

Fate of the thyroid hormone in hyperthyroidised animals. II. Excretion of thyroid hormone by the dog after oral administration of dried thyroid. III. Excretion of thyroid hormone after oral administration of thyroxine. G. ASIMOV and E. ESTRIN. IV. Hyperthyroidisation of fowls with a single dose of thyroid and determination of iodine in tissues. G. ASIMOV, E. ESTRIN, and S. MILETZKAJA (Z. ges. exp. Med., 1931, 76, 380—398, 399—408, 409—418; Chem. Zentr., 1931, ii, 75).—II. Most of the I is excreted in 24 hr.; I appears in the urine and bile after 30 min. and is max. after 12—16 and 15—17 hr., respectively, the ratio of amounts excreted being 20:1. Part is unabsorbed. The urinary I is biologically inactive, but the bile-I accelerates the metamorphosis of axolotls.

III. Most of the I is excreted in 24 hr. The greater part is unabsorbed, and approx. equal quantities are excreted in the urine and bile. The max. is reached in about 5 hr. The urinary I is biologically inactive, and the bile-I is biologically active.

IV. 1.29% of the I administered is found in the egg-yolk; it has practically no biological activity. I is also found in the thyroid, kidneys, liver (as thyroxine), blood, and pancreas. Little I is present in the muscle, fat, brain, and sexual organs.

A. A. ELDRIDGE.

Effect of administration of sugar and insulin on the liver-glycogen of animals receiving thyroxine. G. KNITTEL (Z. ges. exp. Med., 1931, 76, 362—368; Chem. Zentr., 1931, ii, 75—76).—The fall in liver-glycogen, observed in guinea-pigs on administration of thyroxine, is arrested by injection of fructose and insulin, but the effect on body-wt. is unchanged.

A. A. ELDRIDGE.

Anterior pituitary gland and iodine content of the thyroid gland. A. LOESER (Arch. exp. Path. Pharm., 1931, 163, 530—533).—Injection of suspensions of powdered, COMe_2 -dried, anterior pituitary gland into dogs results in a decrease of I content of the thyroid gland in addition to morphological changes.

F. O. HOWITT.

Effect of the ovarian (follicular) hormone on the sensitivity of the uterus towards the posterior pituitary hormone. F. SIEGERT (Klin. Woch., 1931, 10, 734—737; Chem. Zentr., 1931, ii, 258—259).—The hormones are antagonistic.

A. A. ELDRIDGE.

Oestrus-producing hormones. G. F. MARRIAN and A. BUTEXANDT (Science, 1931, 74, 547).—A discussion.

L. S. THEOBALD.

Occurrence of ovarian hormone in urine. E. GLIMM and F. WADEHN (Biochem. Z., 1931, 243, 97—99).—The authors' previously published results on the hormone contents of the urines of children, men, and women have often been higher than those of other authors. The discrepancy is due to differences in the methods of isolation and biological assay.

P. W. CLUTTERBUCK.

Female sexual hormone in unicellular animals. E. E. BAUER (Arch. exp. Path. Pharm., 1931, 163, 602—610).—Injection of EtOH extracts of the protozoan *Colpoda Steini* induces oestrus in spayed mice

within 40 hr. Vegetable matter used for the culture of the protozoa is inactive. Such extracts also cause paralysis in mice, affect the frog's heart in a manner similar to that of bile acids, and exhibit a weak haemolysing action on washed ox erythrocytes.

F. O. HOWITT.

Comparison of the rat and mouse units in the assay of the female sex hormone. T. J. BECKER, C. H. MELLISH, F. E. D'AMOUR, and R. G. GUSTAVSON (J. Pharm. Exp. Ther., 1931, 43, 693—695).—The rat and mouse units of oestrin are approx. equal.

W. O. KERMACK.

Vitamin-A from fish oils. II. P. KARRER, R. MORF, and K. SCHOFF (Helv. Chim. Acta, 1931, 14, 1431—1436).—The unsaponifiable matter of the oil from *Scombrox saurus* is purified as described previously (A., 1931, 1463). The resulting viscous oil (vitamin-A) has M 300—320, the composition $C_{20}H_{30}O$ or $C_{22}H_{32}O$, gives a *p*-nitrobenzoate and an acetate (hydrolysed by EtOH-KOH at 60° to the original material), is oxidised by O_3 giving a considerable amount of geronic acid, and by $KMnO_4$ and CrO_3 , yielding $AcOH = 9.7$ and 16.3% of C-Me groups, respectively. Catalytic reduction affords a *product*, $C_{20}H_{30}O$ which can be distilled in vac. Formulae are suggested.

H. BURTON.

Vitamin-A and carotene. VIII. High-potency vitamin-A concentrates. T. MOORE (Biochem. J., 1931, 25, 2131—2135).—Although the initial blue vals. of liver oils of rats which previously received large amounts of carotene in the form of red-palm oil and of turbot and sole oils varied widely, little difference could be detected in the activities of the final concentrates from these sources, which approached an average val. of 2400 B.U. per mg. (pharmacopoeia colour val. 45,000) in the $SbCl_3$ test corresponding with a min. dose of about 0.001 mg. in rat-growth experiments.

S. S. ZILVA.

Effect of mineral oil administration on the nutritional economy of fat-soluble vitamins. I. Vitamin-A of butter-fat. R. W. JACKSON (J. Nutrition, 1931, 4, 171—184).—With rats, mineral oil causes considerable loss of vitamin-A to the animal organism if the oil is mixed with butter-fat prior to digestion. If the oil is administered separately there is only a very slight diversion of vitamin-A.

CHEMICAL ABSTRACTS.

Effect of xanthophyll on the growth of rats. H. VON EULER, P. KARRER, and M. RYDBOM (Helv. Chim. Acta, 1931, 14, 1428—1431).—Rats grow during 4 weeks on a diet supplemented by xanthophyll, m. p. 192° (dose 0.037 mg.). After this time growth diminishes and then ceases; a continuation can usually be effected by adding carotene in a quantity which is normally insufficient. Xanthophyll cannot replace carotene.

H. BURTON.

Distribution of the vitamin-B complex. III. Fruits. M. H. ROSCOE (Biochem. J., 1931, 25, 2050—2055).—The vitamin- B_1 content of the orange is the highest, being 1/5 that of yeast (dry wts.). The val. of tomato is rather less than 1/10 that of yeast, the banana 1/20, and apple still lower. The vitamin- B_2 content of orange, tomato, and banana is rather less than 1/10 and of apple 1/20 that of

yeast (dry wts.). These vals. are compared with those of other foodstuffs.

S. S. ZILVA.

Effect of coprophagy in rats deprived of the vitamin-B complex. M. H. ROSCOE (Biochem. J., 1931, 25, 2056—2067).—The life of rats receiving cooked diets deficient in the vitamin-B complex or its constituents and containing sol. starch was prolonged considerably when they ate their faeces, whether sterilised or not, and in some cases growth also took place. Death finally occurred as a result of neuritis due to vitamin- B_1 deficiency. A preliminary week of depletion during which coprophagy was not permitted did not prevent this prolongation of life. Growth did not occur when less than 70% of the faeces was consumed and was not proportional to increased consumption. This phenomenon is probably due to the fact that the B-vitamins are synthesised by bacteria in the gut. The synthesis is stimulated by the presence in the diet of a heat-stable factor contained in the autoclaved yeast extracts differing from the B-vitamins. Refection is a condition distinct from that observed in coprophagous rats fed on cooked diets containing sol. starch.

S. S. ZILVA.

Beriberi quotient (Q_b) in nutrition with polished rice and autoclaved grain. V. FAMIANI (Atti R. Accad. Lincei, 1931, [vi], 14, 206—209).—With pigeons fed on polished and washed rice, or on rice autoclaved either dry or wet or in presence of alkali, no appreciable differences are observed in the beriberi quotient or in the symptoms.

T. H. POPE.

Possibility of obtaining persistent beriberi phenomena in the pigeon by deprivation of vitamin-B. G. AMANTEA and V. FAMIANI (Atti R. Accad. Lincei, 1931, [vi], 14, 210—214).—By nutrition with food devoid of vitamin-B, pigeons develop beriberi phenomena which persist for a long time, even when the birds are subjected to prolonged, energetic treatment with beer yeast, associated with a mixed ordinary diet.

T. H. POPE.

Function of torulin. An *in vitro* effect of anti-neuritic vitamin concentrates. N. GAVRILESCU and R. A. PETERS (Biochem. J., 1931, 25, 2150—2161).—The O_2 uptake of minced pigeon's brain is increased on an average some 40% by performing the determinations in O_2 instead of air in the case of cerebrum and the mixed optic lobes and parts below from the normal brain. With the avitaminous (B_1) brain less or even no increase takes place with the optic lobes and lower parts. In the presence of O_2 the lowered O_2 uptakes previously observed in the brain in avitaminosis- B_1 are more marked. Partial restoration of O_2 uptake *in vitro* is observed on addition of vitamin- B_1 concentrates to the mixed optic lobes and lower parts of the avitaminous pigeon. This catalytic action of the concentrates is due to vitamin- B_1 . The effects are not always obtained with the cerebral tissue.

S. S. ZILVA.

Effect of autoclaved cow's milk and of vitamins-B, -C, and -D on the growth of goats. W. CATEL and G. FALLASKE (Jahrb. Kinderheilk., 1931, 81, 313—340; Chem. Zentr., 1931, ii, 263—264).—

Autoclaved cow's milk causes small variations in the serum-Ca and -P. Addition of "vigantol" considerably improves growth and assimilation. Addition of vitamin-B or lemon-juice affords variable results. The results do not require the assumption that a growth vitamin exists. A. A. ELDRIDGE.

Vitamin-C. A. W. OWE (Tidsskr. Kjem. Berg., 1931, 11, 120—124).—The work of Rygh *et al.* has shown that the narcotine present in unripe fruit must be regarded as the precursor of vitamin-C. During the ripening of the fruit the *o*-diphenol derivative is formed, which has a strong antiscorbutic action in a daily dose of about 25×10^{-6} g. It cannot yet be considered definitely proved that the *o*-diphenol derivative is identical with vitamin-C.

H. F. HARWOOD.

Preparation of vitamin-C concentrates from lemon-juice. J. L. SVIRBELY and C. G. KING (J. Biol. Chem., 1931, 94, 483—490).—The vitamin-C of a concentrate prepared from lemon-juice (A., 1930, 119, 381) is extractable by petrol-COMe₂ (1:1), petrol-BuOH (2:1 and 4:1), petrol-PrOH (1:1 and 3:1), AcOEt, BuOH, and PrOH, but not by Et₂O. By the use of such extractants concentrates of 0.03—0.5 mg. of solids per c.c. of lemon-juice are obtained which are fairly stable and appear to contain only one active principle. Passage of NH₃ through solutions in org. solvents destroys the vitamin, which exhibits distinct acidic and reducing properties.

F. O. HOWITT.

Preparation and storage of vitamin-C concentrates from lemon-juice. F. L. SMITH, 2nd, and C. G. KING (J. Biol. Chem., 1931, 94, 491—496).—An aq. concentrate (0.09 mg. per c.c. of lemon-juice) prepared by extraction of solids from a COMe₂ solution with BuOH and cooling to deposit inactive material (cf. preceding abstract) possessed a strong reducing power and gave a positive test with orcinol and resorcinol. Active ppts. were separated from the concentrate at p_H 7.3—7.5. Citric and formic acids were not superior to HCl as stabilising agents. Storage on solid CO₂ in an atm. of N₂ or CO₂ resulted in complete retention of activity for 2—3 weeks.

F. O. HOWITT.

Antirachitic vitamin from irradiated ergosterol. A. WINDAUS and A. LUTTRINGHAUS (Z. physiol. Chem., 1931, 203, 70—75).—The properties of vitamins-D₁ and -D₂ are reviewed. D₂ corresponds with calciferol (A., 1931, 1464). The so-called vitamin-D₁ is now found to be an additive compound of D₂ and an isomeric alcohol, and is resolved by way of the dinitrobenzoate.

J. H. BIRKINSHAW.

Chemical reaction of antirachitic vitamin. E. CRUZ-COKE (Compt. rend. Soc. Biol., 1930, 105, 238—239; Chem. Zentr., 1931, i, 2497—2498).—A drop of HCl added to an EtOH solution of pure ergosterol at 70—80° gives a white ppt. After irradiation of the ergosterol the pptn. is retarded, and redissolution occurs giving a green solution. This is not the case, however, with non-irradiated material. Further addition of HCl re-forms the ppt. With irradiated ergosterol the amount of HCl necessary for this reaction is proportional to concn.

L. S. THEOBALD.

"Viosterol" and cod-liver oil. E. O. PRATHER, M. NELSON, and A. R. BLISS, jun. (J. Amer. Pharm. Assoc., 1931, 20, 1291—1303).—Irradiated ergosterol did not stimulate the growth and development of the body and vital organs (of rats), or prevent infections of the upper respiratory tract or produce the same degree of calcification and growth of the bones as did cod-liver oil.

E. H. SHARPLES.

Vitamin value of cod-liver meal. A. D. HOLMES, M. G. PIGOTT, and D. F. MENARD (J. Nutrition, 1931, 4, 193—201).—Addition of 2% of the best meals is equiv. (chickens) to 0.5% of cod-liver oil. The poorer meals possess little, if any, vitamin val.

CHEMICAL ABSTRACTS.

Heterogeneity of natural products. P. KARRER (Collegium, 1931, 700—710).—Examples are quoted of natural products, e.g., gallotannic acid, hitherto considered to be individual chemical substances, which have been resolved into different components, in some cases themselves not single chemical substances.

D. WOODROFFE.

Dominant starch character in the first generation of the hybrids of two varieties of pea (*Pisum sativum*, L.). L. BHARNGHEM, M. BRIDEL, and (MLL.) C. BOURDOUIL (Compt. rend., 1931, 193, 1135—1137).—A comparison of the soluble carbohydrate and starch contents of two varieties of pea together with their hybrids suggests that ovule transmission determines the dominance of the starch content.

C. C. N. VASS.

Quantitative methods for growth-promoting substances. H. G. VAN DER WEY (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 875—892).—A correlation is established between the amount of growth-promoting substance administered and the bending in normal plants or dissected coleoptiles. The response to growth-promoting substances of plants after multiple shoot-decapitation is greater than after single decapitation. A high temp. during germination of *Avena* reduces the production of growth-promoting substance. Old plants have less bending power and a lower content of growth-promoting substance than young plants. Formation of growth-promoting substance in the coleoptiles of *Zea mays* (as shown by the bending reaction in *Avena*) is dependent on the length of the coleoptiles. The diffusion of growth-promoting substance from dissected coleoptiles into agar plates for the purpose of estimation is restricted to a certain max. limit.

F. O. HOWITT.

Mitogenetic radiation. M. MOISSEJEVA (Biochem. Z., 1931, 243, 67—87).—Further experiments (A., 1931, 1457) are described bringing the no. above 300. An induction in the original sense of Gurwitsch does not exist.

P. W. CLUTTERBUCK.

Effect of various chemical treatments of dormant potato tubers on the peroxidase, catalase, p_H , and reducing properties of the expressed juice. J. D. GUTHRIE (Contr. Boyce Thompson Inst., 1931, 3, 499—507).—The action of a number of org. substances in breaking the dormant period of potato tubers was not closely correlated with changes produced in the peroxidase or catalase activity p_H ,

or reducing power of the juices. A probable relationship is indicated between p_H changes and reducing power. Effective potato dips were either S compounds, or those increasing p_H or reducing power of the juices. The latter effect is associated with an increase in SH compounds in the tuber. A. G. POLLARD.

Increase of sugar utilisation in *Spirogyra* by means of commercial fertilisers. E. WILLIAMS, L. KNEER, G. C. WICKWIRE, D. J. VERDA, and W. E. BURGE (Bot. Gaz., 1931, 92, 321—326).—All fertilisers examined increased the utilisation of sugar from culture solutions by *Spirogyra*, N materials being most active in this respect. Where equal applications of urea, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, $NaNO_3$, and $Ca(NO_3)_2$ were made, plant responses were in the order of the N contents of these substances. A. G. POLLARD.

Oil development in the seed of a growing plant. J. V. EYRE (Biochem. J., 1931, 25, 1902—1908).—In the oil formation in the seed of *Linum usitatissimum* and *L. cribrosum* the acidic constituents are formed first. Whether glycerol is formed at the same time to combine with the fatty acids at a later stage is not established. There is a remarkably rapid oil formation over a period of some 15 days during which a max. of about 36% of oil, calc. on the dry wt. of the seeds, is reached. The unsaturated character of the oil after formation, as measured by its I absorption, continues to increase. S. S. ZILVA.

Soya bean. I. Changes of protein during germination in darkness. W. S. TAO and S. KOMATSU. II. Action of enzymes in seedlings on glycinin. W. S. TAO (Mem. Coll. Sci. Kyoto, 1931, 14, A, 287—292, 293—296).—I. Germination results in loss of wt. mainly due to decrease in fat and nitrogenous matter, in hydrolytic fission of part of the protein, especially globulin, and in liberation of small amounts of NH_3 and urea.

II. The changes in N distribution are due to the action of proteolytic enzymes on glycinin, the protein of the beans. Seedlings exhibit a urease activity greater than that of the seeds. F. O. HOWITT.

Nitrogen metabolism of the lupin seedling. P. McKIE (Biochem. J., 1931, 25, 2181—2188).—The total N of the lupin seedling in the seed and in the early stages of growth consists of insol. N, protein, and asparagine. A close relationship exists between the decrease of insol. and protein-N and increase of asparagine. Protein synthesis begins after 16 days' growth and is accompanied by a fall in asparagine content and a rise in proteose content. NH_3 , amides, NH_2 -acids, and NO_3^- are absent from ungerminated seed. They appear immediately growth begins, rise to a low max. in a few days, and then maintain const. lower level. S. S. ZILVA.

Iodide fission by *Laminaria digitata*. H. KYLIN (Z. physiol. Chem., 1931, 203, 58—65; cf. A., 1931, 132).—The "I liberator" present in *Laminaria* extracts is nitrite formed from nitrate by bacterial action. It is not observed when extracts of fresh material are made sterile by boiling or addition of PhMe. J. H. BIRKINSHAW.

Hemicelluloses of the wood of English oak. I. Effect of the drying of wood on the yields and

composition of hemicellulose-A. M. H. O'DWYER (Biochem. J., 1931, 25, 2017—2022).—With increasingly severe conditions of drying, the hot- H_2O and NaOH extracts of the sapwood or heartwood increase in amount and the yields of hemicellulose-A decrease. S. S. ZILVA.

Detection of woody plant membranes with phloroglucinol and hydrochloric acid. W. PLAHL (Z. Unters. Lebensm., 1931, 62, 603—606).—The defatted specimen is pre-extracted with H_2O to remove sol. matter, and treated with a solution containing equal vols. of 2.5% of phloroglucinol in 96% EtOH and chloral hydrate in H_2O (5:2), to which 4% HCl (d 1.1246) has been added. The colour is a max. after 15 min., and is permanent for a day. J. GRANT.

Pectin of tobacco. C. NEUBERG and M. SCHEUER (Biochem. Z., 1931, 243, 461—471).—A method by which at least part of the pectin can be isolated as pectic acid from the fresh leaves is described. The acid is similar to that obtained from flax and is readily decomposed by tobacco pectase. W. MCCARTNEY.

Non-nitrogenous constituents of tobacco smoke. C. NEUBERG and J. BURKARD (Biochem. Z., 1931, 243, 472—484; A., 1929, 729).—The smoke contains fatty acids (present as salts in the tobacco) and aldehydes and ketones produced by decomp. Rate and temp. of burning of the tobacco, its H_2O content, and the amount of air available for combustion affect the nature and no. of substances produced. The following acids, aldehydes, and ketones can be identified: formic to hexoic acids, C_7 and C_8 acids, traces of unsaturated and OH-acids; CH_2O to $PrCHO$; $COEt_2$ (2:4-dinitrophenylhydrazones, m. p. 149—150°), $COPr_2$ (2:4-dinitrophenylhydrazones), higher and unsaturated ketones. $COMe_2$ is not found. The butyric acid is probably derived from glutamic acid. Substances which yield $BzOH$ on oxidation with Ag_2O are also found. The mixtures of the higher acids and ketones are optically active. Probably the production of the ketones is catalysed by the mineral matter of the tobacco and by the C produced during burning. W. MCCARTNEY.

Lævorotatory carbohydrates of the bulbs of *Lycoris squamigera*, Max. H. BELVAL (Compt. rend., 1931, 193, 891—893).—Lycoride (see this vol., 100) is not hydrolysed by invertase. The accompanying fructoside has $[\alpha] -19^\circ$, and after hydrolysis with HCl $[\alpha] -67^\circ$; it is slowly hydrolysed by invertase. C. C. N. VASS.

Composition of cherry gum. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1931, 53, 4160—4167).—The gum used contained H_2O (10.75%), ash (1.5%), and H_2O -sol. material (14.5%); analysis showed ash (1.3%), galactose (27.7%), arabinose (31.6%), other pentoses (as xylose) (24.5%), and uronic acid (10.1%). Acid hydrolysis gives, initially, pentoses and a complex acid (containing glycuronic acid, mannose, and galactose), which is hydrolysed further to galactose and a complex of glycuronic acid and mannose. The acidic nucleus of the gum contains 2 uronic acid units combined with 1 sugar group instead of the 1:1-combination found

in the aldobionic acids. The mol. proportions of the various constituents are estimated to be arabinose 8, xylose 6, galactose 6, mannose 3, and glycuronic acid 2, whilst the complex acid formed by hydrolysis of the gum with 18% HCl has galactose 6, mannose 3, and glycuronic acid 2. C. J. WEST (b).

Carbohydrate hydrogen sulphate of *Macrocystis pyrifera*. W. L. NELSON and L. H. CRETCHER (J. Biol. Chem., 1931, 94, 147—154).—Extraction of the air-dried fronds with 2% HCl and pptn. with EtOH gives a product containing methylpentose (as fucose) (31.7%), polymeric uronic acid (2.6%), titratable SO_4 (as HSO_4^-) (17.6%), and inorg. SO_4 (ash) (43.8%). Hydrolysis with 2.5% H_2SO_4 affords fucose. H. BURTON.

Presence of a new sugar in dextrorotatory honeys. E. PARISI (Atti R. Accad. Lincei, 1931, [vi], 14, 125—130).—Conifer honeys, which are dextrorotatory, contain (1) a substance yielding an aldehyde-acid of the glycuronic acid group on hydrolysis, and (2) a non-fermentable *glucobiose*, m. p. 180—203°, $[\alpha]_D^{20} +110^\circ$, R_{41-7} [phenylosazone, m. p. 198—200°, $[\alpha]_D^{20} +27.6^\circ$; *p*-nitrophenylosazone, m. p. 135° (? 235°)]. The sugar may exist in the flowers of the tree or it may be produced by enzyme action. T. H. POPE.

Constituents of the cluster base and secondary vegetative growth of bearing spurs of the yellow transparent apple. F. S. LAGASSE (Proc. Amer. Soc. Hort. Sci., 1931, 27, 199—205).—The cluster base contains more H_2O and N (sol., insol., and total), total sugars, free reducing sugars, sucrose, polysaccharides, and total carbohydrates, but less starch, than the secondary growth. Application of NaNO_3 increases the N, but decreases the carbohydrate content. CHEMICAL ABSTRACTS.

Globe artichoke, *Cynara scolymus*, L. G. W. SCOTT (Proc. Amer. Soc. Hort. Sci., 1931, 27, 356—359).—The (dry) leaves contain sugars 10.89, sucrose 3.42, inulin 1.05%. The relation is reversed in the roots, where the inulin may reach 40% (dry wt.). The $\text{NH}_3\text{-N}$ content is 1.51—2.86%; little starch is present. CHEMICAL ABSTRACTS.

Chemical examination of roots of *Rauvolfia serpentina*, Benth. S. SIDDIQUI and R. H. SIDDIQUI (J. Indian Chem. Soc., 1931, 8, 667—680).—Fractionation of the substances extracted from the dry root with 90% EtOH gives a *phytosterol* (termed *serposterol*), $\text{C}_{30}\text{H}_{48}\text{O}_2$, m. p. 159—160°, $[\alpha]_D^{20} -68.5^\circ$ in CHCl_3 , oleic and saturated fatty acids, a mixture of unsaturated alcohols of the composition $\text{C}_{25}\text{H}_{44}\text{O}_2$, and 5 alkaloids (0.5% of dry root) designated (a) *ajmaline*, $\text{C}_{20}\text{H}_{26}\text{O}_2\text{N}_2 + 3\text{H}_2\text{O}$, m. p. 158—160° after losing H_2O at 110° and softening at 150°, $[\alpha]_D^{20} +128^\circ$ in CHCl_3 [hydrochloride + $2\text{H}_2\text{O}$, m. p. 133—134°, m. p. (anhyd.) 253—255°; chloroplatinate, m. p. 217—218°; picrate, m. p. (anhyd.) 223°], (b) *ajmalinine*, $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N} + \text{H}_2\text{O}$, m. p. 180—181° [hydrochloride, m. p. 240—245° (decomp.) (shrinks at 213° and swells at 235°); chloroplatinate, m. p. 254—258° (decomp.)]; picrate, m. p. 200—205° (softens at 175°)], (c) *ajmalicine*, m. p. 250—252° (decomp.) [hydrochloride, m. p. 260—263° (decomp.) after shrinking at 250°; picrate, m. p. 212—215° (decomp.)], (d) *serpentine*, $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}$

+ $1.5\text{H}_2\text{O}$, m. p. 153—154° [hydrochloride, m. p. 260—261° (decomp.) (shrinks at 240°); chloroplatinate, m. p. 217—220° (decomp.)]; picrate, m. p. 261—262° (decomp.)], and (e) *serpentinine*, m. p. 263—265° [hydrochloride, m. p. 260—262°; chloroplatinate, m. p. 260—263° (decomp.)]; picrate, m. p. 225—227°]. Colour reactions of the alkaloids are given.

H. BURTON.

Red colour of the blood-orange. M. B. MALLACK (Plant Physiol., 1931, 6, 729—730).—The presence of acicular crystals of anthocyanin in the juice sacs of blood-oranges is recorded.

A. G. POLLARD.

Dye of red cabbage. I. H. WILLSTAEDT (Biochem. Z., 1931, 242, 303—305).—A procedure for the isolation of the dye is described. It is probably an anthocyanin and is pptd. by $\text{Pb}(\text{OAc})_2$, but not by FeCl_3 or picrolonic acid. It contains about 63% C and 7.0% H. W. MCCARTNEY.

Lycopin. L. CHOLNOKY (Magyar Gyog. Tars. Ert., 1931, 7, 95—107; Chem. Zentr., 1931, i, 3015).—Lycopin preps. from *Tamus communis*, *Solanum dulcamara*, and *Lycopersicum esculentum* are identical. No similar associated compounds could be found.

A. A. ELDRIDGE.

Anthocyanin of *Oryzococcus macrocarpus*, Pers. K. E. GROVE and R. ROBINSON (Biochem. J., 1931, 25, 1706—1711).—The anthocyanin was isolated as the chloride $\text{C}_{22}\text{H}_{23}\text{O}_{11}\text{Cl} \cdot \text{H}_2\text{O}$ and identified as a 3-glucoside of peonidin. S. S. ZILVA.

Carotene in palm oil. K. KOBAYASHI, K. YAMAMOTO, and J. ABE (J. Soc. Chem. Ind., Japan, 1931, 34, 434—436B).—The colour reactions of C_6H_6 or CS_2 solutions of palm oil with dehydrating agents, such as H_2SO_4 , correspond with those of pure carotene. Spectroscopic examination confirms the conclusion that the (principal) pigment of the palm oil is carotene. E. LEWKOWITZCH.

Microchemical detection of volatile fatty acids in plants. I. G. KLEIN and H. WENZL [with N. KEMPERLING] (Mikrochem., 1931, 10, 70—89).—Investigation of the anilides of the fatty acids up to C_7 shows these compounds to be unsuitable as a means of identification of the acids in mixtures, but they may be employed to identify certain of the lower acids on a semi-microchemical scale, either by the crystal form or the m. p., when present alone. Similar conditions obtain for the *p*-toluidides. On the semi-micro-scale (50 mg.) the m. p. of the benzylidene derivatives or the monohydrazides may be employed to identify the acids from C_3 to C_5 , and the m. p. of the monohydrazides those from C_5 to C_8 .

H. F. GILLBE.

Wax constituents of the apple cuticle. A. C. CHIBNALL, S. H. PIPER, A. POLLARD, J. A. B. SMITH, and E. F. WILLIAMS (Biochem. J., 1931, 25, 2095—2110).—The unsaponifiable fraction from the crude plant-wax was treated with phthalic anhydride. The Na phthalates of the primary alcohols were pptd. from the Et_2O solution. After removal of Et_2O the residue was taken up in boiling EtOH, from which the paraffins and ketones crystallised quantitatively, leaving in the mother-liquor the Na salts of the secondary alcohol esters. The mixture of the former

can be separated by Channon and Chibnall's method (A., 1929, 729). The following constituents have been identified: *n*-nonacosane, *n*-heptacosane, *d*- α -nonacosanol, *n*-hexacosanol, *n*-octacosanol, and *n*-triacontanol. S. S. ZILVA.

Wax constituents of forage grasses. I. Cocksfoot and perennial rye grass. A. POLLARD, A. C. CHIBNALL, and S. H. PIPER (Biochem. J., 1931, 25, 2111—2122).—In the case of cocksfoot the chief constituent is a long-chain primary alcohol (nearly pure *n*-hexacosanol). It contains less than 1% of *n*-tetracosanol and about an equal amount of an unidentified longer-chain alcohol. The same alcohol is present in rye grass wax, but the amount of impurities is greater. Hippocoprosterol is identical with ceryl alcohol. S. S. ZILVA.

Seed of *Euphorbia marginata*, Pursh. L. E. HARRIS and M. C. GALLAGHER (J. Amer. Pharm. Assoc., 1931, 20, 1281—1286).—The seeds (6.2% H₂O, 4.0% ash) of *E. marginata* gave about 30% of a drying oil having *d* 0.9222, acid val. 7.76, sap. val. 186, I val. 135.66; the isolated fatty acids contained linolenic, linoleic, stearic, palmitic, and oleic (trace) acids. E. H. SHARPLES.

Existence and distribution of caffeine and theobromine in the tissues of guarana. G. BERTRAND and P. DE B. CARNEIRO (Compt. rend., 1932, 194, 26—28).—The caffeine content of the kernels and teguments of the dried seeds of *Paullinia cupana* is 4.4 and 2.2%, respectively. Theobromine is not present. The dried leaves, roots (excluding the bark), root bark, stems (excluding the bark), stem bark, flowers, and flower stalks contain 0.38, 0.27, 1.74, 0.19, 0.17, 0, 0%, respectively, of caffeine, and 1.2, 0, 0, 0, 0.98, 1.54, 0.38%, respectively, of theobromine. A. LAWSON.

Supposed glutathione of peas. A. KOZŁOWSKI (Biochem. Z., 1931, 241, 407—408).—In the method previously described (A., 1927, 80) a better yield of the substance containing cysteine is obtained by extracting with COMe₂ and pptg. with Cu₂O. It is not certain that the substance is identical with the glutathione of yeast. W. MCCARTNEY.

Dicarboxylic acid nitrogen of proteins. Alcohol-soluble protein from Ragi (*Eleusine coracana*). M. DAMODARAN (Biochem. J., 1931, 25, 2123—2130).—The method is based on the pptn. of dicarboxylic acids from the hydrolysed protein with Ca(OH)₂ and EtOH. Vals. obtained with several proteins are in close agreement with those obtained by direct isolation of the acids by other workers. The N distribution in protamine from Ragi has been determined. S. S. ZILVA.

Occurrence of methylated nitrogen compounds in sea-weed. II. Administration of trimethylamine to cold-blooded animals. R. KAPPELLER-ADLER and F. VERING (Biochem. Z., 1931, 243, 292—309; A., 1930, 1464, 1484).—Neither marine nor fresh-water plants contain NHMe₂ and only the former contain NMe₃, whilst both contain NH₂Me. There is no NMe₃ oxide in marine plants. The NH₂ content of both species varies very widely. Except for *Elodea canadensis*, which contains 0.03% of

NH₂Me, other fresh-water plants contain 0.0015—0.004%. Green and brown marine algae contain 0.01—0.044% and 0.05% of NMe₃, respectively. In red marine algae the NMe₃ content varies greatly (0.017—0.5%) from species to species; the NH₂Me content of these algae is 0.014—0.08%. In the marine plants there is no connexion between botanical relationship and content of methylated amine. When NMe₃.HCl is fed to goldfish small amounts of the substance (but no NMe₃ oxide) are deposited in their musculature, and it is concluded that the methylated amines and NMe₃ oxide found in sea fish may be derived from their food. W. MCCARTNEY.

Wood saps. I. Sap of the red beech (*Fagus sylvatica*). C. G. SCHWALBE and W. ENDER (Cellulosechem., 1931, 12, 316—318).—The sap in the capillaries of the red beech contains considerable amounts of carbohydrates (chiefly hexoses and some pentoses), K, Na, Ca (17.4% of the ash), Mg (9.2%), Cl (6.12%), PO₄, and org. acids (probably lactic acid). N is absent. The carbohydrates are considered as hygroscopic substances responsible for the changes in the wood with varying humidity. R. S. CAHN.

Toxicity of water-soluble extractives of Western Yellow Pine to *Leizites sepiaria*. B. A. ANDERSON (Phytopath., 1931, 21, 927—940).—Hot-H₂O extracts were more toxic than cold, and those from air-seasoned wood more toxic than from kiln-dried. A. G. POLLARD.

Permeability of *Rhoco* cells to ammonia and acetic acid. R. COLLANDER, O. TURPEINEN, and E. FABRITIUS (Protoplasma, 1931, 13, 348—362).—The permeability of epidermal protoplasts of leaves of *R. discolor* to NH₄OAc is controlled by the degree of dissociation of the salt solution, the rate of penetration of undissociated mols. being very small. A. G. POLLARD.

Influence of the potassium : nitrogen ratio on the early growth of the coffee plant. T. DE CAMARGO (Compt. rend., 1931, 193, 1032—1034).—The growth of young *Coffea arabica*, L., plants is greatest when the culture solution has a K₂O : N ratio of 1, the contents of protein, sucrose, starch, and cellulose of the leaves also showing a max., whilst those of glucose and methylpentoses increase with decreasing vals. of the ratio. F. O. HOWITT.

Histological basis of the effect of potash on the "lodging" of barley. C. BLATNY and V. VUKOLOV (Ernähr. Pflanze, 1931, 27, 355—358).—Changes in the tissue structure of barley straw, especially of the nodes, resulting from K manuring are described. A. G. POLLARD.

Can potash and nitrogen deficiencies be determined by chemical tests of parts of living plants? W. KRUGER, G. WIMMER, and H. LÜDECKE (Ernähr. Pflanze, 1931, 27, 425—429, 450—452).—The Hoffer method for detecting K deficiency by means of Fe accumulation at the nodes of maize stems (Washington Agric. Exp. Sta. Bull., 1926, No. 298) gave uncertain results for maize and was inapplicable to oats. Individual plants show considerable variation and climatic conditions affect results. Applications of the NHPh₂ test for NO₃' in freshly-

cut plant stems does not give a satisfactory indication of N deficiency. A. G. POLLARD.

Micro-detection of phosphorus in plant cells. B. ANGELI (Riv. Biol., 1928, 10, 6 pp.; Chem. Zentr., 1931, ii, 95).—Sections are immersed for 20 min. in a $\text{HCl}-(\text{NH}_4)_2\text{MoO}_4$ solution, rapidly washed, immersed in freshly prepared 0.02N- SnCl_2 , washed with H_2O , and moistened with 2.5% aq. NH_3 . Where P is present a blue colour is observed under the microscope. A. A. ELDRIDGE.

Manganese and the growth of *Lemna minor*. E. F. HOPKINS (Science, 1931, 74, 551—552).—Mn is confirmed to be essential for the growth of *Chlorella* (A., 1931, 400). With or without Fe or glucose, it is also essential for the growth of *L. minor*.

L. S. THEOBALD.

Bromine normally present in plants: edible grains, wheat, and bread. A. DAMIENS and S. BLAIGNAN (Compt. rend., 1931, 193, 1460—1462).—The ratio Br/Cl has been determined in various grains, including rice, peas, beans, wheat, and other cereals and also in flour, bread, and yeast. In rice and haricot beans only traces of the halogens were found.

W. O. KERMACK.

Distribution of iodine in grain. E. GLIMM and S. HALASA (Biochem. Z., 1931, 243, 88—96).—The I contents of the seed and the whole plant are determined for a number of cereals (rye, wheat, barley, oats, maize). The I distribution within the grain is not uniform, the content being greatest at the top and least in the middle portion. The abs. I content of the whole plant is distributed fairly evenly between stalk, root, and ear, and relatively is poorest in the ear and richest in the root. Malt is always poorer in I than the barley from which it is obtained.

P. W. CLUTTERBUCK.

Inorganic constituents of the several parts of *Monarda fistulosa*. E. KREMERS and A. A. HARWOOD (J. Amer. Pharm. Assoc., 1931, 20, 1268—1272; cf. B., 1931, 945).—Analyses of the ash of the root, stem, leaf, bract, and corolla are given.

E. H. SHARPLES.

Effects of calcium deficiency on nitrate absorption and on metabolism in tomato. G. T. NIGHTINGALE, R. M. ADDOMS, W. R. ROBBINS, and L. G. SCHEMMERHORN (Plant Physiol., 1931, 6, 605—630).—Ca-deficient tomatoes are characterised by the yellowing of the upper stems and leaves (lower portions remaining green) and by short bulbous roots, brown at the tips with sloughing-off of cells further back. The latter is attributed in part to lack of development of the middle lamella of Ca pectate. Deficiency of Ca results in a lack of ability to assimilate nitrates. The plants accumulate considerable amounts of carbohydrates, but the translocation of sugars and the digestion of starch proceed freely. Nearly all the Ca present in deficient plants is insol. in H_2O and is located chiefly in the older tissues of roots and tops. A portion of this Ca is present as oxalate, but the major part ("combined Ca") occurred in other forms which react with $\text{H}_2\text{C}_2\text{O}_4$ only after treatment with alkali. Both forms of Ca were so slowly utilisable that normal maintenance of tissues was impossible. New cell formation necessitates sufficient Ca to form

the middle lamella and for combination with the materials of the protoplast. In its absence granular proteinaceous inclusions accumulate.

A. G. POLLARD.

Reaction of substrate of *Rumex acetosella*. E. KIVINEN (J. Sci. Agric. Soc. Finland, 1931, 10—16; Proc. Internat. Soc. Soil Sci., 1931, 6, 125—126).—The range of p_{H} of soils in which *R. acetosella* occurs varies with soil type and in general was lower in cultivated than in uncultivated areas. Average vals. were: peats, p_{H} 4.76; silts, 5.01; sands, 5.7; gravels, 6.10.

A. G. POLLARD.

Freezing-point depressions of asparagus shoots determined by a thermo-electric method. E. I. FERNALD (Contr. Boyce Thompson Inst., 1931, 3, 483—497).—Use of a Cu-constantan thermocouple is described. Max. f.-p. depressions of sections of actively growing asparagus shoots occurred at distances of 1 and 3 cm. from the tip when underground and 1.5—3.7 cm. when above ground.

A. G. POLLARD.

Influence of protoplasm rotation on the transport of substances. A. C. A. KOK (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 918—929).—The diffusion of Li salts and of caffeine through the leaves of *Vallisneria spiralis* is hindered by the protoplasm the rotation of the granules of which is without influence on the rate of transport. Et_2O retards the transport to a small extent, not due to inhibition of rotation, but to decrease in permeability of the protoplasm. 0.0001% CuSO_4 used for the initiation of the rotation in leaves in which protoplasmic movement has ceased following removal from light causes either no change or only a slight increase in the transport velocity. Rise in temp. accelerates the diffusion, the temp. coeff. being 1.4.

F. O. HOWITT.

Periodic permeability of iodine solution and of water in the protoplasm of *Zea mays* seeds. R. C. MALHOTRA (Protoplasma, 1931, 13, 374—388).—The rate of intake of H_2O and of 0.05% I solution by maize seeds increases with time of contact and with rise of temp. The actual intake of H_2O was greater from the I solution than from distilled H_2O . Germination of seeds treated with I solution at 25° was normal and seedlings made slightly better growth than controls. No stimulation resulted from I treatment at higher temp.

A. G. POLLARD.

Relation between seeds and micro-organisms. T. R. SATHE and V. SUBRAHMANYAN (J. Indian Inst. Sci., 1931, 14A, 119—139).—There is no direct evidence of the presence of living micro-organisms inside healthy seeds. The micro-organisms usually found on the seed-coat are derived from the soil and are physiologically unrelated to the seed. Treatment of the seed-coat with antiseptic material is not inimical to germination or to the development of the seedling provided the material is removed prior to sowing.

W. G. EGGLETON.

Vital staining of plant cells with erythrosin. S. STRUGGER (Ber. deut. bot. Ges., 1931, 49, 453—476).—The visible effect of plasmolysing erythrosin-stained cells from the epidermis of *Allium cepa* and the root hairs of *Hydromyrtia bogotensis* with aq.

KNO_3 is described. Such staining increases at first the permeability of the cell membrane; the cytoplasm, however, soon ceases to swell, and finally coagulation of the protoplasts takes place. Vital staining occurs up to the point when the nucleus becomes irreversible.

A. LAWSON.

Loss of glucose from dried peas on soaking. W. M. CLIFFORD (Biochem. J., 1931, 25, 1999—2003).—Dried peas lose 0.1—0.15% of glucose on soaking in distilled H_2O for 18—24 hr. The loss is greater after the addition of acids, especially org. acids, but not of alkalis. The uptake of H_2O by dried peas is depressed by the addition of acids, alkalis, or salts. The rate of cooking of peas is unaltered by previously soaking them in acids, alkalis, or salts unless the concn. of alkali or salt is high enough to soften the whole pea in the cold. Such concn. renders the pea inedible.

S. S. ZILVA.

Variations in the Evening Primrose induced by radium. W. H. BRITTINGHAM (Science, 1931, 74, 463—464).

L. S. THEOBALD.

Toxic action. II. Toxicity of normal aliphatic alcohols towards potato. III. Parallelism between surface activity and toxicity of normal aliphatic alcohols. W. STILES and M. L. L. STIERK (Protoplasma, 1931, 13, 1—20, 363—373).—II. The toxicity to potato tuber of aliphatic alcohols as determined by the rate of exosmosis of electrolytes into solutions of the alcohols (cf. *ibid.*, 1927, 2, 577—601) increased with the no. of C atoms in the chain. In the series MeOH to octyl alcohol, addition of 1 C atom increased the toxicity 2.5—4.7 times.

III. In Traube's law concerning the surface tension of solutions of alcohols the factor 3 is approx. only, the average val. for 8 alcohols examined being 3.3. Equi-toxic solutions of different alcohols do not necessarily possess the same surface tension. Surface tension and toxicity increased with mol. wt., but the rise in surface tension was relatively more rapid than that of toxicity.

A. G. POLLARD.

Effect of heavy-metal compounds on plant cells. A. NIETHAMMER (Bot. Archiv, 1931, 33, 41—47).—The effect of solutions of salts of Ni, Hg, Cu, Zn, Co, and Al on the plasmolysis of epidermal leaf cells and of seeds is recorded. Prolonged contact with Hg salts causes the emergence of the plasma and nucleus from cells.

A. G. POLLARD.

Rust-resistance in wheat. V. Physiology of the host. W. F. HANNA (Canadian J. Res., 1931, 4, 134—147).—Catalase activity increases and diastase activity decreases as the plant matures. The oxidase activity and the rates of respiration of the 8 varieties do not differ. The wheats most susceptible to stem rust are those richest in chlorophyll, xanthophyll, and carotene. Photosynthetic processes may take place rapidly and furnish conditions suitable for the growth of the rust mycelium.

A. RENFREW.

Immunological studies on press juice and pigments of leaves. H. HODYO (J. Biochem., Japan, 1931, 13, 273—289).—Sp. immune bodies are formed when rabbits and guinea-pigs are immunised by applications to the skin of the press juice or pigments of leaves mixed with lanolin. Leaves from closely related species can be differentiated, but results with chlorophyll were uncertain.

CHEMICAL ABSTRACTS.

Serological analysis of protein complexes (protenoms) as a method of investigating biological relationships. O. MORITZ (Ber. deut. bot. Ges., 1931, 49, 76—78).—A discussion of the application of immunological methods for the detection of biological relationships.

W. O. KERMACK.

Determination of reducing sugar in syrups, blood, cerebrospinal fluid, milk, and urine. T. UGARTE (Anal. Assoc. Quím. Argentina, 1931, 19, 137—161).—The fluid for analysis is added, until the blue colour disappears, to 1 c.c. of a boiling solution prepared by adding NaOH to CuSO_4 in aq. glycerol. 1 c.c. of reagent containing 0.7% of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 4% of glycerol, and 2% of NaOH is equiv. to 1 mg. of glucose; 1 c.c. containing 0.07% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 4% of glycerol, and 0.4% of NaOH is equiv. to 0.1 mg. of glucose. The details of the determination of sucrose after inversion and of glucose in physiological fluids are described. The accuracy is comparable with that of the Hagedorn-Jensen method.

R. K. CALLOW.

Naphtharesorcinol reaction of alduronic acids. C. NEUBERG and M. KOBEL (Biochem. Z., 1931, 243, 435—450).—In carrying out the reaction 2N-HCl or 50% H_2SO_4 should be used as condensing agent and the mixture heated at 100° . The dye then separates in flocculent form and is best extracted with CHCl_3 or C_6H_6 . (AcOEt , PhMe , or Et_2O can also be used). Glucose, galactose, mannose, xylose, arabinose, maltose, and lactose in ratios not greater than 200 parts to 1 part of uronic acid, fructose in ratios not exceeding 40 : 1 (for galacturonic acid) or 30 : 1 (for glycuronic acid), or sucrose in ratios not exceeding 50 : 1 do not interfere. Simply combined uronic acids (e.g., those in urine) react directly, since they are hydrolysed by the acid used, but the more complex ones must first be hydrolysed with $\text{N-H}_2\text{SO}_4$. If material containing carbohydrates capable of fermenting fails, after fermentation, to react with naphtharesorcinol, but then reacts when a trace of uronate is added, uronic acids are absent. A method of preparing galacturonic acid from orange rind is given.

W. MCCARTNEY.

Determination of cystine in proteins by the method of Folin and Marenzi. S. L. TOMPSETT (Biochem. J., 1931, 25, 2014—2016).—A solution of NaHCO_3 is used instead of that of Na_2CO_3 . The colour produced in the presence of the former is uninfluenced by its concn. and no turbidity occurs. The cystine content of gelatin, caseinogen, edestin, ovalbumin, and serum-albumin has been determined.

S. S. ZILVA.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1932.

General, Physical, and Inorganic Chemistry.

Intensity distribution in the band spectrum of helium (He_2) for the region 6100—6500 Å. C. W. W. READ (Proc. Roy. Soc., 1932, A, 134, 643—657).—An expression is derived for the relative intensities of the band lines throughout a given band. The predicted and experimental distributions are in close agreement. L. L. BIRCUMSHAW.

High resolution in the infra-red. J. D. HARDY (Physical Rev., 1931, [ii], 38, 2162—2167).—Using the resonance radiometer, components of the infra-red spectrum of He I have been resolved; the faint lines of Ne I between 1 μ and 2 μ have been discovered and data for 30 lines are tabulated. N. M. BLIGH.

Band spectrum of beryllium hydride. E. OLSSON (Z. Physik, 1932, 73, 732—746).—An investigation of the BeH spectrum between 4800 and 5600 Å., and an estimation of dissociation consts. from rotation consts. A. B. D. CASSIE.

Two-electron spectrum of boron, B II, and irregular doublets in the series Be I to O V. B. EDLÉN (Z. Physik, 1931, 73, 476—481).—The ionisation potential of the 2^1S_0 term of B II is 25.007 volts, and the 2^3P_2 term lies 4.580 volts above the former. A. B. D. CASSIE.

Negative nitrogen bands. D. COSTER and H. H. BRONS (Z. Physik, 1932, 73, 747—774).

A. B. D. CASSIE.

Red oxygen radiation in the night sky. W. GROTRIAN (Naturwiss., 1932, 20, 85).—Polenical against Sommer (A., 1930, 1226). W. R. ANGUS.

Wave-length standards in the spectra of aluminium. Silicon and bismuth in the Schumann region. R. V. ZUMSTEIN (Physical Rev., 1931, [ii], 38, 2214—2216; cf. A., 1931, 1103).—Between 1900 and 1500 Å. measurements were made by comparison with Fe. Wave-lengths, accurate to 0.02 Å., are, for Si II 1816.922, 1808.01, 1533.42, 1526.71, and for Bi II 1902.33, 1823.71, 1791.82, 1787.39, and 1777.01. N. M. BLIGH.

Broadening of the spectra Al II, Mg I, Be I, Al I. F. PASCHEN (Ann. Physik, 1932, [v], 12, 509—527).—The $3p4s$ and $3p3d$ spectra were investigated. Strong line groups which occur are explained. A. J. MEE.

Spectra of two- and three-valency-electron atoms, Si II, P III, S IV, Si III, P IV, S V. I. S. BOWEN (Physical Rev., 1932, [ii], 39, 8—15).

N. M. BLIGH.

Anomalous fine structure and isotope displacements in the Cl^+ spectrum. S. TOLANSKY (Z. Physik, 1931, 73, 470—481).—The Cl^+ spectrum shows no hyperfine structure, indicating a negligible coupling of the nuclear spin and the outer electronic system. A. B. D. CASSIE.

Rotational structure of the red bands of potassium. F. W. LOOMIS (Physical Rev., 1931, [ii], 38, 2153—2161).—Full data and rotational analysis of four bands are tabulated. The nuclear spin of K^{39} is not zero. N. M. BLIGH.

Magnetic rotation spectrum and heat of dissociation of the potassium molecule. F. W. LOOMIS and R. E. NUSBAUM (Physical Rev., 1932, [ii], 39, 89—98; cf. this vol., 1).—The magnetic rotation spectrum of the near red band system of K_2 was measured. The heat of dissociation of the normal mol. is 0.51 ± 0.02 volt. The % of mols. in the vapour at various temps. is calc. An infra-red edge is predicted and confirmed. N. M. BLIGH.

Broad lines in the arc spectrum of copper. C. W. ALLEN (Physical Rev., 1932, [ii], 39, 42—54).—The anomalous broadening of certain lines was investigated and deductions therefrom are discussed. N. M. BLIGH.

Intensity of quadruplet lines in the arcspectrum of copper. C. W. ALLEN (Physical Rev., 1932, [ii], 39, 55—63; cf. preceding abstract).—Intensity measurements and classifications are tabulated and discussed. N. M. BLIGH.

Third spark spectrum of arsenic (As IV). K. R. RAO (Proc. Roy. Soc., 1932, A, 134, 604—613).—About 60 lines in the spectrum of As IV have been classified. The spectrum consists of a simple triplet and singlet system, and the abs. vals. of the characteristic terms have been estimated. The largest term, $4s^1S_0 = 404,369 \text{ cm}^{-1}$, leads to an ionisation potential of about 49.9 volts. L. L. BIRCUMSHAW.

Spectroscopic evidence of arsenic hydride. R. RYDBERG (Nature, 1932, 129, 167).—No signs of a band spectrum due to AsH could be detected. The previously-reported band (this vol., 103) at $31,802.6 \text{ cm}^{-1}$ is identical with the Q branch in the CH band, and the other bands are considered to be identical with the CH bands, 3143 Å. L. S. THEOBALD.

Krypton arc spectrum. W. GREMMER (Z. Physik, 1932, 73, 620—622).—The results agree with

the Bureau of Standards analysis (Meggers, Humphreys, and de Bruin, A., 1929, 1118; this vol., 2).
A. B. D. CASSIE.

Spectra of inert gases. E. RASMUSSEN (Z. Physik, 1932, 73, 779—790).—An extension of the term systems for Kr and Xe. A. B. D. CASSIE.

Anomalies in fine structure by self-absorption of spectral lines. E. LAU and O. REICHENHEIM (Naturwiss., 1932, 20, 49—50).—Anomalies in the fine structure of the 5461 Å. Hg line are discussed.
W. R. ANGUS.

Polarisation of mercury fluorescence in relation to line hyperfine structure. V. VON KEUSSLER (Z. Physik, 1932, 73, 649—657).—Polarisation and its rotation in weak magnetic fields of Hg resonance radiation agree with the term system of Schüller and Keyston (this vol., 2).
A. B. D. CASSIE.

Metal-inert gas bands in the positive column of electric discharges. H. KREFFT and R. ROMPE (Z. Physik, 1932, 73, 681—690).—Metal-inert gas bands are emitted by the positive column of discharges in mixtures of Tl, In, Zn, Na, K, Rb, and inert gases.
A. B. D. CASSIE.

Paschen-Back effect of hyperfine structure. I. THALLIUM II and III. II. BI II and BI III. J. B. GREEN and J. WULFF (Physical Rev., 1931, [ii], 38, 2176—2185, 2186—2192).—Analysis of the multiplets of the Zeeman patterns gives results in complete agreement with the Goudsmit-Bacher theory of the Paschen-Back effect.
N. M. BLIGH.

Mechanism of electric arcs. W. RAMBERG (Ann. Physik, 1932, [v], 12, 319—352).—Different phenomena of electric arcs are discussed for several metals.
W. R. ANGUS.

Spectra in the vanadium I isoelectronic sequence. (Miss) H. T. GILROY (Physical Rev., 1931, [ii], 38, 2217—2233).—Data obtained for displacements of multiplets and by applications of the regular and irregular doublet law and Landé interval rule, together with new lines and term vals., are tabulated.
N. M. BLIGH.

Existence of the *J*-phenomena. I. BACKHURST (Phil. Mag., 1932, [vii], 13, 28—48).—With special precautions to maintain const. electrical conditions no indication of the *J*-phenomena was found.
H. J. EMELÉUS.

Screening constants for many-electron atoms. Calculation and interpretation of X-ray term values, and of atomic scattering factors. L. PAULING and J. SHERMAN (Z. Krist., 1932, 81, 1—29; cf. A., 1927, 88, 394).—A complete set of screening consts. is deducible from X-ray term vals. and ionisation potentials, but as these are not known for heavy atoms a table of size screening consts. has been prepared partly from theoretical calculations, partly from term vals., which permits a satisfactory interpretation of energy levels of atoms.
C. A. SILBERRAD.

Ionisation in pressure chambers. E. G. STEINKE and H. SCHINDLER (Naturwiss., 1932, 20, 15—16).—Deviation of ionisation from linear increase with pressure is due, not to secondary effects, but to the use of voltages below saturation val.
A. B. D. CASSIE.

L-Discontinuities in X-ray absorption. E. OLSSON (Nature, 1932, 129, 94).—A discussion.
L. S. THEOBALD.

Kramer's theory of X-ray absorption. A. GANGULI (Indian J. Physics, 1931, 6, 453—457).—Theoretical.
E. S. HEDGES.

X-Ray wave-length by the dispersion in quartz. J. A. BEARDEN (Physical Rev., 1932, [ii], 39, 1—7).—High-precision measurements of the refraction of the Cu and Mo *K* series in quartz were made. Wave-lengths deduced from the quantum theory of dispersion are in close agreement with those obtained from crystal gratings; their divergence from results from ruled grating measurements indicates a failure of the optical diffraction theory when applied to X-ray wave-lengths.
N. M. BLIGH.

Appearance of continuous spectra on cathode-ray bombardment. V. Experiments with Lilienfeld and other tubes. W. M. COHN (Z. Physik, 1932, 73, 662—676).—Bluish radiation appears from the anticathode only when gas is present in the tube or when the anticathode is radioactive.
A. B. D. CASSIE.

Compton effect from the classical viewpoint. S. BJÖRCK (Z. Physik, 1931, 73, 541—546).—The Compton effect can be explained as a classical Doppler effect.
A. B. D. CASSIE.

Spectral sensitivity of thin alkali metal films at room and liquid air temperatures. R. SUHRMANN and H. THEISSING (Z. Physik, 1932, 73, 709—726).—Cooling to liquid air temp. increases the work required for emission of electrons from Pt through alkali metal layers, both when the layer is less than and greater than monatomic.
A. B. D. CASSIE.

Ionisation of adsorbed atoms. J. H. DE BOER (Chem. Weekblad, 1932, 29, 34—37).—A lecture.
H. F. GILLBE.

Oxide-coated filaments. II. Origin of enhanced emission. J. A. BECKER and R. W. SEARS (Physical Rev., 1931, [ii], 38, 2193—2213; cf. A., 1930, 127).—Experiments made to test the various theories of electron emission mechanism are described. It is concluded that the active layer is at the outer oxide surface, the activity depending on the concn. of Ba and O₂ on this surface, and on the amount of metallic Ba dispersed through the oxide; the core material mainly affects the ease of production of free Ba by heat-treatment or electrolysis. The thermionic electrons originate in the oxide just beneath the adsorbed Ba; most of the current through the oxide is conducted by electrons, a small portion being carried by Ba and O ions.
N. M. BLIGH.

Lag in photo-electric gas cells. R. FOURMARIER (Compt. rend., 1932, 194, 86—89).—By means of a specially designed cell it is shown that lag in high-pressure gas photo-electric cells is due to ionisation of the gas by positive ions. This explains the fact that such cells, when filled with A, show less lag than when filled with another gas.
C. A. SILBERRAD.

Photo-electric and thermionic properties of palladium. L. A. DUBRIDGE and W. W. ROEHR (Physical Rev., 1932, [ii], 39, 99—107).—The photo-

electric threshold gave a final val. of 2486 Å. after extended outgassing in vac.; the photocurrents excited by monochromatic light increase with rise of temp. Results are in good agreement with Fowler's theory (cf. A., 1931, 1106). The true work function is 4.97 ± 0.01 , and the thermionic work function 4.99 ± 0.04 volts. N. M. BLIGH.

Further experimental test of Fowler's theory of photo-electric emission. L. A. DUBRIDGE (Physical Rev., 1932, [ii], 39, 108—118; cf. preceding abstract and A., 1931, 1106). N. M. BLIGH.

Ionised gases in a magnetic field; proof of existence of the spinning electron. T. V. IONESCU and C. MIHUL (Compt. rend., 1932, 194, 70—72; cf. A., 1931, 285).—The effect on conductance, σ , of a magnetic field, H , parallel to the plates of the ionised gas condenser is shown by a series of σ - H curves for varying wave-lengths, distinguishing conductance due to free electrons from that due to electrons attached to mols. Results indicate that the latter are in a mol. magnetic field of 10.5 gauss which gives them a precessional motion with angular velocity corresponding with the natural frequency of the ionised gas in absence of an external magnetic field. C. A. SILBERRAD.

Diffraction of electrons by single crystals of gold and platinum. J. J. TRILLAT and T. VON HIRSCH (Compt. rend., 1932, 194, 72—74; cf. this vol., 3).—On annealing the Au leaf action begins at 400°; between 400° and 500° all indications of strain disappear, and above that temp. recrystallisation begins, the large oriented crystals breaking up into a confused mass of small crystals and the leaf becoming brittle. Pt leaf gives effects in all respects similar to Au. Results are due to diffraction of electrons by a three- and not by a two-dimensional lattice (cf. A., 1931, 782). C. A. SILBERRAD.

Diffraction of slow electrons at ionic crystals, with special reference to the inner potentials of calcite and aragonite. W. DAMES (Ann. Physik, 1932, [v], 12, 185—210).—Diffraction experiments were carried out with electrons of 20—300 volts with calcite and aragonite. The position of the maxima and the size of the inner potentials were independent of time and the previous history of the crystal. For the crystals used the work of Laue and Rupp is substantiated. For calcite the inner potential is -11.9 ± 3 volts. Aragonite has two inner potentials. A. J. MEE.

Electron microscope. E. BRÜCHE (Naturwiss., 1932, 20, 49).—Photographs are shown of an electron bundle rendered parallel by a double condenser and of an oxide cathode, using high-voltage electrons with an apparatus giving high magnification. W. R. ANGUS.

Complete differential secondary radiation in air for electrons of medium velocity. E. KIPPHAN (Ann. Physik, 1932, [v], 12, 401—432).—Apparatus for investigating the above is described. A. J. MEE.

Electron motion in flames. K. VOGT (Ann. Physik, 1932, [v], 12, 433—476).—Electrical phenomena in pure (metal-free) flames are investigated,

especially those properties which could readily be used for the observation of the mobility of ions or electrons in flames. A. J. MEE.

Determination of the specific charge of the electron from velocity measurements. F. KIRCHNER (Ann. Physik, 1932, [v], 12, 503—508).—The results of a new determination of e/m based on the combination of a direct velocity measurement with a determination of the recombination potential of cathode rays give the val. $1.7590 \pm 0.0015 \times 10^7$ e.m.u. A. J. MEE.

Photo-electrons and negative ions. V. A. BAILEY (Nature, 1932, 129, 166—167).—Wellish's conclusions (A., 1931, 1347) are criticised and evidence is advanced supporting the view that the formation of negative ions by attachment of electrons to mols. in a gas is as frequent as the formation near the cathode. L. S. THEOBALD.

Interaction of radiation and the electron. R. D. KLEEMAN (Phil. Mag., 1932, [vii], 13, 69—76).—Theoretical. H. J. EMELEUS.

Production of high-velocity positive ions by successive accelerations. J. THIBAUD (Compt. rend., 1932, 194, 360—362).—A well-defined pencil of positive ions is passed through a series of tubes (Faraday cages) connected alternately with the terminals of an oscillatory circuit, the length of successive tubes increasing proportionally to the increasing velocity of the ion due to the successive accelerations. The whole is in a vac. H^+ ions of 145 kv. have been obtained with 11 such accelerations, using a.c. of 13 kv. and wave-length 100 m. (cf. A., 1931, 270). C. A. SILBERRAD.

At. wt. of fluorine. E. MOLES (Anal. Fis. Quím., 1931, 29, 605—615).—Existing data on the at. wt. of F have been recalcd. The mean of four modern determinations is 18.999. It is probable that the MeF used by Patterson, Whytlaw-Gray, and Cawood (A., 1931, 1207) contained about 2% of CH_4 . H. F. GILLBE.

Nuclear moment of Se^{80} . K. WURM (Naturwiss., 1932, 20, 85).—From considerations of the spectroscopic data of Se, and a comparison of the rotation term const. for the ground state with the corresponding const. for O^{16} and S^{32} , it is deduced that Se^{80} has no nuclear moment. W. R. ANGUS.

Isotopic constitution and at. wt. of caesium, strontium, lithium, rubidium, barium, scandium, and thallium. F. W. ASTON (Proc. Roy. Soc., 1932, A, 134, 571—578).—The use of a volatile chloride of Ta of unknown composition in the mass spectrograph apparatus failed to give any indication of the lines of Ta, and failure was also experienced with the volatile Pt compound $PtCl_2(CO)_2$. By using a new type of composite anode and improving the vac. in the camera the isotopic constitutions, percentage abundances, packing fractions, and at. wts. of several elements have been determined. Cs is simple, with packing fraction -5.0 ± 2 and at. wt. 132.917 ± 0.02 . Sr has isotopes 86 (percentage abundance, *p.a.*, 10), 87 (*p.a.* 6.6), 88 (*p.a.* 83.3), at. wt. 87.64 ± 0.06 . The ratio of Li^6 to Li^7 has a max. val. 11, giving at. wt. 6.928 ± 0.008 . The ratio of Rb^{85} to Rb^{87} is 3, giving

at. wt. 85.43 ± 0.03 . Ba has isotopes 135 (*p.a.* 5.9), 136 (*p.a.* 8.9), 137 (*p.a.* 11.1), 138 (*p.a.* 74.2), packing fraction -6.1 ± 2 , at. wt. 137.43 ± 0.08 . Sc is simple, with packing fraction -7 and at. wt. 44.96 ± 0.05 . The ratio of Ti^{203} to Ti^{205} is 2.40, packing fraction 1.8 ± 2 , at. wt. 204.41 ± 0.03 . The calc. at. wts. are in good agreement with the accepted chemical vals. with the exception of those of Sc and Cs.

L. L. BIRCUMSHAW.

Mechanical moment of the caesium nucleus from the hyperfine structure of some Cs^+ lines. H. KOPFERMANN (Z. Physik, 1931, 73, 437—451).—The spin of the Cs nucleus is most probably $7/2$.

A. B. D. CASSIE.

Element 87. C. F. GRAHAM (Science, 1931, 74, 665—666).—Curves for the alkali metals showing at. nos. plotted against at. vol., m. p., b. p., and sp. heat are extended to include element 87. The sp. gr. of element 87 should be approx. 2.2.

L. S. THEOBALD.

Nuclear moment of rhenium. L. A. SOMMER and P. KARLSON (Naturwiss., 1931, 19, 1921).—The isotopes of Rh have each a nuclear moment of $5/2$.

A. B. D. CASSIE.

Investigations with a Wilson chamber. II. Range and velocity of recoil atoms. P. M. S. BLACKETT and D. S. LEES (Proc. Roy. Soc., 1932, A, 134, 658—671; cf. A., 1924, ii, 289).—Blackett's method has been used to extend the earlier results (*loc. cit.*) to greater ranges and velocities. Range-velocity curves are given for H particles, α -particles, N, O (O^{16} and O^{17}), and A atoms.

L. L. BIRCUMSHAW.

Charge carried by atoms of radium-D emitted by α -ray recoil from a source of radium-C on a metallic surface, and its relation with the surface forces. J. D. MCGEE (Phil. Mag., 1932, [vii], 13, 1—23).—The charge on a recoil atom is influenced by interaction with the surface from which it escapes; the recoil atom of Ra-D from Ra-C deposited on Ni or Pt has a charge of $+1$.

H. J. EMELEUS.

Regularities between α and β disintegration constants. J. KUDAR (Naturwiss., 1932, 20, 84—85).—Radioactive transformations, in which the transitions α - β , β - α , and β - β occur, are considered. Vals. of the mean life period are given for each transition in the "triad" and an approx. classification can be obtained. The product of the three mean life periods of the transitions concerned gives an approx. const. val. for each "triad."

W. R. ANGUS.

Distribution of energy in the β -ray spectrum of radium-E. F. C. CHAMPION (Proc. Roy. Soc., 1932, A, 134, 672—681).—Using an automatic expansion chamber, the energy distribution of the β -ray spectrum of Ra-E has been studied from H_p 2400 upwards. The existence of a sharp upper limit at about H_p 5500 has been confirmed. No evidence of any gradual tailing off has been found, and it is estimated that less than 1 particle in 2000 is emitted with $H_p > 5500$.

L. L. BIRCUMSHAW.

Increase of absorption of β -rays by molecules of certain constitution. G. FOURNIER and M. GUILLOT (Compt. rend., 1931, 194, 171—173).—The

"normal" relation $\mu/\rho = 15 + 0.142N$, where μ/ρ is the mass coeff. of absorption of β -rays of Ra-D+E and N the at. no. (cf. A., 1925, ii, 176), holds accurately for Li, Be, Ti, and Zr, and also for NaF, NaCl, KCl, AgCl, KBr, AgBr, KI, MgO, and CuO (although not for F, Cl_2 , Br, I, or O_2). The actual figure is in excess of the calc. for C (diamond), SiC, AgI, cuprite, blende, wurtzite, and zincite. Different allotropic forms have different vals. Differences from "normal" vals. in compounds accompany homopolar linkings, and only substances showing such differences exhibit the Raman effect.

C. A. SILBERRAD.

Nuclear γ -radiation excited in beryllium and lithium by α -rays of polonium. (MME.) I. CURIE (Compt. rend., 1931, 193, 1412—1414; cf. A., 1931, 142).—The α -rays from a source of Po of some 100 millicuries acting on Be produce γ -radiation about five times as intense as that from Po, but with coeff. of mass absorption $(\mu/\rho)_{\text{Pb}}$ 0.013, wave-length 0.6—0.7 X, and energy 15 — 20×10^6 electron-volts. Li under similar conditions gives γ -radiation of intensity about equal to that of Po, $(\mu/\rho)_{\text{Pb}}$ 0.15, λ 20 X, and energy 6×10^5 electron-volts. The results do not appear to support the theory that this radiation is due to capture of an α -particle by the light element nucleus.

C. A. SILBERRAD.

Excitation of nuclear γ -rays of boron by α -particles. Quantum energy of the γ -radiation of polonium. F. JOLIO (Compt. rend., 1931, 193, 1415—1417; cf. preceding abstract).—B under similar conditions emits γ -radiation of $(\mu/\rho)_{\text{Pb}}$ 0.02 (that of Po being 0.083), and energy 11×10^6 electron-volts. This result is deemed to support the theory of α -particle capture by the B nucleus.

C. A. SILBERRAD.

Emission of high-velocity protons by the action of very penetrating γ -rays on substances containing hydrogen. (MME.) I. CURIE and F. JOLIO (Compt. rend., 1932, 194, 273—275).—The γ -radiation produced by the action of α -rays from Po on Be and B (cf. preceding abstracts) passed through a thin sheet of Al and 1.5 cm. of Pb is little affected by further passage through thin screens of C, Al, Cu, Ag, Pb, etc., but if passed through a substance containing H, e.g., paraffin, produces greatly increased ionisation. The radiation causing this is due to H-particles, of air path 26 and 8 cm. for those produced from Be and B, respectively, and corresponding with energies of 4.5 and 2×10^6 electron-volts. It is suggested that the photons communicate part of their energy to the protons by a sort of Compton effect. No such effect is obtainable with Th-C.

C. A. SILBERRAD.

Very small ionisation chambers for local measurement of γ -radiation. L. MALLET (Compt. rend., 1932, 194, 370—372).—The arrangement consists of an ionisation chamber which may be as small as 2.8 mm. diameter, which is charged in connexion with the electroscope, then detached therefrom and placed where the radiation is to be measured for a suitable period, and then reattached to the electroscope. Diagrams are given.

C. A. SILBERRAD.

Atomic disintegration measurements. G. HOFFMANN (Z. Physik, 1932, 73, 578—579).—The reality of measurements on *H*-rays is reasserted (A., 1929, 963). A. B. D. CASSIE.

Cathodic evaporation in a magnetic field. E. HENRIOT and O. GOCHE (Compt. rend., 1932, 194, 169—170; cf. A., 1926, 693; 1927, 118; 1931, 407).—When cathodic evaporation occurs in a magnetic field, the cathode (of Ag, Cu, Sn, Zn, Pb, As, Sb, or Si) being in H_2 and the anode in the form of a box with a slit towards the cathode and a screen on the opposite side, an image of the slit is formed on the screen by (magnetically) directed, and a general film by undirected, evaporation. As a rule on dissolving away the evaporated material an image of the slit remains as a slightly blackish film. This is due to C in the cathode, as with a C cathode only the slit image is formed, whilst the H_2 pressure diminishes. This phenomenon affords a method of detecting small quantities of C. C. A. SILBERRAD.

Normal state of the hydrogen molecule. N. ROSEN (Physical Rev., 1931, [ii], 38, 2099—2114).—The dissociation energy, moment of inertia, and fundamental vibration frequency calc. by a variational method are in good agreement with experimental vals. N. M. BLIGH.

Natural units for atomic problems. A. E. RUARK (Physical Rev., 1931, [ii], 38, 2240—2244).—A consistent scheme for the simplification of quantum algebra is described. N. M. BLIGH.

Spinning photon and its scattering by molecules. S. BHAGAVANTAM (Nature, 1932, 129, 167—168).—Mainly a summary. The observed depolarisation of the strongest Raman line of liquid CS_2 agrees with the val. calc. from the theory of spinning photons. L. S. THEOBALD.

Influence of absorption rays of hydrogen on the colorimetric determination of the temperature of stars. V. G. FESENKOV (Bull. Acad. Sci. U.S.S.R., 1931, 787—799).

Pauli's principle and the structure of the atomic nucleus. E. N. GAPON (J. Gen. Chem. Russ., 1931, 1, 641—659).—Theoretical.

R. TRUSZKOWSKI.

Nuclear structure. A. CARRELLI (Physikal. Z., 1932, 33, 73—76).—Mathematical. Using the Gamow model for the nucleus and the empirical Aston data some calculations concerning the structure of the nucleus are made. A. J. MEE.

Photographic study of evaporation rings. E. C. H. DAVIES (Proc. W. Va. Acad. Sci., 1930, 4, 80—85).
CHEMICAL ABSTRACTS.

Simple relations between molecular spectra and structure. H. DESLANDRES (Compt. rend., 1931, 193, 1364—1368; cf. A., 1931, 892).—Previous results are summarised, and it is suggested that the portions of mol. spectra attributed to mol. rotation are really due to the action of the nucleus of one atom on the electrons of one or more rings of the other. C. A. SILBERRAD.

Absorption spectrum of chlorine dioxide. H. C. UREY and (Miss) H. JOHNSTON (Physical Rev.,

1931, [ii], 38, 2131—2152).—Wave-length and energy level data of 134 absorption bands of ClO_2 are tabulated; 5 vibrational levels of the normal electronic state were found. Formulæ for the bands and their isotope separations are given and the normal modes of vibration for the mol. calc. N. M. BLIGH.

Band spectrum of zirconium oxide. F. LOWATER (Proc. Physical Soc., 1932, 44, 51—66).—The band spectrum of ZrO was photographed from λ 2600 to λ 8800; bands were found from λ 3200 to λ 7600, the most prominent being analysed into blue, yellow, and red-infra-red systems, all having the same lower electronic state. Complete data are tabulated. N. M. BLIGH.

Transparency of gypsum and mica in the ultra-violet. T. TAKAGI (Strahlenther., 1931, 40, 189—192; Chem. Zentr., 1931, ii, 819).—Radiation from a quartz Hg lamp which has passed through natural cleavage plates of gypsum is very active towards blood-agar plates and human skin, whilst radiation filtered through mica is apparently inactive. A. A. ELDRIDGE.

Electronic transitions between an inner shell and the virtual outer shells of the ions of the rare earths in crystals. S. FREED (Physical Rev., 1931, [ii], 38, 2122—2130).—The ultra-violet absorption spectra of $CeCl_3 \cdot 6H_2O$ and $Ce(EtSO_4)_3 \cdot 9H_2O$, alone and diluted in the isomorphous La crystals, were investigated at room temp. and at that of liquid N_2 and H_2 . The nature and origin of the observed bands are discussed. It is concluded that the lines of the rare earths in general are associated with inner quantum states. N. M. BLIGH.

Red CN band system. F. A. JENKINS, Y. K. ROOTS, and R. S. MULLIKEN (Physical Rev., 1932, [ii], 39, 16—41).—From measurements of the spectrum excited by CCl_4 vapour mixed with active N complete data and analyses are tabulated for rotational structure, spin and Λ doubling, perturbations, and vibrational structure. N. M. BLIGH.

Bands of CH and CN in stellar spectra. P. SWINGS and O. STRUVE (Physical Rev., 1932, [ii], 39, 142—150).—The upper limit of visibility in the spectral sequence of the CH band at λ 4300 and of the CN band at λ 4200 is *F8*; the heats of dissociation are 110 and 210 kg.-cal. per mol., respectively. The former region is very rich in at. lines, their intensity greatly exceeding that of the mol. lines.

N. M. BLIGH.

Stereochemical studies on hydronaphthalene and derivatives. II. Absorption spectra of hydronaphthalenes. S. KIMURA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 303—316; cf. A., 1931, 1288).—Absorption spectra are recorded for $C_{10}H_8$ (in EtOH), Δ^1 -di-, tetra-, *cis*-octa-, and deca-hydronaphthalene. Those of the last two compounds differ from those of the others, and it is concluded that the formula of $C_{10}H_8$ is asymmetric. R. S. CAHN.

Absorption in ultra-violet and chemical reactivity of organic compounds. (MNE.) P. RAMART-LUCAS and J. HOCH (Compt. rend., 1932, 194, 96—99).—The ultra-violet absorption of substances of the types $Ph[CH_2]_n \cdot CO_2H$, $PhO[CH_2]_n \cdot CO_2H$,

and $\text{PhO} \cdot [\text{CH}_2]_n \cdot \text{OPh}$ is compared; that of the first is very similar to that of PhEt , and of the other two to that of PhOMe . It is concluded that the mutual influences of the chromophores (Ph and $\cdot\text{CO}_2\text{H}$) lead to an increase of absorption when these are joined through C to the chain, but to a decrease when joined by O. Results are discussed in connexion with mol. rearrangement and ring formation. H. A. PIGGOTT.

Absorption of saturated fatty acids in the ultra-violet. O. HARTLEB (Strahlenther., 1931, 39, 442—448; Chem. Zentr., 1931, ii, 682).—Results for propionic, butyric, valeric, lauric, palmitic, and stearic acids are recorded. A. A. ELDRIDGE.

Ultra-violet absorption of the [amino-acid] constituents of proteins. H. GUTHMANN, K. SCHWERIN, and F. STAHLER (Strahlenther., 1931, 39, 401—441; Chem. Zentr., 1931, ii, 682).—From experiments on NH_2 -acids in biological concn., vals. corresponding with the composition of albumin, globulin, and fibrin were calc. Absorption max. are observed for the mixture at 300 and 250 $\text{m}\mu$; these wave-lengths are particularly active in producing light erythema. Greatest absorption was shown by tyrosine, phenylalanine, and glutamic acid. The absorptive power of EtCO_2H , alanine, phenylalanine, tyrosine, histidine, and tryptophan is independent of the mol. wt., but closely dependent on the stereochemical structure. The ultra-violet absorptive power of EtOH and aliphatic amines, acids, and aldehydes falls in the order CHO , NH_2 , CO_2H , OH . A. A. ELDRIDGE.

Absorption of infra-red radiation by small particles. A. H. PFUND and S. SILVERMAN (Physical Rev., 1932, [ii], 39, 64—71).—Investigations with small particles of quartz, calcite, and NH_4Cl coated on the vanes of a special radiometer indicate that the crystals, when sufficiently finely divided, do not reflect well in their regions of metallic reflexion. N. M. BLIGH.

Absorption and reflexion spectra of calcite in the infra-red. S. SILVERMAN (Physical Rev., 1932, [ii], 39, 72—76; cf. A., 1931, 408, and preceding abstract).—Previously unobserved fine structure was detected in the region 6.6—7.4 μ ; possible explanations are discussed. Good agreement between absorption and reflexion wave-lengths within the bands is shown. N. M. BLIGH.

Infra-red absorption bands of water vapour. E. K. PLYLER (Physical Rev., 1932, [ii], 39, 77—82; cf. A., 1931, 892).—Data for 45 lines in the region 1.4 μ and 68 lines in the region 1.90 μ are tabulated. The 1.87 μ band has been further resolved. Observed and calc. intensities are in good agreement; a new classification of the combination bands is given. N. M. BLIGH.

Near infra-red absorption spectrum of methane. J. G. MOORHEAD (Physical Rev., 1932, [ii], 39, 83—88).—Data for the region 1.4—2.6 μ are tabulated; strong bands were found at 1.6 and 2.3 μ , and fine structure was resolved. The vals. deduced for the moment of inertia are 5.32×10^{-40} and 5.17×10^{-40} , respectively. N. M. BLIGH.

Infra-red absorption spectra of aromatic hydrocarbons. P. LAMBERT and J. LECOMTE (Compt.

rend., 1932, 194, 77—79).—The following results were obtained with an improved form of the registering spectrometer (cf. A., 1929, 975): C_6H_6 has a band at 14.8 μ , corresponding with one near 14.4 μ in all alkylbenzenes, the lateral chain giving bands near 13.6 μ . The methylbenzenes show bands characteristic of the *o*-, *m*-, and *p*-positions. 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$, like *m*-xylene, has a band at 14.50 μ , whilst 1 : 3 : 4- $\text{C}_6\text{H}_3\text{Me}_3$ has bands characteristic of *o*- (13.47 μ), *m*- (14.5, 13.02, and 11.43), and *p*- (12.34) -xylenes, and is thus readily distinguished from its isomeride. The spectra of the monoalkylbenzenes in this region differ completely from those of corresponding polyalkyl isomerides. C. A. SILBERRAD.

Infra-red spectra of polyatomic molecules. E. TELLER and L. TISZA (Z. Physik, 1932, 73, 791—812).—The degenerate vibrations of polyat. mols. may have a mean angular momentum, which coupled to the rotation of the mol. gives unusual line separations; the spectra of CH_4 and of the Me halides show this anomalous line separation.

A. B. D. CASSIE.
Use of high dispersion in the study of the Raman effect. P. L. MESNAGE (J. Phys. Radium, 1931, [vii], 2, 403—412).—Raman intensities and wave-lengths, including those for certain new lines and satellites, are reported for C_6H_6 , PhMe , $\text{C}_2\text{H}_5\text{Cl}$, and CS_2 . N. M. BLIGH.

Circular polarisation of light in the Raman effect. J. CABANNES (J. Phys. Radium, 1931, [vii], 2, 381—391; cf. Hanle, A., 1931, 997).—The relation between the sense of polarisation of the Raman lines and the depolarisation factor of the light scattered at right angles to the incident radiation is discussed. N. M. BLIGH.

Anomalous depolarisation of Raman lines in uniaxial crystals. J. CABANNES and (MLLE.) OSBORNE (Compt. rend., 1931, 193, 1410—1412).—Theoretical; the results obtained (cf. A., 1929, 378, 627; 1930, 15) regarding the intensity and depolarisation of the Raman lines produced by the external oscillations of calcite are completely explicable by Kramers and Heisenberg's theory (cf. A., 1924, ii, 644). C. A. SILBERRAD.

Reversal of circular polarisation in Raman scattering. S. BHAGAVANTAM (Indian J. Physics, 1931, 6, 389—400).—A theory of the scattering of circularly polarised light by rotating molecules is developed on classical lines. E. S. HEDGES.

Polarisation rules for Raman lines in liquids. Theoretical and experimental results. J. CABANNES and A. ROUSSET (Compt. rend., 1932, 194, 79—81).—Theory (cf. A., 1929, 752; 1930, 15; 1931, 893) requires that if, during the fundamental oscillation, the deformed mol. does not retain all the elements of symmetry of the undeformed mol. the depolarisation factor, ρ , = 6/7. In no case can $\rho > 6/7$, and lines for which $\rho < 6/7$ correspond with oscillations symmetrical relatively to all the elements of symmetry of the mol. Results contrary to the foregoing are shown to be erroneous. No explanation is so far available for the vals. of ρ deduced from considerations of optical anisotropy being much in excess of experimental vals. C. A. SILBERRAD.

Smekal-Raman effect in some sulphur compounds. J. MEYER (Z. anorg. Chem., 1931, 203, 146—155).—Raman frequencies are given for S (in CS₂), S₂Cl₂, SOCl₂, SO₂Cl₂, ClSO₃H, SO(OMe)₂, SO(OEt)₂, SMe₂, SEt₂, and SMeEt. E. S. HEDGES.

Complete Raman spectrum in relation to infra-red absorption. I. Pyridine and acetic acid. P. KRISHNAMURTI (Indian J. Physics, 1931, 6, 367—387).—An improved technique has revealed numerous new lines in the Raman spectra of C₅H₅N and AcOH and the complete spectra thus obtained reproduce all the max. observed in the infra-red absorption spectra of these liquids. There are no completely inactive frequencies. E. S. HEDGES.

Raman effect and formation of hydrates in solution. P. KRISHNAMURTI (Indian J. Physics, 1931, 6, 401—412).—The Raman frequencies of C₅H₅N, AcOH, and MeOH in aq. solution have been compared with those of the pure liquids. Changes in the position and intensity of the lines indicate the existence of C₅H₅N.2H₂O. The H₂O mols. are attached to the N atom in much the same way as HCl becomes attached. The max. change in the AcOH solution occurs at the composition AcOH.H₂O; in MeOH solution the formation of MeOH.2H₂O is indicated. The frequencies undergoing changes are represented in the infra-red spectrum by strong absorption max. The lines associated with polar groups in the mol. show the max. changes in solution. E. S. HEDGES.

Raman spectra of some cyclohexane hydrocarbons. M. GODCHOT, E. CANALS, and (MLLE.) G. CAUQUIL (Compt. rend., 1932, 194, 176—177).—The Raman lines up to about 3000 cm.⁻¹ of methyl- and 1:2, 1:3-, and 1:4-dimethyl-cyclohexane are tabulated. These differ but slightly from those of cyclohexane, chiefly in showing lines between 800 and 1000. Compared with those of *n*-hexane they indicate that the lines near 500, 1260, and 2925 are characteristic of the ring. C. A. SILBERRAD.

Raman effect for benzene substitution products by improved technique. R. W. WOOD (Physical Rev., 1931, [ii], 38, 2168—2175).—Existing data for C₆H₆, PhMe, *o*-, *m*-, and *p*-xylene, PhBr, Ph₂, Ph₂O, and Ph₂S₂ are revised and corrected. The existence of anti-Stokes lines of C₆H₆, PhMe, and xylene is proved, and data are recorded. N. M. BIGH.

Molecular light scattering in solid bodies. IV. Intensity of light scattered by rock-salt. G. LANDSBERG and S. L. MANDELSTAM (Z. Physik, 1931, 73, 502—510).—Rock-salt is more nearly isotropic than quartz, and light scattered by it obeys more closely theoretical predictions. A. B. D. CASSIE.

Raman effect due to metal electrons. F. W. LOOMIS and J. G. WINANS (Z. Physik, 1932, 73, 658—661).—An unsuccessful attempt to reveal the quantum states of conductivity electrons by the Raman effect. A. B. D. CASSIE.

Use of fluorescence for photometric measurement in the ultra-violet. A. CHEVALLIER and P. DUBOULOZ (Compt. rend., 1932, 194, 174—176).—An adaptation is described of Thover's proposal (cf.

ibid., 1930, 191, 731) to measure ultra-violet radiation by coating a photo-electric cell with fluorescent material. The most suitable material is Na salicylate mixed with dextrin. With this radiation of λ 3900—1900 is measured by the fluorescence produced thereby, and that of longer wave-length directly. C. A. SILBERRAD.

Fluorescence of steam. F. RASETTI (Nuovo Cim., 1931, 8, 191—193; Chem. Zentr., 1931, ii, 1537).—On irradiation of steam under atm. pressure with 2537 Å. fluorescence was observed. The continuum 2520—3500 Å. has a marked max. at 2537 Å. The presence of Hg is unlikely, and the fluorescence (several thousand times as intense as the Raman effect) is apparently due to the H₂O vapour. A. A. ELDRIDGE.

Red fluorescence of glass. L. BRÜNINGHAUS (J. Phys. Radium, 1931, [vii], 2, 398—402).—Polemical against Peters (cf. A., 1931, 150). N. M. BIGH.

Origin of broad absorption and fluorescence bands in solutions of dyes. A. JABLONSKI (Z. Physik, 1931, 73, 460—469).—The Franck-Condon hypothesis is extended to systems with many degrees of freedom, and, together with density fluctuations of the solution near the absorbing or emitting mol., explains the general characteristics of these spectra, including Stokes' rule, independence of the intensity distribution in fluorescence spectra of aq. solutions, and dependence in viscous solutions, on the exciting wave-length, and broadening and displacement of bands on rise of temp. A. B. D. CASSIE.

Analysis of band spectra of the Lenard phosphors. F. SCHMIDT (Ann. Physik, 1932, [v], 12, 211—238).—The emission spectra of Lenard phosphors were investigated and analysed. The emission bands of the phosphor belong to the same series as those of the absorption, but there are more bands. All the phosphors, irrespective of the foreign metal, have the same band series in emission and absorption. A. J. MEE.

Luminous effects produced by rolling amalgams on glass in vacuum. DUFFIEUX and G. TROTEL (Compt. rend., 1931, 193, 1405—1407).—With the same method as that used with Hg (cf. A., 1928, 467) the results with amalgams of Zn, Cd, and Na are similar to those with Hg. C. A. SILBERRAD.

Study of ionic migration in rock-salt crystals by means of phosphorescence. F. BANDOW (Ann. Physik, 1932, [v], 385—400).—The electrical and thermal migration of Ag ions in rock-salt crystals has been studied by phosphorescence means which are described in detail. Rexer's work (A., 1931, 998) is discussed. The emission spectra of certain NaCl phosphors have been investigated. W. R. ANGUS.

Explanation of the destruction of the photo-luminescence of fluorescing systems by oxygen. Formation of active diffusible oxygen molecules by sensitisation. H. KAUTSKY and H. DE BRUIJN (Naturwiss., 1931, 19, 1043).—The destruction by O₂ of the fluorescence and phosphorescence of many dyes which are adsorbed on surfaces has been explained by supposing that the O₂ is rendered active

by a transference of energy from the dye to the O_2 . This active O_2 is short-lived and diffusible, and its action is dependent on its pressure. It is suggested that the active O_2 is in the metastable state.

W. R. ANGUS.

Electrolytic valve action. III. Dielectric constant of the Al_2O_3 buffer layer. IV. Streaming mechanism in the buffer layer of the transpiratory metal. A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1932, 73, 580—585, 586—601; cf. A., 1931, 546, 1130).—III. The dielectric const. of this layer, formed under 400 atm. pressure and 10^7 volts per cm., is 7.45.

IV. The electrical resistance of the buffer layer itself may be great, or it may be small and the greater part of the field intensity may be required at the interface of the buffer layer and electrolyte for liberation of electrons and ions.

A. B. D. CASSIE.

Electrolytic valve action. W. J. MÜLLER (Z. Physik, 1931, 73, 560—564).—Polemical against Günther-Schulze and Betz (A., 1931, 546).

A. B. D. CASSIE.

Effect of pressure on the electrical conductance of salt solutions in water. W. A. ZISMAN (Physical Rev., 1932, [ii], 39, 151—160).—New data are given for a range at 30° of 1—10,000 kg. per sq. cm. and at 75° of 1—11,000 for 0.01*N* solutions at 30° of HCl, LiCl, NaCl, KCl, RbCl, CsCl, NaF, NaBr, NaI, Na_2SO_4 , NaOAc, $CaCl_2$, $BaCl_2$, $ThCl_4$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and at 75° excepting NaF and $ThCl_4$. The observed equiv. conductivity max. cannot be entirely due to a change in the degree of ionic dissociation with pressure; there must be a large change in the diameters of the ions.

N. M. BLIGH.

Absorption of shorter wave-length electric waves by dipolar liquids and electrolytic solutions. J. MALSCH (Physikal. Z., 1932, 33, 19—21).—The absorption coeffs. for alcohols at shorter wave-lengths can be determined from measurements of conductivity for wave-lengths between 76 and 28 m. by means of Debye's conductivity formula. Measurements were also made for solutions of $AgNO_3$ and Fe chlorides in EtOH.

A. B. D. CASSIE.

Dispersion measurements in liquids, particularly in biological solutions, with undamped waves between 1 and 4 metres wave-length. E. MAY and H. SCHAEFER (Z. Physik, 1931, 73, 452—459).—Apparatus for measurement of dielectric consts. at continuously successive wave-lengths is described.

A. B. D. CASSIE.

Retardation of electric waves on passing through an ionised gas. W. HASSELBROCK (Ann. Physik, 1932, [v], 12, 477—502).—The dependence of the absorption of electric waves of length 2—6 cm. on passing through an ionised gas on the electron density and frequency was determined.

A. J. MEE.

Conductivity of complex compounds of platinum. I. I. TSCHERNIAEV and S. I. CHORUNSHENKOV (Ann. Inst. Platine, 1931, 8, 83—92).—Measurements of the conductivity of 33 complex Pt derivatives confirm the structural formulæ assigned to them on chemical evidence. The val. of the con-

ductivity found for amidodiammines is of the same order as for binary electrolytes, but does not vary according to Ostwald's law. The strength of complex bases depends chiefly on the nature of acidic substituents present, on the geometrical isomerism of a given base, and only to a smaller extent on the nature of neutral substituents in the inner sphere. The dissociation consts. of sulphates of hexammines are much smaller than are those of chlorides or nitrates.

R. TRUSZKOWSKI.

Dielectric constants of liquids. V. Aqueous solutions of organic compounds. G. DEVOTO (Gazzetta, 1931, 61, 897—909).—Measurements with solutions of a variety of NH_2 -acids confirm the polar structure of these compounds, as the dielectric const. ranges from 20 to 70. Polar formulæ for methylcarbamide and malonamide are suggested; *s*-dimethylcarbamide is probably of analogous structure, but for the *as*-form the dielectric const. is nearly zero. For solutions of semicarbazide, aminoethyl alcohol, NH_2Ac , succinamide, succinimide, and urethane the const. lies between 0 and —10.

H. F. GILLBE.

Refractive power of santonin and some of its isomerides and derivatives. II. Santoninic and photosantoninic acids and chromosantonin. G. BANCHI and V. E. INFANTE (Gazzetta, 1931, 61, 839—845).—The refractive indices for the H_α , H_β , H_γ , and D lines, and the densities, of $CHCl_3$ solutions are recorded. The observed mol. refraction of santoninic acid agrees with that calc. on the supposition of the ketonic structure. For photosantoninic acid and chromosantonin the calc. and observed vals. differ by 2—3 units; the reasons for the discrepancy are discussed.

H. F. GILLBE.

Optical properties of 1:4-naphthylenebisiminocamphor. J. P. MATHIEU (Compt. rend., 1932, 194, 268—270; cf. J.C.S., 1920, 117, 1599; A., 1930, 1441).—Curves showing for this compound the rotatory and dichroic dispersions, and the absorption for λ 4000—7000, are given. Absorption bands occur at 4300 and 3450 Å. and strong general absorption beyond 2600 Å. The band at λ 4300 has a very high anisotropy factor (cf. A., 1930, 981), and in its neighbourhood the Cotton effect is apparent.

C. A. SILBERRAD.

Rotatory power of naphthylenebisiminocamphor and Kuhn's theory. J. P. MATHIEU (Compt. rend., 1932, 194, 367; cf. preceding abstract).—A corrected calculation shows that the anisotropy factor is small.

C. A. SILBERRAD.

Behaviour of liquid-crystal substances in electrical fields. X-Ray and optical experiments. K. HERRMANN, A. H. KRUMMACHER, and K. MAY (Z. Physik, 1931, 73, 419—436).—X-Rays and optical polarisation determined mol. orientation in an electric field of *p*-azoxyanisole, dianisaldazine, allyl phenetoleazoxybenzoate, and methyl *p*-ethoxybenzylideneaminocinnamate in the amorphous and liquid phases. No orientation appeared in the amorphous phase; in the first liquid phase all four showed orientation of the nematic particles parallel to the field with X-rays, but with optical polarisation the first two appeared normal to the field. Such

discrepancies, also observed in the second liquid phase, are ascribed to a streaming of the particles.

A. B. D. CASSIE.

Magnetic rotatory polarisation. R. DE MALLEMANN and P. GABLANO (Compt. rend., 1931, 193, 1408—1409).—Verdet's const. at 0° and 760 mm. for A (Hg yellow line) is 9.2×10^{-6} ; dispersion for the green and indigo lines is 1.11 and 1.80, respectively. The no. of electrons deduced from this const. and the refractive power is 4.4. As in the case of 11 other substances tabulated, this no. is less than the actual, the disagreement increasing as the no. of electrons is smaller. That this is the case also with A implies that the movements of the peripheral electrons are probably unequally modified by the magnetic field.

C. A. SILBERRAD.

Temperature variation of magnetic birefringence of some fused aromatic compounds. C. SALCEANU (Compt. rend., 1932, 194, 270—273).—Magnetic birefringence-temp. curves for temp. from the m. p. to about 150° in a field of about 39,000 gauss for the Hg yellow line are given for 1-C₁₀H₇-NO₂, and α - and β -naphthonitrile. (C_m/d) $\times 10^{12}$ at 100° is, respectively, 3.69, 3.10, and 4.29, that of C₁₀H₈ being 1.84. For Ph₂, CHPh₃, and benzil C_m is respectively 1.79 (independent of temp. to 150°), 0.89 (at 102°), and 4.72 (at 116°). The birefringence of these three substances changes gradually with continued heating, indicating slow chemical change, possibly oxidation.

C. A. SILBERRAD.

Rotatory dispersion in the ultra-violet of ethyl alcoholic solutions of α - and β -pinenes. R. SERVANT (Compt. rend., 1932, 194, 368—369).—The rotation, in arbitrary units, has been determined from λ 4358 to 2652 for 1:11 and 1:15 EtOH solutions of α - and β -pinene, respectively. α -Pinene shows an increasingly rapid increase in rotation to a max. for λ 2804, then a sharp decrease; β -pinene shows a slight decrease to λ 3650, then a sharp increase to 2804, followed by a very rapid decrease and change of sign. (Cf. A., 1911, ii, 352.)

C. A. SILBERRAD.

Rotation polarisation of a ferromagnetic substance. O. HALPERN (Ann. Physik, 1932, [v], 12, 181—184).—The Heisenberg theory of ferromagnetism can furnish an explanation of the Weiss inner field, which depends on the electrostatic interaction of atoms and ions. The rotation polarisation of a ferromagnetic substance was supposed formerly to be due to a magnetic inner field of the same order as the Weiss field. It is shown how the Heisenberg theory can account for this double refraction in magnetism if a magnetic field of the above size is not present.

A. J. MEE.

Polarisation, susceptibility, and van der Waals forces of atoms with several electrons. J. G. KIRKWOOD (Physikal. Z., 1932, 33, 57—60).—Theoretical. Simple formulæ, derived by an approx. distortion method, are obtained for the polarisation, diamagnetic susceptibility, and the van der Waals forces of atoms with several electrons, for which there is no accurate knowledge of the wave functions. The polarisation and van der Waals forces are brought into relationship with the no. of electrons and the

electrical moment of inertia of the atom. The polarisation is also connected with the susceptibility.

A. J. MEE.

Constitution of B₃N₃H₆. A. STOCK and R. WIERL (Z. anorg. Chem., 1931, 203, 228—234; cf. A., 1931, 1248).—B₃N₃H₆ is extremely stable and has the constitution $\text{NH} \begin{array}{c} \text{BH-NH} \\ \text{BH-NH} \end{array} \text{BH}$. The chemical evidence for a cyclic formula is supported by electron-diffraction diagrams, which show a close similarity between B₃N₃H₆ and C₆H₆. Attention is directed to the similarity between B·N (3+5 valency electrons) and C·C (4+4 valency electrons). E. S. HEDGES.

Nature of single linkings. E. BERGMANN and L. ENGEL (Z. physikal. Chem., 1931, B, 15, 85—96).—A review of the evidence in favour of the view that two parts of a mol. united by a single linking may occupy fixed positions relative to each other, and polemical against Weissberger (A., 1931, 894). The dipole moments of 6:6'-diamino-2:2'-ditolyl, *p*-chloroanisole, Et *p*-chlorobenzoate, *p*-chloro- and *p*-nitro-benzyl chloride have been determined.

R. CUTHILL.

Dipole moments and the structure of organic compounds. X. [Nature of single linkings.] A. WEISSBERGER (Z. physikal. Chem., 1931, B, 15, 97—102; cf. A., 1931, 1113).—A reply to Bergmann and Engel (cf. preceding abstract).

R. CUTHILL.

Chemical linking. II. Interpretation of organic chemistry. F. HUND (Z. Physik, 1932, 73, 565—577).—The hypothesis that σ -linkings are chemically more stable than π -linkings, together with the rules developed for *s*-, *p*-, and *q*-at. valencies (this vol., 10), leads to the system of valencies adopted for org. chemistry. Single linkings are in general of the σ type, double linkings π type, and triple linkings $\sigma\pi\pi$ type; lack of free rotation about π -linkings explains the existence of isomerides, and change from σ - to π -linkings explains the failure of the integer rule for the heat of combustion of (CH₂)_{*n*} when *n* is < 5. This interpretation of valencies leads to alternating single and double linkings between the CH nuclei of the C₆H₆ ring, but such a model ignores the approximations of the theory, the symmetry of the ring requiring a non-localisation of the π -linkings, and must be replaced by an electronic configuration such as Hückel's (A., 1931, 1000).

A. B. D. CASSIE.

Stereochemistry of platinum salts. A. A. GRUNBERG (Ann. Inst. Platine, 1931, 8, 93—114).—In complexes of the type of Peyronne's salt, 1 mol. of H₂C₂O₄ or of glycine combines with Pt, occupying two co-ordinated positions, whilst with those of the type of Reise's base 2 mols. combine, each occupying one co-ordinated position. This observation supports Werner's formulæ for such salts.

R. TRUSZKOWSKI.

Magnus' salts. E. HERTEL and K. SCHNEIDER (Z. anorg. Chem., 1931, 202, 77—80).—X-Ray examination of the green and red forms of [Pt(NH₃)₄][PtCl₄] yields *c/a* ratios of 0.8175 and 0.8340, respectively, and indicates that the complex ions in the two forms are of identical structure and that the PtCl₄ ions are of the same structure as in K₂PtCl₆. The differ-

ence between the two forms is ascribed to differences of co-ordination in the 001 plane. H. F. GILLBE.

Electronic energy levels of the elements with special reference to their connexion with the sizes and electronic states of atoms in metallic crystals. A correction. W. HUME-ROTHERY (Phil. Mag., 1932, [vii], 13, 196—197; cf. A., 1931, 543). H. J. EMELÉUS.

Field of force and form of the carbon dioxide molecule. I. Thermal diffusion in mixtures containing carbon dioxide. II. Variation of the viscosity of carbon dioxide with temperature. III. Form of the carbon dioxide molecule. T. L. IBBS and A. C. R. WAKEMAN (Proc. Roy. Soc., 1932, A, 134, 613—627, 628—635, 636—642).—I. Thermal diffusion measurements have been made on the gaseous mixtures H_2 and CO_2 , N_2 and CO_2 , H_2 and N_2 , and H_2 and A . The two pairs containing CO_2 each show a sharp change in the val. of K_t (the ratio of the coeff. of thermal diffusion to the coeff. of ordinary diffusion) at about 145° . The other pairs show no such change. The results indicate that a change occurs in the nature of the collisions between the CO_2 mols. and the other mols. in the mixture; the change is probably due to an alteration in the field of force of the CO_2 mol., caused by a change in the structure of the mol.

II. The above view receives support from measurements of the variation of viscosity of CO_2 with temp. (over the range 12.5 — 250°). Curves showing the relation between η and \sqrt{T} reveal a discontinuity at about 140° .

III. Examination of the data on the sp. heat of CO_2 confirms the view that there are two kinds of CO_2 mols., a "hard" kind above about 145° , and a "soft" kind below this temp. The "soft" mol. probably corresponds with a straight model, the "hard" mol. with a triangular model.

L. L. BIRCUMSHAW.

Magneto-chemical investigations. V. Magnetic measurements with cupric compounds; theory of magnetism of transition elements. W. KLEMM and W. SCHÜTH (Z. anorg. Chem., 1931, 203, 104—119).—Measurements of the magnetic susceptibility of anhyd. Cu^{++} salts, their hydrates, and ammoniates have been carried out. $CuSO_4$ and $CuCl_2$ are regarded as salts, and CuS and $CuSe$ as intermetallic compounds, whilst CuO and $CuBr_2$ are intermediate in magnetic properties. Cu_2O has been reported as strongly paramagnetic, but its susceptibility is found to be -0.18×10^{-6} . It is suggested that previous investigators have used material containing some CuO .

E. S. HEDGES.

Identification of different varieties of ferric oxide and hydrated ferric oxide by their different magnetic properties. IV. W. H. ALBRECHT and E. WEDEKIND (Z. anorg. Chem., 1931, 202, 209—226; cf. A., 1929, 869).—Susceptibilities of specimens of Fe_2O_3 of different origin have been measured and an attempt is made to interpret the results.

F. L. USHER.

Direct measurement of magnetic susceptibility of liquids by the Curie-Chéneveau magnetic

balance. C. CHÉNEVEAU and C. COURTY (Compt. rend., 1932, 194, 75—76).—Accurate results are more readily obtained with this instrument by calibrating the tube containing the liquid under examination so as to employ exactly equal vols. Measured in this way the coeffs. of magnetisation and susceptibility (both $\times 10^6$) of C_6H_6 are 0.698—0.703 and 0.619, and of CCl_4 0.421—0.424 and 0.690—0.693, respectively. C. A. SILBERRAD.

Diamagnetism of liquid mixtures. J. F. SPENCER and C. G. TREW (Nature, 1932, 129, 95—96).—Re-determinations by the Gouy method reveal certain errors in previous work (A., 1931, 676). Mass susceptibilities for $COMe_2$, $CHCl_3$, and $CCl_3 \cdot COMe_2 \cdot OH$ are -0.60 , -0.51 , and -0.56×10^{-6} , respectively; the last has d_4^{25} 1.49 (cf. A., 1931, 1223).

L. S. THEOBALD.

Magnetic susceptibilities of liquid mixtures. S. P. RANGANADHAM (Indian J. Physics, 1931, 6, 421—431).—A method for the determination of the diamagnetic susceptibilities of liquids is described; the accuracy attainable is claimed to be greater than by other methods. Susceptibilities of the mixtures $C_6H_6 \cdot CCl_4$, $COMe_2 \cdot CHCl_3$, $H_2O \cdot COMe_2$, and $H_2O \cdot EtOH$ have been measured. The magnetic susceptibilities of the liquid mixtures follow an approx. linear law (cf. A., 1931, 676). Deviations due to mol. deformation rarely exceed 1%, whilst those due to compound formation may be 2 or 3%. Compound formation is indicated in the mixtures $COMe_2 \cdot CHCl_3$ and $H_2O \cdot EtOH$.

E. S. HEDGES.

Magnetic saturation phenomena at very low temperatures. O. HALPERN (Ann. Physik, 1932, [v], 12, 169—180).—Theoretical. The magnetic properties of $Gd_2(SO_4)_3$ at high and very low temp. can be quantitatively explained with the aid of simple quantum statistical considerations. The magnetic moment derived agrees with that from spectroscopic data.

A. J. MEE.

Relative permeability of iron, nickel, and permalloy in high-frequency electromagnetic fields. E. M. GUYER (J. Franklin Inst., 1932, 213, 75—88).—The relative magnetic permeability of Fe, Ni, and permalloy presents no anomalous variation in the wave-lengths 70—200 m. and, contrary to previous observers, no evidence of electromagnetic absorption was shown near 100 m. C. A. KING.

Magnetic susceptibility of iron immediately above the Curie point. L. NÉEL (Compt. rend., 1932, 194, 263—265; cf. this vol., 112).—The $1/\chi \cdot T$ curve for Fe for the temp. interval 770 — 777° consists of rectilinear portions corresponding with different Curie consts., decreasing as temp. rises. If the sample be cooled and reheated repeatedly, similar but slightly different curves—indicating smaller susceptibility—are obtained.

C. A. SILBERRAD.

Appearance of ferromagnetism in the system manganese-nitrogen. R. OCHSENFELD (Ann. Physik, 1932, [v], 12, 353—384).—The prep. of $Mn-N_2$ melts is described; the magnetisability and crystal structure are discussed and certain relationships established.

W. R. ANGUS.

Temperature variation of the magnetic susceptibility, gyromagnetic ratio, and heat capacity in Sm^{+++} and Eu^{+++} . (Miss) A. FRANK (Physical Rev., 1932, [ii], 39, 119—129).—Calculations of magnetic susceptibility inclusive of second-order Zeeman terms are extended to the range 0—800° abs., and indicate a min. susceptibility for Sm^{+++} between 375° and 450° abs. Theoretical vals. of the temp. coeffs. of susceptibility are in agreement with experiment when the second-order Zeeman terms are included. N. M. BLYTH.

Atomic moments of some metals. P. WEISS (Nature, 1932, 129, 95).—The ferromagnetic moments of various metals have been determined (by C. SADRON) using solid solutions of the metals in Ni or Co under intense fields and at low temp. Pt, Pd, and Ni have a moment of 3 magnetons, and Cr, Mo, and W one of 19; Mn in Ni gives +15 magnetons, whilst Mn in Co gives —15 magnetons. The ferromagnetic moments plotted against at. nos. lie on 2 straight lines which meet in an apex at V, with a val. of 23 magnetons. L. S. THEOBALD.

Atomic moments. (MLLE.) A. SERRES (Ann. Physique, 1932, [x], 17, 5—95).—Complete data are given for the at. moments of Co, Cr, and Fe. Results indicate that the moment of the Co ion varies in the anhyd. sulphates with the method of prep., and in the crystals with the cryst. structure. Chrome alum gave various vals., attributed to mixtures of different cryst. states. The moment of the Cr ion was 19 in the sulphate, chloride, and chromites. The ferrites of Mg, Pb, Cu, Ni, Cd, and Zn were investigated; the moment of the Fe ion had a low val. in the ferromagnetic compounds, but a normal val. in the paramagnetic $\text{Zn}(\text{FeO}_2)_2$. X-Ray examination of the ferrites showed a similarity of structure. N. M. BLYTH.

Energy relations of inorganic halides. W. HUCKEL (Z. physikal. Chem., 1931, B, 15, 242—247).—Bergmann and Engel's method of calculating at. radii (A., 1931, 1000) involves fundamental errors. R. CUTHILL.

Dependence of specific heat on temperature for elements in the eighth group of the periodic system. F. M. JAEGER (Z. anorg. Chem., 1931, 203, 97—103).—A consideration of previously published sp. heat-temp. curves for metals of group VIII leads to a recognition of two classes, Fe, Co, Ni, Ru and Os, Ir, Pt, with Rh and Pd forming a transition series. E. S. HEDGES.

Grating constant of calcite crystals. J. A. BEARDEN (Physical Rev., 1931, [ii], 38, 2089—2098).—High precision data were obtained for the diffraction angle, density, and grating const. at 20° of 6 calcite crystals from 4 localities. Analysis showed 99.98% purity; vals. of d_{12345} were 3.02769, 3.02799, 3.02805, 3.02807, and 3.02808, respectively. N. M. BLYTH.

Molecular dynamics in crystals. G. TAMMANN (Nachr. Ges. Wiss. Gottingen, 1930, 227—254; Chem. Zentr., 1931, ii, 527—528).—A review. A. A. ELDRIDGE.

New type of crystal fine-structure: lithium ferrite ($\text{Li}_2\text{O}, \text{Fe}_2\text{O}_3$). E. POSNJAK and T. F. W.

BARTH (Physical Rev., 1931, [ii], 38, 2234—2239).—The prep. of two modifications of Li ferrite is described. Interpretation of the X-ray diffraction of the isotropic form obtained at the higher temp. leads to new concepts of the unit cell. Data are: cubic lattice (4b, 4c); unit cube contains one mol., length of edge 4.141 ± 0.005 Å.; d 4.368; n_{Li} 2.40 ± 0.04 .

N. M. BLYTH.

Nature of the metallic state. A. EUCKEN (Z. Metallk., 1931, 23, 293—296, 329—334).—A comprehensive review of recent research on the physical nature of metals with especial reference to the sp. heat, electrical conductivity, thermal conductivity, magnetism, and the Wiedemann-Franz ratio.

A. R. POWELL.

State of undercooled liquids and glasses. F. SIMON (Z. anorg. Chem., 1931, 203, 219—227).—A distinction is made between undercooled liquids, which are in internal thermodynamic equilibrium, and glasses, which are not. E. S. HEDGES.

Reactions of graphite as a disperse laminar system. U. HOFMANN and A. FRENZEL (Kolloid-Z., 1932, 58, 7—14).—The graphite crystal is regarded as a disperse laminar system, consisting of relatively widely-spaced layers of high particle density. These layers remain intact during the chemical reactions of graphite and the products may show the disperse laminar structure to a greater extent than the original graphite. This behaviour is characteristic of the alloying of graphite with alkali metals, the formation of graphitic acid, and the reaction of graphite with conc. H_2SO_4 containing CrO_3 , KMnO_4 , or $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The changes in cryst. space lattice have been observed by X-ray spectrographic examination. The disperse laminar system is responsible for the lubricating properties of graphite. E. S. HEDGES.

Nature of activated carbons. E. BERL, K. ANDRESS, L. REINHARDT, and W. HERBERT (Z. physikal. Chem., 1932, 158, 273—289).—X-Ray diagrams of activated carbons give no indication of the presence of amorphous C and may be satisfactorily explained by supposing that a mesomorphic phase has developed from the three-dimensional graphite lattice. There is no connexion between the activity and the electrical conductivity, which approaches that of graphite the more nearly the higher is the temp. at which the C has been produced. The activity, therefore, cannot be ascribed to the presence of amorphous C, but probably depends both on the development of the surface of the graphite and on the presence of discontinuities or active centres. R. CUTHILL.

Crystal structure of modifications of phosphorus pentoxide. K. BORATYNSKI and A. NOVAKOVSKI (Compt. rend., 1932, 194, 89—91).—50 g. of P_2O_5 "for analysis" (a), sublimed at 300° in O_2 yielded 25 g. of brilliant crystals (b), d 2.100, leaving an amorphous non-volatile residue (c), d 1.80. X-Ray examination showed the crystal structure of (a) and (b) to be similar: rhombohedral, a 11.12, c 1.12 Å., with $12\text{P}_2\text{O}_5$ in the unit cell; (c) gave only a few indistinct rings. Ordinary P_2O_5 is therefore predominantly the cryst. form, and is partly polymerised

to the amorphous form when heated (cf. A., 1930, 1251). C. A. SILBERRAD.

Crystal structure of anhydrous sodium sulphate. W. H. ZACHARIASEN and G. E. ZIEGLER (Z. Krist., 1932, 81, 92—101).—The unit cell has a 5.85, b 12.29, c 9.75 Å., and contains 8 mols.; space-group $Fddd$ (V_h). Previous results (cf. A., 1929, 1212; 1931, 671) are criticised and a different at. arrangement is deduced. C. A. SILBERRAD.

Lattice constant of arsenious oxide. F. LIHL (Z. Krist., 1932, 81, 142—147).—Regler's method (cf. A., 1931, 1217) shows that the unit cell of As_2O_3 has a 11.0457 ± 0.002 Å., and contains 8 mols. C. A. SILBERRAD.

Structure of mercuric bromide. H. BRAEKKEN (Z. Krist., 1932, 81, 152—154).—The unit cell has a 4.624, b 6.798, c 12.445 Å., and contains 4 mols. These dimensions agree with previous results (cf. A., 1931, 671), but the lattice is regarded as a coordination one rather than mol. C. A. SILBERRAD.

Axial ratios of barium hydroxide trihydrate. B. LENGVEL (Z. Krist., 1931, 81, 154).—Revised measurements of the rhombic crystals of $Ba(OH)_2 \cdot 3H_2O$ (cf. A., 1903, ii, 426) give $a : b : c = 0.5225 : 1 : 0.6933$. C. A. SILBERRAD.

Silicate structures of cristobalite type. I. Crystal structure of α -carnegieite. T. E. W. BARTH and E. POSNJAK (Z. Krist., 1932, 81, 135—141).— α -Carnegieite, $NaAlSiO_4$ (cf. A., 1925, ii, 997), at 750° has a unit cell with a 7.37 Å., containing 4 mols., space-group $P2_13$ (T^4); d^{750}_{100} 2.343. C. A. SILBERRAD.

Crystal structure of northupite, bromo-northupite, and tychite. H. SHIDA and T. WATANABE (Compt. rend., 1931, 193, 1421—1423).—Northupite (a), $2Na_2CO_3 \cdot 2MgCO_3 \cdot 2NaCl$, bromo-northupite (b), $2Na_2CO_3 \cdot 2MgCO_3 \cdot 2NaBr$, and tychite (c), $2Na_2CO_3 \cdot 2MgCO_3 \cdot Na_2SO_4$, have been prepared by Schulten's method (cf. A., 1896, ii, 610). The following data are given: n (for white light) and d^{20}_{100} (a) 1.510, 2.366; (b) 1.515, 2.670; (c) 1.510, 2.549. Dimensions of unit cell (cubic) and no. of mols. therein (a) 14.05 Å., 8 (cf. this vol., 12); (b) 14.17, 8; (c) 13.90, 8. C. A. SILBERRAD.

Relations between crystal structure and formula of apatite. M. MEHMEL (Z. physikal. Chem., 1931, B, 15, 223—241).—The lattice consts. are a_0 9.36 and c_0 6.85 Å., the space-group is C_{2h}^6 , and the unit cell contains 2 mols. of $Ca_5(PO_4)_3F$. From the disposition of the atoms in the unit cell, it seems that apatite is a complex salt with F as the central atom, $Ca[F(CaPO_4)_3]Ca$, a structure which accounts for the cleavage, for isomorphous replacement, and for morphotropic changes. Pyromorphite, mimetite, and vanadinite have essentially the same structure as apatite, but the vals. of a_0 and c_0 are 9.95 and 7.32, 10.36 and 7.52, and 10.47 and 7.43 Å., respectively. R. CUTHILL.

Crystal structure of scapolite. E. SCHIEBOLD and G. SEUMEL (Z. Krist., 1932, 81, 110—134; cf. A., 1930, 1100; 1931, 594).—Scapolites from Arendal, d 2.662, and Monte Somma, d 2.690, have respectively

α (d_{110}) 12.09, (d_{100}) 17.24, c 7.580; and α (d_{110}) 12.2, (d_{100}) 17.24, c 7.619 Å., both with 2 mols. of, e.g., $3CaAl_2Si_2O_8 \cdot CaCO_3$ per unit cell. Measurements agree best for space-group C_{2h}^6 , but considerations of at. positions point to the crystals being complicated twins of lower symmetry and to the constitution not being that of a double salt; as in analcime (cf. A., 1931, 550) the Si and Al atoms are mutually interchangeable. C. A. SILBERRAD.

Single-crystal spectrometric data on carbamide. R. W. G. WYCKOFF (Z. Krist., 1931, 81, 102—109).—Single-crystal spectrometric measurements combined with powder data (cf. A., 1931, 550) give results in agreement with those otherwise deduced (cf. A., 1923, i, 760; 1928, 1175) as regards the structure of carbamide and the scattering powers of the atoms therein. C. A. SILBERRAD.

Intensity of total scattering of X-rays by CCl_4 vapour. S. S. LU (Sci. Rep. Nat. Tsing Hua Univ., 1931, A, 1, 111—118).—Woo's theory of the scattering of X-rays by polyat. gases (A., 1931, 1205) using Hartree's at. structure factor are compared with Debye's experimental data (A., 1930, 843). W. R. ANGUS.

[X-Ray] structure of cellulose nitrate films. DESMAROUX and MATHIEU (Compt. rend., 1932, 194, 278—280).—Cellulose nitrate (12% N) films from solution in $COMe_2$ show the same structure as films from Et_2O - $EtOH$ solution (cf. A., 1931, 27, 290, 416). $COMe_2$ solutions of any concn. show a large diffused halo. A smaller halo decreases in intensity and definition with decreased N content, vanishing for $N < 11\%$. With $N > 12.10\%$ reproducible results are obtainable only with films from very dil. old solutions. The solutions themselves in all cases show only the diagram of $COMe_2$. Amorphous cellulose nitrate has lattice planes 4—4.5 Å. measured along the fibre axis. C. A. SILBERRAD.

Piezoelectricity. G. GREENWOOD and D. TOMBOULIAN (Z. Krist., 1932, 81, 30—37).—Using a modification of Hettich's method (cf. A., 1931, 29), and insulating conducting crystals, piezoelectric effects were shown by $Sr(ClO_4)_2$, chalcopyrite, $4KC_4H_4(SbO)_6 \cdot NaCl$, $Pb[C_4H_4(SbO)_6]_2 \cdot 4H_2O$, p -chloroacetanilide, and cinchonine, but not by scolecite or picric acid, although both are reported as pyroelectric, or by $2KC_4H_4(SbO)_6 \cdot LiNO_3 \cdot H_2O$, $2KC_4H_4(SbO)_6 \cdot R(NO_3)_2 \cdot H_2O$ ($R = Zn, Cu, Ni$, or Co), $Ba[C_4H_4(SbO)_6]_2 \cdot 2.5H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Pb(NO_3)_2$, $CaS_2O_6 \cdot 6H_2O$, langbeinite, ullmanite, $Sr(NO_3)_2 \cdot OAc \cdot 1.5H_2O$, or Sr malate. C. A. SILBERRAD.

Ferromagnetic substances in alternating electromagnetic fields. A. ESAU and H. KORTUM (Z. Physik, 1932, 73, 602—619).—Ferromagnetic substances when vibrating under torsion and simultaneously subjected to an alternating longitudinal magnetic field show max. of vibration when the period of the field is slightly less than the natural period of the system. A. B. D. CASSIE.

X-Ray determination of elastic tension in bent crystals. S. KONOBEJEWSKI and I. MIRER (Z. Krist., 1932, 81, 69—91).—Crystals of rock-salt, gypsum, and mica were examined. C. A. SILBERRAD.

Elasticity and breaking of thin quartz fibres. O. REINKOBER (Physikal. Z., 1932, **33**, 32—38).—The elasticity and strength of thin quartz fibres rapidly increase as the cross-section diminishes.

A. B. D. CASSIE.

Influence of foreign particles on cohesion limits and ultramicroscopic sol formation of synthetic rock-salt. I. KCl, CaCl₂, BaCl₂. A. EDNER (Z. Physik, 1932, **73**, 623—648).—99.99 mol.-% pure NaCl crystals were prepared, and had reproducible properties: 0.02 mol.-% of miscible KCl disturbed the properties of the crystals, but the non-miscible halides of Ca and Ba disturbed these properties at 0.002 mol.-%.

A. B. D. CASSIE.

Effect of mechanical working on the state of a solid surface. R. F. HANSTOCK (Phil. Mag., 1932, [vii], **13**, 81—99; cf. A., 1931, 9).—The frictional charges generated and the change in photo-electric properties produced by rubbing two similar bodies together were investigated. The effects produced disappear at approx. the temp. of plastic flow of the material.

H. J. EMELÉUS.

Projection of twinned crystals. P. H. E. TATJE and W. J. VAN WEERDEN (Natuurwetensch. Tijds., 1932, **14**, 17—18).—A simplification of Viola's method is described.

S. I. LEVY.

Alternating torsion tests on zinc crystals. W. FAHRENHORST and E. SCHMID (Z. Metallk., 1931, **23**, 323—328).—In alternating torsion tests of single crystals of Zn the normal and shear stresses in the basal plane gradually increase to a max. and then decrease again with increase in the no. of cycles. The max. occurs much earlier than the appearance of the first fissures which indicate approaching failure. In the earlier stages of the tests the tensile strength and hardness increase rapidly, but later on the metal becomes softer again. No definite relation between the endurance limit and the orientation of the crystal could be established.

A. R. POWELL.

Polish on metals. R. C. FRENCH (Nature, 1932, **129**, 169—170).—The process of polishing Cu and Ag blocks has been investigated by means of electron diffraction rings.

L. S. THEOBALD.

Behaviour of pyroelectric crystals. C. M. FOCKEN (Nature, 1932, **129**, 168).—Pyroelectric phenomena in crystals are best and most easily demonstrated by Bleckrode's method (cf. A., 1931, 23); Kundt's method often fails to give definitive results.

L. S. THEOBALD.

Microscopic cracks produced by electric spark. T. TERADA, M. HIRATA, and R. YAMAMOTO (Nature, 1932, **129**, 168—169).

L. S. THEOBALD.

Transition point of zirconium. R. VOGEL and W. TONN (Z. anorg. Chem., 1931, **202**, 292—296).—Zr is transformed at $862 \pm 5^\circ$ into a new (β) modification, which is denser than the ordinary (α) variety. The heat of transformation is estimated to be about 7.7 g.-cal. per g.

F. L. USHER.

Piezoelectric properties of sodium potassium tartrate crystals. R. D. SCHULWAS-SOROKIN (Z. Physik, 1932, **73**, 700—706).—The piezoelectric modulus of Na K tartrate was found to be 10 times

that recorded; the piezo-effect is a function of the load, and at 50 kg. per sq. cm. becomes independent of temp.

A. B. D. CASSIE.

Electrical resistance law at low temperatures. R. PEIERLS (Ann. Physik, 1932, [v], **12**, 154—168).—An approx. relationship previously used by the author, on which the derivation of the T^4 law for the resistance of metals at low temp. rests, is untenable. A corrected relationship gives results in agreement with those of Bloch (cf. A., 1930, 141).

A. J. MEE.

Influence of the supporting surface on temperature variation of electrical resistance of thin platinum layers. G. BAINTEUR (Z. Physik, 1932, **73**, 691—699).—Sp. resistance of Pt and its temp. coeff. vary with the glass supporting the layer.

A. B. D. CASSIE.

B. [p.] of metals and alloys at atmospheric pressure. W. LEITGEBEL (Z. anorg. Chem., 1931, **202**, 305—324).—Re-determination of the b. p. of some metals in a high-frequency furnace gave the following results: Mg $1097 \pm 3^\circ$; Zn $907 \pm 2^\circ$; Cd $767 \pm 2^\circ$; Tl $1457 \pm 10^\circ$; Pb $1740 \pm 10^\circ$; Sb $1635 \pm 8^\circ$; Bi $1560 \pm 5^\circ$. B.-p. curves for the systems Al-Mg, Al-Zn, Bi-Pb, Bi-Sb, Cd-Pb, Cd-Mg, Cd-Zn, Cu-Zn, Mg-Pb, Mg-Sb, Mg-Zn, Pb-Sb, Pb-Tl, Pb-Zn, and Sb-Zn, and the b.-p. surface for the system Cd-Pb-Zn, have also been determined. Bi-Sb and Pb-Sb give mixtures of max. b. p.

F. L. USHER.

B. p. of ethyl alcohol. W. SWIENTOSLAWSKI, A. ZMACZYNSKI, and J. USAKIEWICZ (Compt. rend., 1932, **194**, 357—358; cf. A., 1930, 1356).—EtOH prepared (a) by a distillery, and after dehydration by azeotropic distillation with (b) C₆H₆, and (c) CS₂ has b. p. (ebullioscopic) (a) 78.320° , (b) 78.318° , and (c) 78.319° ; d^{25}_4 0.78518—0.78525; n^{15}_D (λ 5876) 1.36333—1.36344.

C. A. SILBERRAD.

Specific heat in relation to Raman effect data. S. PARAMASIVAN (Indian J. Physics, 1931, **6**, 413—420).—Sp. heats calc. from Raman effect data agree well with the observed vals.

E. S. HEDGES.

Specific heats of solid hydrogen at helium temperatures. K. MENDELSSOHN, M. RUHEMANN, and F. SIMON (Z. physikal. Chem., 1931, **B**, **15**, 121—126).—The calorimeter used in the determinations previously reported (A., 1930, 282) is described and results are given in detail.

R. CUTHILL.

Determination of the ratio of the two specific heats of gases by Kundt's tube method. A. K. SHAHA (Indian J. Physics, 1931, **6**, 445—451).—An improved method is described the error of which is only 0.045%. The following results for γ have been obtained: MeCHO (30°) 1.145, Pr^oOH (110°) 1.272, PrⁿOH (110°) 1.590, *n*-C₅H₁₂ (40.2°) 1.382, amylene (43°) 1.432.

E. S. HEDGES.

Relaxation period of the specific heat of diatomic gases. A. EUCKEN, O. MUCKE, and R. BECKER (Naturwiss., 1932, **20**, 85—86).—Deviations from theoretical vals. are considered for O₂, N₂, and Cl₂. Results obtained by different experimental methods are discussed.

W. R. ANGUS.

Specific heat of gases, C_p , at high pressures. I. N. GODNEV (J. Gen. Chem. Russ., 1931, 1, 684—688).—Mathematical. R. TRUSZKOWSKI.

Exact determination of the true specific heats of tungsten, rhodium, palladium, ruthenium, osmium, and iridium at temperatures between 0° and 165°. F. M. JAEGER and E. ROSENBOHM (Rec. trav. chim., 1932, 51, 1—46).—Earlier determinations of the sp. heat of W, Pd (cf. A., 1930, 1103), Os, and Rh (cf. A., 1931, 674) have been confirmed and the apparatus employed has been further modified and used for similar measurements on Ir and Ru. In all cases C_p rises above the limiting val. $3R$ at comparatively low temp., 100—150°, and Rh and Pd have max. at high temp. The C_p -temp. curve for Ru is discontinuous, owing to transitions through the successive allotropic forms, α -, β -, γ -, and δ -Ru. There is not sufficient data available to calculate the val. of C_p for Ru. The transition from α - to β -Ru at 1030—1040° is accompanied by an absorption of heat of approx. 0.69 g.-cal. per g. M. S. BURR.

Atomic heats of ruthenium, rhodium, and palladium and coefficients of expansion of rhodium and palladium at high temperatures. H. HOLZMANN (Siebert Festschr., 1931, 147—172).—The coeff. of linear expansion of Rh is $7.628 \times 10^{-6} + 4.537(t^\circ - 20) \times 10^{-9}$ and that of Pd $10.637 \times 10^{-6} + 9.187(t^\circ - 20) \times 10^{-9} - 4.564(t^\circ - 20)^2 \times 10^{-12}$. The sp. heat of Ru is $0.057439 + 0.018921t^\circ \times 10^{-3}$, of Rh $0.060467 + 0.018303t^\circ \times 10^{-3}$, and of Pd $0.0584 + 0.015853t^\circ \times 10^{-3}$. The at. heats of Pd and Rh at const. vol. calc. from the above sp. heats agree with those calc. from the Born-Brody theory but not with those of Jaeger and Rosenbohm (A., 1930, 1103).

A. R. POWELL.

Significance of the chemical constant. K. S. G. DOSS (Indian J. Physics, 1931, 6, 459—461).—Theoretical. E. S. HEDGES.

Physical properties of compressed gases. II. Carbon monoxide. W. E. DEMING and (Miss) L. E. SHURE (Physical Rev., 1931, [ii], 38, 2245—2264; cf. A., 1931, 53).—Theoretical. N. M. BLIGH.

Van der Waals equation for inert gases. E. NEUSSER (Physikal. Z., 1932, 33, 76—81).—At high temp. the van der Waals consts. a and b become independent of pressure, and both decrease with rise of temp. At very high temp. a becomes zero. The temp. for which the pressure dependence is noticeable has no definite relation with the crit. temp. Below the crit. temp. the behaviour of the inert gases is similar to that of H_2 and CO_2 . Accurate vals. of the at. wts. of He, Ne, and Ar are obtained which are in agreement with Aston's mass-spectrograph determinations. A. J. MEE.

Determination of the vapour pressure of ice at low temperatures. C. DEI (Nuovo Cim., 1931, 8, 71—77; Chem. Zentr., 1931, ii, 393).—Measurements of discharge potentials gave the following vals.: -22.3° , 0.58 ± 0.23 ; -55° , 0.0166 ± 0.0008 ; -66° , 0.0037 ± 0.0002 . A. A. ELDRIDGE.

Joule-Thomson effect in air. II. J. R. ROEBUCK (Proc. Amer. Acad. Arts Sci., 1930, 64, 287—334).—Apparatus is described and vals. are recorded

for the Joule-Thomson coeff., sp. heat, entropy, rate of change of heat content with pressure, pv , coeff. of expansion, Joule coeff., elastic coeff., const.-pressure air scale, intrinsic energy variation with vol., and const.-vol. air scale. The calc. Kelvin temp. of the triple point for H_2O is 272.79° .

CHEMICAL ABSTRACTS.

Kelvin scale temperature of freezing water. F. G. KEYES (Proc. Amer. Acad. Arts Sci., 1931, 66, 349—355).—Roebuck's results (preceding abstract) are criticised. The triple point temp. of H_2O under atm. air pressure is 273.135° .

CHEMICAL ABSTRACTS.

Chemistry of alloys. A. WESTGREN (Angew. Chem., 1931, 45, 33—40).—A lecture dealing principally with the application of X-ray analysis to the elucidation of the composition of the phases present in alloys and to the classification of the compounds formed. Simple stoichiometric proportions may occur in alloys, not merely as a result of regular at. groupings, but also because of the existence of simple relationships between the nos. of atoms and valency electrons present. The author's previous definition of a true intermetallic compound as one in which structurally equiv. atoms are chemically identical is therefore invalid. H. F. GILLBE.

Formation and shape of segregations in metallic solid solutions. H. HANEMANN and O. SCHRÖDER (Z. Metallk., 1931, 23, 271—273, 297—300).—The differences in the shape and rate of separation of constituents from supersaturated solid solutions on cooling or on ageing lead to the conclusion that their shape and method of separation are governed by the at. arrangement in the solid solution. The following hypotheses are put forward. When the atoms of one constituent of the solid solution occupy lattice lines which are free from atoms of the second constituent and at the same time are at a max. distance from atoms of the second constituent, the atoms of the first constituent can move freely along these lines; this movement is designated "perfusion." The formation of segregates by perfusion proceeds rapidly, is difficult to repress by quenching, and leads to the formation of relatively large crystals of the segregate which form needles and layers in symmetrical positions to the directions of perfusion. In perfusion neighbouring atoms can be drawn into the lines of perfusion; examples of this occur in the development of the Widmannstätten structure and in the shape of the α -brass segregates from homogeneous β - or γ -solid solutions. On the other hand, if the atoms of neither of the constituents fulfil the above conditions changes in concn. occur only by interchange of the positions of the atoms; this type of movement is designated "diffusion." The formation of segregates by diffusion occurs slowly, is easily repressed, and leads to the formation of very small crystals which frequently assume an almost spherical form. Several modifications of these two typical cases of segregate formation are described and their mechanism is discussed. The external shape of segregates from solid solutions is governed chiefly by the orientation of the original mixed crystal and not by the orientation of the segregate crystal itself, but this shape may be modified

if recrystallisation occurs. Several typical examples of the breakdown of supersaturated solid solutions are discussed and it is shown that α -brass separates along an octahedral plane and γ -brass apparently along a cube axis.

A. R. POWELL.

Diffusion of molybdenum in tungsten. J. A. M. VAN LIEMPT (Rec. trav. chim., 1932, 51, 114—132).—A formula is deduced for the diffusion of two regular uniaxial metals forming a continuous series of mixed crystals. $D=8/3 \cdot p^2 \gamma e^{-3b/T}$, where p is the min. at. separation in the metal into which diffusion takes place, γ the characteristic monochromatic at. frequency of the diffusing metal, T , the m. p. of the diffusing metal, T' the temp. at which diffusion is measured, b is approx. 2, and the factor 3 varies in accordance with the deviations of the metal from Dulong and Petit's law. The formula is in good agreement with the diffusion of Mo into a single crystal of W and may in this case be reduced to $\log_{10} D = -17,500/T - 3.20$. The rate of diffusion of Mo into polycryst. W is greater, being made up of two factors, inter-at. and inter-cryst., the latter depending on the character of the structure of the W. No general formula can, therefore, be deduced. A colorimetric method is employed for the determination of amounts less than 2% Mo in W.

M. S. BURR.

X-Ray examination of iron-chromium alloys. G. D. PRESTON (Phil. Mag., 1932, [vii], 13, 419—425).—The Fe-Cr system forms a continuous series of solid solutions. The val. of a increases from 2.860 Å. for 100% Fe to 2.879 Å. for 100% Cr.

H. J. EMELEUS.

Alloys of platinum with copper and with nickel. N. S. KURNAKOV and V. A. NEMILOV (Ann. Inst. Platine, 1931, 8, 5—16, 17—24).—Solid Pt-Cu alloys heated at 850° exhibit recalcence at 700—800°, with a max. of 807.5° at 50 at.-% Pt, pointing to the formation of a compound, PtCu, from solid solutions which exist at higher temp. The existence of this compound is confirmed by measurements of the hardness, conductivity, and temp. coeff. of conductivity of reheated and tempered alloys.

No compound formation takes place between Pt and Ni, the alloys consisting of two types of solid solution, one containing less, and the other more, than 20 at.-% Pt.

R. TRUSZKOWSKI.

X-Ray examination of alloys of the gold-platinum system. W. STENZEL and J. WEERTS (Siebert Festschr., 1931, 300—308).—The lattice parameter of quenched homogeneous Au-Pt alloys is a linear function of the composition. The solubility of Pt in Au is 43, 30, and 25 at.-%, and that of Au in Pt is 19, 7, and 3.5 at.-% at 1100°, 900°, and 700°, respectively. The range of heterogeneity extends to a max. at 1180° with 60 at.-% Pt; i.e., all alloys are homogeneous solid solutions above this temp. (cf. Johansson and Linde, A., 1930, 1102).

A. R. POWELL.

Palladium-iron alloys. A. T. GRIGORIEV (Ann. Inst. Platine, 1931, 8, 25—36).—No compound formation occurs in fused Pd-Fe alloys and the solid phase which separates on cooling consists of an unbroken series of solid solutions, with a min. f. p.

of 1290° at 50 at.-% Pd. Solid alloys containing about 75 at.-% Pd exhibit recalcence on cooling, pointing to the existence of a compound, Pd₃Fe, with a transformation point at about 800°. The existence of this compound is confirmed by hardness, conductivity, and temp. coeff. of conductivity curves.

R. TRUSZKOWSKI.

Lattice constants of silver-palladium and gold-palladium alloys. W. STENZEL and J. WEERTS (Siebert Festschr., 1931, 288—299).—For pure Pd, $a_{20}=3.8809+0.0005 \text{ Å.}$, for Au-Pd alloys a is a linear function of the composition, and for Ag-Pd alloys almost a linear function of the composition, the max. contraction in a being 0.007 Å. with the 1:1 alloy.

A. R. POWELL.

Alloys of palladium with platinum and rhodium. G. TAMMANN and H. J. ROCHA (Siebert Festschr., 1931, 309—320).—Max. hardness of Pd-Pt alloys occurs at 10—20% Pd when the alloys are quenched from 1400°, at 30% Pd when they are quenched from 1200°, and at 40% Pd when they are annealed at 600° for 12 hr.; quenched alloys, except that containing 38% Pd, are all harder than annealed alloys. The solubility of H₂ in Pd-Pt alloys is very small when less than 40% Pd is present, then increases rapidly with rise in Pd content; the solubility is slightly greater in alloys quenched from 1300° than in alloys annealed at 700°. Pd-Pt alloys with more than 74 at.-% Pd become coated with Au when immersed in HAuCl₄ solution and those with more than 50 at.-% Pd are blackened by alcoholic I. Alloys with less than 30% Pd have a granular, and those with more than 40% Pd a dendritic, microstructure. These results are held to indicate that the system is not a continuous series of solid solutions. Pd-Rh alloys have a smooth hardness curve with a max. at 50—60 at.-% Rh; max. solubility of H₂ occurs in the alloy with 10 at.-% Rh, and the reaction limit with I at 75 at.-% Rh.

A. R. POWELL.

Ternary system iron-nickel-phosphorus. R. VOGEL and H. BAUR (Arch. Eisenhüttenw., 1931—1932, 5, 269—278).—The equilibrium diagram of the ternary system Fe-Ni-P up to 15% P shows four binary phosphides, Fe₃P, Ni₃P, Ni₅P₂, and Fe₂P, but no ternary phosphide. Fe₃P and Ni₃P form a continuous series of solid solutions the Fe-rich members of which correspond with the schreibersite of meteoric Fe. There is a transitional four-phase equilibrium at 970° in the field Fe-Fe₃P-Ni₃P-Ni, viz., liquid + α solid solution = γ solid solution + schreibersite. On cooling below this temp. the α -phase (kamasite) and the γ -phase (taenite) decompose with the separation of schreibersite in the form of fine rods, the rhabdite of meteoric Fe. An addition of P to Fe restricts the γ -field, whereas addition of Ni to Fe broadens this field; the heterogeneous field below 970° in the ternary system at first becomes narrower with fall in temp. and then broadens again, so that on heating certain of the alloys the schreibersite or rhabdite first dissolves, is then pptd. again, and finally forms homogeneous α or γ . These variations in solubility give rise to the characteristic twinning and formation of layers of plate-like crystals which are frequently observed in meteoric Fe.

A. R. POWELL.

Refractive index of liquid mixtures. I. Binary systems with piperidine as one component. N. A. PUSHIN and P. G. MATAVULJ (*Z. physikal. Chem.*, 1932, **158**, 290—296).—For mixtures of piperidine with phenols n passes in many cases through a max. and the composition for which the deviation of n from the val. calc. by the additive principle is a max. corresponds in several systems with a compound the existence of which is indicated by the f.-p. curve. The temp. coeff. of n may deviate similarly from the additive behaviour.

R. CUTHILL.

Influence of cellulose nitrates of different stability on the refraction of liquid mixtures. III. Stabilisation process. T. TOMONARI, C. TROGUS, and K. HESS (*Angew. Chem.*, 1932, **45**, 99—104, 126—129).—For solutions of cellulose nitrate in COMe_2 -MeOH or in COMe_2 -EtOH n varies with the method of prep. and subsequent treatment of the cellulose nitrate. All operations which increase the stability of the nitrate tend to lower n to a limiting val. For solutions in pure COMe_2 the val. of n is independent of the stability of the cellulose nitrate. Its variation in mixtures is due to the presence of a foreign substance, which has been isolated but not identified. This substance appears to contain 3 NO, and 2 SO_3 groups to 2 C_6 groups and has a marked effect on n when the solvent is either of the above mixtures on any of the following: COMe_2 with PrOH, BuOH, isoamyl alcohol, or $\text{CH}_2\text{Ph}\cdot\text{OH}$; cyclohexanone with MeOH, EtOH, PrOH, BuOH, isoamyl alcohol, or $\text{CH}_2\text{Ph}\cdot\text{OH}$.

E. S. HEDGES.

Heat capacities of the system acetic acid-water at various temperatures. M. B. NEUMANN (*Z. physikal. Chem.*, 1932, **158**, 258—264).—The sp. heat, c , of mixtures containing 5—100% AcOH has been determined at 24°, 42°, 60°, and 80°. For the pure acid $c=0.463\pm0.00091t$, where t is the temp., but for the mixtures c is not a linear function of t . At all temp. and concns. c exceeds the val. calc. by the additive principle.

R. CUTHILL.

Heat capacities of aqueous solutions of sulphuric acid. A. S. SOCOLIK (*Z. physikal. Chem.*, 1932, **158**, 305—312).—Vals. of the sp. heat, s , at 20°, 40°, 60°, and 80° of solutions containing 5—100% H_2SO_4 are recorded. For solutions containing 40% and upwards, s increases with rise of temp., and the curve connecting percentage increase for a given temp. change with concn. exhibits a well-defined min. at $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$. The sp. heat of an equimol. mixture of H_2SO_4 and H_2O is additively related to the sp. heats of the components, but for other mixtures the additivity principle is not valid.

R. CUTHILL.

B. p. of saturated solutions of the system $(\text{K},\text{NH}_4)(\text{NO}_3,\text{Cl})$. S. I. ARONOVA and Z. N. LUNSKAJA (*J. Chem. Ind. Russ.*, 1931, **8**, No. 18, 23—27).—The b. p. of solutions saturated with respect to KCl and NH_4Cl (7.99% KCl and 40.81% NH_4Cl) is 117°; 121.8° for KCl and KNO_3 (9.31% KCl and 68.27% KNO_3), and 133.3° for KCl, KNO_3 , and NH_4NO_3 (15.93% KCl, 49% KNO_3 , 30.21% NH_4NO_3 , 4.89% H_2O , or 15.93% NH_4Cl , 64.93% KNO_3 , 14.28% NH_4NO_3 , 4.86% H_2O). NH_4NO_3 is

stable at all temp. up to 270° if traces of H_2O are present.

R. TRUSZKOWSKI.

Influence of impurities on the critical temperature of aqueous solutions of phenol. R. DOLIQUE (*Compt. rend.*, 1932, **194**, 289—291).—Experiments with PhOH, m. p. 40.85° (cf. A., 1919, i, 482), give $66.5\pm0.1^\circ$ and 34% PhOH for the crit. solution temp. and concn. The effect of the addition of small quantities of C_6H_6 , C_{10}H_8 , and $\text{C}_5\text{H}_5\text{N}$ is to raise the crit. temp., whilst the crit. concn. (% PhOH) is raised by C_6H_6 , but diminished by C_{10}H_8 and $\text{C}_5\text{H}_5\text{N}$ (cf. A., 1922, ii, 743).

C. A. SILBERRAD.

Solubility of gas and coefficient of dilatation by adsorption. J. HORIUTI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, **17**, 125—256).—Data for the coeff. of dilatation δ and the solubility γ are recorded for the gases SO_2 , MeCl, Me_2O , CO , N_2O , C_2H_6 , C_2H_4 , C_2H_2 , CH_4 , O_2 , N_2 , CO , and H_2 in the solvents CCl_4 , PhCl, C_6H_6 , COMe_2 , AcOMe, Et_2O , and in some cases CHCl_3 , at varying temp. between 0° and 140°. Apparatus for use with gases of large, medium, and small solubility and methods of preparing very pure samples of the different gases are described. Ångström's rule that the ratio of δ for any pair of gases is independent of the nature of the solvent, and Just's similar rule for γ is valid only for gases of lower b. p. For H_2 , N_2 , and CO the order of solubility is identical with that of the crit. temp. of the solvent. As the b. p. of the solute becomes higher the solubility in polar solvents containing O increases, but diminishes in normal solvents when the solute is unsaturated or polar. The opposite is the case for normal solutes. The internal heat of dissolution is shown to be a linear function of temp. and various other mathematical relationships are discussed.

M. S. BURR.

Absorption of gaseous nitrogen by a benzene solution of rubber and guttapercha hydrocarbon in sunlight. A. W. K. DE JONG (*Rec. trav. chim.*, 1932, **51**, 133—134).—A solution of crepe rubber in C_6H_6 absorbs N_2 as well as O_2 when exposed to sunlight through either quartz or glass. Similar behaviour is observed with a C_6H_6 solution of guttapercha hydrocarbon separated from sheet balata by crystallisation from light petroleum and purified by subsequent recrystallisation. In the latter case a gel is sometimes formed.

M. S. BURR.

Solubility of iodine in ethyl acetate. E. KNOTT (*Pharm. J.*, 1932, **128**, 84—85).—The solubility (parts per 100 of solvent) of I in AcOEt is: 0°, 10.48; 8°, 11.1; 10—12°, 12.39; 30°, 16.15.

E. H. SHARPLES.

Solubilities and activity coefficients of silver sulphate in certain salt solutions. J. B. CHLOUPEK and V. Z. DANEŠ (*Coll. Czech. Chem. Comm.*, 1932, **4**, 8—19).—The solubility of Ag_2SO_4 in H_2O and in aq. solutions of K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and KNO_3 has been determined at 25° and activity coeffs. have been calc. from the data. A new type of thermo-regulator and a filtering pipette having a sintered glass disc are described.

E. S. HEDGES.

Solubility of radium sulphate in water at 20°. O. ERBACHER and B. NIKITIN (*Z. physikal. Chem.*,

1932, 158, 216—230; cf. A., 1918, ii, 144).—100 c.c. of H_2O dissolve 1.40×10^{-4} g. The solute is strongly adsorbed by filtering materials. $RaSO_4$ slowly decomposes under the influence of its own radiation, but this change occurs chiefly on the surface whether the surrounding medium is air or H_2O .

R. CUTHILL.

Validity of mass law. I. Solubility of radium sulphate in sulphuric acid and sodium sulphate solutions. B. NIKITIN and O. ERBACHER (Z. physikal. Chem., 1932, 158, 231—236).—The activity solubility product of $RaSO_4$ at 20° has approx. the same val. in H_2O , 0.0001 — $0.1N-H_2SO_4$, and 0.01 — $0.1N-Na_2SO_4$.

R. CUTHILL.

Solubility of water in granite magmas. R. W. GORANSON (Amer. J. Sci., 1931, [v], 22, 481—502).—The percentage solubility of H_2O in granite glass at 900° and a pressure P bars is given approx. by the equation $x = P/(92.76 + 0.0808P)$. Its percentage solubility at 980 bars is given by $x = 0.47$ — $0.00305t$.

C. W. GIBBY.

Distribution of iodine between kerosene and aqueous solutions. M. I. KORSHUN (J. Chem. Ind., Russia, 1931, 7, 698—701).— $K (=C_k/C_s)$ increases markedly with decrease in the concn. of I. With increase in concn. of $NaCl$, K decreases to a min. and then increases. K is affected by alkalinity, but not by acidity. The extraction capacity of the kerosene increases with use, since part of the I forms with it a resinous compound.

CHEMICAL ABSTRACTS.

Adsorption of gases and gas mixtures on wood charcoal. A. MAGNUS and A. KRAUSS (Z. physikal. Chem., 1932, 158, 161—196).—The adsorption of C_2H_2 , C_2H_4 , and CO_2 by purified activated charcoal at pressures of about 0.1 — 760 mm. and at temp. between 0° and 100° conforms to the adsorption formula previously deduced (A., 1929, 1139); the purer is the charcoal the closer is the agreement. Owing to its dipole character Me_2O is, however, adsorbed more strongly than the formula indicates. The data are not in agreement with Langmuir's isotherm. The adsorption of mixtures of C_2H_2 and Me_2O has been determined at 0° , 20° , and 40° . If A_1 and A_2 are the respective amounts of the two gases adsorbed per g. of adsorbent when they are present at pressures p_1 and p_2' in a mixture and also when they are present singly under pressures p_1 and p_2 , then $p_1' = p_1 + f(A_1) \cdot A_2$ and $p_2' = p_2 + f'(A_2) \cdot A_1$, approx. A complete approx. equation for the adsorption of a mixture of dipole-free gases is given.

R. CUTHILL.

Sorption of carbon disulphide at low pressures by activated charcoals. A. J. ALLMAND and J. L. LIZIUS (Proc. Roy. Soc., 1932, A, 134, 554—570).—Isostere measurements on six different charcoals, previously degassed at 110° and carrying various charges of CS_2 , have been made, and heats of adsorption and isothermals at 25° calc. therefrom. In all cases the heat of adsorption rises continuously as the charge on the charcoal decreases at pressures below 10^{-1} mm. Above this pressure it decreases sharply. The isothermal given by a particular charcoal is reversible. The mechanism of the dis-

placement of the O_2 charge on a charcoal surface by the adsorption of a vapour is examined, with special reference to differences shown by CCl_4 and CS_2 .

L. L. BIRCUMSHAW.

Behaviour of sugar carbon in the adsorption of monobasic aliphatic acids. F. KRCZIL (Kolloid-Z., 1932, 58, 68—76).—Experiments on the adsorption of monobasic fatty acids by sugar charcoal have not succeeded in establishing any general relation between adsorptive capacity and particle size over the range 200 — 30μ . The increase often observed is attributed to the greater activity of the smaller particles already present in the original material. Particles between 50 and 30μ , obtained by fractional sedimentation, show a decreased adsorptive capacity after drying at 120° . After heating for 2 hr. at 500° in a limited supply of air the normal sequence of adsorbability of the acids is reversed. This appears not to be due to a change of particle size, but to the activating influence of atm. O_2 , for after heating for 4 hr. at 600° in vac. the adsorptive capacity increases with fineness of subdivision, but the order of adsorption of the acids is not reversed.

F. S. HEDGES.

Adsorption of ethylene and carbon dioxide on gold. A. MAGNUS and R. KLAR (Siebert Festschr., 1931, 235—239).—Isotherms for the adsorption of CO_2 and C_2H_4 on finely-divided Au have been constructed for 0° , 20° , and 40° and pressures up to 520 mm. of Hg. At low pressures the adsorption does not follow Henry's law, adsorption being always greater than that corresponding with the law; this is attributed to the presence of sharp corners and edges and of narrow hollow spaces with a higher adsorption potential than the remainder of the powder.

A. R. POWELL.

Adsorption of electrolytes by crystalline surfaces. L. DE BROUCKERE (Bull. Acad. roy. Belg., 1931, [v], 17, 1249—1261).—The adsorption of KCl , $CuCl_2$, and KI from aq. solution by cryst. $BaSO_4$ has been investigated. The amount adsorbed increases with the concn. of the solution, reaching asymptotically a const. val. independent of temp. It is about the same for the two chlorides, but much greater for KI . This supports the view that a unimol. layer is formed and that the greater part of the electrolyte is fixed by direct adsorption of the anion, an equiv. no. of cations being retained by electrostatic attraction.

J. W. SMITH.

Adsorption and surface reaction of alizarin on vacuum-sublimed films of alkaline-earth halides. J. H. DE BOER [with J. Broos] (Z. physikal. Chem., 1932, B, 15, 281—299).—Alizarin vapour is powerfully adsorbed by films of vac.-sublimed CaF_2 , BaF_2 , and SrF_2 at 100° , but reaction between adsorbent and adsorbate sets in at once, HF being liberated. At higher temp. reaction proceeds more rapidly, and, as the absorption spectra of the films show, comes to an end when the no. of alizarin mols. fixed by reaction is equal to the no. originally adsorbed. The reaction is confined to the surface and consists in the replacement of the F^- ions of the surface by half their no. of anions formed by removal of H^+ from the two OH groups of alizarin. $BaCl_2$ also adsorbs

alizarin, but at 100° there is no detectable chemical reaction. Above 200°, however, the rate of reaction is appreciable, and for each mol. of alizarin fixed by reaction 2 mols. of HCl are set free. From the position of the adsorption max. of the compounds it appears that the alizarin ion is polarised most in the Ca compound. The absorption max. of alizarin which is simply adsorbed is nearer the ultra-violet on BaCl₂ than on CaF₂; this is presumably due to the polarising action of the H⁺ being counteracted to a greater extent by F⁻ than by Cl⁻. R. CUTHILL.

Adsorption on vacuum-sublimed films of barium chloride and determination of specific surface. J. H. DE BOER (Z. physikal. Chem., 1932, B, 15, 300—310).—When a vac.-sublimed film of BaCl₂ adsorbs I vapour, the max. no. of I atoms fixed by the surface is equal to four times the no. of alizarin mols. which the surface could take up. Since one alizarin mol. displaces two Cl⁻ ions (cf. preceding abstract), and in the adsorption of I the no. of adsorbing centres is twice the no. of Cl⁻ ions because I atoms may also be adsorbed between Cl⁻ ions, it follows that the max. adsorption of I corresponds with the formation of a monat. layer. It is deduced that the mean thickness of the separate lamellae of the salt film varies from 5 mols., with rapid sublimation, to 11 mols., and that the sp. surface is 100—250 × 10⁴ sq. cm. per g. R. CUTHILL.

Adsorption of anthraquinone derivatives by cotton cellulose. K. BRASS and K. LAUER (Kolloid-Z., 1932, 58, 76—78).—The vat dyes 1-benzamidoanthraquinone, 1:4- and 1:5-dibenzamidoanthraquinone, and 1:2-dianthrimide in dry EtOH or C₆H₆ solution are not adsorbed by cotton. The 1-aminoanthraquinones and their Ac and other derivatives in abs. EtOH solution are taken up by cotton reversibly in accordance with Henry's law.

E. S. HEDGES.

Surface molecular potential, and the dielectric constant of the medium. Dependence of heat of adsorption and of adsorption capacity on the dielectric constant of the adsorbed gas. B. V. ILJIN (J. Gen. Chem. Russ., 1931, 1, 750—759).—Mathematical. R. TRUSZKOWSKI.

Effect of light on the surface tension of Boys' soap solution. L. D. MAHAJAN (Nature, 1932, 129, 133). L. S. THEOBALD.

Reade's iriscope, and the "wettability" of solid and liquid surfaces. M. GUILLOT (Compt. rend., 1932, 194, 166—169).—The effects obtained with the iriscope and soap solutions are also observed with other substances, *eg.*, lactic acid, Et lactate, glycerol, linseed oil, and also with BzOH, CH₂PhCl, C₁₀H₈, camphor, olive oil, etc. dissolved in volatile solvents. The effects are shown directly on certain solids, *eg.*, freshly-broken glass [but not glass which is only sufficiently clean to comply with Devaux' criteria for "wettability" (cf. A., 1931, 1229), although all surfaces giving the effect are "wetable"], on fresh cleavage surfaces of many crystals, but not on metallic substances, and on some liquids, *eg.*, linseed or olive oil. C. A. SILBERRAD.

Osmotic systems containing three liquids separated by two membranes. F. A. H. SCHREINEMAKERS and J. P. WERRE (Rec. trav. chim., 1932, 51, 51—60).—Systems in which a variable liquid is separated by membranes from two invariable liquids are considered. In all cases one of the invariable liquids is H₂O and the other aq. NaCl and Na₂CO₃, the composition of which varies in the different experiments. The variable liquid is aq. NaCl, aq. Na₂CO₃, or pure H₂O. The two membranes are either pig's bladder or cellophane. Data are given showing the time taken for the variable solution to attain the composition of the invariable solution and the change in vol. of the former which accompanies the process. The two types of membrane behave differently, since with the pig's bladder the vol. of the invariable liquid continuously decreases, whilst with the cellophane it increases. M. S. BURR.

Electrokinetic phenomena. V. Small constant source of error in viscosity measurements. H. A. ABRAMSON (J. Gen. Physiol., 1932, 15, 279—281).—A const. error in the use of the Ostwald viscosimeter is ascribed to electrokinetic effects and its magnitude is calc. and shown to decrease with increasing radius of the capillary. H. DAVSON.

Measurement of the electrokinetic potential on a ceramic diaphragm and on a parchment-paper membrane by the method of streaming potentials. J. BABOROVSKY and B. BUREL (Coll. Czech. Chem. Comm., 1931, 3, 563—577).—Details are given of a method for measuring the electrokinetic potential ζ at the boundary between KCl solution and a porous ceramic diaphragm; ζ falls continuously with increasing concn. of the electrolyte, and at low concn. electrokinetic phenomena produce abnormally high conductivity of the solution in the pores of the diaphragm. Application of the method to a parchment-paper diaphragm shows that even in pure H₂O no charge develops on the diaphragm; the vals. obtained by Baborovsky's method for determining the hydration of ions, using a paper membrane, therefore do not need correction for electro-osmotic effects. H. F. GILBE.

Diffusion of gases under pressure. V. V. IPATIEV, jun., and V. I. TICHOMIROV (J. Gen. Chem. Russ., 1931, 1, 736—739).—The diffusion coeff. of H₂ in H₂O has the same val. at 1 as at 100 atm. pressure, *viz.*, 3.02; in 20% NaOH solution the val. at 100 atm. is 0.89, in MeOH 14.52, and in C₆H₆ 20.94.

R. TRUSZKOWSKI.

Diffusion coefficients and particle sizes of colourless substances. H. SULLMANN (Protoplasma, 1931, 13, 546—566).—The diffusion coeffs. of sucrose, maltose, lactose, glucose, fructose, glycerol, hexamethylenetetramine, and carbamide are determined and shown to be dependent on the concn. of the solutions and on the size of the dissolved particles.

A. G. POLLARD.

Effect of electrolytes on the dielectric constant of water. III, IV. R. T. LATTEY and W. G. DAVIES (Phil. Mag., 1932, [vii], 13, 444—455; cf. this vol., 120).—The dielectric const. of solutions of CdBr₂, BaCl₂, Mg(NO₃)₂, La(NO₃)₃, Th(NO₃)₄, and Zr(NO₃)₄ increases linearly with concn. For CuSO₄

and MgSO_4 it falls from linearity at higher concns. CdBr_2 and $\text{Mg}(\text{NO}_3)_2$ cause the same increase at equiv. concns.: this is considerably less than the val. for BaCl_2 . The 1 : 3 salts and the 1 : 4 salts are equally effective within the limit of experimental error. The molar polarisation of these salts is calc.

H. J. EMELÉUS.

Regular arrangements of small metal spheres. F. STÖBER (Kolloid-Z., 1932, 58, 14—17).—Systems of small metal spheres of approx. equal size, distributed in another solid medium, formed by cooling a dispersion of metallic globules in a melt, are found to be arranged according to a definite pattern. It is inferred that Newton's laws of attraction are applicable to these metallic particles.

E. S. HEDGES.

Constitution of colloidal gold. W. PAULI and E. RUSSE (Kolloid-Z., 1932, 58, 22—44).—Measurements of $[\text{H}^+]$, $[\text{Cl}^-]$, electrical conductivity, and coagulation val., and examination of the effects of electro-dialysis and of freezing of conc. Au sols have shown definitely that these sols contain ionogenic Au complexes in the Werner sense. The purified sols, prepared by the reduction method, do not differ essentially from those prepared by disintegration methods.

E. S. HEDGES.

Preparation and standardisation of colloidal gold for the Lange test. J. PATTERSON (Brit. J. Exp. Path., 1931, 12, 143—146).—The Au sol is prepared after a preliminary test made by adding 1, 2, 3, etc. drops of 0.02N-NaOH to tubes containing 5 c.c. of a solution made from distilled H_2O (50 c.c.), 1% $\text{K}_2\text{C}_2\text{O}_4$ (0.5 c.c.), and 1% $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$ (0.5 c.c.), and heating the tubes rapidly in a water-bath. The right proportions are present in the tube which is the lowest in the series to give (after 1 min. at 100°) a bright red, clear sol which exhibits a very faint sheen. The stock is adjusted to the correct stability for immediate use in the Lange test by the addition of small quantities of acid, using the stability of the sol against oxyhæmoglobin as indicator.

CHEMICAL ABSTRACTS.

Magnetism of precipitates of colloidal silver. V. I. VAIDYANATHAN and B. S. PURI (Nature, 1932, 129, 170).—The sp. susceptibility of colloidal Ag, prepared by two different methods, varied from 0.133 to 0.166×10^{-6} as against 0.2×10^{-6} for massive Ag (cf. A., 1931, 1231).

L. S. THEOBALD.

Highly-polymerised compounds. LIX. Viscosity laws. H. STAUDINGER (Helv. Chim. Acta, 1932, 4, 213—221).—The η_{sp} of equally conc. solutions of hydrocarbons of high mol. wt. depends entirely on the length of the chain and is independent of other structural considerations. Viscosity measurements thus enable the mol. wt. of highly-polymerised compounds to be calc. The high viscosity of colloidal solutions of these substances is due not so much to strong hydration as to the chain-like form of the mols., which may cause their effective vol. to be 1000 or more times as great as their true vol. "Mol. colloids" are recognised as a distinct type.

E. S. HEDGES.

Solvation equilibrium in colloidal solutions. G. V. SCHULTZ (Z. physikal. Chem., 1932, 158, 237—257).—Published data for the osmotic pressure, P ,

of colloidal solutions may be represented by the equation $P(V-b) = nRT$, if it is assumed that the mol. wt. of the disperse phase does not vary with the concn., and that b , the vol. correction, varies with the concn. in consequence of changing solvation. When such a system is in equilibrium, P must be exactly counter-balanced by the tendency of the disperse phase to become solvated, a tendency which may be regarded as a "solvation pressure." If s is the vol. occupied in the sol by unit wt. of the disperse phase together with the solvent bound by it, it is found that $P = k(1/s)^v$, where k and v are consts., and it is known that swelling pressure can be expressed by an equation of the same form, in which $1/s$ is replaced by c , the concn. in the swollen vol. In both equations the val. of v is about 3, and from available data it appears that the effective sp. covol. (quotient of b by the concn.) of a sol for a given osmotic pressure is practically equal to the val. of $1/c$ obtained by extrapolating swelling pressure data for the same two components to a pressure equal to the osmotic pressure. It thus seems that solvation and swelling are manifestations of the same cause.

R. CUTHILL.

Solvation of cellulose acetate sols. A. Y. DRINBERG (J. Appl. Chem., Russia, 1931, 4, 87—116).—Although the sp. degree of solvation decreases with increase in concn., the total vol. of the hydrated phase increases inversely as the degree of depolymerisation. The relative length of mol. chains decreases with increase in depolymerisation. Increase in mol. vol. of peptising agents increases the viscosity and degree of solvation; increase in the mol. vol. and concn. of aromatic hydrocarbons used as coagulants also increases the viscosity. Sols containing EtOH have smaller viscosity and degree of solvation the higher are the concn. of EtOH and the mol. wt. of peptising agents. Increase in the mol. wt. of acid radicals of esters used as peptising agents increases the viscosity of sols. The viscosity and degree of solvation with a homologous series of peptising agents increase with the mol. polarisation, dipole moment, and (EtOH) coagulation val. Higher temp. decrease viscosity and degree of polymerisation of sols with the same peptising agent, and of sols for which the ratio of the coagulating agent to peptising agent is less than the peptising val.; when this ratio lies between the peptising and coagulating vals. coagulation takes place as the temp. is raised.

CHEMICAL ABSTRACTS.

Determination of cataphoretic velocity. J. M. ALBAREDA [with BUJAKOVSKI] (Anal. Fis. Quim., 1931, 29, 688—698).—A modified form of apparatus for moving boundary measurements is described. Ultramicroscopic determination of the electrokinetic transference velocity of suspensions of kaolin in 0.001N solutions of alkali and alkaline-earth hydroxides confirms Wiegner's lyotropic series.

H. F. GILLBE.

Suspension effect of Wiegner and Palmann. II. Suspension effect and the surface of the disperse phase. J. M. ALBAREDA (Anal. Fis. Quim., 1931, 29, 681—687).—Addition of CaCl_2 and BaCl_2 to an aq. suspension of kaolin shows that coagulation has no influence on the magnitude of the

suspension effect. Since the hygroscopically-bound H_2O is also independent of coagulation, the surface of the disperse phase does not alter during coagulation by electrolytes. With increase of the size of the dispersed particles the effect diminishes, the magnitude of the change being in accordance with the variation of other properties which are a function of the surface of the particles.

H. F. GILLBE.

Theory of coagulation of homogeneous aerosols. H. S. PATTERSON (Phil. Mag., 1932, [vii], 13, 523—527).—Theoretical.

H. J. EMELÉUS.

Theory of the coagulation of dilute clay suspensions. E. W. RUSSELL (J. Agric. Sci., 1932, 22, 165—199).—A résumé of current views on the electrical behaviour of soil colloids.

A. G. POLLARD.

Flocculation of colloidal solutions. I. Mutual flocculation of oppositely-charged colloids. A. LOTTERMOSER and K. MAY (Kolloid-Z., 1932, 58, 61—68).—Experiments on the flocculation of negatively-charged sols of CdS , V_2O_5 , SnO_2 , mastic, HgS , Sb_2S_3 , As_2S_3 , and Prussian-blue by a standard positively-charged $Fe(OH)_3$ sol demonstrate that complete flocculation occurs when the electrochemical equivs. of the oppositely-charged colloids are equal.

E. S. HEDGES.

Displacement of equilibrium in ferric hydroxide sols by heating. K. JABŁCZYŃSKI and W. LASKOWSKI (Rocz. Chem., 1931, 11, 817—819).—The velocity of coagulation of undialysed $Fe(OH)_3$ sol by KCl is reduced by 18% after heating 30 min. at 52° ; on keeping 13 hr. the velocity returns to its original val. When the temp. is raised to 84° the reduction is 66% and the change is irreversible; at the same time the dimensions of the micelles are reduced, probably owing to elimination of hydration H_2O . As a result the density of the charge on the micelles increases, rendering them more resistant to coagulation by KCl .

R. TRUSZKOWSKI.

Rejuvenation of colloidal solutions. K. JABŁCZYŃSKI and E. EMIN (Rocz. Chem., 1931, 11, 805—816).—The ageing of colloidal solutions is associated with a decline in the velocity of coagulation to a min. val. and, conversely, rejuvenation is associated with an increase in this velocity to a max. val. Both processes are accompanied by an increase in the sp. conductivity of the solution, pointing to diffusion of ions from the micelles into the perimicellar fluid. In the case of dialysed colloidal $Fe(OH)_3$, the Cl ions formed within the micelle by ionisation of basic Fe^{+++} chloride diffuse out, thus augmenting the positive charge of the micelles, and making them more resistant to the coagulative action of electrolytes. In the case of undialysed $Fe(OH)_3$ sols, the H^+ ions formed as a result of hydrolysis diffuse out of the micelles, thereby augmenting the negative charge of the latter, and rendering them more susceptible to the action of electrolytes. In both processes auto-coagulation is absent, and the dimensions and degree of dispersion of the colloid are unchanged. The behaviour of $Fe(OH)_3$ sols towards electrolytes depends, therefore, entirely on whether and to what

extent the sols have been previously purified by dialysis.

R. TRUSZKOWSKI.

Absorption of water by gelatin. VII. Influence of temperature on swelling in acid solutions and the combination of gelatin with hydrochloric, nitric, or sulphuric acid. W. B. PLEASS (Biochem. J., 1931, 25, 1943—1948).—Raising the temp. causes an increase in H_2O absorption until at 25° in all solutions more acid than p_H 3.2 the gelatin is too soft to weigh. Max. swelling occurs at p_H 3.0 at 18° , at 2.6 at 12° , and at p_H 2.4 at 0° . Curves for the combination of gelatin with HCl , HNO_3 , and H_2SO_4 from p_H 5.0 to 1.7 are practically identical, exhibiting a flat portion from p_H 2.4 to 1.9, and indicate a combining wt. for gelatin of 1180 and K_b 5×10^{-11} . There is no hydrolysis of gelatin in these acid solutions ($p_H > 1.5$ at 18 — 20°).

S. S. ZILVA.

Constitution and properties of gelatinised substances. J. V. RUBIO (Anal. Fis. Quím., 1931, 29, 516—537).—Views on the colloidal state are reviewed, attention being directed towards the unsatisfactory nature of current nomenclature. Gels should be regarded as two-phase systems, and jellies as homogeneous.

H. F. GILLBE.

Action of electric field on gelatin: effect of indicators. (MLLE.) S. VEIL (Compt. rend., 1932, 194, 454—456).—A film of gelatin in the form of a gel not yet dried is deformed by an electric field throughout the entire space between and not merely near the electrodes (cf. A., 1925, ii, 292). Incorporation in the gelatin of various indicators, covering a p_H range of 0.15—13.0, shows abrupt changes of p_H at various places, which appear to be the immediate cause of the deformations (cf. A., 1931, 1368).

C. A. SILBERRAD.

Disperse ferromagnetics. H. SACHSE (Kolloid-Z., 1932, 58, 18—22).—The magnetisability of Fe_3O_4 or Fe , dispersed in gelatinous $Al(OH)_3$, SiO_2 , or $SrSO_4$, decreases with increasing dispersity of the ferromagnetic substance and increases with ageing, especially at higher temp.

E. S. HEDGES.

Effect of hydrogen-ion concentration on the precipitating and protective action of mixtures of two proteins on colloidal gold and gum-benzoin. R. H. HOPKINS, W. O. KERMAK, and W. T. SPRAGG (Biochem. J., 1931, 25, 1860—1873).—Mixtures of ovalbumin and gelatin, ovalbumin and oxyhaemoglobin, and of oxyhaemoglobin and gelatin were investigated with regard to the protective action of these mixtures against pptn. of the lyophobic colloids by 1.25% $NaCl$. The results previously obtained (A., 1931, 1009) with single proteins apply to the above mixtures. If the influence of a protein on the charge of the lyophobic particles is distinguished from its protective effect, the two proteins appear to act additively with respect to each of these effects.

S. S. ZILVA.

Refractivity of protein colloids. N. F. VERMOLENKO (J. Gen. Chem., Russia, 1931, 1, 21—30).—Change in n on mixing equal vols. of 3% glutin and 0.5*N*- Li , Na , K , Mg , Ca , Ba , Al , or Fe chloride is additive; n of glutin and ovalbumin varies linearly

with concn. (0.4–2.5%). Increase in n of H_2O on addition of gelatin treated with NaCl solution is greater than that for H_2O - or $CaCl_2$ -treated gelatin. Increasing aggregation of gelatin has no effect on refractivity. 2.5% gelatin dispersions subjected to different thermal treatment have the same val. of n . For 1% gelatin sols n is minimal in the neighbourhood of the isoelectric point. **CHEMICAL ABSTRACTS.**

Union of biocolloids. III. Uric acid-protein. S. J. PRZYŁECKI, M. Z. GRYNBERG, and D. SZRAJBER (Biochem. Z., 1932, 244, 190–213).—The dependence of the combination of uric acid and protein on the condition of the protein (sol, gel), the nature of the protein, the concn. of protein and uric acid, and the presence of electrolytes and alcohol is investigated. Experiments with caseinogen, gelatin, albumin, and globulin and with mixtures of albumin and globulin show that in the sol condition no combination with uric acid occurs. In the gel condition, all these proteins combine with uric acid on the alkaline side ($p_H > \text{isoelectric point}$). The combination is reversed when the protein passes from the gel to the sol condition and when the concn. of uric acid is decreased. The combination of globulin and albumin with uric acid is partly reversible and after a long time irreversible. The mode of combination is discussed (cf. A., 1931, 1090).

P. W. CLUTTERBUCK.

Reactions between colloids. II. Reactions between pigment sols and proteins. W. PAULI and L. SINGER (Biochem. Z., 1932, 244, 76–127).—Further work is described (cf. A., 1929, 395) on the colour change of pure Congo-red and -blue sols and the mechanism (constitutional mol. change, change of dispersion, etc.) is discussed. Tables summarise the quant. investigation of the modifying effects on Congo-blue sol of temp., CO_2 , EtOH, electrolytes, proteins, and NH_2 -acids. P. W. CLUTTERBUCK.

Proteins. III. Uniform solubility of the protein fraction of orange-seed meal in solutions of various sodium salts. L. K. ROTH and F. SAUNDERS (J. Amer. Chem. Soc., 1932, 54, 342–345; cf. A., 1931, 661).—*N*-Solutions of NaCl, NaBr, NaI, $NaHCO_3$, Na_2CO_3 , Na_2SO_4 , Na_3BO_3 , Na_2HPO_4 , Na_3PO_4 , NaOAc, NaOBz, Na salicylate, and Na tartrate extract the same amount of N from orange-seed meal; there is no evidence for the existence of a lyotropic series in this particular system. Pomelin, the globulin of the meal, is equally sol. in *N*-solutions of salts of strong bases and weak acids as in neutral salt solutions. The presence of acid apparently decreases the amount of N extracted, as is the case with NaH_2PO_4 . C. J. WEST (b).

Denaturation and the viscosity of protein systems. M. L. ANSON and A. E. MIRSKEY (J. Gen. Physiol., 1932, 15, 341–350).—The conditions for producing very viscous solutions with small concns. of denatured protein are examined. Denaturation produces an increase of η which, in the presence of carbamide, is not due to aggregation but hydration of protein particles. H. DAVSON.

Fibrinogen. E. HEKMA (Kolloid-Z., 1932, 58, 85–96).—The morphological habits of fibrinogen are

described. In the presence of alkali or acid, fibrinogen readily forms clear hydrosols, containing adsorption complexes with OH^- or H^+ combined with much H_2O . When kept, the swollen micelles arrange themselves into chains and produce a homogeneous gel. The formation of needles and fibrils is due to dehydration. A solid, hard substance is obtained by complete drying. E. S. HEDGES.

Structure-viscosimetric investigations of aqueous and alcoholic tannin systems of various concentrations. H. ERBING and Y. NISIZAWA (Kolloid-Z., 1932, 58, 79–85).—Determinations with the overflow viscosimeter show that aq. and EtOH solutions containing >5% of tannin show structure-viscosity. The systems in EtOH have a higher abs. viscosity and greater structure-viscosity than those in H_2O . This is ascribed to difference in solvation of the tannin. H_2O -EtOH mixtures containing 30% of tannin show structure-viscosity. The systems investigated are transitional between mol. and colloidal disperse systems. E. S. HEDGES.

Equilibrium between carbon and its oxides. P. E. HENRY (Ann. Mines, 1931, 19, 5–25; Chem. Zentr., 1931, ii, 1243–1244).—Lewis and Randall's curves correlating $\log K$ with T for the equilibrium $C + CO_2 \rightleftharpoons 2CO$ are in accord with Boudouard's results at 550–800° and Lewis and Randall's results at 850–1200°. With the aid of Lewis and Randall's formula $K, \log K$, and the ratio $CO : CO_2$ for $p_{CO} + p_{CO_2} = 0.001$ –10 atm., for 450–1100°, are calc. The ratio $[CO]/([CO] + [CO_2])$ as a function of T is shown graphically for the above pressures.

A. A. ELDRIDGE.

Apparent dissociation constants of certain amino- and aminohydroxy-acids and the changes of free energy and entropy caused by ionisation. E. J. CZARNETZKY and C. L. A. SCHMIDT (Z. physiol. Chem., 1932, 204, 129–134).—The apparent acid and basic dissociation consts. of valine, hydroxyvaline, *dl*- α -aminobutyric acid, and aminohydroxybutyric acid have been determined. The length of the C chain has no marked influence on the vals. The effect of the OH group is to increase the basic and to lower the acidic const. The apparent change of free energy, heat of ionisation, and change of entropy are calc. J. H. BIRKINSHAW.

Activities and the standard state. I. Activity coefficients. II. Electrode potentials. A. MACFARLANE and O. GATTY (Phil. Mag., 1932, [vii], 13, 283–291, 291–300).—From an examination of 6 concn. scales it is shown that by expressing concn. in g.-mols. of salt in a fixed quantity of solvent the physical interpretation of the activity coeff. is simplified, and the latter can be definitely related with the partial molal heat and the dilution of the solute to infinite dilution. The concn. of the solute in the standard states is, in general, a function of the temp. and pressure of the solution.

II. The vals. of the standard electrode potentials of the anions depend on the choice of units of concn. of solutions, and the use of the vol. normality scale is advocated. From the vals. of the electrode potentials in different solvents the partial molal free energies

for the transfer of electrolytes at infinite dilution can be calc. N. M. BLIGH.

Study of hydrolytic dissociation of salts by Raman effect. P. KRISHNAMURTI (Indian J. Physics, 1931, 6, 345—352).—Hydrolysis in solutions of carbamide and hexamethylenetetramine hydrochlorides is shown by the appearance of lines characteristic of the base as well as those of the salt in the Raman spectra, and an estimate may be made of the degree of hydrolysis from the relative intensities of the two sets of lines. In *N* solution $\text{CO}(\text{NH}_2)_2 \cdot 2\text{HCl}$ shows less hydrolysis than is indicated by reaction velocity methods. Hexamethylenetetramine is a weaker base than carbamide. J. W. SMITH.

Physico-chemical studies of complex formation involving weak acids. IV. Alkali solutions of lanthanum tartrate. H. T. S. BRITTON and W. E. BATTRICK (J.C.S., 1932, 196—207).—On adding NaOH to an aq. suspension of La tartrate some interaction, with formation of Na tartrate, is followed by dissolution of the ppt.; this occurs earlier when excess of Na tartrate is present. A suspension containing NaOH just insufficient to cause dissolution sets, on keeping, to a gel.

C. W. DAVIES.

Equilibria in the boric acid-diol-water system. I. N. VERMAAS (Rec. trav. chim., 1932, 51, 67—92).—Colorimetric determinations of p_H show that in solutions of 0.1*M*- H_3BO_3 and varying quantities of diol, the concn. of BD' (D representing the diol residue) from the complex HBD is negligible compared with the concn. of BD_2' from the complex HBD_2 (cf. A., 1930, 1018). Potentiometric determinations of p_H during neutralisation of solutions of H_3BO_3 and diol by KOH give curves below p_H 7 for many diols, indicating the presence of strong acids. The results confirm the existence of BD_2' . By potentiometric titration of mixtures of H_3BO_3 and diol with KBO_2 the ratio K_2/K_1 for a number of polyhydric alcohols has been determined ($K_2 = [\text{H}'] \times [\text{BD}_2'] / [\text{HB}] \times [\text{D}]^2$ and $K_1 = [\text{H}'] \times [\text{BD}'] / [\text{HB}] \times [\text{D}']$). For fructose, mannitol, sorbitol, mannitan, and glycerol the vals. are 30, 40, 40, 300—400, and 3, respectively.

M. S. BURR.

Acidity of arsenious acid and its diol compounds in aqueous solution. B. ENGLUND (Rec. trav. chim., 1932, 51, 135—142).—Colorimetric titration curves of aq. H_3AsO_3 by KOH, with and without the addition of diols, indicate that mannitol, sorbitol, or α -mannitan increases the acidity, but not to the same extent as in the case of H_3BO_3 . The results indicate that the chief complex ion in the solution is AsD_2' , D representing the diol residue. A form of H_3AsO_3 , which is a weaker acid than the normal form, is obtained by heating sublimed As_2O_3 with H_2O on the water-bath for 5 hr. By boiling this solution for 7 hr. under a reflux it attains the normal acidity.

M. S. BURR.

Complex formation in the system MoO_3 - H_2O . A. V. NOVOSELOVA (J. Gen. Chem. Russ., 1931, 1, 668—683).—The molybdic acid present in 1.4% solutions of MoO_3 contains 4 atoms of Mo per mol.; the mol. wt. of the complex falls with increasing dilution. The dissociation const. of molybdic acid is

7×10^{-3} . Permanent change in the degree of association of molybdic acid complexes is not observed on heating aq. MoO_3 and then cooling. The composition of Ag molybdates varies with the p_H of the medium; $\text{Ag}_2\text{O} \cdot \text{MoO}_3$ is pptd. from 0.4% aq. MoO_3 of p_H 4.2 by AgOAc , whilst at $p_H < 2$ AgNO_3 ppts. $\text{Ag}_2\text{O} \cdot 3\text{MoO}_3$. In the electro-titration of aq. MoO_3 by NaOH or $\text{Ba}(\text{OH})_2$ the p_H falls with addition of alkali from p_H 6.5 to 5, after which it again rises; this effect is due to hydrolysis of complex mols. When weak bases are used the titration curves exhibit two breaks, corresponding with the formation of two salts, $\text{Na}_2\text{O} \cdot 4\text{MoO}_3 \cdot n\text{H}_2\text{O}$ at p_H 4, and $\text{Na}_2\text{O} \cdot \text{MoO}_3$ at higher p_H . The mol. wt.-concn. curve of MoO_3 solutions exhibits a break at 5.25%, above which heteropolymerides appear in solution. R. TRUSZKOWSKI.

Thermal dissociation of oxides and peroxides.

I. Manganese dioxide. **II. Sodium peroxide.** M. BLUMENTHAL (Rocz. Chem., 1931, 11, 855—864, 865—869).—I. The dissociation pressure of natural, cryst., and amorphous MnO_2 has been determined over the range 369—544°. The reaction is in all cases reversible, and the heats of dissociation, *Q*, given by $\log p - Q/4.6T + 1.75 \log T + 2.8$, are 27.9 and 28.5 kg.-cal. for amorphous and cryst. MnO_2 , respectively, and 37.1 for pyrolusite. No compound or solid solution formation between MnO_2 and Mn_2O_3 is observed below 850°.

II. The heat of dissociation of Na_2O_2 , m. p. 460°, is 38.2 kg.-cal. No evidence of the existence of Na_2O_3 was obtained. R. TRUSZKOWSKI.

F.p. of the system hydrogen chloride-sulphur monochloride. H. TERREY and H. SPONG (J.C.S., 1932, 219—226).—The system shows two eutectics, between which there is a region of incomplete miscibility. The upper layer in this region has a const. f. p. and probably contains a compound for which the formula $\text{H}_4\text{S}_2\text{Cl}_6$ is suggested. C. W. DAVIES.

Compound formation between nitrobenzenes.

D. L. HAMMICK, L. W. ANDREW, and J. HAMPSON (J.C.S., 1932, 171—174).—F.p. curves show that PhNO_2 (A) gives with *m*-dinitrobenzene (B) a compound AB, and with *s*-trinitrobenzene (C) a compound A_2C . B gives no compound with C, nor A with trinitrotoluene. C. W. DAVIES.

Thermodynamics of concentrated solutions.

I. Eutectic systems. E. KORDES (Z. physikal. Chem., 1931, 158, 1—34; cf. A., 1928, 117; 1929, 994).—On the assumption that no change occurs in the total no. of mols. and that there is no formation of solid solutions, it is shown that the f.p. curves exhibit certain additive relations in which the f. p. of the pure components, the eutectic temp., and the mol. differential heats of dissolution of the components are involved. R. CUTHILL.

Oxide hydrates and active oxides. XLVIII.

Different kinds of binding of water, with special reference to osmotic binding in gels. G. F. HUTRIG (Kolloid-Z., 1932, 58, 44—61).—A review of the literature, particularly relating to the v. p.-temp. curves and the X-ray spectrograms of substances containing H_2O , leads to the recognition of the following types of binding: (1) cryst. hydrates of stoicheio-

metric composition, (2) mixed crystals, (3) amorphous hydrates of stoichiometric composition, (4) hydrogels with capillary bound H_2O , (5) cryst. and amorphous substances containing osmotically bound H_2O (e.g., zeolites and permutites), (6) sorbed H_2O , (7) mixed types, which can be expressed in terms of the preceding. E. S. HEDGES.

System water-carbon dioxide-ammonia. E. JANECKE and E. RAHLFS (Z. Elektrochem., 1932, 38, 9—12; cf. A., 1930, 1373).—Previous work is completed by examination of the ternary systems $\text{NH}(\text{CO}\cdot\text{NH}_2)_2\text{--NH}_4\text{HCO}_3\text{--CO}(\text{NH}_2)_2$ and $\text{NH}(\text{CO}\cdot\text{NH}_2)_2\text{--}(\text{CN}_2\text{H}_2)_2\text{--CO}(\text{NH}_2)_2$, and the binary system $\text{NH}(\text{CO}\cdot\text{NH}_2)_2\text{--NH}_3$. The metastable solubility curve of $\text{NH}_2\cdot\text{CO}_2\cdot\text{NH}_4$ at 0° has been determined. From the NH_3 pressures of the above-mentioned binary system the existence of the compound $\text{NH}(\text{CO}\cdot\text{NH}_2)_2\cdot 2\text{NH}_3$ is deduced. A complete diagram is given. F. L. USHER.

System $\text{K}_2\text{CO}_3\text{--KHCO}_3\text{--H}_2\text{O}$ at 42° . Z. P. STARKOVA (J. Gen. Chem. Russ., 1931, 1, 747—749).—The solid phases in the system are KHCO_3 and $\text{K}_2\text{CO}_3\cdot 1\frac{1}{2}\text{H}_2\text{O}$. No compound formation takes place. K_2CO_3 free from KHCO_3 can be cryst. out at 42° only when the KHCO_3 concn. is $< 2.46\%$.

R. TRUSZKOWSKI.

System $\text{H}_3\text{PO}_4\text{--Ba}(\text{OH})_2\text{--CO}_2\text{--H}_2\text{O}$. R. PALLU (Compt. rend., 1931, 193, 109—111).—If CO_2 is passed into solutions of $0.248N\text{--BaO}$ and H_3PO_4 at 17° until equilibrium is attained (about 1 month) conductivity determinations indicate the formation of BaHPO_4 , but not of $\text{Ba}_3(\text{PO}_4)_2$, although the latter is formed in the absence of CO_2 (cf. A., 1931, 684). When the ratio $\text{BaO}/\text{H}_3\text{PO}_4$ is > 1 the solid phase is BaHPO_4 ; with more BaO the ppt. contains increasing amounts of BaCO_3 , to a max. of 70.8%. $\text{Ba}_3(\text{PO}_4)_2$ is therefore completely decomposed by aq. CO_2 at room temp.

C. A. SILBERRAD.

System $\text{H}_3\text{PO}_4\text{--Ca}(\text{OH})_2\text{--CO}_2\text{--H}_2\text{O}$. R. PALLU (Compt. rend., 1932, 194, 458—460; cf. preceding abstract).—If CO_2 is passed into mixtures of CaCO_3 and $N\text{--H}_3\text{PO}_4$ until equilibrium is reached (about 2 months) the conductivity curve shows the formation of CaHPO_4 with no indication of $\text{Ca}_3(\text{PO}_4)_2$; without CO_2 a colloidal substance for which $\text{P}_2\text{O}_5/\text{CaO} = 0.28\text{--}0.30$ is also formed (cf. A., 1925, ii 770; 1929, 651). The solid phase for mixtures with the ratio $\text{CaO}/\text{H}_3\text{PO}_4$ is > 1 is CaHPO_4 ; as the ratio increases CaCO_3 is present in increasing proportion. CO_2 increases the amount of P_2O_5 in solution.

C. A. SILBERRAD.

Polytherms of ternary systems containing water, an alkali sulphate, and a sulphate of the vitriol type. V. A. BENRATH and C. THONENSEN (Z. anorg. Chem., 1932, 203, 405—416; cf. A., 1931, 310).—Solubilities of CdSO_4 in H_2O between 0° and 100° and limits of stability of the several solid phases have been redetermined. The system $\text{CdSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$ has been systematically studied and the existence of the following compounds established: $3\text{CdSO}_4\cdot\text{K}_2\text{SO}_4\cdot 5\text{H}_2\text{O}$, $3\text{CdSO}_4\cdot\text{K}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, $3\text{CdSO}_4\cdot 2\text{K}_2\text{SO}_4\cdot \text{H}_2\text{O}$, and $\text{CdSO}_4\cdot\text{K}_2\text{SO}_4\cdot 1.5\text{H}_2\text{O}$, in addition to $\text{CdSO}_4\cdot\text{K}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ previously described. Polythermal diagrams are given. With Ti_2SO_4 the

compounds $3\text{CdSO}_4\cdot\text{Ti}_2\text{SO}_4\cdot 5\text{H}_2\text{O}$ and $2\text{CdSO}_4\cdot\text{Ti}_2\text{SO}_4$ have been prepared; and with Rb_2SO_4 the compounds $3\text{CdSO}_4\cdot\text{Rb}_2\text{SO}_4\cdot 5\text{H}_2\text{O}$, $\text{CdSO}_4\cdot\text{Rb}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, and $2\text{CdSO}_4\cdot\text{Rb}_2\text{SO}_4$, in addition to $\text{CdSO}_4\cdot\text{Rb}_2\text{SO}_4\cdot 6\text{H}_2\text{O}$ previously described. Polytherms for the last two systems have also been determined. F. L. USHER.

Calcium saccharates. E. ANGELESCU and C. VLADESCU (Z. ver. Deut. Zucker-Ind., 1931, 81, 700—720).—The temp. at which a solution of CaO and sucrose ppts. $\text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot 3\text{CaO}$ rises as the ratio $\text{CaO}/\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is diminished, and with increasing dilution reaches a min., which is assumed to indicate a change in the sol. phase to $\text{Ca}(\text{OH})_2$. These results are to be expected from the effects of temp. and dilution on the reactions $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{CaO} \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot\text{CaO}$; $3\text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot\text{CaO} \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}\cdot 3\text{CaO} + 2\text{C}_{12}\text{H}_{22}\text{O}_{11}$. The ppt. is frequently of a highly-disperse, lyophile nature, and its composition is profoundly affected by adsorption, which accounts for the large number of "compounds" described by previous workers. The viscosity of the system in these cases is high and shows the hysteresis characteristic of colloids. The degree of dispersion of the ppt. increases with the ratio $\text{CaO}/\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in agreement with von Weimarn's theory.

N. H. HARTSHORNE.

Chromium halides. F. HEIN and I. WINTNER-HOLDER (Z. anorg. Chem., 1931, 201, 314—322).—The reduction equilibria $2\text{CrX}_3 + \text{H}_2 \rightarrow 2\text{CrX}_2 + 2\text{HX}$ have been measured by Jelinek's method at different temp. for CrCl_3 and CrBr_3 . Heats of formation are calc.

F. L. USHER.

Methods and apparatus in use at the Bureau of Physico-Chemical Standards. VII, VIII. Heats of combustion. III. Succinic acid. IV. Other substances. M. BECKERS (Bull. Soc. chim. Belg., 1931, 40, 571—610).—Succinic acid is a suitable secondary standard in calorimetry; its heat of combustion is 3026.3 g.-cal. per g. (in vac.). The recryst. material should be dried over P_2O_5 after compression, the latter causing disruption of vacuoles enclosing solvent. The val. 9604.9 is found for C_{10}H_8 , giving 1.5200 for the ratio $\text{C}_{10}\text{H}_8/\text{BzOH}$ (wts. in vac.). Vals. are also reported for cetyl alcohol, 10,302.7; dotriacontane, 11,146.0; anthracene, 9457.6; anthraquinone, 7427.2; COPh_2 , 8529.3; salol, 6819.3.

C. W. DAVIES.

Heat of formation of ozone. P. GUNTHER, E. WASSMUTH, and L. A. SCHRYVER (Z. physikal. Chem., 1932, 158, 297—304).—The heat of formation determined directly by the explosion method is -34.22 ± 0.24 kg.-cal. per mol. at const. vol. R. CUTHILL.

Determination of heat of combustion of cellulose nitrate and cellulose. M. PRETTE (Mem. Poudres, 1930—1931, 24, 223—233).—Experiments were carried out in a 600-c.c. stainless steel bomb at 25 kg. pressure. The heats of combustion of cellulose nitrates of 11.16, 11.97, 12.13, 13.25, 13.45, and 13.89% N were 2598.5, 2477.5, 2459.2, 2300.6, 2267, and 2207.2, and the heats of formation 713, 669, 655, 586, 578, and 549 g.-cal. per g., respectively. By extrapolation, the heat of combustion of cellulose is 4180; tests on 6 samples of ramie fibre gave a mean of 4173.7 g.-cal. per g. The heat of combustion of

cellulose nitrate between 11.12 and 14.15% N is given by $C_v = 4173.7 - 141.3x$, and the heat of formation by $F_v = 1409.7 - 62.3x$ g.-cal./g., where $x = \% \text{ N}$.
W. J. WRIGHT.

Calorimetric investigation of dehydrated kaolin. E. KLEVER and E. KORDS (Veroff. Kaiser Wilhelm-Inst. Silikatforsch., 1930, 3, 17—22; Chem. Zentr., 1931, i, 2443—2444).—The heat of dissolution in 40% HF of samples of Zettlitz kaolin heated to various temp. shows an increase at 420—550°; this corresponds with the endothermic removal of H_2O . The heat of hydration of kaolin obtained is 34.8 kg.-cal. Between 550° and 900° the heat of dissolution shows the existence of a compound, metakaolin or kaolin anhydride; the heat of formation of this from the oxides is -15.8 ± 2.5 kg.-cal. per mol. For samples heated at 900—1000° the heat of dissolution corresponds with the sum of those of the free oxides, so that decomp. of metakaolin into the oxides can be assumed. Between 1170° and 1220° there is a second exothermal effect which points to the formation of sillimanite. L. S. THEOBALD.

Interpretation of electrolytic conduction in amalgams and other alloys. C. WAGNER (Z. physikal. Chem., 1932, B, 15, 347—352).—An approx. equation giving transport numbers in dilute binary alloys in terms of diffusion coeffs. of solvent and solute, and derived by the methods previously described (A., 1931, 171), leads to results in qual. agreement with existing transport data for dil. amalgams. Since the derivation of the equation postulates that metal ions and electrons move independently of each other, and that the metals are largely ionised into ions and electrons, these assumptions seem to be justified. R. CUTHILL.

Influence of sucrose on the conductivity of aqueous salt solutions. E. LANDT and C. BODEA (Z. ver. Deut. Zucker-Ind., 1931, 81, 721—773).—The conductivities of dil. solutions of KCl, NaCl, BaCl_2 , and NEt_4 picrate in H_2O and in 10, 20, 40, 60, and 67% sucrose solutions have been measured at 20°, and, in a few cases, at 35° and 50° also. Kohlrausch's square-root law holds in all cases in the most dil. solutions, and its region of validity increases with the sugar concn. The Debye-Hückel-Onsager theory is in qual. agreement only with the results. Walden's rule, $\lambda_\infty \cdot \eta = \text{const.}$, is not obeyed, but for NEt_4 picrate approaches validity with rise of temp. The ions migrate faster than the rule requires. An explanation of this, based on association of the sugar mols., is advanced.

N. H. HARTSHORNE.

Electrolytes in clays. L. M. ZARUDSKI (J. Appl. Chem., Russia, 1931, 4, 9—33).—The sp. conductivity of H_2O extracts of clays is given by $k = \beta C^{1/3} D$, where C is the wt. in g. of clay extracted with 100 c.c. H_2O , β is the conductivity at $C=1$, and D is the proportionate decrease in conductivity when the clay : H_2O ratio is increased tenfold. The change in conductivity on evaporation is expressed by $k' = \beta' C'^{1/3} D$, where k' is the conductivity when the extract is conc. C' times. The amount of electrolytes adsorbed by clays is characterised by increase in D and is a measure of the "fatness" of the clay. CHEMICAL ABSTRACTS.

Transport of electricity through phase boundaries. System I (glass-gas). I. Introduction of hydrogen into glass by electrolysis. E. MANEGOLD and F. A. SCHNEIDER (Z. physikal. Chem., 1932, 158, 197—215; cf. A., 1929, 521).—The electrolytic displacement of Na^+ by H^+ in Thuringian glass at about 300° has been accomplished in an apparatus consisting of a metal anode surrounded by H_2 contained under low pressure in a glass vessel having an outer metallic coating serving as cathode. The vol. of H_2 introduced into the glass and the wt. of Na displaced are both in accordance with Faraday's law. By passing the current in the reverse direction the Na^+ can be displaced by other metal ions, such as those of Al, Cu, and Ag. Attempts to introduce N_2 or He into the glass failed. R. CUTHILL.

[Ionic] transport in glasses. R. SCHWARZ and J. HALBERSTADT (Z. anorg. Chem., 1932, 203, 365—372; cf. A., 1931, 1012).—Electricity is carried solely by Na ions in both plain soda glass and Thuringian glass, the K ions in the latter being immobile. The observations were made at different temp. between 400° and 620°. F. L. USHER.

Standard electrode potentials in ethyl alcohol. A. MACFARLANE and (SIR) H. HARTLEY (Phil. Mag., 1932, [vii], 13, 425—443; cf. A., 1929, 1240).—A study has been made of reference electrodes and liquid junction potentials in EtOH. The electrode potentials of Li, Na, Tl, Ag, Cl, Br, and I, and the solubility products of AgCl, AgBr, AgI, AgCNS, and TlCl in EtOH are recorded. From the results the partial molal free energies of transfer of a number of electrolytes are calc. and compared with vals. derived from the Born equation. The dissociation const. of EtOH is 1.9×10^{-19} . H. J. EMELEUS.

Study of liquid-liquid junctions with a view to eliminate the potential difference thereat. J. V. LAKHANI (J.C.S., 1932, 179—182).—A const. and reproducible p.d. is set up at a junction consisting of two impinging jets. It is established instantaneously. C. W. DAVIES.

Hydrogen effect. F. TODT (Z. Elektrochem., 1932, 38, 12—13).—Hydrolytic adsorption at a platinised Pt surface, as found by Kolthoff and Kameda (A., 1929, 1410) in phosphate buffer solutions containing KCl, gives rise to acid in amount sufficient to account for the change in p_H attributed by Wolf to a "H effect." F. L. USHER.

Behaviour of the hydrogen-palladium diffusion electrode when supplying current. A. KOENIG (Siebert Festschr., 1931, 179—192).—The cell used comprised a horseshoe-shaped thin-walled Pd tube immersed in a Pd dish perforated at the bottom and filled with a eutectic mixture of KNO_3 and NaNO_2 ; H_2 was passed through the Pd tube and O_2 through the bottom of the dish, which was covered with Pd sponge to break up the bubbles and prevent spurting. At 250° this cell had an e.m.f. of 0.75 volt when no current was taken from it; with increasing c.d. at the Pd- H_2 electrode the voltage fell, the optimum current yield being 0.7 amp. per sq. dm. at 0.5 volt over prolonged periods. A. R. POWELL.

Physico-chemical studies of complex formation involving weak acids. III. Conductometric and potentiometric titrations of metallic acetates. H. T. S. BRITTON and F. H. MEEK (J.C.S., 1932, 183—196).—The order of increasing hydrolysis of the acetates is Pb, Cu, Be, Th, Al. The solubility of PbSO_4 in NaOAc is attributed to the formation of basic Pb acetate.

C. W. DAVIES.

Electrolytic reduction potentials of organic compounds. VII. Dinitrobenzenes. VIII. Dinitrophenols. IX. Allyl alcohol. Action of a catalyst on electrolytic reduction. X. Azobenzene. M. SHIKATA, N. HOZAKI, and I. TACHI (Mem. Coll. Agric. Kyoto, 1931, No. 17, 1—19, 21—33, 35—44, 45—55).—VII. The electrolytic reduction of $\text{C}_6\text{H}_4(\text{NO}_2)_2$ at 25° , as investigated polarographically at the dropping Hg cathode, takes place in two stages, 2 H atoms taking part in each stage. Each reduction stage, therefore, belongs to the type $\text{NO}_2\text{--NO}$ and the reduction potentials (R.P.) of the two NO_2 -groups differ from one another. The reducibility in the first stage decreases for the three isomerides in the order *o*, *p*, and *m* in acid solutions, *e.g.*, p_H 1, whilst the order is *p*, *o*, and *m* in strongly alkaline solutions, *e.g.*, p_H 13. The corresponding orders for the second stage are *o*, *m*, and *p*, and *m*, *p*, and *o*, respectively. In accordance with the authors' "negativity rule," the first R.P. of $\text{C}_6\text{H}_4(\text{NO}_2)_2$ is, for all isomerides, more positive than the R.P. of PhNO_2 or $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{OH}$. Unlike the *o*- and *m*-compounds, *p*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$ has a third R.P. in solutions of p_H 10 or more. The solubilities of the three $\text{C}_6\text{H}_4(\text{NO}_2)_2$ at 25° , determined polarographically, are: *o*, 0.1308, *m*, 0.8075, *p*, 0.1195 g. per litre.

VIII. Reduction of 2:4-, 2:6-, and 2:5- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OH}$ takes place in two stages, due to the two NO_2 -groups. The reducibility decreases in the order 2:5, 2:6, 2:4, for the first and 2:6, 2:4, 2:5, for the second stage, in both strongly acidic and strongly alkaline solutions. The relations vary in solutions of intermediate p_H . In their relations with other NO_2 -compounds they obey the "negativity rule." The solubilities of the three isomerides at 25° , determined polarographically, are: 2:4 0.0865, 2:6 0.2853, 2:5 0.1123 g. per litre.

IX. The reduction of allyl alcohol takes place with some difficulty and its R.P. is -2.14 volts. Comparison with previous work on the reduction of compounds with a double linking indicates that the group does not increase the electronegativity of the mol. so much as CO_2H or nuclear N. The catalytic effect of colloidal Pt-black on the reduction is very slight. Other effects observed, due to Pt-black, however, are: change in deposition potential of K' in accordance with Shikata's theory (A., 1930, 413); increase of H' concn. in neutral aq. electrolyte, assumed to be due to selective adsorption or the exchange of ions between colloid and solution; development of a more positive deposition potential of H'; depolarising action in electrolytic decomp. of H_2O .

X. Electrolytic reduction of azobenzene by the dropping Hg cathode gives a reversible azo-hydrazo-system for p_H 1.2—5.0, and similarly for a stationary Hg cathode of area 0.785 sq. m. The polarograms for the latter always show a max. due to accumulation of

the reduction product on the cathode. A Pt cathode, 0.785 sq. mm., gives R.P. 0.15—0.2 volt more negative than the other two.

M. S. BURR.

Acidic property of sugars. F. URBAN and P. A. SHAFFER (J. Biol. Chem., 1932, 94, 697—715).—The electrometric titration of glucose, fructose, and sucrose with NaOH, using the H electrode, indicates that these sugars behave as dibasic acids with the following dissociation consts. (pK_1 and pK_2) at 25° : glucose, 12.09, 13.85; fructose, 11.68, 13.24; sucrose, 12.60, 13.52. At high alkalinity a third acidic group appears to come into play with each sugar (cf. A., 1929, 765; 1930, 747).

F. O. HOWITT.

Cathode oscillograph measurements of the voltage effect in electrolytic solutions. W. FUCHS (Ann. Physik, 1932, [v], 12, 306—318).—A cathode oscillographic method of measuring small changes in resistance, which appear when the voltage has been applied for only a short time, is described and applied to solutions of electrolytes. By means of these oscillograms Wien's concn. effects are rendered visible. The dependence of the effect on ionic charge and concn. and its variation with field strength are discussed. Characteristic graphs for $\text{Ba}_2\text{Fe}(\text{CN})_6$, $\text{Ba}_3[\text{Fe}(\text{CN})_6]_2$, and MgSO_4 are given. W. R. ANGUS.

Characteristic curves of the aluminium rectifying cell. L. L. BARNES (Phil. Mag., 1932, [vii], 13, 76—81).—The characteristics of a cell with Al and Pb electrodes in aq. Na borate have been obtained. Rectification decreases rapidly above 25° and ceases at 95° .

H. J. EMELÉUS.

Electrolytic transfer of platinum in hydrochloric acid solution. G. GRUBE, F. OETTEL, and H. REINHARDT (Siebert Festschr., 1931, 108—120).—In conc. HCl electrolytically deposited Pt dissolves anodically more rapidly than rolled Pt sheet. Dissolution of active Pt begins at $e_H = +1$ volt, whilst Cl_2 begins to be evolved at a passive Pt anode at 1.2—1.4 volts. Pt can be transferred electrolytically from anode to cathode in *M*-solutions of H_2PtCl_6 in 5*N*-HCl at 75° ; at a low c.d. Pt dissolves at the anode as Pt^{IV} , but at a very high c.d. part dissolves as Pt^{II} (cf. A., 1931, 914).

A. R. POWELL.

Influence of a magnetic field on the anodic behaviour of iron. U. SBORGI (Gazzetta, 1931, 61, 846—882).—The potentials of various kinds of Fe in 0.5—2*N*- HNO_3 , 3*N*-HCl, 3*N*- H_2SO_4 , and 3*N*- H_2SO_4 containing FeSO_4 have been measured at const. c.d. and under the influence of magnetic fields of various intensities. In all cases the field prolongs the period of activity of the Fe, and its influence is not altered by anodic or cathodic treatment of the electrode. In H_2SO_4 the effect is a max. at a concn. of 2—3*N*, and decreases with increase of the FeSO_4 concn.; at lower acid concn. secondary effects occur. Increase of the field strength has less influence at high than at low FeSO_4 concn. These and other observations are discussed in considerable detail. H. F. GILLBE.

Present position of the theory of local [galvanic] elements. J. ECKELL (Z. Elektrochem., 1932, 38, 13—24).—A crit. review of recent experimental work.

F. L. USHER.

Graphical methods for the calculation of constants. II. Function $y = (1 + t/\tau_0)^{-1/(n-1)}$ as an equation of chemical kinetics. M. CRESPI (Anal. Fis. Quim., 1931, 29, 571—583).—The general kinetic equation (cf. A., 1930, 1377) is converted into the form $y = (1 + t/\tau_0)^{-1/(n-1)}$, where $1/\tau_0 = K(n-1)a^{n-1}$, and various graphical methods of employing this curve are demonstrated. H. F. GILLBE.

Velocity coefficients of uni- and bi-molecular reactions. S. ROGINSKI and L. ROSENKEVITSCH (Z. physikal. Chem., 1931, B, 15, 103—115).—The theory of activation in a unimol. reaction and recent velocity data are examined from the point of view of the theory previously developed (A., 1930, 1377). The const. B in Arrhenius' equation $K = Be^{-A/RT}$ is connected with the no. of quadratic terms in the expression for the energy of activated mols.

R. CUTHILL.

Supposed law of flame speeds. W. A. BONE (Chem. and Ind., 1932, 116—118; cf. A., 1927, 424).—Polemical. The evidence against Payman and Wheeler's "law" is restated.

J. G. A. GRIFFITHS.

Oxidation and inflammation of combustible gaseous mixtures. M. PRETTE (Ann. Office Nat. Combust. liq., 1931, 6, 7—42; Chem. Zentr., 1931, ii, 1260).—Methods for the determination of ignition temp. are criticised, and the pyrometer method is described. The results are accurate to $\pm 5^\circ$. Air- H_2 mixtures containing 10 and 90.5 vol.-% H_2 inflame respectively at 456° and 540° . Up to 60 vol.-% the ignition temp. rises linearly with the H_2 content, but at higher H_2 concns. it rises more rapidly. The temp. is very sensitive to the products of combustion. If an equal vol. of $N_2 + O_2$ is substituted for air, the ignition temp. falls for small H_2 concns.; substitution of N_2 by A somewhat raises the temp., and the presence of products of combustion again has a large effect. Addition of CO_2 considerably raises the temp.; up to 60 vol.-% H_2 it is almost const., and thereafter rises. The flame is violet and C separates. The material or vol. of the vessel is without effect.

A. A. ELDRIDGE.

Homogeneous first-order gas reactions. I. Decomposition of ethylidene diacetate. C. C. COFFIN (Canad. J. Res., 1931, 5, 636—647; cf. A., 1931, 1372).—Apparatus and method for measuring the rate of decomp. of $CHMe(CO_2Me)_2$ vapour at temp. in the neighbourhood of 230° are described. The velocity coeff. at a given pressure and temp. is independent of the ratio surface/vol. of the containing vessel, and the decomp. is strictly homogeneous and unimol. The results are discussed.

F. L. USHER.

Slow combustion of methane. W. A. BONE and R. E. ALLUM (Proc. Roy. Soc., 1932, A, 134, 578—591; cf. A., 1930, 1529; 1931, 45).—A study of the slow combustion of CH_4 at atm. pressure and over the temp. range 423 — 447° indicates that the process is a direct hydrocarbon oxidation, uncomplicated by any sign of "peroxidation." The most reactive $CH_4 + O_2$ mixture is that corresponding with the alcohol-forming proportion (i.e., $2CH_4 + O_2$).

L. L. BIRCUMSHAW.

Formation of methyl alcohol and formaldehyde in the slow combustion of methane at high pressures. D. M. NEWITT and A. E. HARTNER (Proc. Roy. Soc., 1932, A, 134, 591—604; cf. preceding abstract).—Large proportions of MeOH can be isolated from the products of the slow combustion of CH_4 at high pressures. Initial mixtures with the composition $2CH_4 + O_2 + (6-6.5)X$ (where $X = CO_2, N_2, H_2O$, or CH_4) were used. The rate of formation of MeOH increases with the CH_4/O_2 ratio as combustion proceeds in an $8.1CH_4 + O_2$ mixture, until the concn. of H_2O and CO_2 in the products exerts a retarding effect. At any pressure there is a definite temp. at which max. survivals of MeOH and CH_2O are obtained. The effect of increasing the pressure over the range 10—150 atm. increases the survival of MeOH and to a smaller extent of CH_2O , and also increases the ratio MeOH/ CH_2O . The reaction under the experimental conditions is mainly a surface effect and exhibits a marked induction period.

L. L. BIRCUMSHAW.

Kinetics of two bimolecular reactions in solution and in the vapour phase. E. A. MOELWYN-HUGHES and C. N. HINSHELWOOD (J.C.S., 1932, 230—240).—The kinetics of the formation of NEt_4I and the esterification of Ac_2O by EtOH have been studied in the gaseous phase and in solution in CCl_4 and hexane. The rates of both reactions in solution are about 10^8 times slower than a hypothetical gaseous reaction with the same crit. increment. This discrepancy is not due to deactivation by solvent mols. because rates of the same order of magnitude are obtained for the gaseous reactions.

F. J. WILKINS.

Photographic investigation of flame movements in gaseous explosions. IV—VI. W. A. BONE and R. P. FRASER (Phil. Trans., 1931, A, 230, 363—385; cf. A., 1929, 771).—Photographic records show that "shock waves" set up by igniting detonators surrounded by N_2 at or near the same instant as a mixture of CO and O_2 is ignited in the same explosion tube, are extremely potent in abruptly accelerating the initial flame movement and ultimately causing detonation. In a sufficiently explosive medium detonation may be set up at the instant of ignition, provided that the ignition is sufficiently intense and that the flame is simultaneously struck by a powerful shock wave. Auto-ignition of a flame moving with a velocity greater than that of sound may be produced by the close proximity of a shock wave moving ahead of it. Several such auto-ignitions may occur before detonation is set up. Experiments on the spin of detonating flames of various explosive mixtures indicate that it is not due to a helical rotation of the gas as a whole, nor to vibrations in the explosion tube itself. The phenomenon is discussed.

N. H. HARTSHORNE.

Velocity of polymerisation of hydrocarbons of the divinyl and allene series. E. N. GAPON (J. Gen. Chem. Russ., 1931, 1, 779—784).—The possible number of primary polymerides of hydrocarbons of the divinyl series, as well as of *s*-substituted allene hydrocarbons, is equal to the number of types of active mol., whilst in the case of *as*-allenes it is greater. The velocity of polymerisation of *s*-substituted hydro-

carbons is greater than is that of the *as*-, and diminishes with increase in homologous series; the introduction of a Me group into divinyl hydrocarbons reduces the velocity by 80%, and into allene hydrocarbons by 33%. Retardation of velocity due to introduction of a substituent is greater when the terminal than when the central atoms of the chain are affected. C_5H_8 hydrocarbons of the divinyl series have a higher velocity of polymerisation than their structural isomerides of the allene series, whilst the reverse is the case for C_6H_{10} hydrocarbons. The velocity coeff. of polymerisation, K , at 150° of divinyl hydrocarbons becomes 6^n times smaller when n Me groups are introduced into the mol. K is greatly increased in those cases in which conjugated chains are converted by polymerisation into conjugated rings, and this effect is greater the fewer atoms enter into the rings. K falls for both di- and poly-meride formation in homologous series. Increase in the mol. wt. or number of substituents in the terminal atoms of butadienes reduces, and in the central atoms increases, the polymeride content of the product. The reaction of polymerisation is characterised by its low temp. coeff. and energy of activation, as compared with bimol. reactions in gases. R. TRUSZKOWSKI.

Velocity of polymerisation. V. Hydrocarbons of the divinyl series. VI. Hydrocarbons of the allene series. E. N. GAPON (J. Gen. Chem. Russ., 1931, 1, 765—769, 770—778).—V. The velocity coeffs. of the polymerisation of 13 hydrocarbons have been calc. from Lebedev's data (A., 1913, i, 1285).

VI. The process of polymerisation of hydrocarbons of the allene series differs from that of the divinyl series in that in the latter case monomeride mols. combine with each other, and with the polymeride, whilst in the former both this process and that of combination between polymeride mols. take place. The velocity coeffs. of 6 hydrocarbons are calc. from Lebedev's data. R. TRUSZKOWSKI.

Propagation of combustion along surface of an inflammable liquid. III. T. KINBARA (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 104—119).—A flame travels along the surface of an inflammable liquid in a covered vessel at a steady rate provided that the temp. is below or considerably above the temp. at which the flame speed in an open vessel is a max.; at this temp. the flame speed is const. for some time after the flame has started, then the flame begins to oscillate, explosion ultimately resulting. Flame speeds in a closed vessel are, in general, much lower than in a similar open vessel at the same temp., the decrease being due mainly to the gas current produced by the combustion. In a covered vessel open at both ends the flame travels with gradually increasing speed as it progresses, the initial velocity in the case of C_6H_6 being greater or less than that in a similar vessel closed at one end according as the temp. is below or above 7° . The rate of travel of a flame over EtOH in an open vessel tends to increase as the depth of the vessel increases. R. CUTHILL.

Theory of explosive reactions. H. MURAOUR (Compt. rend., 1932, 194, 280—282).—The difference between the behaviour of explosives which give rise to

an explosive wave when ignited in free air (e.g., PbN_6) and that of explosives which merely burn rapidly is attributed to the occurrence of a chain reaction in the former case, spreading the decomp. in all directions, whilst in the latter ignition is carried forward by shock due to impact of the gaseous mols. produced. The velocity of propagation of the former action is independent of, of the latter proportional to, the pressure, although checks to the escape of the gases may raise the pressure sufficiently to produce an explosive wave. C. A. SILBERRAD.

Kinetics of oxidation of the nitrite ion with hydrogen peroxide. E. A. SHILOV, A. A. RIUBAKOV, and M. A. PAL (Bull. inst. polytech. Ivanovo-Vosnesensk, 15, 85—105).—The order of the reaction with respect to H_2O_2 depends on the relative concns. of H_2O_2 , NO_2 , and HNO_2 . The reactions are probably (a) $2HNO_2 + H_2O_2 = N_2O_4 + 2H_2O$; $N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$ (temp. coeff. 2.7); or (b) $N_2O_4 + H_2O_2 \rightarrow N_2O_4 \cdot H_2O_2$; $N_2O_4 \cdot H_2O_2 + 2HNO_2 = 2N_2O_4 + 2H_2O$ (temp. coeff. 10—20°, 2.6). Raschig's "supernitric acid," probably $N_2O_4 \cdot H_2O_2$, reacts with H_2O_2 thus: $N_2O_4 \cdot H_2O_2 + H_2O_2 = O_2 + 2H_2O + N_2O_4$.

CHEMICAL ABSTRACTS.

Kinetics of ionic reactions. IV. Neutral salt effect of the ferric-iodide reaction in concentrated salt solutions. A. KISS and I. BOSSÁNYI (Magyar Chem. Fol., 1931, 37, 121—133; Chem. Zentr., 1931, ii, 2410).—In conc. salt solutions only chlorides affect the mechanism of the reaction; from 1 mol. of salt upwards the simple laws of chemical kinetics hold, and the sp. ionic effect is very marked in conc. salt solutions. A. A. ELDRIDGE.

Kinetics of reactions involving collisions between solute and solvent molecules. E. A. MOELWYN-HUGHES (J.C.S., 1932, 95—107).—Einstein's treatment of the Brownian movement has been modified in order to give the rate of collision between solute and solvent mols. If it is assumed that every such collision which occurs with an energy in excess of the crit. increment leads to reaction it is possible to account satisfactorily for the rates of many unimol. reactions in solution. In other cases it is necessary to assume further that the energy of activation is distributed between several degrees of freedom. The no. of degrees of freedom required is not greater than 8, and may vary for a given reaction from solvent to solvent. F. J. WILKINS.

Kinetics of the esterification of acetic anhydride in ethyl-alcoholic solution. E. A. MOELWYN-HUGHES and A. C. ROLFE (J.C.S., 1932, 241—246).—The esterification of Ac_2O in EtOH solution is unimol. with a velocity coeff. given by $k - 4.4 \times 10^{-8} e^{-18,800/RT}$. The observed rate lies between those calc. on the assumptions that reaction occurs when Ac_2O mols. collide with EtOH mols. with an energy of activation of 21,100 g.-cal., or with OEt' with an energy of activation of 13,200 g.-cal. F. J. WILKINS.

Hydrolysis of polysaccharides. I. Influence of neutral salts on the acid inversion of sucrose. S. KOMATSU and G. NOMURA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 267—272).—Rates of inversion of sucrose by $N-H_2SO_4$ have been measured in presence of sulphates of K, Cu, Al, Fe^{II} , and Fe^{III} . Fe^{III} acceler-

ates and Fe^{II} retards the inversion, whilst the other salts have no influence. Neither a change in the degree of ionisation of the acid nor the presence of $(\text{H}_2\text{O})_1$ in the solvent is considered adequate to explain the results.

F. L. USHER.

Studies of stereokinetics. II. Heat of activation and action constant of some benzene derivatives. G. SEMERANO (*Gazzetta*, 1931, 61, 921—943; cf. A., 1931, 1241).—Measurements have been made of the rates of hydrolysis of NHPhAc and of its derivatives methylated in the Ph nucleus in order to study steric hindrance effects in this series. The experimental results satisfy only very approx. the formula $k = \alpha e^{-q/RT}$, where q is the activation energy and α the action const., and are in better agreement with the formulæ derived by Hückel (A., 1928, 987). The greater stability found in the Me derivatives is probably due to an increase in the activation energy after introducing the Me group. With rise in temp., however, this effect decreases and the steric effect becomes more pronounced.

O. J. WALKER.

Reactions between gas and solid. II. T. Aono (*Bull. Chem. Soc. Japan*, 1931, 6, 319—324; cf. this vol., 128).—Dry CO_2 does not react appreciably with dry CaO . The absorption of CO_2 from a moist air- CO_2 mixture by $\text{Ca}(\text{OH})_2$ follows fairly closely the equation $W_t = 30(1 - e^{-0.0135t})$, where W_t is the % increase of wt. in time t , and C is the concn. of CO_2 in the gas phase. When dry CO_2 is absorbed by $\text{Ca}(\text{OH})_2$, the H_2O first set free is held by the $\text{Ca}(\text{OH})_2$ for a time and then evolved. The curve showing the increase of wt. with time has a max., because it represents the net result of the velocity of absorption of CO_2 , which follows an equation of the above type, and the velocity of evolution of H_2O which follows the equation $-dm_t/dt = km_t - 24.3\beta e^{-\beta t}$, where m_t is the amount of H_2O held by the solid at the time t , and k and β are consts.

N. H. HARTSHORNE.

Aqua regia and base metals. Rate of corrosion of iron and nickel by aqua regia as a function of composition and time of mixture. C. F. BONILLA (*Ind. Eng. Chem. [Anal.]*, 1932, 4, 128—130).—Aqua regia (4 : 1) does not dissolve base metals so readily as other HCl-HNO_3 mixtures. Ni is attacked most rapidly by a 3 : 40 mixture, and low-C steel by 7 : 20 mixture.

E. S. HEDGES.

Effect of addition of various reagents on the dissolution of copper in sulphuric acid. V. ZEMLANITZIN and N. BODREVA (*J. Chem. Ind. Russ.*, 1931, 8, No. 18, 34—36).—The accelerative effect of the addition of various substances on the velocity of dissolution of Cu or Pb in H_2SO_4 is in the order: $\text{HNO}_3 > \text{K}_2\text{Cr}_2\text{O}_7 > \text{HCl} > \text{MnO}_2 > \text{CuSO}_4 > \text{PbO}_2$. The CuSO_4 cryst. in the presence of $\text{K}_2\text{Cr}_2\text{O}_7$ is contaminated by Cr alum.

R. TRUSZKOWSKI.

Kinetics of dissolution of readily soluble substances. K. JABECZYNSKI, J. GUTMAN, and A. WALCZUK (*Z. anorg. Chem.*, 1931, 202, 403—417).—Rates of dissolution of a no. of sol. cryst. inorg. and org. substances in H_2O and EtOH , respectively, have been measured spectrophotometrically. The same laws are followed as in the case of substances with slight solubility.

F. L. USHER.

Mode of reaction of cellulose, an instance of a system with a highly developed internal surface. K. HESS and C. TROGUS (*Z. physikal. Chem.*, 1931, B, 15, 157—222).—The course of the reaction of cellulose fibres with a variety of liquid reagents has been followed by velocity measurements and X-ray examination of the solid phase. The results show that the theory of a permutoid mode of reaction is untenable. In all the reactions investigated three phases can be distinguished: first the cellulose X-ray diagram alone is visible, then the interferences of the product of reaction appear, and finally the cellulose interferences disappear and only those of the product of reaction remain. Since the reaction may have made considerable progress before the second phase is reached, it seems that the first phase represents a surface reaction occurring on the crystallite surfaces. Swelling of the fibre promotes reaction at this stage, for by enlarging the intermicellar spaces it renders the micelles more readily accessible. In the second and last phases the reaction progresses from the surface of the micelles to their interior, and the rate of this topochemical heterogeneous reaction depends on the velocity of diffusion of the liquid reactants through the surface layer which has already reacted to the unattacked cellulose nucleus, the seat of reaction being the boundary surface between these two portions of the micelle. At this stage the rate of reaction is influenced by substances which render the layer of resultant permeable to the reactant mols., e.g., by forming a double compound with larger lattice consts. The actual rate of the surface reaction is great compared with rate of diffusion.

R. CUTHILL.

Catalytic action of hydrogen on the carbon monoxide flame. C. E. H. BAWN and W. E. GARNER (*J.C.S.*, 1932, 129—138).—The nature of the wall has no effect on the intercept made by the pressure-radiation curve at the pressure axis. The pressure at which the step in this curve occurs is, however, modified, probably because of the different rates at which H_2 is removed from the gas phase by different surfaces. CO_2 and SO_2 cause the step to appear at higher pressure due to the removal of H_2 from the flames by these gases.

F. J. WILKINS.

Dynamics and catalysis of thermal decomposition of hydrogen carbonates in aqueous solution. I. Decomposition of pure calcium or magnesium hydrogen carbonate solutions at boiling temperature. II. Decomposition of hydrogen carbonate in solutions of mixed calcium and magnesium hydrogen carbonate. III. Influence of rate of evaporation and of free carbonic acid on the rate of decomposition of hydrogen carbonates. R. STUMPER (*Z. anorg. Chem.*, 1931, 202, 227—260, 261—269, 270—276).—I. In boiling solutions of $\text{Ca}(\text{HCO}_3)_2$ the decomp. is bimol., and is probably determined by the reaction $2\text{HCO}_3' \rightarrow \text{CO}_3'' + \text{H}_2\text{CO}_3$. $\text{Mg}(\text{HCO}_3)_2$ behaves similarly, but the rate of decomp. is smaller than with $\text{Ca}(\text{HCO}_3)_2$ owing to hydrolysis of the more sol. MgCO_3 . At concns. 0.0025—0.020N the order of the reaction is between 1 and 2.

II. From solutions containing both $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$, CaCO_3 is pptd. first. The rate of decomp.

decreases regularly as the proportion of Mg in the mixture is increased. When Mg : Ca is <0.4 the order of the reaction is 2, but becomes smaller and indefinite with larger proportions of Mg.

III. The coeff. of the velocity of decomp. of $\text{Ca}(\text{HCO}_3)_2$ in boiling solutions is proportional to the rate of evaporation. The decomp. of both $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ is retarded by free H_2CO_3 .

F. L. USHER.

Dark reaction between mercuric chloride and ammonium oxalate catalysed by ammonium persulphate. Proof of formation of an intermediate compound of mercuric chloride and the oxalate ion. I. C. GHOSH and B. C. CHAKRAVARTY (*Z. physikal. Chem.*, 1932, 158, 265—272).—For a given $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concn. the quotient of the reaction velocity by the concn. of the intermediate compound $\text{HgCl}_2(\text{CO}_2)_2$ is a const. at 50° and at 60° . The val. for the dissociation const. of the compound deduced from extinction coeff. measurements with solutions of $\text{H}_2\text{C}_2\text{O}_4$ and HgCl_2 agrees quantitatively with the velocity data.

R. CUTHILL.

Reaction of formaldehyde on potassium ferrocyanide in aqueous solution. IV. T. KIRIGAKUBO (*J. Soc. Chem. Ind. Japan*, 1931, 34, 479—481B; cf. A., 1930, 454).—The evolution of H_2 by the action of $\text{K}_4\text{Fe}(\text{CN})_6$ on aq. CH_2O decreases with increased dilution, is promoted somewhat by $\text{H}_4\text{Fe}(\text{CN})_6$, is decreased by KCN, and is increased only to a limited extent by increasing the concn. of KOH between 0.004 and 0.1N. The alkalinity increases and then decreases with increasing dilution. The yield of $\text{K}_2\text{Fe}_2(\text{CN})_6$ agrees with the alkalinity produced. $\text{K}_4\text{Fe}(\text{CN})_6$ evolves H_2 from CH_2O in conc. alkali solution at room temp., probably owing to the formation of $\text{Fe}(\text{OH})_3$ by the action of alkali on the $\text{K}_2\text{Fe}_2(\text{CN})_6$.

D. K. MOORE.

Ozonisation of benzaldehyde and the role of ozone as an oxidation catalyst. II. E. BRINER, A. DEMOLIS, and H. PAILLARD (*Helv. Chim. Acta*, 1932, 15, 201—213).—When $\text{O}_2 + \text{O}_3$ is passed through a solution of PhCHO (in hexane, CCl_4 , or CHCl_3) the amount of BzOH formed is greatly in excess of the O_3 consumed. When the concn. of O_3 is low the amount consumed is negligible. The effects of concn., temp., and solvent on this catalytic reaction have been examined. A higher concn. of O_3 causes some BzO_2H to be formed. The energy of reaction of a very small quantity of O_3 is believed to initiate reaction chains which would not be produced if O_2 were present alone.

E. S. HEDGES.

Mixed catalysts in the Friedel-Crafts reaction. Yields in typical reactions using ferric chloride-aluminium chloride mixtures as catalysts. W. A. RIDDELL and C. R. NOLLER (*J. Amer. Chem. Soc.*, 1932, 54, 290—294; cf. A., 1931, 91).—In all cases studied the yield with AlCl_3 alone is directly proportional to the amount of catalyst up to the optimum quantities (1 mol. for acid chlorides and 2 mols. for acid anhydrides). The yield falls rapidly when more than these optimum amounts are used. The reaction of C_6H_6 with CCl_4 (with excess of one reagent) also requires 1 mol. of catalyst even although no O compounds are involved. With mixtures of AlCl_3 and

FeCl_3 and an excess of C_6H_6 as solvent, two types of reactions are found : those in which the yield decreases proportionally to the amount of FeCl_3 added (all carbonylic chlorides with C_6H_6 and of C_6H_6 with excess of CCl_4), and those in which the yield first decreases, then rises to a max. at about 50 mol.-% FeCl_3 , and then decreases to the yield obtained with pure FeCl_3 (all acid anhydrides, $p\text{-MeC}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$, and CCl_4 with excess of C_6H_6). All reactions appear to be of the first type when carried out in CS_2 . The results are given in a series of curves.

C. J. WEST (b).

Catalysts for the production of hydrogen by means of the water-gas reaction. III. X-Ray examination of iron-chromium catalysts. IV. Activity of catalysts prepared by evaporation and by fusion. R. YOSHIMURA (*J. Soc. Chem. Ind. Japan*, 1931, 34, 484—488B).—X-Ray diffraction photographs of catalysts consisting of Fe_2O_3 , Cr_2O_3 , and mixtures, after use, show that the Cr_2O_3 is present, as before use, in the form of solid solution. Fe_2O_3 is reduced by use to Fe_3O_4 , the crystals of which are prevented from growing by barriers of solid solution. The activity of catalysts prepared by fusion of Fe_2O_3 with or without Cr_2O_3 between C electrodes in a graphite crucible is inferior to that of those prepared by evaporation of nitrates or by pptn., the last two being equal. This is probably due to surface conditions affected by the temp. of treatment.

C. IRWIN.

Fixation of vanadium by preparation of complex vanadio-zeolite catalysts, and their properties. I. E. ADADUROV and others.—See B., 1932, 145.

Complex catalysts for synthesis of methyl alcohol. V. A. PLOTNIKOV and others.—See B., 1932, 137.

Catalytic activity of platinum metals in the decomposition of methyl alcohol. G. F. HUTTIG and E. WEISSBERGER (*Siebert Festschr.*, 1931, 173—178).—The catalytic activity of metals of the Pt group deposited on asbestos on the reaction $\text{MeOH} = 2\text{H}_2 + \text{CO}$ is generally very erratic in the early stages of use, but finally reaches a const. val. which decreases in the order Pd, Os, Rh, Ru, Ir, Pt. In the first few hr. the activity of Os rises to more than 15 times its final const. val., then falls rapidly, whereas the vals. for Pd, Pt, and Rh undergo relatively little variation. The ultimate vals. are in all cases much higher than that of a ZnO catalyst.

A. R. POWELL.

Catalytic oxidation of toluene. G. CHARLOT (*Compt. rend.*, 1932, 194, 374—376).—Data are given showing the extent of the partial and complete oxidation of PhMe by air at various temp. in presence of Fe_2O_3 . The catalytic effect of a series of oxides has been studied. In each case, the extent of the partial oxidation passes through a max., but becomes almost zero at 550° .

J. L. D'SILVA.

Formation of acetone by catalytic decomposition of acetic acid. G. MALQUORI (*Mem. R. Accad. d'Italia*, 1931, 2, [Chim., 2], 15 pp.).—The rate of formation of COMe_2 from AcOH by contact with MgO , MgCO_3 , CaCO_3 , SrCO_3 , and BaCO_3 at temp. between 370° and 530° has been studied. The

apparent heat of activation increases with increase of the radius of the cation, *i.e.*, in the order Mg, Ca, Sr, Ba. The temp. coeff. of the reaction velocity is almost independent of the method of prep. and the available surface of the catalyst. At low temp. MgO and basic Mg carbonates are the most active of the catalysts studied.

H. F. GILLBE.

Alkylation of amines as catalysed by nickel. C. F. WINANS and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 306—312).—The formation of *sec.* from primary amines during the hydrogenation (Ni catalyst) of nitriles, oximes, etc. may result thus: (1) reaction of amines with alcohols with elimination of H₂O; (2) elimination of NH₃ from 2 mols. of an amine; (3) reaction of alkylideneimines with themselves or with amines. Reactions of types 1 and 2 are induced by the Ni catalyst at temp. above 160—170°, and account wholly or partly for the *sec.*-amines formed. Reactions of type 3 do not require a catalyst and occur spontaneously at room temp.; they account for the formation of *sec.*-amines in the hydrogenation of nitriles and oximes and probably of other N compounds, which can be reduced below approx. 175°. The use of more active Ni catalysts minimises the above types of reactions. The following preps. have been effected in yields of 14—93% using a Ni catalyst usually in H₂ at 200°/100 atm.: *N*-ethylcyclohexylamine from cyclohexylamine and EtOH; *N*-ethylpiperidine from piperidine and EtOH; *N*-ethyl-2-methylpiperidine from 2-methylpiperidine and EtOH; *N*-butyl-β-phenylethylamine from BuOH (or PrCHO) and β-phenylethylamine; *N*-butyl-2-methylpiperidine from BuOH and 2-methylpiperidine; *N*-cyclohexylpiperidine from cyclohexanol and piperidine; *N*-butylpiperidine from PrCHO and piperidine; dicyclohexylamine from cyclohexylamine and cyclohexanone; *N*-butylcyclohexylamine from PrCHO and cyclohexylamine; diamylamine and dicyclohexylamines from the corresponding primary amines; amyl- and diamyl- amines from BuCN; NH₂·CH₂Ph and NH(CH₂Ph)₂ from hydrobenzamide; *p*-NMMe₂·C₆H₄·NH₂ from methyl-orange; NH₂·CH₂Ph from CHPh·NOH and NH₂·[CH₂]₃·Ph from cinnamald-oxime.

C. J. WEST (b).

Catalytic decomposition of kerosene. E. W. KANNING and O. W. BROWN.—See B., 1932, 135.

Enzymes and organic catalysis. W. LANGENBECK (Angew. Chem., 1932, 45, 97—99).—The similarity of enzymes to certain complex org. catalysts is indicated. Thus these catalysts include those which form the same reaction products from α-keto-acids when carboxylase is employed. The kinetics, side reactions, and structural specificity of many reactions of the two types are also parallel. F. O. HOWTIT.

Electrodeposition of chromium from trivalent chromium salt solutions. I. Chromium chloride and sulphate baths. H. T. S. BRITTON and O. B. WESTCOTT.—See B., 1932, 150.

Electrolysis of chromium oxalates. A. MAZZUCHELLI [with U. VIVALDI, U. BACCI, and E. ROSSI] (Mem. R. Accad. d'Italia, 1931, 2, [Chim., 1], 15 pp.).—Electrolysis of solutions of Cr₂(C₂O₄)₃ or of K Cr oxalate does not yield a satisfactory deposit, but with

18—20% solutions of Cr(NH₄C₂O₄)₃·3H₂O a bright adherent deposit is produced at room temp.; at temp. above 50° no metallic deposit is formed. The influence of the c.d. has been studied; the yield rises from about 1% at 25 amp. per sq. dm. to about 1.5% at 42 amp. per sq. dm., which is the highest c.d. at which a coherent deposit is obtained, and to 4.4% at 150 amp. per sq. dm. Slightly improved yields are obtained by adding Cr₂(C₂O₄)₃ to the bath. The electrolytic reduction of solutions of Cr₂(C₂O₄)₃ and K Cr and NH₄ Cr oxalates has been examined polarographically. Whereas the curve given by the first-named exhibits one inflexion at about -0.85 volt and an ill-defined inflexion at -1.4 volt, those of the two double salts exhibit only the second inflexion, which corresponds with deposition of the metal. The break at -0.85 volt is attributed to partial reduction of Cr₂(C₂O₄)₃ to CrC₂O₄.

H. F. GILLBE.

Molybdenum bronzes. W. G. BURGERS and J. A. M. VAN LIEMPT (Z. anorg. Chem., 1931, 202, 325—328; cf. A., 1930, 558).—Electrolytic reduction of fused acid Na molybdates of varying composition with Mo electrodes gives rise to either MoO₂ or "molybdenum blue," but not to products resembling the W bronzes.

F. L. USHER.

Electrolytic deposition of polonium from an alkaline medium. M. HAÏSSINSKY (Compt. rend., 1932, 194, 275—277).—Using pure Au electrodes, previously cathodically polarised, and aq. NaOH of varying concn. containing 2—4 × 10⁻⁹ g.-atom Po per litre, the Po is deposited on both electrodes—with *N*-NaOH at about equal velocity; the velocity diminishes for the anode for variation of concn. in either direction, but for the cathode remains nearly const. The crit. potential of the anion varied little with alkalinity, averaging +0.53 (relative to the HgCl electrode); that of the cation fell from -0.21 for 0.28*N*. to -0.45 for 4*N*-NaOH. Po in NaOH of >0.2*N* is mainly in ionic solution. Little Po is separable by centrifuging its solution in aq. NaOH of concn. >*N*.

C. A. SILBERRAD.

Electrochemistry of rhenium. I Reduction products formed in the electrolysis of aqueous solutions of potassium perrhenate. H. HOLMANN (Z. anorg. Chem., 1931, 202, 277—291).—In neutral and slightly acid (H₂SO₄) solutions of KReO₄ metallic Re and ReO₂·2H₂O are deposited at Pt or Hg cathodes. With the latter Re amalgam is formed. In strongly acid solution violet and green intermediate reduction products are formed.

F. L. USHER.

Linear crystallisation velocity *KG* of cathode silver in the electrolysis of silver nitrate. A. GLAZUNOV, C. O. RADA, and C. L. BALCAR (Chem. Listy, 1932, 26, 12—15).—The val. of *KG* varies directly with the density of current, and inversely with the concn. of AgNO₃ and with the viscosity of the medium.

R. TRUSZKOWSKI.

Platinum in electrochemistry. K. ARNDT (Siebert Festschr., 1931, 1—11).—When Pt electrodes are used at high c.d. slow loss of Pt may occur; thus in 50% H₂SO₄ with a c.d. of 0.8 amp. per sq. cm. the anode develops pits and becomes covered with reddish-yellow or brown spots of hydrated PtO₃, whilst the

cathode suffers loss by disintegration of the surface caused by the violent evolution of H_2 . Similar effects may occur in the prep. of perborates and cause a serious reduction in the efficiency of the electrolysis as minute particles of Pt in the solution produce a catalytic decomp. of the perborate. A. R. POWELL.

Cathodic disintegration of metallic alloys. II. L. BELLADEN (*Gazzetta*, 1931, 61, 952—958; cf. A., 1930, 172).—The relationships between the composition of the alloy, ease of disintegration, and composition of the disintegrated metal have been determined for Ni-Cu, Cd-Sb, and Sb-Cu alloys.

O. J. WALKER.

Anodic oxidation of cobaltous and nickelous chlorides. C. SCHALL (*Z. Elektrochem.*, 1932, 38, 27—31; cf. A., 1929, 892).—Anodic oxidation of a solution of $CoCl_2$ in alcoholic HCl containing $CaCl_2$ gives, at -70° , a green solution of (probably) $CoCl_3$. Addition of $CsCl$ to the green liquid leads to pptn. of a green solid which, after washing and drying at room temp., consists of a mixture of known double chlorides of Cs and Co^{II} . Both the original solution and the $CsCl$ ppt. become yellow at -80° . $HClO_3$ in cold conc. aq. HCl gives similar results. Additive products of the oxidised substance with C_5H_5N have also been obtained. Analogous behaviour of $NiCl_2$ is not established with certainty.

F. L. USHER.

Passivity of anodes in nickel baths. O. GRUBE.—*See B.*, 1932, 113.

Electrodeposition of iron, copper, and nickel alloys from cyanide solution. II. L. E. STOUT and C. L. FAUST.—*See B.*, 1932, 109.

Electrolytic reduction of ketones. C. SCHALL (*Z. Elektrochem.*, 1932, 38, 31—32). A misinterpretation by Shima (A., 1930, 1291) of conclusions reached by Schall and Kirst (A., 1924, i, 63) is corrected.

F. L. USHER.

Electrolytic reduction of nitrobenzene to p-aminophenol. F. M. BRIGHAM and H. S. LUKENS.—*See B.*, 1932, 112.

Ignition voltage of helium for small values of pd . F. M. PENNING (*Naturwiss.*, 1931, 19, 1042).—The curve connecting the ignition voltage with the product of the pressure of the gas and the distance between the electrodes is given and discussed.

W. R. ANGUS.

Negative photo-effects in gas discharges. F. M. PENNING (*Physica*, 1931, 11, 183—196; *Chem. Zentr.*, 1931, ii, 1680).

Band spectroscopy and photochemistry. R. MECKE (*Physikal. Z.*, 1932, 33, 1—14).—A résumé of the applications of the results of band spectroscopy to photochemistry, including reactions of activated mols., of mols. dissociated by optical excitation, and of "predissociated" mols.

A. B. D. CASSIE.

Detection of hydrogen atoms in reaction of hydrogen with chlorine. K. H. GEIB and P. HARTECK (*Z. physikal. Chem.*, 1931, B, 15, 116—120).—The H atom concn. in the photochemical union of H_2 and Cl_2 has been determined by following the reaction $H_{para} + H = H_{normal} + H$ by thermal conductivity measurements (cf. A., 1931, 1252).

R. CUTHILL.

Spectrum and photochemical decomposition of chlorine monoxide. W. FINKELNBURG, H. J. SCHUMACHER, and G. STIEGER (*Z. physikal. Chem.*, 1931, B, 15, 127—156).—The absorption spectrum over the range 2200—8500 Å. and under pressures of 10—600 mm. is continuous. Absorption begins at 6600 Å., corresponding with the dissociation $Cl_2O = ClO + Cl$, the Cl probably being excited. Max. on the absorption coeff. curve at 5300 and 4100 Å. represent dissociation into the same products, but at other stages of excitation, whilst a max. at 2560 Å. is due to the dissociation $Cl_2O = Cl + Cl + O$. For light of wave-lengths 436, 365, and 313 mμ, the rate of photochemical decomp. is proportional to the amount of light absorbed and therefore independent of whether Cl, or Cl_2O is the absorbent, and is independent of the Cl_2 pressure and also of the Cl_2O pressure until it falls below a certain limit. The quantum yield is about 3.5, varying by only about 10% between the extreme wave-lengths, and the temp. coeff. is about 1.1 at room temp., but increases as the temp. rises. Reaction is initiated by the dissociation into ClO and Cl, and the reaction chain $Cl + Cl_2O = Cl_2 + ClO$, $ClO + Cl_2O = Cl_2 + O_2 + Cl$ is set up. Among the intermediate products of reaction are ClO_2 and a higher Cl oxide of unknown formula. The smaller quantum yield in the decomp. in CCl_4 solution (A., 1931, 48) is explained by supposing that the reactions $Cl + Cl = Cl_2$ and $Cl + ClO = Cl_2O$ occur so much more frequently in the solution than in the gaseous state that they compete with the reaction $Cl + Cl_2O = Cl_2 + ClO$.

R. CUTHILL.

Gasometric and polarimetric investigations on the photolysis of fructose and glucose. A. L. BERNOULLI and R. CANTIENI (*Helv. Chim. Acta*, 1932, 15, 119—139).—Analysis of the gases evolved during the photolysis of fructose solutions by the radiation of a quartz-Hg vapour lamp shows that CO_2 , H_2 , and CO are formed. The amount of CO_2 produced decreases as the light intensity is increased and varies with the concn.; it is least at concns. between 10 and 25%. At room temp. the solution remains neutral, but acids are produced at higher temp. (about 80°). CO is not formed directly from fructose, but through an intermediate compound. Addition of NaCl accelerates the rate of evolution of gases, but addition of acids or bases has the reverse effect. The same gases are produced in the photolysis of glucose solutions, but at first more H_2 is formed than CO, whilst at a later stage the CO exceeds the H_2 . The CO is again a secondary product. H_2SO_4 and HCl accelerate the rate of evolution of gases from glucose solutions, whilst alkalis inhibit it.

E. S. HEDGES.

Photosynthesis of carbohydrates *in vitro*. J. BELL (*Nature*, 1932, 129, 170).—Repeated examination revealed no adsorption of org. matter by the catalysts used in attempted photosyntheses of carbohydrates (this vol., 29).

L. S. THEOBALD.

Photosynthesis of carbohydrates in ultra-violet light from activated carbon dioxide solutions. G. MEZZADROLI and E. VARETON (*Atti R. Accad. Lincei*, 1931, [vi], 14, 347—352).—The formation of CH_2O , glycinaldehyde, and reducing

sugars on exposure of CO_2 solutions to ultra-violet light is enhanced by the presence of finely-divided or colloidal CaCO_3 or MgCO_3 and especially by activating the CO_2 solution by means of the electric discharge or radium emanation. T. H. POPE.

Photographic action of slow cathode rays. V. WEIDNER (Ann. Physik, 1932, [v], 12, 239—264).—The photographic action of slow cathode rays of velocities 0—1100 volts on different AgBr emulsions was studied. The reciprocal law is in general obeyed, although in a few cases there are deviations. The blackening curves of plates poor in gelatin have linear increase in blackening with no. of electrons. For ordinary gelatin plates there is a delayed increase in the blackening with amount of charge. The sensitiveness of the gelatin-poor plate increases linearly with the radiation energy above 60 volts. The lowest velocity for which photographic action has been found is 22 volts, for all emulsions. The abs. vals. of sensitivity are given. A. J. MEE.

Exothermic reactions at high temperatures. D. BINNIE and T. S. WHEELER.—See B., 1932, 100.

Lithium cyanamide. A. PERRET and R. PERROT (Compt. rend., 1932, 194, 95—96).—Pure C_2N_2 and Li above 175° give LiCN and $(\text{CN})_n$; above 350° the LiCN is partly decomposed to Li_2CN_2 and C. Li in excess of HCN up to 570° , or Li_2O to 650° give LiCN (with decomp. products of HCN). If Li is in excess much Li_2CN_2 is formed, as also occurs if the product from Li_2O and HCN is heated in vac. at 650° . If a mixture of 70% Li_2O and 30% LiCN is heated above 300° the LiCN is gradually transformed to Li_2CN_2 . $\text{Li}_4\text{Fe}(\text{CN})_6$ heated not above 500° behaves as $\text{K}_4\text{Fe}(\text{CN})_6$; above that temp. Li_2CN_2 is formed in increasing proportion (cf. B., 1911, 956).

C. A. SILBERRAD.

Decomposition of sodium hydrogen carbonate in aqueous solution. A. V. FILOSOFOV (J. Gen. Chem. Russ., 1931, 1, 743—746).—In the reaction $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3$, in boiling aq. solution the val. of the ratio of decomposed NaHCO_3 to residual NaHCO_3 falls with increasing concn. This effect is due to H^+ and OH^- present. R. TRUSZKOWSKI.

Dehydration of cupric oxide. G. CHAMPETIER and U. V. THUAV (Compt. rend., 1932, 194, 93—94).—X-Ray examination shows that there is no intermediate compound, e.g., $4\text{CuO} \cdot \text{H}_2\text{O}$, between the blue hydroxide, $\text{Cu}(\text{OH})_2$ (cf. A., 1931, 444), and anhyd. CuO , the structure of which does not differ in spite of the difference in colours of products prepared in different ways. The basic nitrate, chloride, and sulphate prepared by Sabatier (cf. A., 1897, ii, 491) appear to exist, each giving a characteristic X-ray diagram. C. A. SILBERRAD.

Simple reactions which proceed at high temperature; chemical composition of the atmospheres of stellar bodies. G. PICCARDI (Mem. R. Accad. d'Italia, 1931, 2, [Chim., 7], 54 pp.).—The thermochemistry of the reaction between Mg and H_2O is discussed at length. The spectrum of the Mg arc when produced in a H_2O -vapour atm. is accompanied by those of MgH , MgO , OH , and by the H_α line. The MgO bands are fainter than those of

MgH , and the Mg lines diminish in intensity as the H_2O -vapour concn. increases. The results show that the homogeneous reaction between Mg and H_2O passes through a series of equilibria and results in the simultaneous formation of MgO and MgH . Similar reactions occur in the case of Al, Zn, and Cd, hydrides of the type MH being formed. The occurrence in sunspots of oxides and hydrides and of H_2 is discussed, together with chemical considerations relating to the composition of stellar atms. H. F. GILLBE.

Preparation of crystalline calcium hydroxide. C. NOGAREDA (Anal. Fis. Quim., 1931, 29, 556—559).—By adding 30—20 c.c. of 15—20% KOH solution to 1 litre of saturated $\text{Ca}(\text{OH})_2$ solution the solubility product of the latter is exceeded and macrocryst. $\text{Ca}(\text{OH})_2$ is pptd. The two cryst. forms appear to be capable of co-existence, the formation of the one or the other being dependent solely on the rate of crystallisation. H. F. GILLBE.

Formation of calcium nitride from its elements. I. A. VON ANTROPOFF. II. H. H. FRANCK and C. BODEA (Angew. Chem., 1932, 45, 49—50, 51—52).—I. Arguments in favour of views previously expressed, and attacked by Franck and Bodca (A., 1931, 807).

II. A reply.

H. F. GILLBE.

Study of carbides by methane synthetic method. R. SCHENCK, F. KURZEN, and H. WESSELSKOCK (Z. anorg. Chem., 1931, 203, 159—187).—The synthesis of carbides from the metals and CH_4 has been studied. The results for the Fe-C system agree with those obtained by thermal analysis. CH_4 reacts with Cr at 600 — 800° , forming Cr_5C_2 and a C-rich mixed-crystal phase containing 11.5% C in equilibrium with the Cr_5C_2 phase. The C content of the mixed-crystal phase can be increased to 12.5% by further treatment with CH_4 ; this phase probably contains Cr_7C_3 . W and CH_4 react at 800° , forming WC, whilst at 700° W_5C_2 is formed together with a C-rich mixed-crystal phase of uncertain composition. Mo gives the stable Mo_2C at 800° and the metastable MoC at 700° . Re reacts with CH_4 initially, but the film of carbide protects the remaining metal. The composition of the film is unknown. E. S. HEDGES.

Oxides of gallium. A. BRUKL and G. ORTNER (Z. anorg. Chem., 1931, 203, 23—25).— Ga_2O is formed as a dark brown sublimate by heating an intimate mixture of Ga_2O_3 and Ga in a stream of H_2 at 500 — 700° . It is stable in dry air at room temp., but reduced cold dil. H_2SO_4 to H_2S . Attempts to prepare GaO resulted in the formation of a mixture of Ga_2O_3 and Ga, having a composition approximating to GaO. E. S. HEDGES.

Non-metallic films persisting after the dissolution of tin. A. KUTZELNIGG (Z. anorg. Chem., 1931, 202, 418—420).—Yellowish-white films, amounting to about 0.02 wt.-% of the metal taken, remain when the purest commercial Sn foil is dissolved in 10% FeCl_3 . The films are sol. in aq. HCl and insol. in HNO_3 , and give reactions for Sn^{IV} .

F. L. USHER.

Displacement of metals by hydrogen under pressure. II. Separation of group V metals

from solutions of their chlorides by hydrogen under pressure. V. V. IPATIEV, jun., and V. P. TEODOROVITSCH (J. Gen. Chem. Russ., 1931, 1, 729—735).—As is quantitatively pptd. from solutions containing AsCl_3 and SbCl_3 or BiCl_3 by H_2 under 100 atm. at 225° , whilst Sb cannot be separated from Bi by this method. R. TRUSZKOWSKI.

Action of potassium cyanate on arsenic, antimony, and tin. J. DALIETOS (Praktika, 1931, 6, 92—96; Chem. Zentr., 1931, ii, 1687).— NH_3 arising from the reaction $\text{KCNO} + 2\text{H}_2\text{O} = \text{KHCO}_3 + \text{NH}_3$ ppts. $\text{Sn}(\text{OH})_2$, which is determined by means of I. SbCl_3 gives a cryst. ppt.; As^{III} gave no ppt. In presence of $\text{C}_5\text{H}_5\text{N}$, SnCl_2 gave $[\text{Sn}(\text{C}_5\text{H}_5\text{N})_6](\text{CNO})_2$, or in presence of hexamethylenetetramine (X) in EtOH $[\text{SnXEtOH}](\text{CNO})_2$. In both cases Sb affords $\text{Sb}(\text{OH})_3$. Excess of KCNO with SnCl_2 gradually forms the grey metal. A. A. ELDRIDGE.

Preparation of sulphuric acid free from nitric acid. W. R. G. ATKINS (Nature, 1932, 129, 98).—Traces of HNO_3 can be removed from H_2SO_4 by the cautious addition of $(\text{NH}_4)_2\text{S}$ or, preferably, H_2S . The amount of S formed is invisible. L. S. THEOBALD.

Hydrated chromic chlorides. [Preparation of triaquotrichlorochromium.] A. RECOURA (Compt. rend., 1932, 194, 229—232).— $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ is prepared in two ways: (a) green tetra-aquodichlorochromic chloride is dried in vac. for 2—3 days, losing $2\text{H}_2\text{O}$, and then treated with Et_2O for a few days, when triaquotrichlorochromium dissolves out forming a brown solution: $3[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} = 2[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] + [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$. Prolonged drying of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ in vac. slowly converts it all into $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$, e.g., 51% in 1 year. (b) Dissolution of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ in COMe_2 has the same effect as Et_2O on the dehydrated compound, but the brown $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ must be pptd. by excess of Et_2O . H_2O decomposes it. C. A. SILBERRAD.

Combination of iodine in molecular aggregates. K. A. HOFMANN (Sitzungsber. preuss. Akad. Wiss., 1931, 25, 7 pp.).—After prolonged treatment with warm 2% $(\text{NH}_4)_2\text{CO}_3$ solution both Tussah and mulberry silk adsorb I and this is much less readily removed than from cellulose fibre. When adsorbed from EtOH solution about half the I does not react with $\text{Na}_2\text{S}_2\text{O}_3$. It is concluded that this is due to definite chemical combination. Solid $\text{Mg}(\text{OH})_2$ absorbs I vapour up to a composition of about $5\text{Mg}(\text{OH})_2 \cdot \text{I}$. This is not extractable with CHCl_3 or CCl_4 and can be titrated only after acidification. The structure of starch iodide is also discussed.

J. W. SMITH.

Affinity. LVI. Affinity of rhenium to sulphur. II. Rhenium heptasulphide. W. BILTZ and F. WEIBKE (Z. anorg. Chem., 1931, 203, 3—8).—The substance pptd. by acting on KReO_4 with H_2S has a const. composition, corresponding with Re_2S_7 . When heated, the substance decomposes to ReS_2 and S. Re_2S_7 has $d_{25}^{25} 4.866 + 0.006$. The relation to corresponding compounds of Mn and Os is discussed.

E. S. HEDGES.

Mechanism of oxidative processes and autoxidation of bivalent iron. W. MANCHOT and H.

SCHMID (Ber., 1932, 65, [B], 98—109).—Determinations of the absorption of O_2 by Fe^{II} with As_2O_3 in Na_2CO_3 solution as acceptor show the consumption to increase first rapidly, then more slowly with increase of As, finally approaching asymptotically a limit of 2 equiv. The ratio $\text{Fe}:\text{As}$ is ultimately raised to 1:600. $\text{Fe}(\text{OH})_2$ therefore consumes 2 equiv. or activates 1 equiv. of O_2 . Experiments in aq. Na_2CO_3 are more trustworthy than in aq. KOH , since the As is not then autoxidised. In presence of KOH with $\text{AsO}_3^{\text{III}}$ as acceptor the authors fail to confirm the observation of Wieland and Franke (A., 1928, 965) that the O_2 consumption can rise above 2 equiv., although they have extended the ratio $\text{Fe}:\text{As}$ to 1:200, or that of Gire (A., 1920, ii, 544) that the maximal O_2 absorption occurs at $\text{As}:\text{Na}=1:2$. With NaH_2PO_2 in acid solution as acceptor about 12 equiv. of O_2 are absorbed. A chain reaction is here assumed to occur, which throws little light on primary processes. The occurrence of O_3 indicates the conversion of hypophosphite into a lower oxide of P which is very rapidly oxidised. By the use of anthraquinone as H acceptor the experiments with arsenite acceptor have been conducted along the path of indirect autoxidation and dissected into completely known changes; the same total consumption of O_2 has been observed as by direct autoxidation. H. WREN.

Convenient method of preparing anhydrous aluminium bromide. R. P. BELL (J.C.S., 1932, 338—339).—Less than the calc. amount of Br is added gradually to Al turnings in CS_2 at room temp., and the solution filtered and evaporated in vac.

H. A. PIGGOTT.

Constitution and properties of cobalt nitrosyl tricarbonyl. F. REIFF (Z. anorg. Chem., 1931, 202, 375—381).—Substitution of NO for one of the CO groups in $\text{Co}(\text{CO})_4$ results in the formation of a substance with properties similar to those of $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$. The magnetic susceptibility of $\text{Co}(\text{NO})(\text{CO})_3$ has been measured, and the val. observed indicates that the substance possesses the electronic configuration of Kr. Thermal decomp. of the vapour yields a metal of great purity and large surface.

F. L. USHER.

Use of active racemic compounds for the determination of the configuration of homomerides. Cobalt and rhodium triethylenediamines. M. DELÉPINE and R. CHARONNAT (Bull. Soc. Franç. Min., 1930, 53, 73—84; Chem. Zentr., 1931, i, 2448—2449).—The method depends on the fact that compounds of the same configuration form only mixed crystals or mixtures of both components, whilst otherwise racemic compounds possessing residual optical activity are formed. Rh^{III} salts have: *d*-chloride, $[\alpha]_D +78^\circ$; *l*-bromide, $[\alpha]_D -66^\circ$; *l*-iodide, $[\alpha]_D -52^\circ$; Co^{III} salts have: *d*-bromide, $[\alpha]_D +123^\circ$; *l*-bromide, $[\alpha]_D -120^\circ$; *d*-chloride, $3\text{H}_2\text{O}$, $[\alpha]_D +126^\circ$. Rh and Co en₃ form a racemic compound, $[\text{Co}_5\text{Rh}_{10}\text{en}_3]\text{Br}_3 \cdot 3\text{H}_2\text{O}$, $[\alpha]_D +84^\circ$ (calc. $+86.5^\circ$), whether or not the salts are mixed in mol. ratio. Hence *d*- Co^{III} and *d*- Rh^{III} triethylenediamine compounds are enantiomorphous. *d*- $[\text{Co en}_3]\text{Cl}_3$ and *d*- $[\text{Rh en}_3]\text{Cl}_3$ give a racemic compound, $[\alpha]_D +103^\circ$; the *l*-iodide compounds give a racemic com-

pound, $[\alpha]_D -73^\circ$. d -[Rh en₃]Cl₃ and l -[Co en₃]Cl₃ form mixed crystals.

[With M. MATHEU.] Racemic [Rh en₃]Br₃·3H₂O has the same structure as [Co_{0.5}Rh_{0.5} en₃]Br₃·3H₂O.

A. A. ELDRIDGE.

Action of hydrazine on aqueous solutions of nickel salts. C. PAAL and L. FRIEDERICI (Ber., 1932, 65, [B], 19—24).—N₂H₄ does not reduce aq. solutions of Ni or Co salts at 100° in absence or presence of NH₃. Addition of small amounts of Pd causes more or less quant. pptn. of Ni partly as a lustrous mirror, partly as a black sponge. Reduction also occurs in alkaline tartrate solution. Pt acts similarly but more slowly. Change is attributed to catalytic decomp. of N₂H₄ into N₂, NH₃, and H₂ and action of H₂ adsorbed by Pd or Pt. H. WREN.

Thermal decomposition of luteo-rhodium halides. E. BIRK and H. KAMM (Siebert Festschr., 1931, 12—30).—At 210° [BrRh(NH₃)₅]Br₂ is quantitatively converted into [Br₃Rh(NH₃)₃], light brown crystals insol. in H₂O, acids, or alkalis; at 280° the triammine is converted into Rh(NH₃)Br₃, dark brown powder insol. in H₂O but sol. in conc. acids. The corresponding chloride and iodide compounds cannot be prepared by thermal decomp. of the hexammine compounds. A. R. POWELL.

Isomerism of the compounds [(NH₃)₂PdCl₂]. F. KRAUSS and K. MAHLMANN (Siebert Festschr., 1931, 215—234).—Treatment of the yellow and rose-coloured compounds [(NH₃)₂PdCl₂] in aq. suspension with Cl₂ affords a compound which can be formulated only as [Pd(NH₃)₄][PdCl₂]; this, when boiled with H₂O, yields Cl₂ and the yellow diammine. Treatment of [Pd(NH₃)₄]Cl₂ with K₂HgCl₄, H₂OsCl₃, or picric acid yields the corresponding mercurichloride, chlorosmate, or picrate, whereas a HCl solution of H₂PdCl₄ yields either the rose or yellow [(NH₃)₂PdCl₂], according to the concn. of the HCl; hence it is suggested that both compounds are bimolar. Further work has shown that neither *cis-trans* nor co-ordination isomerism can exist; hence it is concluded that the two forms bear a pseudomonotropic relation to one another, the rose compound being the more labile.

A. R. POWELL.

Nitro-compounds of platinum. IX. Methylamino-derivatives. X. Reaction of nitration. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1931, 8, 37—53, 55—71).—IX. Three of the four possible stereoisomerides of (en MeNH₂PtNO₂Cl₂)Cl have been prepared, and the compounds en MeNH₂Cl₂NO₂PtX, en MeNH₂NO₂ClNO₂PtX, and en (C₅H₅N)NO₂ClNO₂PtX have been separated into their optical antipodes. The above methylamines are converted into methylimides by the action of alkalis.

X. Non-electrolytic *cis*-Pt^{IV} derivatives can be nitrated directly by HNO₃, and the NO₂-group so introduced is attached by one of the newly-formed valency linkings. The NH₃-groups of Cleve's and of Peyronne's salts are shown by Kerner's abs. method to be in the *cis*-position. The amido-reaction can take place in non-electrolytic Pt^{IV} compounds. Migration of the substituents can in certain cases occur during nitration. R. TRUSZKOWSKI.

Platinum pentammines. I. I. TSCHERNIAEV and A. N. FEDEROVA (Ann. Inst. Platine, 1931, 8, 73—82).—*Dichloro-* and *nitrochloro-platinum trans-tetrammines*, of the types en (NH₃)₂Cl₂PtX₂ and en (NH₃)₂NO₂ClPtX₂, have been prepared. The former compound reacts reversibly with aq. NH₃ to yield a mixed *pentammine*, en (NH₃)₃ClPtX₂, and *hexammine*, en (NH₃)₄PtX₄. R. TRUSZKOWSKI.

Ammines and amides of quadrivalent platinum as acids and bases. A. A. GRÜNBERG and G. P. FAERMAN (Ann. Inst. Platine, 1931, 8, 115—166).—The basicity of Pt amides is in the order: amidodiammines > amidotriammines > amidotetrammine, solutions of the most basic salt, [en (NO₂)₂NH₂ClPt], possessing the same order of alkalinity as aq. NH₃ in equiv. concn., and being more alkaline than C₅H₅N or NH₂Ph. The alkalinity of solutions of the above salts falls on heating, as a result of the reaction R·Pt·NH₃ ⇌ R·Pt·NH₂' + H⁺; this reaction is also responsible for the acidity of [Pt6NH₃]Cl₄, [Pt5NH₃Cl]Cl₃, and [Pt4NH₃Cl₂]Cl₂, the strength of these acids falling with increase in the number of NH₃-groups present. Hydroxylated Pt^{IV} ammines behave as ampholytes in solution. R. TRUSZKOWSKI.

Action of oxides on platinum at high temperatures. E. J. KOHLMAYER and J. W. WESTERMANN (Siebert Festschr., 1931, 193—214).—Pt is unattacked by Bi₂O₃ or PbO in a neutral atm. at temp. up to 1200°, but at 1300° slow dissociation of the oxides takes place and the Pt gradually absorbs Bi or Pb with the formation of brittle fusible drops, whilst at 1400° rapid perforation of the Pt occurs. When Al₂O₃, MgO or "Marquardt mass" is heated in a Pt crucible the surface begins to roughen and assumes a cryst. appearance at 1600° and at 1700° failure of the crucible rapidly ensues owing to absorption of Al, Mg, or Al and Si by the Pt.

A. R. POWELL.

Rapid gravimetric phase analysis with the centrifuge. W. KUNITZ (Zentr. Min. Geol., 1931, A, 225—232; Chem. Zentr., 1931, ii, 1165).—A fractional method starts with a heavy liquid which is progressively diluted.

A. A. ELDRIDGE.

Recommended specifications for analytical reagent chemicals. W. D. COLLINS and others (Ind. Eng. Chem. [Anal.], 1932, 4, 154—156).—Specifications and tests recommended by the American Chemical Society's Committee on Analytical Reagents are given for Ba(OAc)₂, Na₂B₄O₇·10H₂O, CdSO₄, FeCl₃, Fe(NO₃)₃, litmus-paper, K₂SO₄ (fused). Corrections are given for MgO, MeOH, KIO₃, KBr, and NaHSO₄.

E. S. HEDGES.

Magneto-optical method of analysis as a new research tool. F. ALLISON (Ind. Eng. Chem. [Anal.], 1932, 4, 9—12).—The val. of the magneto-optical method of analysis in qual. and quant. analytical procedure, the study of isotopes, and the detection of intermediate compounds in certain reactions is indicated.

E. S. HEDGES.

Micro-analytical methods as time and labour savers. E. M. CHAMOT (Ind. Eng. Chem. [Anal.], 1932, 4, 7—8).—A discussion of the advantages of micro-methods.

E. S. HEDGES.

Certain essential corrections in the analysis of gases. C. A. L. HORSTMANN and F. E. C. SCHEFFER (Rec. trav. chim., 1932, 51, 143—152).—An Amagat correction has been deduced for application to the calculation of the vol. of mixed gases when the respective vals. of the factor α in the equation of state differ widely, and also an Avogadro correction for use in the calculation of densities when the gas in question differs appreciably from an ideal gas. The latter correction can be determined with the greater accuracy. Examples are given of the application of the corrections to experimental data. M. S. BURR.

Analysis of mixtures of hydrogen, methane, ethane, and propane. C. A. L. HORSTMANN and F. E. C. SCHEFFER (Rec. trav. chim., 1932, 51, 153—158; cf. A., 1931, 54).—The mixture of gases is separated into two fractions by condensation in liquid air. These are then burnt separately and the composition is determined from the amount of CO_2 , on the assumption that the first fraction contains only H_2 and CH_4 and the second C_2H_6 and C_3H_8 . After isolating the first fraction, the second must be volatilised and re-condensed to determine whether any appreciable amount of CH_4 has been absorbed by the liquid. In such a case it is necessary to add a measured quantity of H_2 to prevent absorption of the CH_4 . This adsorption takes place only if the ratio $\text{C}_2\text{H}_6:\text{C}_3\text{H}_8$ is > 3 . The Avogadro correction (cf. preceding abstract) must be applied, but the Amagat correction can be neglected if the vols. of the 2 separate fractions only (and not the total vol.) are used in the calculation. M. S. BURR.

Detection of the colour changes of indicators in turbid or coloured media. G. PICHARD and R. CHAMINADE (Ann. Falsif., 1931, 24, 538—542).—The indicator is extracted from the medium by an immiscible solvent such as Bu^tOH , C_6H_6 , or petroleum. Data are given concerning the colours of various indicators at different p_{H} vals. in various solvents, especially Bu^tOH . As examples, the titration of the acidity of a wine and the determination of the approx. p_{H} of a soil are described. W. J. BOYD.

Behaviour of some unattackable electrodes. I. LIFSCHITZ and M. REGGIANI (Gazzetta, 1931, 61, 915—921).—The use of electrodes of W, Ta, Mo, W-bronze, and carborundum for potentiometric titrations is described. For oxidation-reduction reactions Ta is suitable, and carborundum can be used as a reference electrode, since its potential is not affected by oxidising or reducing agents. For acidimetric titrations all the above electrodes except Ta are satisfactory. O. J. WALKER.

Rapid method for fixing end-point of potentiometric titration. F. FENWICK (Ind. Eng. Chem. [Anal.], 1932, 4, 144—146).—A mathematical formula for determining the end-point of a potentiometric titration reduces the necessary plotting to a min. E. S. HEDGES.

Double quinhydrone micro-electrode. W. KUNTARA (Z. physiol. Chem., 1932, 204, 54—56).—A micro-apparatus for p_{H} determinations on one drop of liquid is described. J. H. BIRKINSHAW.

Thallium carbonate as a standard in volumetric analysis. R. HAC and K. KAMEN (Chem.

Listy, 1932, 26, 6—12).—The stability and const. composition of Tl_2CO_3 prepared by different methods render it a valuable reagent for the standardisation of acids. R. TRUSZKOWSKI.

Acidimetry and alkalimetry by the use of *s*-diphenylguanidine. H. H. CHAKMAKJIAN (J. Chem. Educ., 1931, 8, 2060—2061).—For the standardisation of 0.1*N*-HCl, diphenylguanidine (1 g. in 50 c.c. EtOH) is titrated in presence of Me-red.

CHEMICAL ABSTRACTS.

Colorimetric method for measuring the hydrogen-ion concentration of natural waters. D. GOULSTON (J. Proc. Roy. Soc. N.S.W., 1931, 65, 37—39).—The p_{H} of various sea-waters was determined by comparing the intensity of colour produced when $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ was added to the H_2O with that of a standard solution of the indicator in a Duboscq colorimeter. N. H. HARTSHORNE.

Volumetric determination of chloride. J. S. PIERCE and J. L. COURSEY (Ind. Eng. Chem. [Anal.], 1932, 4, 64—65).—A modification of Deniges' method is proposed. The accuracy is about 0.1%. The procedure may be used to determine Cl^- in presence of many substances which interfere with the Volhard or Mohr methods, but $\text{Fe}(\text{CN})_6^{4-}$ should be absent. E. S. HEDGES.

Pseudo-halogens. XVI. Determination of perchloric acid and perchlorates. L. BIRCKENBACH and J. GOUBEAU (Z. anorg. Chem., 1931, 203, 9—17).— ClO_4^- can be determined by treating with conc. H_2SO_4 and an oxidising agent [preferably $\text{K}_2\text{Cr}_2\text{O}_7$, KNO_3 , or $(\text{NH}_4)_2\text{S}_2\text{O}_8$], and absorbing the evolved Cl_2 in a mixture of 10% Na_2SO_3 and 10% NaOH solutions. Anions other than those containing halogens do not interfere; the latter must either be removed or determined separately and deducted. I^- , IO_3^- , and IO_4^- do not interfere and the procedure is therefore specially suitable for determining ClO_4^- in caliche. E. S. HEDGES.

Determination of small quantities of iodides. JEAN (Bull. Soc. Pharm. Bordeaux, 1931, 69, 41—46; Chem. Zentr., 1931, ii, 748).—Excess of Br solution is added to the neutralised liquid and reduced after a few min. with CH_2O and NaOH; AcOH is added, followed by KI, and the I titrated with $\text{Na}_2\text{S}_2\text{O}_3$. CN^- or NH_3 must be removed, but SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, and $\text{C}_2\text{O}_4^{2-}$ do not interfere. A. A. ELDRIDGE.

Determination of iodine in coal. R. KOHLER (Mitt. Lab. Preuss. Geol. Landesanst., 1931, No. 13, 1—9; Chem. Zentr., 1931, ii, 748).—The max. results are obtained in Fellenberg's process when 5 c.c. of the K_2CO_3 solution are used for 10 g. of coal; 90% of I added could be found. A. A. ELDRIDGE.

Determination of minute quantities of iodine. V. KURELAC (Magyar Chem. Fol., 1931, 37, 93—103; Chem. Zentr., 1931, ii, 600).—Fellenberg's method is generally applicable; Schwaibold's is suitable for small quantities of material rich in I. Pfeiffer's method is best for liquid substances; if sufficient care is exercised, Glimm and Isenbruch's modifications are unnecessary. A. A. ELDRIDGE.

Determination of minute quantities of reducible sulphur. P. C. SCHERER, jun., and W. W. SWEET (Ind.

Eng. Chem. [Anal.], 1932, 4, 103—104).—The compounds of S are reduced to H_2S by means of Al and HCl and the gas stream passes over a strip of dry $Pb(OAc)_2$ paper. The length and colour of the stain produced give a measure of the amount of H_2S . The method is accurate for 0.000001—0.000015 g. of reducible S and may be used for the approx. determination of S up to 0.0001 g. The procedure is applicable to the determination of reducible S in blood, urine, and other biological products, rayon, synthetic org. compounds, etc. S present as SO_4^{2-} is not determined.

E. S. HEDGES.

Iodometric titration of sulphites. J. LUKAS (Chem. Listy, 1932, 26, 26—34).— Na_2SO_3 cannot be determined by titration of its solutions by I, owing to rapid spontaneous oxidation, amounting, at concns. such as are used for volumetric work, to 5% in 5 min., 30% in 30 min., and 100% in 12 hr. Na_2SO_3 may be determined by adding a small quantity to 0.05N-I, weighing, and titrating excess of I with $Na_2S_2O_3$. Oxidation of Na_2SO_3 solution may be retarded for not more than 6 hr. by the addition of 2—4% erythritol, 5—10% glycol, or 5—10% EtOH. The form of sulphite most stable in the dry state or in solution is $Na_2S_2O_5 \cdot 0.5H_2O$.

R. TRUSZKOWSKI.

Identification of persulphates and of blood (peroxidases) by means of 2:7-diaminofluorene hydrochloride. J. SCHMIDT and W. HINDERER (Ber., 1932, 65, [B], 87—90).—2:7-Diaminofluorene hydrochloride in H_2O is unaffected by air or dil. HNO_3 . The presence of 0.00000017 g. Cl_2 per c.c. of H_2O is detected by a blue coloration after a time; the reagent is three times as sensitive as benzidine. Persulphate in H_2O (1:100,000) gives a blue colour after 5 min.; the test is applicable in presence of much SO_4^{2-} . Traces of blood in presence of H_2O_2 give a blue colour, but the test should not be applied on filter-paper. The $SnCl_2$ -hydrochloride complex cannot be substituted satisfactorily for the hydrochloride. Fresh milk yields colorations with 2:7-diaminofluorene or phenylenediamine within 10 min. at room temp.; boiled milk gives no colour with the fluorene derivative after 2 hr., and only a pale yellow after 24 hr., whereas with phenylenediamine the colour is as intense after 24 hr. as if fresh milk had been used. Reaction is delayed by AcOH and inhibited by mineral acid. A constitution analogous to that of benzidine appears essential for the reaction, since 2:5-diaminofluorene has no action.

H. WREN.

"Ring test" for detection of nitrate ions. E. SCHROER (Z. anorg. Chem., 1931, 202, 382—384).—It is shown that the two factors determining the "brown ring" reaction are (1) a strongly acid medium in which free HNO_3 can be formed and (2) a temp. sufficiently high (30—70°) to initiate thermal decomp. of the HNO_3 . If HNO_2 is prevented from accumulating (e.g., by adding carbamide), no reaction is obtained.

F. L. USHER.

Removal of bromide and iodide for detection of nitrate. M. J. MURRAY and A. W. AVENS (Ind. Eng. Chem. [Anal.], 1932, 4, 58).—The brown-ring test for NO_3^- may be carried out with a solution originally containing Br^- and I^- by first pptg. these as $AgBr$

and AgI with a solution of Ag_2SO_4 in aq. NH_3 . The result is satisfactory with solutions containing more than 0.5 mg. NO_3^- per c.c. E. S. HEDGES.

Elimination of correction for nitrites in nitrate determinations. G. H. NELSON, M. LEVINE, and J. H. BUCHANAN (Ind. Eng. Chem. [Anal.], 1932, 4, 56—58).—The conditions of decomp. of nitrites and nitrates when evaporated to dryness with other reagents have been examined. In presence of AcOH, nitrites are decomposed at p_H 3 and nitrates at p_H 2. In presence of NH_4Cl or $(NH_4)_2SO_4$ no nitrite is lost at p_H 11, but nitrites are decomposed when the p_H is lower. No decomp. of nitrites takes place with aq. NH_3 or NH_4HCO_3 . It is suggested that the usual correction for nitrites may be eliminated by evaporating a neutral solution with NH_4Cl or $(NH_4)_2SO_4$, or with AcOH at p_H 3.

E. S. HEDGES.

Determination of phosphates in waters. J. E. FARRER and G. E. YOUNGBURG (Ind. Eng. Chem. [Anal.], 1932, 4, 107—109).—The colorimetric method of Kuttner and Cohen (A., 1928, 336) is adapted for the analysis of natural waters. 1 part of PO_4^{3-} can be detected in 10^8 parts of H_2O . Fe^{2+} , Cu^{2+} , or Al^{3+} does not interfere until the amount present exceeds 50 times that of PO_4^{3-} . Fe^{3+} interferes at concns. greater than 6 p.p.m. CO_3^{2-} , SO_4^{2-} , and NO_3^- in considerable quantity do not interfere.

E. S. HEDGES.

Iodometric determination of hypophosphorous and phosphorous acids. V. HOVORKA (Chem. Listy, 1932, 26, 19—26).— CO_2 is passed for 3—5 min. through a boiling solution containing 50 c.c. of 0.1N-KIO₃, 20 c.c. of 12% $Hg(ClO_4)_2$, 5—10 c.c. of 10% H_2SO_4 , and not more than 0.07 g. of H_3PO_2 or 0.15 g. of H_3PO_3 , 35 c.c. of 20% KI are added to the cooled solution, and excess of I is titrated with 0.1N- $Na_2S_2O_3$. Practically identical results are obtained by this method, by Vsetička's (Chem. Listy, 1914, 8, 259), and by Brukl and Behr's methods (A., 1924, ii, 566).

R. TRUSZKOWSKI.

Electrochemical determination of small quantities of arsenic. SCHEERMESSE (Pharm. Ztg., 1932, 77, 112).—The substance is introduced into the cathode (As-free Pb) compartment of a cell containing 10% H_3PO_4 . The evolved H_2 and AsH_3 pass through an empty U-tube to the dissociation tube, where the AsH_3 is decomposed by a high-tension a.c. giving a mirror of As which may be examined by the usual methods. The AsH_3 need not be absolutely dry; $CaCl_2$, NaOH, and even glass-wool adsorb and decompose AsH_3 .

E. H. SHARPLES.

Determination of boron in waters. Direct determination of boric acid. F. J. FOOTE (Ind. Eng. Chem. [Anal.], 1932, 4, 39—42).—In the presence of sufficient mannitol, H_3BO_3 is completely neutralised at p_H 7.6. Standard NaOH is used for the titration and CO_2 must be rigorously excluded.

E. S. HEDGES.

Electrometric titration of boric acid. L. V. WILCOX (Ind. Eng. Chem. [Anal.], 1932, 4, 38—39).— H_3BO_3 in the presence of mannitol is titrated with NaOH, using the quinhydrone electrode. The procedure is recommended for irrigation and drainage

waters between p_R 7 and 8, in which the content of PO_4''' and SiO_3'' is low. E. S. HEDGES.

Determination of silica and alumina in refractory materials. C. PERTUSI and E. DI NOLA.—See B., 1932, 147.

Determination of silicic acid in mineral waters. L. FRESSENIUS (Angew. Chem., 1932, 45, 132—133).—A discussion of necessary precautions.

E. S. HEDGES.
Binary system carbon tetrachloride-ethylene dichloride. B. p. and sp. gr. as aids to analysis. H. D. YOUNG and O. A. NELSON (Ind. Eng. Chem. [Anal.], 1932, 4, 67—69).—Curves have been constructed showing the relation between (a) sp. gr., (b) b. p. and composition of CCl_4 - $C_2H_4Cl_2$ mixtures. The sp. gr.-composition curve is linear. The b. p.-composition curve shows that there is a min. b. p. at 75.30° at a concn. of approx. 70 mol.-% CCl_4 .

E. S. HEDGES.
Micro-analytical test for carbon disulphide. N. TISCHLER (Ind. Eng. Chem. [Anal.], 1932, 4, 146).—1 c.c. of 1% NH_4Et_2 in abs. EtOH and 5 drops of 0.05% $Cu(OAc)_2$ in abs. EtOH are added to 1 c.c. of the solution to be tested. Colourless solutions in CO_2 , HCl , Et_2O , and EtOH give a golden-yellow colour at a CS_2 concn. of 1 in 10^5 and a perceptible yellow colour at 1 in 10^7 . A ppt. is formed in aq. solution, but the sensitivity is the same. Pure thioacetic acid gives a similar reaction. E. S. HEDGES.

Iodometric determination of carbon disulphide. M. P. MATUSZAK (Ind. Eng. Chem. [Anal.], 1932, 4, 98—101).—The determination of CS_2 by iodometric titration of xanthate is both accurate and rapid. The solution of KOH in EtOH should be freshly prepared, the formation of free xanthic acid should be avoided as far as possible, and the xanthate should be titrated with I immediately after its formation.

E. S. HEDGES.
Removal of phosphoric ion as lead phosphate in determination of sodium. J. BOUGAULT and E. CATTELAINE (J. Pharm. Chim., 1932, [viii], 15, 97—99).—The application of the general process previously described (this vol., 136) in the determination of Na by the Mg U acetate method is described.

Quantitative spectrographic studies of coprecipitation. I. Magnesium in calcium oxalate. S. POPOFF, L. WALDBAUER, and D. C. MCCANN (Ind. Eng. Chem. [Anal.], 1932, 4, 43—46).—Mg in CaC_2O_4 can be determined by spectrographic analysis when the amount of Mg is between 1 and 0.001%. The amount of Mg pptd. with Ca by $(NH_4)_2C_2O_4$ depends on the time of digestion after making the solution alkaline, on the time of pptn., and on the amount of $(NH_4)_2C_2O_4$, but not on the amount of NH_4Cl used. For complete pptn. of Ca, sufficient $(NH_4)_2C_2O_4$ must be present for both Ca and Mg.

E. S. HEDGES.
Analysis of beryllium minerals. F. G. HILLS (Ind. Eng. Chem. [Anal.], 1932, 4, 31—32).—Existing methods are critically compared.

Titration of zinc with potassium ferrocyanide. Use of diphenylamine or diphenylbenzidine as internal indicators. I. M. KOLTHOFF

and E. A. PEARSON (Ind. Eng. Chem. [Anal.], 1932, 4, 147—150).—The results obtained in this titration depend mainly on the speed and the temp. No indicator correction is necessary with diphenylbenzidine, but when 1% $NHPh_2$ is used 0.033 c.c. of 0.025M- $K_3Fe(CN)_6$ must be added as a correction per drop of indicator. The use of $NHPh_2$ is preferred as the colour changes are more pronounced.

E. S. HEDGES.
Rotating mercury electrode and its use in electrolysis. P. S. TUTUNDZIC (Z. anorg. Chem., 1931, 202, 297—304).—A rotating Hg cathode, requiring only 12—15 g. Hg, is described. Accurate results were obtained with it in the determination of Hg and of Cu, and slightly too high with Zn.

F. L. USHER.
Conductometric titration of a solution of tetraisoamylammonium iodide in zinc diethyl with sodium ethyl in zinc diethyl. F. HEIN and H. PAULING (Z. Elektrochem., 1932, 38, 25—27).—Titration of the above substances at 35° in an atm. of N_2 shows the occurrence of reaction between equimol. quantities.

F. L. USHER.
Electrometric titration of copper salts by sodium hydroxide. R. A. BEEBE (J. Physical Chem., 1931, 35, 3677—3683).—Titration curves for $(CCl_3CO_2)_2Cu$, $Cu(OAc)_2$, and $Cu(ClO_3)_2$ obtained with the quinhydrone electrode are reproduced, and point to the existence of a basic salt, $(CCl_3CO_2)_2Cu \cdot 3Cu(OH)_2 \cdot xH_2O$. The order of stability of basic Cu salts is chloride > sulphate > trichloroacetate > nitrate > chlorate > acetate.

W. T. HALL (c.).
Determination of aluminium in certain aluminium compounds. C. G. PORE (Biochem. J., 1931, 25, 1949—1953).—The Al is pptd. with 8-hydroxyquinoline and the latter is determined by dissolving the ppt. in HCl, adding excess of $KBrO_3$, and then determining the excess of Br by adding KI and titrating with $Na_2S_2O_3$. Amounts of Al between 0.3 and 1.0 mg. present in suspension can be analysed.

S. S. ZILVA.
Colorimetric determination of traces of manganese and chlorine with benzidine. R. C. STRATTON, J. B. FICKLEN, and W. A. HOUGH (Ind. Eng. Chem. [Anal.], 1932, 4, 2).—The bluish-green colour obtained by adding benzidine hydrochloride has been adapted to the determination of small quantities of MnO_4' in the absence of free Cl_2 , or the determination of Cl_2 in the absence of MnO_4' . The colour fades quickly, but an artificial colour standard may be made by mixing $CuSO_4$ and picric acid solutions. The procedure is most accurate with 0.0001—0.001 mg. of MnO_4' or 0.001—0.001 mg. of Cl_2 in 100 c.c. of solution.

E. S. HEDGES.
Detection of manganese as permanganate in presence of chlorides, e.g., in sea-water. G. DENIGÈS (Compt. rend., 1932, 194, 91—92; cf. A., 1888, 873; 1901, ii, 350).—For this purpose ClO' or BrO' is an efficient oxidiser, especially in presence of Cu'' . Thus, to 10 c.c. of the solution under examination 1 drop of 5% aq. $CuSO_4$, and for each 0.2 mg. (probable) of Mn'' 1 drop of commercial aq. $NaOCl$ are added; the liquid is boiled, cooled, and centrifuged

to remove CuO. 1—2 mg. of Mn⁺⁺ are detectable in presence of 100 g. NaCl per litre.

C. A. SILBERRAD.

Di-*o*-anisidine as internal indicator in the dichromate method for [determining] iron. M. E. WEEKS (Ind. Eng. Chem. [Anal.], 1932, 4, 127—128).—Di-*o*-anisidine in glacial AcOH is recommended as internal indicator. The solution is stable to light.

E. S. HEDGES.

Thiosulphate titration of small amounts of iron in glass sands. L. B. SKINNER.—See B., 1932, 104.

Precipitation of iron, aluminium, and chromium hydroxides in pure, dense, easily filtered form. F. L. HAHN (Ber., 1932, 65, [B], 64—65).—The reagent is prepared by dissolving 15 g. of NaNO₂ and 15 g. of NaN₃ in H₂O (250 c.c.), warming with 2 c.c. *M*-FeCl₃ to remove silicate, filtering, and diluting the filtrate to 500 c.c. The test solution is nearly neutralised with aq. NH₃, diluted to 100—150 c.c. per m.-mol. of metal, and treated with 2—3 g. of NH₄Cl and 10 c.c. of precipitant. The mixture is warmed on the water-bath; when the ppt. has subsided, the usual procedure is adopted, NH₄Cl and precipitant being added to the first wash waters. In presence of a tenfold amount of Mn, the pptd. Fe(OH)₃ carries down only 0.1% of Mn.

H. WREN.

Inoculation crystals. C. ZEGGELI (Praktika, 1928, 3, 392—399; Chem. Zentr., 1931, ii, 1035—1036).—Illegible documents written in Fe ink are rendered legible by moistening with H₂O and exposure to (NH₄)₂S vapour; those in C ink are exposed to I vapour and treated, after exposure to air, with starch solution. The formation of ppts. in new test-tubes is non-uniformly slower than in tubes already used for the same purpose.

A. A. ELDRIDGE.

Characteristic reaction for violet solutions of chromium salts. III, IV. C. MONTEMARTINI and E. VERNAZZA (Ind. Chim., 1931, 6, 630—632, 739—742; Chem. Zentr., 1931, ii, 1396, 1689).—III. An aq. suspension of Cd(OH)₂ forms with K Cr alum solution a green ppt. which immediately becomes lilac, and blue on washing. The compound Cr₂O₃.4CdO.SO₃ is partly decomposed on boiling with H₂O. If a solution of Cr(NO₃)₃.9H₂O is treated with Na₂SeO₄ and then with a suspension of ZnCO₃, the lilac compound Cr₂O₃.4ZnO.SeO₃ is obtained; in the corresponding greenish violet-blue compound obtained with K₂TeO₄ the ratio Cr₂O₃ : ZnO : TeO₃ is 1 : 4.67 : 0.36.

IV. The lilac ppt., Cr₂O₃.4ZnO.SO₃, obtained from Cr₂(SO₄)₃ solution and ZnCO₃ or Zn(OH)₂, when heated or in vac. over H₂SO₄, becomes darker in colour and still contains 7H₂O. Cr₂O₃.4ZnO.SeO₃ and Cr₂O₃.4CdO.SO₃ behave analogously, the latter losing H₂O only in vac. over H₂SO₄. Washing with anhyd. Et₂O or EtOH affords Cr₂O₃.4ZnO.SO₃.11H₂O. The lilac ppt. is considered to be [Cr₂(H₂O)₈(HZnO₂)₄][SO₄]. Although zincates are formed, Cd(OH)₂ affords chromites.

A. A. ELDRIDGE.

Electrometric determination of chromium and vanadium in ferrous alloys. W. WERZ.—See B., 1932, 149.

Colorimetric determination of molybdenum. L. H. JAMES (Ind. Eng. Chem. [Anal.], 1932, 4, 89—90).—The method of Maag and McCollam (B., 1925, 504) is modified by substituting HClO₄ for H₂SO₄ and BuOAc for Et₂O as extracting agent. Ni, Cr, V, Si, and Cu in small quantities do not interfere. The procedure is not recommended where the sample contains more than 0.8% Mo.

E. S. HEDGES.

Analysis of traces of Morogoro pitchblende. F. HECHT.—See B., 1932, 145.

Determination of uranium in pitchblende. V. A. MATULA (Chem. Obzor, 1931, 6, 124—126; Chem. Zentr., 1931, ii, 748).—The potentiometric determination of U in presence of Fe with TiCl₃ is preferred; other elements of group III and P₂O₅ do not interfere.

A. A. ELDRIDGE.

Cathode-ray effect in X-ray spectrum analysis. M. ISHIBASHI (Z. anorg. Chem., 1931, 202, 372—374).—When a mixture of TiO₂ with BaSO₄ is placed on the anticathode of an X-ray tube the ratio of the intensities of the lines Ti K_{α1} and Ba L_{α1} undergoes a change which can easily be measured. Such measurements have been made and used to correct earlier determinations of the Ti content of meteorites.

F. L. USHER.

Germanic sulphide. Quantitative conversion of sulphide into dioxide by hydrolysis. J. H. MÜLLER and A. EISNER (Ind. Eng. Chem. [Anal.], 1932, 4, 134—136).—A suspension of GeS₂ in H₂O is quantitatively converted into GeO₂ by passing steam through the liquid. The procedure is recommended for the determination of Ge.

E. S. HEDGES.

Colorimetric determination of vanadium. T. GEDEON (Magyar Chem. Fol., 1931, 37, 89—92; Chem. Zentr., 1931, ii, 749).—V compounds in 10% H₂SO₄ solution give with H₂O₂ brown to brownish-red pervanadic acid, the colour being proportional to the V content and unchanged by 5—40% acids or colourless inorg. salts. The limit of determination of pervanadic acid is 1 : 625,000; Mo interferes, whilst in presence of Fe 5% of H₃PO₄, and in that of Ti HF, is added.

A. A. ELDRIDGE.

Use of hydroxyquinoline, strychnine, and brucine for the gravimetric determination of vanadium, and of quinoline for the separation of vanadium from chromium. A. JÍLEK and V. VICOVSKÝ (Coll. Czech. Chem. Comm., 1932, 4, 1—7).—V may be determined by pptg. a solution of Na₃VO₄ by adding AcOH solutions of 8-hydroxyquinoline, strychnine, brucine, or quinoline. The ppt. is ignited and weighed as V₂O₅. Among these reagents, only quinoline serves to separate VO₄^{'''} and CrO₄^{'''}. The ppt. formed by adding quinoline in AcOH is ignited to V₂O₅, the filtrate is reduced by SO₂, and the Cr pptd. by aq. NH₃ and ignited to Cr₂O₃.

E. S. HEDGES.

Application of 8-hydroxyquinoline, strychnine, brucine, and quinoline to the separation of vanadium from arsenic. A. JÍLEK and V. VICOVSKÝ (Chem. Listy, 1932, 26, 16—18).—VO₄^{'''} is quantitatively pptd. in acid solutions by the above substances; AsO₄^{'''}, which remains in solution, can be pptd. as As₂S₅ by H₂S after addition of HCl.

R. TRUSZKOWSKI.

Recovery of platinum and standardisation of platinic chloride solution. W. B. BYERS (Chemist-Analyst, 1931, 20, No. 5, 5—6).—The K_2PtCl_6 is dissolved in hot dil. HCl, the Pt is pptd. with Zn, washed, and dissolved in HCl- HNO_3 . HNO_3 is removed with HCl and the diluted solution is standardised against KCl; the K_2PtCl_6 ppt. is weighed.

CHEMICAL ABSTRACTS.

Determination of small quantities of iridium in chloroplatinates. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1931, 8, 167—171).— $(NH_4)_2PtCl_6$ is reduced to $(NH_4)_2PtCl_4$ by NH_4 oxalate, and $(NH_3Cl)_2Pt$ is pptd. from the solution by aq. NH_3 . The mother-liquor is heated with aq. NH_3 , thereby converting all Pt compounds into $(NH_3)_4PtCl_2$, and this is oxidised by HNO_3 to $(NH_3)_4Cl_2PtCl_2$. The filtrate is evaporated until NH_4Cl crystallises, when black $(NH_4)_2IrCl_6$, containing 0.02—0.03% of $(NH_4)_2PtCl_6$, ppts.

R. TRUSZKOWSKI.

Thermo-regulators. Thermostat for temperatures from 20° to 1000°. H. BRUNING (Chem. Fabr., 1932, 17—19).—A thermo-regulator is described in which the Pt-Hg contact is broken in an atm. of H_2 and the level of the Hg in the capillary is adjustable by a steel micrometer screw which serves also for the electrical connexion to the Hg. An improved relay, regulator, and heater circuit is described. A thermostat for use up to 350° consists of a double-walled vessel containing Hg which functions both as a heat reservoir and as the temp. regulator. For temp. between 350° and 1000° a quartz vessel containing air serves to operate a special Hg regulator which is not influenced by atm. temp. and pressure changes.

H. F. GILLBE.

Thermo-regulator for adiabatic calorimeters. H. RIECHE and R. GRAU (Z. tech. Physik, 1931, 12, 284—286; Chem. Zentr., 1931, ii, 747).—A modification of Kangro's all-metal calorimeter (A., 1928, 729) is described.

A. A. ELDRIDGE.

Thermostat [for electric furnace] without relay. A. SIMON and P. RATH (Chem. Fabr., 1932, 33).—The contact breaker is a cylindrical Fe float (in Hg) 5 mm. high which makes contact with a horizontal Pt spiral by means of a Pt wire threaded through a hole in the upper end. This float is not liable to be pushed down into the Hg and with good workmanship will give a constancy to 0.5° at up to 650°.

C. IRWIN.

Potentiometric pyrometer. T. R. HARRISON (J. Sci. Instr., 1932, 9, 19—21).—An automatic recording instrument is described. The galvanometer attached to a null type potentiometer operates a mechanism to rebalance the circuit for each change of c.m.f.

C. W. GIBBY.

Silvering of small mirrors. E. A. BAKER (J. Sci. Instr., 1931, 8, 392).—Mirrors only a few mm. in diameter are held on the end of a glass tube sliding within another slightly larger glass tube. The latter is constricted at its lower end, and the silvering solution and washing water are drawn up as into a pipette.

C. W. GIBBY.

Polarising system for spectrophotometers. J. H. DOWELL (J. Sci. Instr., 1931, 8, 382—384).—

Three Nicols are arranged in tandem, the two fixed end ones transmitting light polarised in the same plane and the middle one rotating. Better readings are obtained at high density than with the ordinary form.

C. W. GIBBY.

Colour measurement by analytical methods. J. A. A. KETELAAR (Chem. Weekblad, 1932, 29, 6—9).

—Various methods of analysing colours are described. The Helmholtz-Exner method is discussed in some detail and is shown to be unsuitable for practical measurements, since (1) it is complicated, (2) the results cannot be simply expressed, (3) the method is uncertain, especially as regards the brightness factor, and (4) the coeffs. obtained do not suffice for reproduction of a colour.

H. F. GILLBE.

Pentagonal comparison prism for spectroscopes. S. D. BRYDEN, jun. (Rev. Sci. Instr., 1932, [ii], 3, 51).—The usual right-angled prism is replaced by a pentagonal prism mounted on a vertical slide in front of the slit.

D. R. DUNCAN.

Photo-electric photometer and its use in comparing X-ray intensities. E. DERSHEM (Rev. Sci. Instr., 1932, [ii], 3, 43—50).—An apparatus for measuring photographic densities by means of a photo-electric cell is described, no dark-room being required. The instrument is specially useful for work on very soft X-rays, and has been used to measure the absorption coeff. of gases (cf. A., 1931, 1346), the reflexion of X-rays, and for the analysis of the Doppler effect in the H_β line from a homogeneous beam of H positive rays.

D. R. DUNCAN.

Wedge spectrograms without an absorbing wedge. O. E. MILLER (Rev. Sci. Instr., 1932, [ii], 3, 30—42).—A review of the methods of producing wedge spectrograms. The author's instrument, an improvement on Hansen's condenser (Z. Physik, 1924, 29, 356), has been used for measuring the spectral sensitivity of photographic plates, and could readily be converted into a photographic spectrophotometer.

D. R. DUNCAN.

Device to measure the amount of plane polarised light in low intensity radiations and to measure small rotations of the plane of polarisation. D. R. MOREY (Rev. Sci. Instr., 1932, [ii], 3, 24—29).—The photo-electric polariscope described has been used in the study of fluorescence. The % polarisation can be measured accurately down to 10^{-5} ft.-candle. A rotation of 1" can be detected.

D. R. DUNCAN.

X-Ray stereocinematography and the testing of materials. G. KOEGL (Angew. Chem., 1932, 45, 43—44).—A discussion of the advantages and practical difficulties of the method.

H. F. GILLBE.

Self-contained X-ray apparatus for crystal analysis. R. A. STEPHEN (J. Sci. Instr., 1931, 8, 385—387).—A compact instrument is described.

C. W. GIBBY.

Sources of monochromatic red and yellow light. F. ESCLANGON (Compt. rend., 1932, 194, 266—268).—The electrodeless discharge operates a Na or Cd lamp satisfactorily only if the lamp is heated from time to time. This is avoided if the tube contains A at 0.1 mm. Hg. Zn and Hg can then

replace Na or Cd. The arc spectra of the metals are obtained. In this way Cd and Zn, respectively, give, with suitable screens, the lines 6438 and 6362 of brilliances 0.25 and 1.0 candles and breadth 0.045 Å. The A not only starts the discharge but also lowers the temp. required for its passage; its action appears to be connected with its high resonance potential and the Ramsauer effect. C. A. SILBERRAD.

Luminous spectrograph based on transmission of non-canalised X-rays across a curved sheet of mica. (MILLÉ.) Y. CAUCHOIS (Compt. rend., 1932, 194, 362—365).—A method is described whereby a spectrum of non-canalised X-rays is obtained by transmission across, and selective reflexion from, the non-cleavage planes of a cylindrically curved sheet of mica. C. A. SILBERRAD.

Automatic apparatus, with selenium rectifier, for conductivity measurements. E. ROTHER, G. JANDER, and O. PFUNDT (Chem. Fabr., 1932, 19—20).—The resistance of the bridge wire, rectifier, and measuring instrument must be approx. equal. The apparatus may be operated by the electric mains, but if the voltage is not sufficiently const. an induction coil may be used. Results obtained by the deflexion method are given. H. F. GILLBE.

Theory of diaphragm electrolyzers. F. GIOR-DANI (Mem. R. Accad. Ital., Sci. Fis. Mat. Nat., 1930, 1, Chim. No. 6, 70 pp.; Chem. Zentr., 1931, ii, 25).—Current yields have been calc. The dilution law for NaOH and NaCl was studied; the results accord with Ghosh's approximation. A new diaphragm electrolyser on the counter-current principle is proposed. A. A. ELDRIDGE.

Portable apparatus for precise gas analysis. H. R. AMBLER (J. Sci. Instr., 1931, 8, 369—373).—The overall size of the apparatus previously described (A., 1929, 1262) has been reduced. C. W. GIBBY.

Compensator for constant-volume gas burettes. H. R. AMBLER (J. Sci. Instr., 1931, 8, 374—376).—The top of the manometer is connected to artificial atm. the pressure of which is adjusted so that the vol. of air in a bulb, originally filled at atm. pressure, is kept const. C. W. GIBBY.

Measurement of low, continuously varying pressures. L. A. M. HENRY (Bull. Soc. chim. Belg., 1931, 40, 657—664).—A counterpoised glass bulb resting on the Hg surface in one arm of a manometer is attached to a lightly-supported horizontal glass tube carrying a mirror. Small changes in level cause rotation of the tube and mirror around a horizontal axis, and are observed with lamp and scale. C. W. DAVIES.

Soxhlet extraction apparatus. D. S. BINNINGTON (Ind. Eng. Chem. [Anal.], 1932, 4, 125—126).—In the improved apparatus cork stoppers and rubber or ground-glass connexions are eliminated. E. S. HEDGES.

Fractionating column for diminished pressure. M. T. BUSH and A. M. SCHWARTZ (Ind. Eng. Chem. [Anal.], 1932, 4, 142—143).—The apparatus can be used for 50—400 c.c. of material having a b. p. up to 200° at pressures down to 1 mm. E. S. HEDGES.

Greaseless valve. J. L. WILSON (J. Physical Chem., 1931, 35, 3353).—A glass Hg valve for transferring small quantities of gas or liquid which does not attack Hg from the storage to the reaction system, is described. J. BALOZIAN (c).

Small electromagnetic gas pump. E. LEHRER (Chem. Fabr., 1932, 33—34).—The pump is intended to handle 3—5 litres of gas per min. against pressures up to 30 cm. of H₂O. The magnetically operated cylinder consists of a glass tube filled with strips of sheet Fe and as the apparatus is in its main parts of glass it is suitable for many gases. The cylinder is suspended on a spring and the pump is actuated preferably by a.c. C. IRWIN.

Separation of large samples of minerals with large differences in sp. gr. with heavy liquids. S. KLEIN (Zentr. Min. Geol., 1932, A, 244—250; Chem. Zentr., 1931, ii, 1165).—Brogger's apparatus is modified. A. A. ELDRIDGE.

Apparatus for determination of volatile solids by sublimation. L. HART (Chemist-Analyst, 1931, 20, No. 6, 14).—A pair of Petri dishes is employed. CHEMICAL ABSTRACTS.

Micro-condenser and constant liquid flow apparatus. E. W. BLANK (Chemist-Analyst, 1931, 20, No. 6, 20).—The condenser is made from two T-tubes and rubber tubing. Const. liquid flow is obtained by means of a separating funnel and a reservoir. CHEMICAL ABSTRACTS.

Measurement of slow gas flow. D. H. KILFER (Ind. Eng. Chem. [Anal.], 1932, 4, 97—98).—The method described depends on measurement of the change of temp. of the gas when supplied with a measured heat input. E. S. HEDGES.

Gas sampling. R. A. KOLLIKER (Chem. Fabr., 1932, 1—3).—A small metal injector operated by compressed air delivered at const. pressure from a steel bottle draws the air or gas to be examined through absorbing liquid contained in two sintered glass scrubbing flasks. Using 2 litres of air compressed to 150 atm. more than 1000 litres of gas can be drawn at the rate of 25—80 litres per min. The rate of suction is practically const. until the pressure falls below 25 atm., provided no ppt. is formed in the absorption vessels. The apparatus is portable. F. L. USHER.

Ultra-centrifuge and its field of research. J. B. NICHOLS (Ind. Eng. Chem. [Anal.], 1932, 4, 12—17).—Two types of ultra-centrifuge, giving forces up to 10,000 and 100,000 times that of gravity, respectively, are described. Published work on sedimentation analysis is reviewed. E. S. HEDGES.

Bicycle-chain stirrer. S. B. LIPPINCOTT (Ind. Eng. Chem. [Anal.], 1932, 4, 93).—The stirrer is recommended where it is desired to keep a solid worked free from the wall of a flask. E. S. HEDGES.

Precision sodium cutter. E. B. HERSHBERG and E. H. HUNTRESS (Ind. Eng. Chem. [Anal.], 1932, 4, 100—101).—Constructional details are given. The pellets produced are reproducibly uniform in wt. and suffer no oxidation during the process. E. S. HEDGES.

Jelly strength tester. C. R. FELLERS and J. A. CLAGUE (Ind. Eng. Chem. [Anal.], 1932, 4, 106—107).—The pressure necessary to break the jelly is read directly on a scale which registers the tension of a spring. E. S. HEDGES.

Mechanical shaking device. O. W. CHAPMAN and F. CINOTTO (Ind. Eng. Chem. [Anal.], 1932, 4, 126). E. S. HEDGES.

Determination of the refractive indices of a material such as muscovite mica. F. RECORD and W. D. JONES (J. Sci. Instr., 1932, 9, 24—25).—Strips of suitable size are cut respectively parallel and perpendicular to the extinction planes (previously determined with a polariscope) and placed in an Abbé refractometer. C. W. GIBBY.

Preparation of thin sections of Portland cement and other clinkers for petrographic

examination. H. G. FISK (Amer. J. Sci., 1932, [v], 23, 172—176).—"HyraX," a synthetic resin said to be a compound of $C_{10}H_8$, dissolved in C_6H_6 may with advantage be substituted for Canada balsam.

Vapour-pressure nomograph. V. W. WILSON and C. R. BLOOMQUIST (Ind. Eng. Chem. [Anal.], 1932, 4, 136—137). C. W. GIBBY. E. S. HEDGES.

Nomography. W. SCHREIBER (Chem. Fabr., 1932, 3—4).—A nomogram is given for converting results of a gas analysis from vol.-% into kg. per cu. m. F. L. USHER.

Discovery and properties of rhenium. O. COLLENBERG (Svensk Kem. Tidskr., 1931, 43, 265—281).—An account of the discovery, prep. and properties of Re and its compounds.

H. F. HARWOOD.

Geochemistry.

Structure and development of temperature inversions in the atmosphere. S. MAL, S. BASU, and B. N. DESAI (Nature, 1932, 129, 97).

L. S. THEOBALD.

Italian natural gases. M. LEVI and C. PADOVANI (Atti III Cong. Naz. Chim. pura appl., 1929, 688—717; Chem. Zentr., 1931, ii, 520).—Gases from mountains and hills contain considerably greater quantities of higher hydrocarbons than of CH_4 ; otherwise there is little difference between the gas from mountains and those from valleys. In exceptional cases large amounts of N_2 were present.

A. A. ELDRIDGE.

Radioactivity of the springs of Bareges. R. MASSY (Bull. Soc. Pharm. Bordeaux, 1930, 68, 235—238; Chem. Zentr., 1931, ii, 980).—Bastan cold springs are frequently more strongly radioactive than the sulphurous thermal springs. A. A. ELDRIDGE.

Spectrographic determination of the cations in some Spanish medicinal mineral waters. II. S. PINA DE RUBIES (Anal. Fis. Quím., 1931, 29, 653—658).—A report that certain mineral waters contained Cr, Co, Ni, Zn, and Hg is shown to be erroneous.

H. F. GILLIE.

Variations of the hydrogen-ion concentration of sea-water. D. GOULSTON (J. Proc. Roy. Soc. N.S.W., 1931, 65, 43—50).—The p_H of various Australian sea-waters was 8.4—8.6, which was perceptibly greater than that of the H_2O taken from the river mouths. This reduction is probably due to a lessening in the amount of $Ca(OH)_2$ and $Mg(OH)_2$, an efflux of fresh, brackish H_2O , and a proportional increase in the org. life. Measurements on the influence of the CO_2 pressure on the p_H of sea H_2O show that the latter is slightly buffered. The results are discussed in relation to the distribution of org. life in the ocean. N. H. HARTSHORNE.

Microgenetic habit-studies of recent barytes formations. F. BUSCHENDORF (Z. Krist., 1932, 81, 38—68; cf. A., 1931, 459).—A detailed account is given of the fan-shaped etc. aggregates in the

Silberbach mine (Stolberg). Some crystals show zoning with material of different optical properties; analysis thereof showed only $BaSO_4$ 99.43, $CaSO_4$ 0.27, SiO_2 0.38, $(Al, Fe)_2O_3$ 0.23%, and a trace of Sr, which is insufficient to explain the differences observed. The mode of deposition previously suggested (through loss of CO_2) is confirmed by analyses of (a) H_2O dropping in the drusy cavity, and (b) H_2O in a pool below the barytes deposit, showing (in g. per 1000 litres): Fe^{II} (a) 2.6, (b) 1.4; Ba 3.3, 0.7; Ca 24.7, 11.0; Mg 6.6, 1.6; Na 8.6, 13.4; Cl 9.0, 11.0; SO_4 32.4, 18.5; HCO_3 83.1, 38.3%. C. A. SILBERRAD.

Formula of vesuvianite. E. MACHATSCHKI (Z. Krist., 1932, 81, 148—152).—32 analyses of vesuvianite are tabulated and discussed with reference to their mutual discrepancies and the X-ray structure. It is concluded that the author's formula, $X_{19}Y_{13}Z_{18}(O, OH, F)_{76}$, where $X=Ca, Na, K, Mn$; $Y=Al, Fe^{III}, Fe^{II}, Mg, Ti, Zn, Mn$, etc.; and $Z=Si, B$, and to a small extent Al (cf. Zentr. Min. Geol., 1930, A, 284), expresses the normal type better than that of Warren and Modell (cf. A., 1931, 1116).

C. A. SILBERRAD.

Rocks bearing kyanite and sillimanite in Bhandara district, C.P. [India; occurrence of dumortierite]. S. K. CHATTERJEE (Rec. Geol. Surv. India, 1931, 65, 285—305).—Associated usually with kyanite, dumortierite occurs at Mogra and Girola, 15 miles S.E. of Bhandara town: d 3.27, n_a 1.678, n_b 1.685, n_c 1.688; pleochroic lilac and colourless; analysis: SiO_2 29.78, Al_2O_3 63.39, Ti_2O_3 0.18, B_2O_3 5.49, Fe_2O_3 0.26, H_2O+ 0.96, H_2O- 0.04, FeO and MnO trace, total 100.10%; corresponding approx. with $6\frac{1}{2}SiO_2, 8Al_2O_3, B_2O_3, \frac{2}{3}H_2O$ (cf. A., 1903, ii, 158; 1905, ii, 263). In the neighbourhood occur rocks containing one or more of the above-mentioned minerals and tourmaline, rutile, sillimanite, topaz, corundum, roscoelite mica, chlorite, and muscovite, the origin of which by pneumatolytic and hydrothermal metamorphism due to granitic intrusions is suggested. C. A. SILBERRAD.

Calaverite. V. GOLDSCHMIDT, C. PALACHE, and M. PEACOCK (Neues Jahrb. Min., 1931, A, 63, Beil.-Bd., 1—58; Chem. Zentr., 1931, ii, 2442).—A crystallographic study. A. A. ELDRIDGE.

Mineralogy and origin of the natural beach sand concentrates of New South Wales. H. F. WHITWORTH (J. Proc. Roy. Soc. N.S.W., 1931, 65, 59—74).—The natural concentrates of heavy minerals found at many points on the coast of New South Wales consist mainly of zircon, ilmenite, and rutile, the remaining 2—8% comprising several other minerals including minute amounts of Au and platinoid metals. The origin of the concentrates is discussed.

N. H. HARTSHORNE.

Rillensteine. J. D. LAUDERMILK and A. D. WOODFORD (Amer. J. Sci., 1932, [v], 23, 135—154).—Attempted artificial production of rilled limestone leads to the conclusion that the rills are caused by dissolution by H_2CO_3 during occasional rainstorms. Modifications may be caused by cleavage and other cracks. Wind erosion smooths out the rills.

C. W. GIBBY.

Geology of the Big Snowy Mountains, Montana. F. REEVES (U.S. Geol. Surv. Prof. Paper 165, 135—149).—A general study.

N. H. HARTSHORNE.

Geology of the eastern part of the Santa Monica Mountains, Los Angeles County, California. H. W. HOOTS (U.S. Geol. Surv. Prof. Paper 165, 83—134).—An account of the oilfields in this region is included.

N. H. HARTSHORNE.

Lithologic studies of fine-grained upper cretaceous sedimentary rocks of the Black Hills region (N.E. Wyoming). W. W. RUBEY (U.S. Geol. Surv. Prof. Paper 165, 1—54).—A comparative study of the mineralogy, chemical and mechanical composition, density, porosity, fissility, and lamination discloses several relations which throw light on the geological history of the region and perhaps on its oil and gas possibilities.

N. H. HARTSHORNE.

Mineralogy of the silver-lead-zinc deposits of N.S. Wales, with special reference to the Barrier Ranges silver field. G. SMITH (J. Proc. Roy. Soc. N.S. Wales, 1930, 64, 224—263).—The modes of formation of minerals are discussed. C. W. GIBBY.

Geology of the Wellington district, N.S. Wales, with special reference to the origin of the upper Devonian series. A. J. MATHESON (J. Proc. Roy. Soc. N.S. Wales, 1930, 64, 171—190).—Analyses are given.

C. W. GIBBY.

Occurrence of stannite in Spain. Composition. S. PINA DE RUBIES (Anal. Fis. Quim., 1931, 29, 699—705).—A specimen of stannite from Valduerna had the composition Cu_2SnFeS_4 ; the Fe may be partly replaced by Zn. The petrology of the mineral is described.

H. F. GILLBE.

Petrology of the quartz-diorite of Estaca de Vares, Galicia [Spain]. I. P. PONDAL (Anal. Fis. Quim., 1931, 29, 552—555).—The mineral contained SiO_2 64.10, Al_2O_3 15.37, $Fe_2O_3 + FeO$ 4.55%, and smaller quantities of alkalis and alkaline earths, TiO_2 , and P_2O_5 . It consisted principally of plagioclase, biotite, quartz, hornblende, and orthoclase, together with chlorite, apatite, zirconite, and ilmenite.

H. F. GILLBE.

Bauxite deposits in Gorizia. D. COSTA (Giorn. Chim. Ind. Appl., 1931, 13, 564).—Samples of bauxite from large deposits recently discovered in the Forest of Piro, Gorizia, contain: (1) red variety, Al_2O_3 53.04, Fe_2O_3 17.16%; (2) yellowish-brown varieties, Al_2O_3 47.14—63.10, Fe_2O_3 5.37—14.03%. T. H. POPE.

Spectrographic investigation of the distribution of the platinum metals in the minerals of the South African platinum deposits. H. SCHNEIDERHOHN and H. MORITZ (Siebert Festschr., 1931, 257—285).—In the sulphide-pyroxenite zone of the Merensky horizon the Pt metals are all conc. in the sulphide minerals, the concn. being the greater the older is the mineral; no true Pt mineral (sperrylite, cooperite, or stibiopalladinite) is present in the unaltered sulphides, all the Pt metals being in solid solution in the sulphides, especially in Ni pyrites, pyrrhotite, and, to a smaller extent, pentlandite. The pyroxenite itself is practically free from Pt metals. Unaltered dunite contains the Pt metals as native grains between the silicate minerals or as fine inclusions in the chromite, which may contain up to 10—15 g. per metric ton. The individual older silicates, diopside, hortonolite, hyalosiderite, olivine, hornblende, and mica, all contain about 1 g. of Pt per metric ton, whereas the newer silicates, especially plagioclase, are free from Pt. These facts indicate that in the crystallisation of the liquid magmatic rocks the Pt went almost completely into the sulphide portion when S was present in the liquid mass, and when S was absent the Pt crystallised out as free metal associated with chromite; the small quantities of Pt which did not separate in either of these ways were eventually pptd. with older silicates in the pneumatolytic and contact-pneumatolytic phases. The minerals produced by weathering of dunite are free from Pt, whereas in the weathering of the sulphide pyroxenitic ores considerable changes in the Pt distribution occur.

A. R. POWELL.

Examination of rocks in Wood's light. L. ROYER (Bull. Soc. Franç. Min., 1930, 53, 515—518; Chem. Zentr., 1931, ii, 834).—Nepheline, leucite, and sodalite fluoresce red, white, or orange in ultra-violet light; zinc spar shows white fluorescence, whilst willemite does not fluoresce. Galena and anglesite are differentiated by the yellow fluorescence of the latter. The arsenious opal of St. Nectaire does not fluoresce, but phosphoresces after exposure to ultra-violet light. The arsenious limestone of Hamman-Meskoutine shows a white fluorescence and a greenish phosphorescence. Solid and liquid hydrocarbons in rocks can be detected since the latter give a yellow, and the former no, fluorescence. Anthracitic and graphitic can be differentiated from bituminous and carboniferous rocks.

A. A. ELDRIDGE.

Two chlorites (grochauites) of corundum rocks. S. PAVLOVITCH (Bull. Soc. Franç. Min., 1930, 53, 535—538; Chem. Zentr., 1931, ii, 696).—Chlorite from Corundum Hill, Mecon City, N. Carolina, d 2.697, $9SiO_2, 5Al_2O_3, 16MgO, 14H_2O$; grochauite from the Urals, d 2.705, $9SiO_2, 5Al_2O_3, 15MgO, 14H_2O$.

A. A. ELDRIDGE.

Geology and lead ore deposits of Mawson [of Bawzaing, Shan States, Burma]. J. C. BROWN (Rec. Geol. Surv. India, 1931, 65, 394—433).—The ore consists almost entirely of galena and cerussite irregularly distributed in clay in fissures in limestone. The metallic contents are almost pure Pb (0.30% Zn, 8—14 oz. Ag per ton). The origin of the ores is discussed. C. A. SILBERRAD.

Felspar substitute from Vischnevsky Gory, Ural. D. S. BELIANKIN (Zentr. Min. Geol., 1931, A., 190—196; Chem. Zentr., 1931, ii, 834).—"Can-crinite" from Vischnevsky Gory is renamed vischnevite. It is grouped with the hexagonal sodalites and is $3\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{Na}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$; n 1.489.

A. A. ELDRIDGE.

Subterranean oxidation of shale. K. LUTS (Brennstoff-Chem., 1932, 13, 10).—Definite evidence has been found of the oxidation of a deep-lying bed of shale by O_2 present in H_2O which has penetrated to the shale through fissures in the superposed strata and in the shale itself.

A. B. MANNING.

Occurrence of iodine in water and coal; fertiliser experiments with iodine salts. R. WACHE (Mitt. Lab. Preuss. Geolog. Landesanst., 1931, No. 13, 43—52; Chem. Zentr., 1931, ii, 981).—Fellen-berg's method showed various river and spring waters to contain $1.3\text{—}11.2 \times 10^{-6}$ g. I per litre; no regular dependence on other factors (Fe or salt content; geological formation of area, passage through towns, etc.) was observed. On filtration, water supplies lose only about 13% of their I. Brown coal contained 1.35—5.71 mg. I per kg. of dry, ash-free coal; bituminous coal contained 0.9—13 mg. Fertilisation of rye with CaI_2 or $\text{Ca}(\text{IO}_3)_2$ alone in pot experiments showed that about 9% of the I was assimilated; with Na iodobenzoate the percentage was much greater. No effect on the growth was observed, neither were the plants damaged by 2—8 mg. I per 400 g. of soil.

A. A. ELDRIDGE.

Fossil timber from the Sydney Harbour Colliery. R. T. BAKER (J. Proc. Roy. Soc. N.S.W., 1931, 65, 96—111).—The specimen is described and the reason for the presence of CaCO_3 in it is discussed.

N. H. HARTSHORNE.

Pine soils of the sea dunes of Wollin Island. R. H. GANSSEN (Mitt. Forstwirts. Forstwissens., 1931, 422; Proc. Internat. Soc. Soil Sci., 1931, 6, 161).—The process of podsol formation in these areas is traced.

A. G. POLLARD.

Russian studies on soil profiles. J. S. JOFFE (J. Amer. Soc. Agron., 1932, 24, 33—57).—A comprehensive review of the investigations of soil formation and classification in Russia. A. G. POLLARD.

Electrical capacity and conductivity of soil blocks. G. H. CASHEN (J. Agric. Sci., 1932, 22, 145—164).—Changes in the equiv. parallel capacity of soils with decreasing H_2O content were of similar general type for all soils examined, and indicated four characteristic moisture contents. Of these, one corresponds with Atterberg's "Schwindungsgrenze" (moisture content at which air enters the pores), and another with his "Ausrollgrenze" (lower plastic limit). A third may be related to the shrinkage and cohesion of soils at low H_2O contents.

A. G. POLLARD.

Soils of the Nile and Gash. V, VI. P. VAGELER and F. ALTEN (Z. Pflanz. Dung., 1932, 23 A, 149—207, 208—339).—Further investigations of the composition, structure, H_2O relationships, and nutrient vals. of these soils are recorded. A. G. POLLARD.

Brown steppe soils in the Thessalian plain. N. LIATSIKAS (Compt. rend., 1932, 194, 308—311).—Mechanical and chemical analyses are given of a soil from the Thessalian plain having a low humus and high CaCO_3 content and closely resembling the brown steppe soils.

W. O. KERMAK.

Organic Chemistry.

[Preparation of hydrocarbons and alcohols by reduction of fats under high pressure.] W. SCHRAUTH (Ber., 1932, 65, [B], 93—95; cf. A., 1931, 932).—A question of priority (cf. Schmidt, A., 1931, 1268). H. WREN.

Isoprene and caoutchouc. XXXVII. Homologous polypranes. H. STAUDINGER and E. O. LEUPOLD (Helv. Chim. Acta, 1932, 15, 221—230).—The val. of K_m (for polymerised hydrocarbons with branched chains) in the relationship $\eta_{sp}/c = K_m M$, where η_{sp} = viscosity in C_6H_6 or tetrahydronaphthalene and c is the concn. of a molar solution of the unit hydrocarbon (C_5H_{10} for polypranes, whence $c = 7\%$ solution) is approx. const. (3.6×10^{-4}). A closer relationship between η and M is evidenced when "chain equiv." solutions are used (chain equiv. wt. = mol. wt./no. of C atoms in the unbranched chain = n , equiv. solution = $0.1n\%$). Such solutions of various hydrocarbons with chain mols. of the same mol. wt. have the same sp. viscosity in any given solvent, i.e.,

$\eta_{sp}(\text{eqt.}) = K_{\text{eqt.}} \times M$, $k_{\text{eqt.}}$ being a const. (0.85×10^{-4} in tetrahydronaphthalene, 1.0×10^{-4} in C_6H_6) for all hydrocarbons irrespective of the nature of the side-chain. Hence it is possible to calculate either η_{sp} or n in a 1.4% solution from the relationship $\eta_{sp} = k_{\text{eqt.}} \times 14 \times n\% = (\text{in tetrahydronaphthalene}) 1.2n \times 10^{-3}$. These conclusions are confirmed by determination of η with various polymerised hydrocarbons of known mol. wt. (e.g., di- and tetra-bixin, hexahydrosqualene), and the mol. wt. of hydrocaoutchouc is thus found to be about 50,000. This and other evidence based on the serial gradation of other physical properties (solubility, b.p., d) of chain-polymerised hydrocarbons with increasing mol. wt. fails to support the micelle theory for solutions of such polymerides. J. W. BAKER.

Thermal chlorination of methane. J. MASON (Nature, 1932, 129, 97—98).—The 4 H atoms of CH_4 are not, apparently, simultaneously and equally available for chlorination, but after substitution of 1 H the remainder appear to be equally available (cf. A., 1931, 1267, 1372). L. S. THEOBALD.

Action of benzoyl peroxide on triethylmethane [γ -ethylpentane]. J. BOESEKEN and A. J. WILDSCHUT (Rec. trav. chim., 1932, 51, 168—173).— $\text{C}_6\text{H}_5\text{OH}$ (best prepared from MgEtBr and $\text{Et}\cdot\text{CO}_2\text{Et}$) is dehydrated by boiling with a little conc. H_2SO_4 and the resulting γ -ethyl- Δ^2 -pentene hydrogenated (Ni) at 150°/90 atm. to γ -ethylpentane (I). When (I) is boiled with Bz_2O_2 , CO_2 , BzOH , (probably) heptylbenzene and a heptyl benzoate, and (mainly) a non-distillable viscous product are formed. A *tert*-alcohol is not produced (cf. A., 1930, 316). H. BURTON.

Synthesis and crystal spacings of certain long-chain paraffins, ketones, and secondary alcohols. S. H. PIPER, A. C. CHIBNALL, S. J. HOPKINS, A. POLLARD, J. A. B. SMITH, and E. F. WILLIAMS (Biochem. J., 1931, 25, 2072—2094).—The following have been synthesised and their crystal spacings determined: tricosan- μ -one (laurone), nonacosan- α -one, and hentriacontan- π -one (palmitone) from the Ba salts of the fatty acids; heptacosan- ξ -one (myristone) and pentatriacontan- σ -one (stearone) from the fatty acids; by Channon and Chibnall's method (A., 1929, 729) nonacosan- μ -one, m. p. 74.5° (oxime, m. p. 47—47.5°); nonacosan- κ -one, m. p. 74.3—74.8° (oxime, m. p. 49.5—50°); nonacosan- ι -one, m. p. 73.5—74.2° (oxime, m. p. 48.5—49°); by reduction of the ketones with Na nonacosan- ω -ol, m. p. 83.6—83.8°, setting point 83° (acetate, m. p. 50.5—51°); nonacosan- ξ -ol, m. p. 79—79.3°, setting point 78.4° (acetate, m. p. 41—42°); nonacosan- μ -ol, m. p. 74—74.5°, setting point 73° (acetate, m. p. 44—45°); nonacosan- κ -ol, m. p. 74.8—75°, setting point 74.2° (acetate, m. p. 45—45.5°); nonacosan- ι -ol, m. p. 75.3—75.6°, setting point 74.8° (acetate, m. p. 44.5—45°). Clemmensen reduction of the corresponding ketones gave *n*-nonacosane, m. p. 62.7—63.0°, *n*-heptacosane, *n*-hentriacontane, and *n*-pentatriacontane; Gascard's method gave *n*-octacosane, m. p. 61.4—61.5°, setting point 61.1°; *n*-dotriacontane, m. p. 69.5—69.7°, setting point 69.3°; *n*-hexatriacontane, m. p. 75.7—75.9°, setting point 75.4°; *n*-hexacosane, m. p. 56.4—56.6°, setting point 56.1°; *n*-triacontane, m. p. 65.6—65.8°, setting point 65.5°; and *n*-tetratriacontane, m. p. 72.5—72.8°, setting point 72.4°. If the m. p. of a pure paraffin is determined in the way described it is possible to determine two transition temp. at which a visible change of structure occurs. The lower of these is markedly affected by impurities. The m. p., transition points, and crystal spacings of a comprehensive series of mixed paraffins have been determined. Evidence which makes it possible to suggest the composition of a mixture of paraffins as obtained in biochemical research is advanced. S. S. ZILVA.

Velocity of polymerisation of hydrocarbons. E. N. GAPON.—See this vol., 232, 233.

Conversion of butenes into liquid hydrocarbons. A. MAILHE and RENAUDIE (Ann. Office Nat. Combust. liq., 1931, 6, 79—81; Chem. Zentr., 1931, ii, 1270).—In presence of SiO_2 gel at 650—700° Δ^2 -butene forms liquid unsaturated hydrocarbons and C_6H_6 , PhMe, and *m*-xylene, together with propylene and CH_4 (40% each of gases); "methylbutene" forms rather less CH_4 . Δ^3 -Butene at a higher temp.

gives more C_6H_6 and PhMe, together with C_{10}H_8 and anthracene. A. A. ELDRIDGE.

Allylic rearrangement of crotyl bromide and magnesium crotyl bromide. W. G. YOUNG and A. N. PRATER (J. Amer. Chem. Soc., 1932, 54, 404—405).—Crotyl bromide with Zn and dil. EtOH, or Mg crotyl bromide with dil. acid, gives a mixture of Δ^1 - and Δ^2 -butenes, containing approx. 10% of the former, the presence of which must be due to an allylic rearrangement. C. J. WEST (b).

Formation of methyl alcohol and formaldehyde in the slow combustion of methane at high pressures. D. M. NEWITT and A. E. HAFFNER.—See this vol., 232.

Colorimetric determination of methyl alcohol. Interference of dimethyl ether. B. F. DODGE (Ind. Eng. Chem. [Anal.], 1932, 4, 23—24).—The determination of MeOH by oxidising to CH_2O with KMnO_4 and applying a modified Schiff's reagent is inaccurate when Me_2O is also present. The error is such that 1 g. of Me_2O is equiv. to 0.93 g. of MeOH. E. S. HEDGES.

Determination of small amounts of ethyl and butyl alcohols. M. J. JOHNSON (Ind. Eng. Chem. [Anal.], 1932, 4, 20—22).—The alcohols are oxidised by a mixture of 3*N*- $\text{K}_2\text{Cr}_2\text{O}_7$ and 10*N*- H_2SO_4 , and the acids produced are distilled and determined by titration with $\text{Ba}(\text{OH})_2$ in the presence of phenol-red. The procedure is suitable for determining 3—15 mg. of EtOH or BuOH or their mixtures. E. S. HEDGES.

Alkyl bromomethyl ethers. C. M. BLAIR and H. R. HENZE (J. Amer. Chem. Soc., 1932, 54, 399—401).—The following alkyl bromomethyl ethers are prepared by saturating a cooled mixture of 75 c.c. of aq. CH_2O and 1 mol. of the appropriate alcohol with HBr: Pr, b. p. 48°/20 mm., 133.3°/747.5 mm.; Bu, b. p. 57.2°/20 mm., 159°/749.5 mm., and amyl, b. p. 83°/15 mm., 178—180° (decomp.)/748.3 mm. The stability of the ethers decreases with increasing mol. wt. C. J. WEST (b).

Cyclic esters of sulphuric acid. II. Constitution of methylene and glyoxal sulphates, and the reaction of methylene sulphate with tertiary bases. W. BAKER and (in part) F. B. FIELD (J.C.S., 1932, 86—91; cf. A., 1931, 1047).—The following observations are not in accordance with the structure

CH_2SO_2 (Delepine, A., 1900, i, 130) for methylene sulphate (I): (a) CH_2 ethers of simple compounds usually have lower m. p. and b. p. than the Me_2 ethers; (b) ethylene sulphate, dimorphous forms both with m. p. 99°, and trimethylene sulphate, m. p. 63°, prepared from Ag_2SO_4 and the appropriate dibromide in xylene, possess normal mol. wts. and are readily sol. in org. solvents; (c) the mol. wt. of (I) in C_6H_6 is about 211. (I) is, therefore, $\text{SO}_2\text{CH}_2\text{SO}_2$.

Glyoxal sulphate is considered to be $\text{SO}_2\text{CH}(\text{O})\text{CH}(\text{O})\text{SO}_2$ and not $(\text{SO}_2\text{CH}(\text{O})\text{CH}(\text{O}))_2$; it reacts with EtOH and $(\text{CH}_2\cdot\text{OH})_2$ to give glyoxal Et₄ acetal and 2:3-ethylenedioxydioxan, m. p.

137°, respectively. The last-named compound is identical with the naphtho-1:4:5:8-dioxan, m. p. 133—136°, of Boeseken *et al.* (A., 1931, 1162; cf. Donciu, A., 1895, i, 319).

(I) and aq. pyridine give *pyridine methylenosulphate*, $C_6H_5N \cdot CH_2 \cdot O \cdot SO_2 \cdot O$, m. p. about 228° (decomp.), hydrolysed by prolonged heating with H_2O to pyridine, CH_2O , and H_2SO_4 . *Quinoline*, m. p. 260—265° (decomp.) (darkens at about 230°), and *NPhMe*, m. p. about 168—169° (decomp.), *methylenosulphates* are prepared; the latter is stable to hot dil. NaOH.

The following m. p. are recorded: ethylene glycol $:CH_2$, -95°, and Me_2 , -58°, ethers; trimethylene glycol $:CH_2$, -45°, and Me_2 , -82° (b. p. 106°/753 mm.), ethers; pyrocatechol $:CH_2$, ether, -18°.

H. BURTON.

Crystalline sodium α -glycerophosphate. CHARPENTIER and BOCQUET (Compt. rend., 1932, 194, 104—107).—Na α -glycerophosphate ($+6H_2O$) is isolated from the technical mother-liquors after removal of the β -salt, and identified by resolution with quinine and conversion into an active Me_3 derivative (cf. A., 1926, 383, 818). An active Li H salt is obtained (in solution) from the strychnine salt and LiI, and is converted into active Me_3 and $Na_2 Me_2$ ($[\alpha]_D -7.2^\circ$) derivatives. A product of the same nature is obtained by seeding the mixture of glycerophosphates prepared from allyl phosphate.

H. A. PIGGOTT.

Compounds of metallic salts with organic sulphides. P. C. RAY (J. Indian Chem. Soc., 1931, 8, 537—540).—Presidential address. J. W. BAKER.

β -Hydroxyethylsulphonium derivatives. V. ETTTEL and A. KOHLIK (Coll. Czech. Chem. Comm., 1931, 3, 583—592).— β -Hydroxydiethyl sulphide (I) and an excess of EtCl at 100° (bath) give the very hygroscopic β -hydroxytriethylsulphonium chloride; the bromide and iodide, m. p. 97°, are prepared similarly from (I) or from Et_3S and $OH \cdot CH_2 \cdot CH_2Br$ (I). $\beta\beta'$ -Dihydroxytriethylsulphonium chloride, m. p. 119°, bromide, m. p. 85°, and iodide, decomp. readily, are prepared from (I) and the requisite halogenohydrin, whilst tri- β -hydroxyethylsulphonium chloride (II), m. p. 127°, bromide, m. p. 104°, and iodide, decomp. 65°, are obtained similarly from $\beta\beta'$ -dihydroxydiethyl sulphide (III). Unstable sulphonium hydroxides are obtained from the above iodides and AgOH. The hydroxyethylsulphonium halides are not affected by HCl, whilst (III) and HCl give sulphonium chlorides as secondary products (cf. Davies and Oxford, A., 1931, 463). (II) and $SOCl_2$ give tri- β -chloroethylsulphonium chloride, decomp. above 100°, which is non-vesicant.

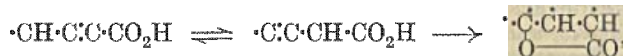
H. BURTON.

Conversion of d - β -octyl chloroformate into dextrorotatory β -chloro-octane and action of the chlorides and oxychloride of phosphorus on d - β -octanol. A. H. J. HOUSSA and H. PHILLIPS (J.C.S., 1932, 108—114).—When d - β -octyl chloroformate (I) is heated at 130° for 14 hr. CO_2 and a dextrorotatory β -chloro-octane (II), $\alpha_{365}^{20} +17.5^\circ$ ($l=1$), are formed. (II) is probably produced without inversion of configuration; it is assumed that during the decomp. the octet of the *asym.*-C atom remains intact, and if the optically active radical becomes free

at any stage, it must exist as the anion $C_6H_{13} \cdot CHMe$, which subsequently combines with Cl^\ominus . The previously proposed (A., 1930, 61) mechanism for the production of d - β -octyl acetate from (I) and KOAc is substantiated by the observation that (I) and MeCOSK give COS and β -octyl acetate, -1.78° ($l=0.25$). The action of PCl_3 , PCl_5 , and $POCl_3$ on d - β -octanol in Et₂O in presence and absence of $ZnCl_2$ or pyridine is investigated; levorotatory β -chloro-octane is produced in all cases but in varying amount and with varying rotation. In presence of pyridine, only PCl_5 gives an appreciable quantity of the chloro-octane; with PCl_3 , the main product is di- β -octyl H phosphite, b. p. 116—118°/ <0.1 mm., $\alpha_{365}^{20} +18.84^\circ$ ($l=1$), together with a little β -octyl H_2 phosphite, whilst β -octyl H_2 phosphate (mainly) and di- β -octyl H phosphate are formed using PCl_4 or $POCl_3$.

H. BURTON.

Olefinic acids. VI. Lactonisation and allied additive reactions. I. System $\alpha\beta$ -acid- $\beta\gamma$ -acid- γ -lactone. R. P. LINSTAD (J.C.S., 1932, 115—129).—Contrary to Fittig's statements (A., 1893, i, 189; 1895, i, 204), $\alpha\beta$ -unsaturated (e.g., *n*- Δ^6 -hexenoic) acids can be converted into γ -lactones by boiling 50% H_2SO_4 . The production of γ -lactones from $\alpha\beta$ - and $\beta\gamma$ -acids is represented by the scheme



and three (possibly four) types of acids are distinguished, viz., (i) lactonisation much faster than tautomeric change but both processes slow (acids with one γ - and no β -alkyl group), (ii) lactonisation fast, tautomeric change slow ($\gamma\gamma$ -dialkylated acids), (iii) tautomeric change faster than lactonisation (acids with one γ - and one β -alkyl group), and (iv) (?) tautomeric change fast and irreversible in the direction $\beta\gamma \rightarrow \alpha\beta$, no lactonisation being possible (acids without γ -substituents). The rates of lactonisation of Δ^6 - and Δ^8 -*n*- [type (i)] and of Δ^6 - and Δ^8 -*iso*- [type (ii)] -hexenoic acids are studied. Both Δ^6 -acids are lactonised almost completely by boiling 50% H_2SO_4 in 1 hr., but with cold 60% H_2SO_4 , lactonisation is inappreciable. The $\beta\gamma$ -acids are, however, lactonised (under suitable conditions) by cold 60% H_2SO_4 , and mixtures of the $\alpha\beta$ - and $\beta\gamma$ -acids can be analysed by determination of the acid-lactone content of the mixture after treatment with 60% H_2SO_4 ; this method is, of course, limited to acids of types (i) and (ii). The production of a γ -lactone from an $\alpha\beta$ -acid shows that Fittig's method of analysis of mixtures of $\alpha\beta$ - and $\beta\gamma$ -acids is useless. Δ^6 -*iso*-Hexenoic acid, m. p. -22° (corr.), is converted by prolonged boiling into the γ -lactone. *n*- and *iso*-Hexolactones could not be isomerised (by boiling or treatment with 60% H_2SO_4) to unsaturated acids.

Pyroterebic acid, m. p. -4.5° (corr.), as usually prepared from terebic or Δ^6 -*iso*hexenoic acid, is always contaminated with γ -*iso*hexolactone. A lactone-free specimen of the acid is equilibrated by alkali to a mixture containing 22—23% of the $\alpha\beta$ -acid [and not 5% as previously reported (A., 1928, 1214)], a val. in agreement with those found for the higher homologues (A., 1930, 1405).

H. BURTON.

Selective hydrogenation of unsaturated fatty acids. S. UENO, T. YUKIMORI, and S. UEDA (J. Soc. Chem. Ind., Japan, 1931, 34, 481—483B).—Mixtures of Me clupanodonate and oleate (containing linoleate and linolenate?) were hydrogenated over a Ni catalyst at 60°/1 atm. and the liquid fatty acids (Twitchell) of the products were separated and examined for thiocyanogen val., bromides, etc. Selective hydrogenation was apparent; nevertheless, at high pressure (as in the case of a Pt catalyst at atm. pressure) some of the less unsaturated acids were hardened together with the highly unsaturated acids. E. LEWKOWITSCH.

Unsaturated fatty acids and their derivatives. V. Constitution of linolenic acid (linseed oil). Y. INOUE and B. SUZUKI. VI. Configuration of oleo- and elaido-dibromostearic acid. T. MARUYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 375—378, 379—382).—V. Oxidation by Armstrong and Hilditch's method (A., 1925, i, 355) of Me linolenate (by debromination of hexabromostearic acid from linseed oil) affords propionic, azelaic, suberic, oxalic, and malonic acids. Partial oxidation with cold KMnO_4 yields linusic and isolinusic acids. Hydrogenation by methods described previously (B., 1930, 956; A., 1931, 601) has given the following results: from 1/3 hydrogenated, by bromination, tetrabromostearic acid, by oxidation oxalic, malonic, hexoic, sativic, and azelaic acids, and no suberic acid; 2/3 hydrogenated, by oxidation, nonoic, azelaic, and no suberic acid, and oleodihydroxystearic with a trace of stearic acid; complete hydrogenation, stearic acid only. The results indicate that linoleic, oleic, and stearic acids are formed successively.

VI. Debromination with KOH-EtOH at room temp. of oleo- and elaido-dibromostearic acids gives respectively Δ^1-0 - (I) (oxidised to octoic and α -bromosebacic acids) and Δ^9-0 - or - ι -bromo-octadecenoic acids (II) (oxidised to nonoic and azelaic acids). Further debromination occurs only at higher temp., (I) losing HBr at 80—100° between C atoms η and θ , forming $\Delta^{\eta\theta}$ -octadecadienoic acid and (II) at 170° giving stearolic acid. F. R. SHAW.

Determination of pyruvic acid and preparation of lithium pyruvate. W. B. WENDEL (J. Biol. Chem., 1932, 94, 717—725).—Conditions are described for the rapid and apparently complete reduction of pyruvic to lactic acid by Zn-Cu in H_2SO_4 and determination of lactic acid by the Friedemann-Cotonin-Schaffer method. *Li pyruvate* is described.

F. O. HOWITT.

Addition of sodium enol-alkylmalonic ester to phenyl styryl ketone. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1932, 54, 407—409; cf. A., 1931, 67, 803).—Polemical with Holden and Lapworth (A., 1931, 1272). C. J. WEST (b).

Constitution of maleic acid. *l*-Menthyl and *l*-bornyl esters of maleic and citraconic acids. Alkaloidal salts of methyl hydrogen and cyclohexyl hydrogen maleates and of maleamic acid. A. WASSERMANN (Annalen, 1932, 492, 266—277).—The previously described *l*-menthyl H maleate of m. p. 56° (A., 1931, 1160) is shown to be a mol. (1 : 1) compound (I) of *l*-menthyl H maleate (II), m. p. 85°,

and *l*-menthyl H fumarate (III), m. p. 49°. (II) rearranges partly into (III) when heated at 155° for 4–5 hr.; the mixture affords (I). (I) is also obtained from (II) and (III) in pentane when the solution is cooled at -10° for 7 hr.; cooling at -10° for 2–5 hr. gives mixed crystals. *l*-Borneol and maleic anhydride at 100°/1 hr. or 155°/4 hr. afford *l*-bornyl H maleate, m. p. 50°, $[\alpha]_D^{25} -56.9^\circ$ in CHCl_3 ; at 155°/6–5 hr., *l*-bornyl H fumarate is the sole product. *l*-Bornyl maleate has m. p. 81°, $[\alpha]_D^{25} -55^\circ$ in EtOH , -61° in CHCl_3 . The *l*-bornyl H citraconates, m. p. 82.5° and 150°, of Hartwall (A., 1903, ii, 3), now obtained with m. p. 86° (IV) and 152° (V), respectively, are not stereoisomerides. (V) is reduced catalytically (PtO_2) in EtOH to *l*-bornyl H methylsuccinate, m. p. 73° $[\alpha]_D^{25} -34^\circ$ in EtOH , also obtained by similar reduction of *l*-bornyl H mesaconate (VI), m. p. 106° [cf. Hartwall (*loc. cit.*), whose ester of m. p. 116.5° could not be prepared], whilst (IV) is reduced to an oily ester. (V) and Br in Et_2O in sunlight give a compound, m. p. 106° [apparently not (VI)], whilst (IV) similarly affords an oil.

The morphine salt ($+\text{H}_2\text{O}$), decomp. 185—190°, $[\alpha]_D^{25} -86.9^\circ$ in H_2O , of Me H maleate, the quinine salt, softens at 85°, melts to a turbid liquid at 100°, and clears at 120°, $[\alpha]_D^{25} -121.2^\circ$, of cyclohexyl H maleate, m. p. 64°, and the brucine salt, amorphous, $[\alpha]_D^{25} -36.5^\circ$ to -46.2° in H_2O , of maleamic acid (NH_4 salt, decomp. about 140°) are prepared. The H esters regenerated from the alkaloid salts are optically inactive, and thus afford no evidence for the asymmetric structure of the H maleates.

H. BURTON.

Modified Curtius reaction. V. Reaction with saturated dicarboxylic acids. C. NAEGELI and P. LENDORFF (Helv. Chim. Acta, 1932, 15, 49—59).—By methods previously described (A., 1929, 540, 1456) sebacyl chloride is converted directly into octamethylenediamine (52% yield), its hydrochloride (76% yield), and its Ac derivative, m. p. 121—122° (73% yield), and adipyl chloride into tetramethylenediamine hydrochloride (68% yield), whilst succinyl chloride affords ethylenediamine hydrochloride (75% yield), but the action of AcOH on the carbimide is abnormal in this case, giving not the Ac_2 derivative, but the cyclic compound (I), m. p. 122°: $\text{CH}_2\text{N}^+\text{CO} \rightarrow \text{CH}_2\text{N}^+\text{CO}$

$\text{CH}_2\text{N}^+\text{Ac} > \text{CO} \rightarrow \text{CH}_2\text{N}^+\text{Ac} > \text{CO}$ (I), and a substance, $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_2$, m. p. 172°. Lauryl chloride is converted in AcOH into undecylacetamide (17%) and *s*-diundecylcarbamide, the main product being lauric acid (77%) obtained thus: $\text{C}_{11}\text{H}_{23}\cdot\text{COCl} + \text{AcOH} \rightleftharpoons \text{C}_{11}\text{H}_{23}\cdot\text{CO}_2\text{H} + \text{AcCl}$, NHMeAc also being formed.

J. W. BAKER.

Structure of glutamic acids and esters. II. α -Substituted derivatives of β -methylglutamic acid. G. A. R. KON and E. M. WATSON (J.C.S., 1932, 1—11).—Ozonolysis experiments show that Et α - β -dimethylglutamate prepared from Et isodehydracetate by Feist's modification (A., 1922, i, 521) of Bland and Thorpe's method (J.C.S., 1912, 101, 1567), is a mixture consisting mostly of the $\beta\gamma$ -isomeride; Et potassio- β -methylglutamate and MeI in Et_2O give a product containing even more of the $\beta\gamma$ -form.

The Ag salt of the less fusible form of dimethylglutaconic acid (*loc. cit.*) and EtI in Et₂O afford, however, nearly pure Et $\alpha\beta$ -dimethyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylate, b. p. 141°/18 mm. (ozonolysis products, CH₃Ac·CO₂Et, Ac·CO₂Et, and traces of H₂C=O and CHMeAc·CO₂Et). The "labile" (? *trans*- Δ^2 -form) $\alpha\beta$ -dimethylglutaconic acid, m. p. 103°, has not yet been obtained in sufficient quantity for further investigation.

The "normal" form, m. p. 148°, of α -benzyl- β -methylglutaconic acid (I) (J.C.S., 1912, 101, 1740) is esterified (Ag salt method) to Et *cis*- α -benzyl- β -methyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylate (II) [ozonolysis products, CH₃Ac·CO₂Et and Et phenylpyruvate (*semicarbazone*, m. p. 159—160°], whilst the "labile" form, m. p. 134°, of (I) similarly gives Et *trans*- α -benzyl- β -methyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylate (III) (ozonolysis products, CH₃Ph·CHAc·CO₂Et and traces of CH₃Ac·CO₂Et and Bz·CO₂Et). Et α -benzyl- β -methylglutaconate, prepared essentially by Bland and Thorpe's method, contains approx. equal amounts of (II) and (III). Successive treatment of (II) or (III) with KOEt (in Et₂O) and dry BzOH gives a mixture of (II) and the Et ester of α -phenyl- γ -methyl- Δ^2 -butene- $\beta\delta$ -dicarboxylic acid (α -benzylidene- β -methylglutaric acid), m. p. 173°; this acid is not isomerised by alkali under conditions which cause interconversion of the *cis*- $\alpha\beta$ - and *trans*- $\beta\gamma$ -acids. The "normal" and "labile" forms of β -methyl- α -ethylglutaconic acid are similarly shown to be *cis*- β -methyl- α -ethyl- Δ^2 - and *trans*- β -methyl- α -ethyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylic acids, respectively. Et *trans*- β -methylglutaconate is ethylated (EtI on K derivative) to the Et ester of (IV), whilst Et *cis*- β -methylglutaconate similarly affords a new Et β -methyl- α -ethyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylate, b. p. 146°/22 mm., from which a solid acid has not yet been obtained.

H. BURTON.

Dilactylic acids. M. GODCHOT and P. VIELES (Compt. rend., 1931, 193, 1430—1432).—*dl*-Dilactylic acid, m. p. 112—113° (cf. A., 1907, i, 471), and Ac₂O give the anhydride, b. p. 110—111°/13 mm., hydrolysed to the same acid, but the *meso*-acid, m. p. 73°, does not react with Ac₂O. The Et ester yields with aq. NH₃ the dilactylamides (*dl*-, less sol., m. p. 183°; *meso*-, m. p. 135°); each is hydrolysed by *N*-H₂SO₄ to the corresponding acid, but with 10% NaOH each gives the *dl*-acid, which may also be obtained by the action of NaOH on the *meso*-acid. Each amide is converted by NH₃ at 200° into the same imide, m. p. 122°. Anilides (*dl*-, m. p. 168°; *meso*-, m. p. 120°) and *p*-toluidides (*dl*-, m. p. 179—180°; *meso*-, m. p. 147°) are prepared from the Et ester and are hydrolysed by NaOH to the *dl*-acid only, due to the greater stability of this acid.

F. R. SHAW.

Dehydration temperature of citric acid. F. PERCIABOSCO (Atti III Cong. Naz. Chim. pura appl., 1929, 509—512; Chem. Zentr., 1931, ii, 220).—Powdered citric acid is practically dehydrated in 8 hr. at 70°; at higher temp. slight decomp. and discoloration appear. Anhyd. citric acid can be prepared by crystallisation of the conc. solution at 60° in vac., or at 100° at atm. pressure.

A. A. ELDRIDGE.

Nature of humic acid, the chief constituent of brown coal. W. FUCHS (Ges. Abhandl. Kennt.

Kohle, 1930, 9, 176—181; Chem. Zentr., 1931, ii, 1657).—Humic acid, C₆₉H₅₂O₃₀, contains 4 CO₂H, 4 OH, one CH₃·CO, and one CO group. The formation of peat is attributed principally to the action of enzymes.

A. A. ELDRIDGE.

Constitution of Schiff's bases. K. VON AUWERS and H. WUNDERLING (Ber., 1932, 65, [B], 70—79; cf. Short and Watt, A., 1930, 1571).—Aldehydes and ketones, R·CO·CH₂Alk (R=an aliphatic or aromatic, substituted or unsubstituted hydrocarbon residue, or H, and a H atom of the CH₂ or methenyl group can be replaced), afford true Schiff's bases which behave as aldimines and ketimines and function as enamines only to a minor extent during certain transformations. Derivatives of the compounds R·CO·CH₂Ar are Schiff's bases of the type R·C(NR')·CH₂Ar which show no tendency towards transformation; the isomeric compounds R·C(NHR')·CHAr obtained in other manners are also stable, so that imine and enamine forms are equally justified. When a CH₂ or methenyl group with mobile H is vicinal to the C:NR group and the possibility of forming a conjugated system exists, enamines are formed which, under certain conditions, can function as ketimines. These conditions are fulfilled by $\alpha\gamma$ -diketones, β -ketonic esters, and α -cyano-ketones. Ph cannot replace the latter radical, since it does not render the H atom sufficiently mobile. Spectroscopic data are recorded for the following compounds: *isobutaldanil*, *trimethylacetaldanil*, *acetoneanil*, *methylisopropenylaniline*, *benzylidenebenzylamine*, *benzylidene- α -phenylethylamine*, α -phenylethylamine, *benzylidene- β -phenylethylamine*, β -phenylethylamine, *benzylideneisoamylamine*, *acetophenonebenzylimine*, *isoamylidenebenzylamine*, b. p. 112—114°/11 mm., from benzylamine and *isovaleraldehyde* at room temp., *benzylidene-*p*-anisidine*, *p-anisylideneaniline*, *acetophenoneanil*, *cinnamylideneethylamine*, *Et styrylcarbamate*, β -phenylpropylidene-*isoamylamine*, b. p. 138—141°/13 mm. H. WREN.

Oxidation of acetaldehyde. W. H. HATCHER, E. W. R. STEACIE, and F. HOWLAND (Canad. J. Res., 1931, 5, 648—650).—MeCHO with O₂ or air rapidly gives a substance which in H₂O has the properties of a per-acid.

R. S. CAHN.

Carbon rings. XVIII. Comparison of the velocity of reaction of cyclic and analogous aliphatic ketones with hydroxylamine. L. RUZICKA and J. B. BUIJS (Helv. Chim. Acta, 1932, 15, 8—17).—The % oxime formation in a given time and the bimol. velocity coeff. have been determined for a series of cyclic ketones containing 3—8 and 15 or 16 C atoms by determination of the excess NH₂OH by titration with 0.03*N*-I at *p*_H 7.5. The results, together with those of Petrenko-Kritschenko (A., 1906, ii, 341), show that % oxime formation (1 hr.) with aliphatic Me ketones (I) and with isomeric ketones with the CO group in the middle of the chain (II) is almost unaffected by the no. of C atoms in the mol., (I) being consistently > (II) (e.g., COMePr² 75%; COEt₂ 44%), but with the cyclic ketones (CH₂)_n>CO, the val. approximates to that of (I) when *n*=4 (77%), reaches a max. in *cyclohexanone* (*n*=5, 98%), falls rapidly almost to the val. of (II) at *n*=7 (40%), whilst *cyclopentadecanone* (*n*=14; 70%) gives the

same val. as Me tetradecyl ketone. Although duplicate results obtained with the same ketone and NH_2OH solutions are concordant, small unexplained differences ($>$ experimental error) are observed in the vals. obtained when different solutions of the reagents are used. J. W. BAKER.

Formation of acetone by catalytic decomposition of acetic acid. G. MALQUORI.—See this vol., 235.

***n*-Propyl *n*-amyl ketone.** P. KARRER, A. WATTSTEIN, W. FROWIS, and R. MORF (Helv. Chim. Acta, 1932, 15, 231—235).—Contrary to Bryant and Clemo (A., 1931, 1399) this ketone prepared either by Bouveault and Locquin's method (A., 1905, i, 18) or by ZnPr^{I} on *n*-hexoyl chloride [synthesised thus: $\text{Bu}^{\text{I}}\text{Br} + \text{CHNa}(\text{CO}_2\text{Et})_2 \longrightarrow \text{CHBu}^{\text{I}}(\text{CO}_2\text{Et})_2 \longrightarrow \text{C}_6\text{H}_{11}\cdot\text{CO}_2\text{H}$] is analytically pure, and the semicarbazone, m. p. 65—66° (const.; correct analysis), of either specimen gives no m. p. depression with that of the ketone from lupinine, all having identical X-ray spectra. The m. p. 73—74° of the former authors is unexplained. Finally all three specimens of the ketone give identical *p*-nitrophenylhydrazones. J. W. BAKER.

Partition principle as applied to the structure of enolic sodium derivatives of $\alpha\gamma$ -diketones and β -keto-esters. II. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1932, 54, 387—397; cf. A., 1931, 1035).—The action of ClCO_2Et on Et γ -ketobutane- $\alpha\alpha\beta$ -tricarboxylate (I), m. p. 34°, further demonstrates the greater reaction velocity of the Na enol malonic ester group as compared with the Na enol acetoacetic ester group, which is again shown to be a function of the degree of neutralisation of the reactive element (Na) in that group. A solution of (I) in MeOH contains 0.3% of enol; its behaviour toward NaOH indicates that the pure enolic form is exceedingly labile even at temp. below 0°. (I) and ClCO_2Et in EtONa give Et γ -ketobutane- $\alpha\alpha\beta$ -tetracarboxylate (II), b. p. 182°/2 mm. (phenylhydrazone, m. p. 104°), also prepared from $\text{CMe}(\text{ONa})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ and $\text{CBr}(\text{CO}_2\text{Et})_3$. Et γ -ketobutane- $\alpha\alpha\beta$ -tetracarboxylate, b. p. 175°/2 mm., obtained from AcCl and the Na enol of Et ethane- $\alpha\alpha\beta$ -tetracarboxylate, with $\text{NH}_3\cdot\text{NHPh}$ gives $\text{NHAc}\cdot\text{NHPh}$ and $[\text{CH}(\text{CO}_2\text{Et})_2]_2$. (I) and ClCO_2Et in pyridine give a liquid, b. p. 182—184°/2 mm., which is apparently a mixture (A) of approx. equal amounts of $\text{CMe}(\text{O}\cdot\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}(\text{CO}_2\text{Et})_2$ and (II); A and $\text{NHPh}\cdot\text{NH}_3$ in Et_2O afford the phenylhydrazones of (I) and (II) and $\text{NHPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$. (II) shows no enol content; the variation in enolisation in these and in similarly constituted esters is opposed to the "Claisen rule." The action of H_2 in presence of a Pt oxide catalyst on Et *O*-carbethoxyacetate, *O*-carbethoxyacetomalonnate, *O*-acetylacetomalonnate, acetylmethanetricarboxylate, and methanetetracarboxylate shows that with increase in the no. of acyl groups about the ethylenic C atoms, reduction proceeds with difficulty or not at all. The facility of catalytic reduction of ethylenic compounds with reference to structure is discussed.

C. J. WEST (b).

Method for the identification and determination of the 6-hydroxyl group in glucose. J. W. H.

OLDHAM and J. K. RUTHERFORD (J. Amer. Chem. Soc., 1932, 54, 366—378).—The OH group on C_6 of glucose can be identified (when not already substituted) by conversion of the sugar into the corresponding glucoside, converting the residual OH into $\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ -*p* groups, and heating the product with NaI in COMe_2 at 100° (whereby the $\text{C}_6\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ -*p* group is replaced quantitatively by I). Determination of I in the I-compound is effected with AgNO_3 in boiling MeCN; the corresponding nitrate is formed, and this is subsequently converted into the corresponding OH compound, thereby affording an accurate identification and determination of the 6-OH group. These properties are strictly confined to the 6-position of glucose. 2 : 3-Dimethyl- β -methylglucoside (I) and fuming HNO_3 in CHCl_3 give 78% of the 4 : 6-dinitrate, m. p. 98—99°, $[\alpha]_D -20.8^\circ$ in CHCl_3 , converted by NaI in COMe_2 at 100° into 6-iodo-2 : 3-dimethyl- β -methylglucoside (II), m. p. 52—55°, $[\alpha]_D -7.1^\circ$ in CHCl_3 , which with AgNO_3 in MeCN affords 2 : 3-dimethyl- β -methylglucoside 6-nitrate, b. p. 140°/0.3 mm., $[\alpha]_D -27.7^\circ$ in CHCl_3 . Methylation of this with Ag_2O and subsequent reduction gives 2 : 3 : 4-trimethyl- β -methylglucoside. (I) and PhSO_2Cl in pyridine at room temp. give 4 : 6-dibenzenesulphonyl-2 : 3-dimethyl- β -methylglucoside, m. p. 119—120°, $[\alpha]_D -21^\circ$ in CHCl_3 , converted by NaI in COMe_2 into 6-iodo-4-benzenesulphonyl-2 : 3-dimethyl- β -methylglucoside, m. p. 72—73°, $[\alpha]_D -7.7^\circ$ in CHCl_3 , also formed from (II) and PhSO_2Cl . Reduction of 4-benzenesulphonyl-2 : 3-dimethyl- β -methylglucoside 6-nitrate, m. p. 96—97°, gives 4-benzenesulphonyl-2 : 3-dimethyl- β -methylglucoside, m. p. 86—87°, $[\alpha]_D -42.6^\circ$ in CHCl_3 , methylated to the 2 : 3 : 6-Me₃ derivative, m. p. 83—84°, $[\alpha]_D -35.6^\circ$ in CHCl_3 , also prepared from 2 : 3 : 6-trimethyl- β -methylglucoside. 2 : 3-Diacetylbenzylidene- β -methylglucoside, m. p. 169—170°, $[\alpha]_D -95.2^\circ$ in CHCl_3 , is hydrolysed by $\text{N}/40\text{-HCl}$ to 2 : 3-diacetyl- β -methylglucoside, $[\alpha]_D -55.3^\circ$ in CHCl_3 . The 4 : 6-di-*p*-toluenesulphonyl derivative, m. p. 160—161°, $[\alpha]_D -12.7^\circ$ in CHCl_3 , of this and NaI in COMe_2 gives 6-iodo-2 : 3-diacetyl-4-*p*-toluenesulphonyl- β -methylglucoside, m. p. 160—161°, $[\alpha]_D -19.9^\circ$ in CHCl_3 ; the 6-nitrate, m. p. 128—129°, $[\alpha]_D -32.9^\circ$ in CHCl_3 , is reduced to 2 : 3-diacetyl-4-*p*-toluenesulphonyl- β -methylglucoside, m. p. 165—166°, $[\alpha]_D -55.4^\circ$ in CHCl_3 (2 : 3 : 6-Ac₃ derivative, m. p. 116—117°). 2 : 3-Diacetyl- β -methylglucoside 6-nitrate has m. p. 134—136°, $[\alpha]_D -29.9^\circ$ in CHCl_3 . The tetra-*p*-toluenesulphonyl derivative, m. p. 177—178° (decomp.), $[\alpha]_D -6.6^\circ$ in CHCl_3 , of β -methylglucoside with NaI in COMe_2 affords 6-iodo-2 : 3 : 4-tri-*p*-toluenesulphonyl- β -methylglucoside, m. p. 211—212°, $[\alpha]_D -1.2^\circ$ in CHCl_3 ; the corresponding 6-nitrate has m. p. 166—168°, $[\alpha]_D -21.1^\circ$ in CHCl_3 . 2 : 3 : 4-Tribenzenesulphonylglucosan and 2 : 3 : 6-trimethyl-5-*p*-toluenesulphonyl- γ -methylglucoside did not react with NaI.

C. J. WEST (b).

Identity of Pacsu's 4-methylglucose with Brigl's 2-methylglucose. E. PACSU (Ber., 1932, 65, [B], 51—54).—Levene's observation of the absence of the OMe group from the osazone of Pacsu's methylglucose is confirmed. The osazone, m. p. 160°, from the syrupy compound regarded as 4 : 5 : 6-trimethylglucose (A., 1925, i, 515) contains 1 OMe. H. WREN.

Specificity of β -glucosidase of emulsin. Derivatives of 3- and 4-methyl-*D*-glucose. B. HELFERICH and O. LANG (J. pr. Chem., 1932, [ii], 132, 321—334).—3-Methyl- β -methyl-*D*-glucoside (I) (syrup), $[\alpha]_D^{20}$ —26.9°, is prepared from β -tetra-acetyl-3-methyl-*D*-glucose, m. p. 95—96° (Ac₂O and KOAc), by action of HBr in AcOH followed by treatment of the crude acetobromo-compound with MeOH and Ag₂CO₃, and hydrolysis of the resulting 2:4:6-triacetyl-3-methyl- β -methyl-*D*-glucoside (II), m. p. 90—90.5°, with *N*-NaOH. Its identity is proved by its ready acetylation to (II), and the presence of the pyranose ring is confirmed as follows: 2-acetyl-3-methyl- β -methyl-*D*-glucoside, m. p. 144—144.5°, is obtained by the action of NaOMe in MeOH on (II), and is converted by successive action of CPh₃Cl and Ac₂O in pyridine into 2:4-diacetyl-3-methyl-6-triphenylmethyl- β -methyl-*D*-glucoside, m. p. 176.5—177.5°, hydrolysed by HBr in AcOH to 2:4-diacetyl-3-methyl- β -methyl-*D*-glucoside, m. p. 140—142.5°, the *p*-toluenesulphonyl derivative, m. p. 91—91.5°, of which with dry NaI in COMe₂ gives 2:4-diacetyl-3-methyl- β -methylglucoside-6-iodohydrin, m. p. 100.5—101.5°; this is readily converted by AgF in pyridine into the corresponding olefine, m. p. 76.5—77.5°, which does not itself reduce Fehling's solution but readily does so after hydrolysis by acid. (4?) Methyl- β -methyl-*D*-glucoside (III) (syrup) is prepared by alkaline hydrolysis of its 2:3:6-Ac₃ derivative (from 2:3:6-triacetyl- β -methyl-*D*-glucoside, MeI, and Ag₂O), and freed from any accompanying 6-methyl- β -methyl-*D*-glucoside by conversion into and regeneration from its CPh₃ derivative. Neither (I) nor (III) is hydrolysed by emulsin under a variety of conditions. isoPropylidene-3:5-diacetyl-*D*-glucose-6-iodohydrin, m. p. 75—76°, prepared from the *p*-toluenesulphonyl derivative and NaI, was not converted into the olefine under the above or various other conditions. H. A. PIGGOTT.

Reactivity of alcohols with chlorotriphenylmethane. K. JOSEPHSON (Annalen, 1932, 493, 174—180).—Diisopropylidenegalactose and CPh₃Cl in pyridine at room temp. for 3 days give the 6-triphenylmethyl derivative; tri(isopropylidene-glucose-3) phosphate (A., 1930, 1166) similarly yields a tri(triphenylmethyl) derivative, m. p. about 130°, $[\alpha]_D^{16}$ —24.7° in COMe₂. Hydroaromatic *sec*-alcohols can be distinguished from the *tert*-alcohols, since the latter do not react with CPh₃Cl under the above conditions, whilst the former do. *l*-Menthyl, m. p. 139—140° (corr.), *d*-bornyl, m. p. 118—119° (corr.), $[\alpha]_{D, 16}^{\text{yellow}}$ +48.1° in CHCl₃, *cholesteryl*, m. p. 139—140° (corr.), $[\alpha]_{D, 16}^{\text{yellow}}$ —29.8° in CHCl₃, and *betulyl* CPh₃ ethers are described. CMe₂Et·OH does not give a CPh₃ ether. H. BURTON.

Possible source of error in determining the constitution of di- and poly-saccharides. J. C. IRVINE and R. P. MCGLYNN (J. Amer. Chem. Soc., 1932, 54, 356—363).—2:3:6-Trimethylglucose (I) in MeOH containing 0.3% HCl at room temp. shows $[\alpha]_D +70.5^\circ \rightarrow -23.5^\circ$ in 100 hr.; the yield of 2:3:6-trimethyl- γ -methylglucoside (II), b. p. 180°/0.05 mm., is nearly quant. The constitution of (II) follows from its rotation, its instability to dil. acid, and its conversion into 2:3:5:6-tetramethyl- γ -glucose. When

(II) is hydrolysed, the liberated 2:3:6-trimethyl- γ -glucose passes into the stable, cryst. variety, which is the only form isolated. Oxidation of (I) by Br gives either the corresponding γ - or δ -lactone according to variations in the concn. of HBr present; in the presence of CaBr₂ and CaCO₃ the δ -lactone results, whilst with Br in H₂O the γ -form is produced. These results show that the formation of (I) in the constitutional studies of carbohydrates by the methylation method is ambiguous, as are the results of oxidation methods in certain cases. C. J. WEST (b).

Derivatives of 4-glucosidomannose. H. S. ISBELL (Bur. Stand. J. Res., 1931, 7, 1115—1131).—Hepta-acetyl-4-glucosido- γ -methylmannose (I), m. p. 167° (dimorphic), $[\alpha]_D^{20}$ —12.7° in CHCl₃, prepared from the corresponding Br-compound and Ag₂CO₃, is completely hydrolysed by 0.25*N*-H₂SO₄, but only 6 Ac groups are removed by 0.1*N*-Ba(OH)₂. Its $[\alpha]_D^{20}$ in MeOH containing HCl rapidly changes to +12.8°. (I) is converted by dry HCl in MeOH followed by aq. Ag₂CO₃ into hexa-acetyl-4-glucosidomannose (II), m. p. 171°, $[\alpha]_D^{20}$ +21.7° in CHCl₃, which can be acetylated to the corresponding Ac₈ derivative. It is suggested that (I) possesses the ortho-ester structure, the ortho-Ac being split off to give (II). (I), dissolved in CHCl₃, is converted by HCl into chlorohepta-acetyl-4-glucosidomannose. Bromohepta-acetyl-4-glucosidomannose with Ag₂CO₃ in cold COMe₂ gives hepta-acetyl-4-glucosidomannose, m. p. 110°, $[\alpha]_D^{20}$ +11.7° in CHCl₃ (α -Ac₈ derivative). 4-Glucosido- β -mannose, m. p. 203—205° (decomp.), now obtained cryst. (cf. Haworth and others, A., 1931, 200), gives the β -Ac₈ derivative, m. p. 165°, $[\alpha]_D^{20}$ —12.96°.

Hepta-acetyl-4-glucosido- β -methylmannose, m. p. 178°, $[\alpha]_D^{20}$ —23.2° in CHCl₃, is obtained together with the γ -derivative, and may be deacetylated by Ba(OMe)₂ to 4-glucosido- β -methylmannoside (+0.5H₂O), m. p. 229°, $[\alpha]_D^{20}$ —48.5° in H₂O, which may be reconverted into the Ac₇ compound. The corresponding α -methylmannose, m. p. 185°, $[\alpha]_D^{20}$ +29.3° in CHCl₃ (cf. A., 1931, 200), has also been obtained from crystallising the β - and γ -compounds.

The optical rotations of the derivatives of 4-glucosidomannose are correlated with those of the analogous derivatives of mannose, and are similarly exceptional in certain cases. Since 4-glucosidomannose cannot form a 1:4-ring, these exceptional rotations are not caused by existence of that structure. F. R. SHAW.

Existence of α -diamylose. A. MIEKELEY (Ber., 1932, 65, [B], 69; cf. A., 1930, 1414).—A reply to Pringsheim and others (A., 1931, 1276). H. WREN.

Differential analysis of starches. J. B. MCNAIR (Field Museum, Chicago, Bot. Ser., 1930, 9, 1—44).—The following methods are used for the characterisation of starches of different origin: microscopical examination; polarisation; I reaction; gentian-violet reaction; safranin reaction; temp. of gelatinisation; chloral hydrate-I reaction; CrO₃ reaction; pyrogallol reaction; FeCl₃ reaction; Purdy solution reaction. CHEMICAL ABSTRACTS.

Phosphorus, nitrogen, and silicon content of starch fractions. M. SAMEO (Helv. Chim. Acta,

1932, 15, 43—47).—Polemical against Karrer and Kraus (A., 1930, 72), whose technique does not effect the separation of P-containing and P-free starch fractions. The author's conclusion (A., 1930, 584) that the physico-chemical behaviour of starch emulsion is dependent on the P, N, and Si content is maintained.

J. W. BAKER.

[Phosphorus, nitrogen, and silicon content of starch fractions.] P. KARRER (Helv. Chim. Acta, 1932, 15, 48).—A reply to Samec (preceding abstract).

J. W. BAKER.

Mode of reaction of cellulose. K. HESS and C. TROGUS.—See this vol., 234.

Reactions relating to carbohydrates and polysaccharides. XXXIX. Structure of the cellulose synthesised by the action of *Acetobacter xylinus* on glucose. H. HIBBERT and J. BARSHA (Canad. J. Res., 1931, 5, 580—591; cf. this vol., 42).—"Cellulose," prepared by the action of *A. xylinus* on glucose, consists of closely-packed membranes containing 2% of dry substance, has great tensile strength, but no fibrous structure, and is sol. in Schweitzer's reagent, cuproammonium sulphate, and the usual organic solvents. With Ac_2O , AcOH , and SO_2Cl_2 or H_2SO_4 , it yields a triacetate (I), which, when partly deacetylated, gives a product (II), containing 40% Ac, completely sol. in COMe_2 ; (I), when dry spun in CHCl_3 and deacetylated with 2*N*-alcoholic NaOH , gives a regenerated "cellulose" showing the X-ray structure of natural cellulose fibres. "Cellulose," regenerated from (I) (not spun) with HCl in MeOH gives α - and β -methylglucosides (94% yield) and with HCl and ZnCl_2 glucose (almost quant. yield). Deacetylation and methylation of (II) gives trimethylcellulose (84% yield), hydrolysis of which affords 2:3:6-trimethylmethylglucoside (92.3% yield) and then 2:3:6-trimethylglucose (83.5% yield). The octa-acetate, m. p. 221—221.5°, was also obtained. The rotations of natural and "synthetic" cellulose and their derivatives are almost identical.

R. S. CAHN.

Aliphatic $\alpha\beta$ -diamines. H. REIHLEN, G. VON HESSLING, W. HUHN, and E. WEINBRENNER (Annalen, 1932, 493, 20—32).— α -Amino-nitriles readily eliminate HCN on attempted catalytic reduction and so poison the catalyst. α -Acetamido-nitriles are, however, readily converted by catalytic reduction (Adams) (in Ac_2O only) (cf. Carothers and Jones, A., 1926, 161) at 50—60° into $\alpha\beta$ -diacetamido-compounds in yields of 75—90%. Hydrolysis of the Ac_2 derivatives to the $\alpha\beta$ -diamines presents little difficulty unless an NHAc group is attached to a *tert.*-C atom, in which case a piperazine is the main product. Thus, α -acetamidopropionitrile gives $\alpha\beta$ -diacetamidopropane; α -acetamidophenylacetoneitrile, m. p. 113°, affords a little of a Ac_2 derivative, m. p. 166°, of phenylethylenediamine (I) and 80—90% of $\alpha\beta$ -diacetamidophenylethane, m. p. 159°, which is hydrolysed by conc. HCl at 100° to the dihydrochloride of (I); α -acetamidoisobutyronitrile furnishes $\alpha\beta$ -di(acetamido)- β -methylpropane, m. p. 99—100°, which is hydrolysed by evaporating with conc. HCl at 100° (bath) (variable results often obtained) to $\alpha\beta$ -isobutylenediamine dihydrochloride, and by boiling with

conc. HCl to 2:2:5:5-tetramethylpiperazine dihydrochloride (34% yield); α -acetamido- α -methylbutyronitrile, m. p. 15—20° (not obtained pure), yields $\alpha\beta$ -diacetamido- β -methylbutane, m. p. 95°; α -acetamido- α -phenylpropionitrile, m. p. 166°, gives $\alpha\beta$ -diacetamido- β -phenylpropane, m. p. 147°, hydrolysed by 20% HCl to the dihydrochloride of $\alpha\beta$ -diamino- β -phenylpropane, b. p. 80°/high vac., and (mainly) 2:5-diphenyl-2:5-dimethylpiperazine dihydrochloride; 1-acetamido-1-cyanocyclohexane, m. p. 90°, affords (the reduction occurs readily at room temp.) 1-acetamido-1-acetamidomethylcyclohexane, m. p. 167°, hydrolysed by dil. HCl to 1-amino-1-aminomethylcyclohexane dihydrochloride, m. p. 120—122° (decomp.).

2-Cyanopyridine, b. p. 103°/12 mm., f. p. 26°, from pyridine-2-carboxylamide and P_2O_5 , is similarly reduced to 1-acetyl-2-acetamidomethylpiperidine, m. p. 105°; when the reduction is carried out above 60°, di-(1-acetyl-2-piperidylmethyl)amine, b. p. 116°/high vac., is often the main product. 2-Aminomethylpiperidine dihydrochloride is prepared. Phenyl- and isopropyl-malononitriles are similarly reduced to $\alpha\gamma$ -diacetamido- β -phenyl-, m. p. 144°, and $\alpha\gamma$ -diacetamido- β -isopropyl-propane, m. p. 128°, respectively.

H. BURTON.

$\beta\beta'$ -Dihalogenodiethylamines. V. PRELOG, G. DRIZA, and V. HANOUSEK (Coll. Czech. Chem. Comm., 1931, 3, 578—584).—A cold mixture of $\beta\beta'$ -dihydroxydiethylamine (I) (290 g.) and HCl (*d* 1.19; 750 g.) is treated with gaseous HCl (270 g.) and the resultant product heated, first at 100—120°, and then at 180—200°; $\beta\beta'$ -dichlorodiethylamine hydrochloride (II), m. p. 210° [corresponding chloroplatinate, m. p. 224° (decomp.)], and *picrate*, m. p. 111—112°, is thereby obtained in about 65% yield. (II) and KCNO give 2-imino-3- β -chloroethylloxazolidine hydrochloride, m. p. 152° (corresponding chloroaurate, m. p. 101—102°, chloroplatinate, m. p. 178—179°, and *picrate*, m. p. 129—130°); with KCNS , 2-imino-3-chloroethylthiazolidine, m. p. 188—189° (*picrate*, m. p. 143—144°), results. (I) and HBr give $\beta\beta'$ -dibromodiethylamine hydrobromide, which with KCNO and KCNS affords 2-imino-3- β -bromoethylloxazolidine hydrobromide, m. p. 161° (corresponding *picrate*, m. p. 120°), and 2-imino-3- β -bromoethylthiazolidine, m. p. 207° (hydrobromide, m. p. 148°; *picrate*, m. p. 144—145°), respectively. The free $\beta\beta'$ -dihalogenodiethylamines are not stable. The Bz_2 derivative of *as*- $\beta\beta'$ -dihydroxydiethylcarbamide [obtained as an oil from (I) and KCNO] has m. p. 108°.

H. BURTON.

Bis-halogenoethylamines. II. V. PRELOG and J. DRIZA (Coll. Czech. Chem. Comm., 1932, 4, 32—38).—Treatment of 2-imino-3- β -bromoethylloxazolidine hydrobromide (cf. preceding abstract) with 2 mols. of NaOEt in EtOH , and subsequent addition of picric acid, affords 2-amino-3-vinylloxazolinium *picrate*, m. p. 178° (I) (gives MeCHO with 33% H_2SO_4), converted by aq. HBr into NH_4Br , crotonaldehyde, and $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{NH}_2$ (as *picrate*). From the mother-liquor of (I) by heating with fuming HBr at 180° is obtained $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\cdot 2\text{HBr}$ (insol. in MeOH) and *N*- β -bromoethylethylenediamine dihydrobromide, m. p. 172° (*dipicrate*, sinters at 170°, decomp. 231°),

also synthesised by the action of 48% HBr at 160—170° on $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ (II) (A., 1903, i, 153) and converted by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ into bis- p -toluenesulphonylpiperazide (A., 1899, i, 750). In an attempt to prepare the hypothetical intermediate $\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$ (III, $\text{X}=\text{Br}$) in these decomp., (II) was condensed with Et_2CO_3 at 180° to give $N\cdot\beta$ -hydroxyethylimidazolidone (III, $\text{X}=\text{OH}$), which gave no cryst. product with HBr. The same products are similarly obtained from 2-imino-3- β -chloroethyloxazolidine dihydrochloride.

J. W. BAKER.

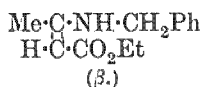
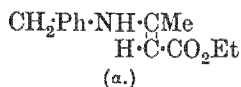
Preparation and properties of α - and β -methylcholine and γ -homocholine. R. T. MAJOR and J. K. CLINE (J. Amer. Chem. Soc., 1932, 54, 242—249).—Et α -dimethylaminopropionate (I) is obtained in 57% yield from NHMe_2 and $\text{CHBrMe}\cdot\text{CO}_2\text{Et}$ in $\text{Et}_2\text{O}\cdot\text{EtOH}$; α -methylcholine (II) is prepared from (I) by Karrer's method (A., 1922, i, 813). (II) is the only true α -methylcholine so far prepared. Acetyltrimethylammonium chloride, m. p. 140°, when reduced (Adams' method) gives 50% of β -methylcholine chloride, m. p. 165° (corresponding *picrate*, m. p. 168°), also formed from $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl}$ and NMe_3 at 100°. $\text{OH}\cdot[\text{CH}_2]_3\text{Cl}$ and NMe_3 give 92% of γ -homocholine chloride, m. p. 173°. The work of Partheil (A., 1892, 950) on the prep. of γ -homocholine has been repeated; NH_4 and β -methylcholine salts were isolated.

C. J. WEST (b).

Interference of reducing sugars in ninhydrin reaction for amino-acids and related compounds as applied to carbohydrates. J. A. AMBLER and J. B. SNIDER (Ind. Eng. Chem. [Anal.], 1932, 4, 37).—The presence of more than 10 mg. of glucose or 1 mg. of fructose is objectionable when testing for NH_2 -acids with ninhydrin.

E. S. HEDGES.

Isomerism of the condensation products from benzylamine and ethyl acetoacetate and of the products of acylation of β -aminocrotonic ester. K. VON AUWERS and H. WUNDERLING (Ber., 1932, 65, [B], 79—86).—The spectroscopic behaviour of the two products from $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ and Et acetoacetate in 1-methylnaphthalene, AcOEt, and MeOH is explicable only on the assumption that they are stereoisomeric ethylenic compounds (α and β). This con-



ception is supported by the behaviour of the "phenylhydrazones of Et acetoacetate" [Et β -phenylhydrazinocrotonate]. The exaltations of the CH_2Ph derivatives are remarkably small; this is true also of the products from $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ and acetylacetone. The hypothesis that they are not true enamines but, when melted or dissolved, are equilibrium mixtures of the ketimine and enamine forms, is untenable, since the same behaviour is exhibited by the N -ethylbenzylamine derivative of acetylacetone in which the imine form is impossible. Some unexplained peculiarity of $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ derivatives appears to be involved. The β -acylamido-derivatives of Et crotonate are similarly shown to be ethylenic derivatives, but

difficulties are encountered in assigning configurations to the two forms. Optical data are recorded for the following compounds: Et β - β -benzylaminocrotonate and Et α - β -benzylaminocrotonate in 1-methylnaphthalene, AcOEt, and MeOH; α -benzylaminoethylidenecrotonate; α - N -ethylbenzylaminoethylidenecrotonate, b. p. 196—198°/12 mm.; Et β -benzamidocrotonate, m. p. 46—48° and m. p. 95—96°, in substance and in 1-methylnaphthalene; Et β -acetamidocrotonate, m. p. 63°.

H. WREN.

Synthesis of i - β -hydroxyglutamic acid. C. R. HARRINGTON and S. S. RANDALL. **The dissociation constants.** G. M. RICHARDSON (Biochem. J., 1931, 25, 1917—1930).—Et α -oximinocrotonededicarboxylate, prepared from Et acetonedicarboxylate, HCl, and Et nitrite in Et_2O , was reduced by Hartung and Munch's method (A., 1929, 1066) in presence of Pd-C and subsequently by means of Pd-C activated by H_2PtCl_6 and a trace of Fe. The product was hydrolysed with HCl, the acid removed, and the NH_2 -acid isolated through its Ag salt. Alternatively the compound was obtained in cryst. form by concentrating the product of hydrolysis and then saturating with HCl, filtering the hydrochloride, and isolating the NH_2 -acid by the above method from the mother-liquor. The following derivatives were prepared: *hydrochloride*, m. p. 187°; *Et ester hydrochloride*, m. p. 168.5°, and *Ag, Cu, and Ca H salts*. Dissociation consts. at 25°, mol. concn. 0.02, pK_1 2.09, pK_2 4.18, pK_3 9.20. There are marked discrepancies between the behaviour of the synthetic product and that of the compound isolated by Dakin (A., 1919, i, 150).

S. S. ZILVA.

Compounds of lysine with cupric chloride. F. WREDE (Z. physiol. Chem., 1931, 203, 162—164).—*dl*-Lysine forms with 1 mol. of CuCl_2 two compounds: blue (+2 H_2O), m. p. about 250—255° (decomp.), and green, m. p. about 170° (decomp.). The green form is converted into the blue by boiling with an excess of CuCl_2 . *d*-Lysine behaves similarly: blue (+2 H_2O), m. p. 260° (decomp.), green (+ H_2O), m. p. 180° (decomp.).

J. H. BIRKINSHAW.

Action of halogens on mercury fulminate. G. ENDRES [with H. BOTTMANN] (Ber., 1932, 65, [B], 65—69).—The action of Cl_2 on Hg fulminate suspended in H_2O gives dichloroformoxime (yield 40%) and (?) $\text{CCl}_3\cdot\text{NO}$. If $N\cdot\text{HCl}$ is substituted for H_2O , the yield of dichloroformoxime is increased to 65%. The main product of the action of Br on Hg fulminate suspended in H_2O is dibromofuroxan (30%), accompanied by minor amounts of $\text{CBr}_3\cdot\text{NO}$, CBr_4 , and dibromoformoxime. In presence of mineral acid, dibromoformoxime (yield 60%) is mainly formed, whereas *tribromonitrosomethane*, b. p. 36—38°/14 mm., is prepared in 40% yield from KOBr and Hg fulminate in ice-cold H_2O .

H. WREN.

Ethylenic nitriles. Δ^2 -Pentenitrile. P. BRUYLANTS and G. JMOUDSKY (Bull. Acad. roy. Belg., 1931, [v], 17, 1161—1173).—By repeated fractionation and removal of the $\beta\gamma$ -compound as its dibromide (cf. A., 1931, 205) Δ^2 -pentenenitrile is separated into the form (I, ? *trans*), b. p. 143—144°/761 mm., 73—74°/72 mm., and the form (II, ? *cis*), b. p. 127—128°/765 mm., 59—59.5°/72 mm. The

nitrile was prepared (1) by dehydration of *n*-butaldehyde cyanohydrin with P_2O_5 , (2) by the action of quinoline on α -chloro- (higher total yield and less of the $\beta\gamma$ -compound formed) and β -chloro-*n*-valeronitrile, and (3) by condensation of $EtCHO$ with cyanoacetic acid in the presence of pyridine (small yield and much $\beta\gamma$ -compound obtained); all methods gave a mixture of both forms. Both (I) and (II) are partly isomerised to the Δ^{β} -compound by $NaOPh$, but with conc. H_2SO_4 each gives the corresponding *form*, m. p. 150—151° and 68—68.8°, respectively, of the amide, of which the latter is isomerised by irradiation to a mixture (approx. 50%) of the two forms, whilst similar treatment of the *form*, m. p. 150—151°, causes no appreciable isomerisation. J. W. BAKER.

Ethylenic nitriles. Δ^{α} -Hexenonitrile. P. BRUYLANTS and L. ERNOULD (Bull. Acad. roy. Belg., 1931, [v], 17, 1174—1179).—Dehydration of the cyanohydrin of *n*-valeraldehyde [azeotropic mixture with H_2O (14% H_2O), b. p. 80.6—80.7°/747 mm., best prepared by $K_2Cr_2O_7$ oxidation of *n*-amyl alcohol] with P_2O_5 and fractionation after removal of the $\beta\gamma$ -compound (cf. preceding abstract), gives the *form* (*trans*), b. p. 164—165°/755 mm., and the *form* (*cis*), b. p. 149—150°/757 mm., of Δ^{α} -*n*-hexenonitrile, converted by conc. H_2SO_4 into the *trans*-, m. p. 124.6—125°, and *cis*-, m. p. 67—68°, *amide*, respectively.

J. W. BAKER.

Compounds of the type $BCl_{3-n}(OR)_n$. E. WIBERG and W. SUTTERLIN (Z. anorg. Chem., 1931, 202, 1—21).— $MeOH$ and $EtOH$ react vigorously with BCl_3 at -60° to -90° , with the quant. production of compounds $BCl_{3-n}(OR)_n$. The following are described: $BCl_2 \cdot OMe$, m. p. -14.9° to -15° , b. p. 58° ; $BCl(OMe)_2$, m. p. -87.5° to -87.8° , b. p. 74.7° ; $BCl_2 \cdot OEt$, b. p. 77.9° ; $BCl(OEt)_2$, b. p. 112.3° . $B(OMe)_3$ has m. p. -28.9° to -29.0° , b. p. 68.7° , and $B(OEt)_3$ b. p. 117.4° . The v. p.-temp. equations, mol.-latent heats of evaporation, and the Trouton's consts. are given. All the compounds form colourless liquids and are hydrolysed readily by H_2O ; those containing Cl react with excess of alcohol. Whereas BCl_3 and $BCl_2 \cdot OR$ react with Et_2O , even at -80° , to form additive compounds, $BCl(OR)_2$ and $B(OR)_3$ do not react even at 100° . $BCl_2 \cdot OR$ decomposes at 50—70°, yielding the compound $BOCl$, whereas $BCl(OR)_2$ and $B(OR)_3$ are stable at this temp.

H. F. GILLBE.

Action of substituents on boron trichloride.

I. Action of ether. II. Action of alcohol. III. Electronic interpretation of the action of ether and alcohol on boron trichloride, and some consequences of the theory. E. WIBERG and W. SUTTERLIN (Z. anorg. Chem., 1931, 202, 22—30, 31—36, 37—48).—I. The compound $BCl_3 \cdot Me_2O$, m. p. 76° , is formed by the action of Me_2O on BCl_3 at -80° ; it hydrolyses readily. When heated at 80° for some hrs. $BCl_2 \cdot OMe$, $CHCl_3$, B_2O_3 , and $BOCl$ are formed. $BCl_2 \cdot OMe$ and Me_2O at -80° yield a *cryst. compound* ($BCl_2 \cdot OMe)_2 \cdot Me_2O$, m. p. below 0° (decomp.); the thermal decomp. yields $BCl(OMe)_2$ and $BCl_3 \cdot Me_2O$. Thermal decomp. (0°) of $(BCl_2 \cdot OEt)_2 \cdot Et_2O$ yields $BCl_3 \cdot Et_2O$, $BCl(OEt)_2$.

II. BCl_3 and NMe_3 at -40° yield $BCl_3 \cdot NMe_3$, m. p.

243° , which is stable at 250° and does not react with warm $EtOH$. $BCl_3 \cdot Et_2O$ and $EtOH$ react vigorously at -40° to yield a *compound* $(BCl_2 \cdot OEt)_2 \cdot Et_2O$, which readily decomposes into $BCl_3 \cdot Et_2O$ and $BCl(OEt)_2$.

III. It is suggested that in the B atoms of the additive compounds described above there are operative 4 covalencies and 1 electrovalency and that the latter is directed towards an atom which is already held by a covalency linking. This view affords a satisfactory explanation of the types and behaviour of the compounds obtained, and has been further confirmed by experiments with BCl_3 and other compounds. Thus BCl_3 and HF at about -140° yield BF_3 and HCl , and, probably, a *compound* $BF_3 \cdot HCl$; BCl_3 and $NHMe_2$ yield at -60° a mixture of the *compounds* $BCl_2 \cdot NMe_2$ and $BCl(NMe_2)_2$; whilst $CHMe_3$ does not react with BCl_3 . The possibility of preparing optically active compounds containing an asymmetric O atom is indicated. H. F. GILLBE.

Gallium triethyl monoetherate, gallium triethyl, and gallium triethylamine. L. M. DENNIS and W. PATNODE (J. Amer. Chem. Soc., 1932, 54, 182—188).—The prep., properties, and reactions of $GaEt_3$, its monoetherate, and Ga triethylamine are described. Hydrolysis of these compounds probably gives $GaEt_2OH$. M. McMAHON (b).

Conjugated double linkings. XXI. Formation of aromatic hydrocarbons from diene-carboxylic acids. R. KUHN and A. DEUTSCH (Ber., 1932, 65, [B], 43—49).—The hydrocarbon obtained by decarboxylation of sorbic acid with anhyd. $Ba(OH)_2$ has the composition $C_{10}H_{14}$ and not $C_{10}H_{16}$ (Doebner, A., 1904, i, 149; 1907, i, 203, 204) and is identified as *o*-propyltoluene, b. p. $65—68^\circ/14$ mm., d_4^{20} 0.8747, by oxidation to phthalic acid and hydrogenation to 1-methyl-2-propylcyclohexane, b. p. $175.5—176^\circ/755.5$ mm., d_4^{20} 0.8130; isomeric hydrocarbons do not appear to be produced. Decarboxylation of vinylacrylic acid gives mainly trimeric products, but the dimeride is identified as $PhEt$; Doebner's tri-cyclooctane should be deleted from the literature. Cinnamylacrylic acid yields a *hydrocarbon*, $C_{20}H_{18}$ (?), β -phenyl- α -*o*-diphenyllethane, b. p. $205—210^\circ/10$ mm., d_4^{17} 1.0484, hydrogenated to the *compound* $C_{20}H_{36}$, b. p. $195—202^\circ/12$ mm., and oxidised to $BzOH$. The bearing of the results on the production of *m*-xylene from bixin is discussed. H. WREN.

Catalytic oxidation of toluene. G. CHARLOT.—See this vol., 235.

Nuclear chlorination of toluene derivatives. E. WERTYPOROCH (Annalen, 1932, 493, 153—165).—Chlorination of $CPhCl_3$, $CPhF_3$, $CPhClF_2$, $CPhCl_2F$, CH_2PhCl , and $PhMe$ in presence of $SbCl_5$ (0.01 mol.) usually at about room temp., gives 58—80, 53—67, 37, 23, 59, and 77—86%, respectively, of monochloro-derivatives; the yields are much higher (and the amounts of polychloro-derivatives lower) than with I as catalyst. The composition of the mixtures of monochloro-compounds is determined by conversion into the mixed chlorobenzoic acids and subsequent analysis by a modification of Hope and Riley's method (J.C.S., 1922, 121, 2510) (the nos. given in parentheses are the % *o*-, *m*-, and *p*-isomerides, respectively):

CPhCl₃ (3.3, 69.5, 27.27); CHPhCl₂ (I as catalyst; SbCl₅ cannot be used owing to its condensation action) (5.64—6.94, 45.94—47.64, 43.1); CH₂PhCl (51.56, 0, 48.44); PhMe (55—58, 0, 42—45); CPhF₃ (—, 80, 10—15); CPhCl₂F (56.2, 37.5, 6); CPhClF₂ (92.5, 3.5, 3.5).
H. BURTON.

Ozonides of *o*-xylene and the structure of the benzene ring. A. A. LEVINE and A. G. COLE (J. Amer. Chem. Soc., 1932, 54, 338—341).—Ozonisation of *o*-xylene in Ac₂O (most suitable solvent) and subsequent decomp. with ice, gives (CHO)₂, Ac₂, and AcCHO. The formation of these products indicates that *o*-xylene exists in two isomeric forms.

C. J. WEST (b).

Molecular compounds of 4:6-dichloro-1:3-dinitrobenzene. H. S. JOIS and B. L. MANJUNATH (J. Indian Chem. Soc., 1931, 8, 633—636).—Mol. compounds are obtained by fusing this substance (A) with various second components (B) and thus are obtained the compounds with C₁₀H₈, m. p. 68°; α-, m. p. 105°, and β-, m. p. 78.5°, -naphthol; α-, m. p. 91° [converted by boiling in EtOH into 2:4-dinitro-5-chlorophenyl-α-naphthylamine (dimorphous), orange form converted at 145—150° into a yellow form, m. p. 204—205°], and β-, m. p. 72—73° [2:4-dinitro-5-chlorophenyl-β-naphthylamine (dimorphous), labile yellow changing to stable orange form, m. p. 186—187°], -naphthylamine; pyridine (AB₂+2H₂O), converted by warming into a halogen-free substance, decomp. 235°, and benzidine (A₂B). Except where otherwise stated, all are of the type AB.

J. W. BAKER.

Stereoisomeric *p*-di-α-hydroxybenzylbenzenes and *p*-di-α-chlorobenzylbenzenes. A. WEISSBERGER and H. BACH (Ber., 1932, 65, [B], 24—32).—*p*-Xylene is converted by Br at 140—160° into *p*-bis-dibromomethylbenzene, transformed by conc. H₂SO₄ at 120—130° in a current of air under diminished pressure into terephthalaldehyde, m. p. 115—116°, in 90% yield. MgPhBr in Et₂O transforms the aldehyde into *p*-di-α-hydroxybenzylbenzene, m. p. 174—175° (corr.) (cf. A., 1931, 471), and an isomorphous mixture, m. p. 142—143° (corr.), of this compound and its stereoisomeride. Treatment of the mixture with Ac₂O followed by fractional pptn. of the product from Et₂O by light petroleum affords *p*-di-α-acetoxybenzylbenzene, m. p. 145—145.5° (corr.), and iso-*p*-di-α-acetoxybenzylbenzene, m. p. 95—96°, hydrolysed to iso-*p*-di-α-hydroxybenzylbenzene, m. p. 130.5—131.5° (corr.). The isomerides are unchanged when heated at 200—205°. Treatment of *p*-di-α-hydroxybenzylbenzene in AcOH with HCl is accompanied by slight isomerisation, but permits the isolation of *p*-di-α-chlorobenzylbenzene, m. p. 129.5—131.5° (corr.) to 133.5—135.5° (corr.), according to the manner of heating. Trituration of the substance is sufficient to cause partial isomerisation to iso-*p*-di-α-chlorobenzylbenzene, m. p. 67—70°, which is best prepared by boiling *p*-di-α-chlorobenzylbenzene in CHCl₃, extraction of the solid residue with light petroleum, and repetition of the operations with the residue. When heated at 130—133°, either isomeride affords the same equilibrium mixture. The small difference between the dipole moments of the stereoisomeric Cl-com-

pounds in contrast with that between the isomeric stilbene dichlorides (A., 1930, 1093) is considered to support the authors' theory of the absence of free rotation around the ethane C-C linking (cf. Bergmann and Engel, A., 1930, 1501).

H. WREN.

Isomeric dinitrobenzenes. O. WYLER (Helv. Chim. Acta, 1932, 15, 23—43).—An accurate ternary m.-p. diagram for mixtures of *o*-, *m*-, and *p*-C₆H₄(NO₂)₂ is plotted by means of which the composition of any mixture is obtained. The *o*-+*p*-compounds may also be determined (error ±0.2%) by boiling with a slight excess of a 5% solution of NaOMe or KOMe in MeOH and titrating the excess with *N*-AcOH in MeOH, using α-naphtholphthalein as indicator, correcting for the acid content of the sample. Under these conditions the *m*-compound is unattacked whilst the *o*- and *p*-isomerides react quantitatively: C₆H₄(NO₂)₂+NaOMe → C₆H₄(OMe)·NO₂+NaNO₂. By these methods the formation of all three isomerides by nitration of PhNO₂ with mixed acids is confirmed, the *m*-content varying from 95% (at -17° to -10°) to 85% (at 25—29°) and 80% (at 90—100°). The *o/p* ratio increases from 51/49 at -17° to 97/3 at 129°. Under all conditions subsequent purification is necessary to obtain pure *m*-C₆H₄(NO₂)₂. Vacuum distillation removes extraneous impurities without altering the *o*:*m*:*p* ratio. Crystallisation from MeOH or EtOH gives pure *m* but in small yield, and chemical methods are best. The use of aq. NaHSO₄, NH₂OH, or NaOH is unsatisfactory, and NH₃ in MeOH gives a pure product but in small yield. Purification is best effected with Na₂S_x in MeOH or EtOH (followed by vac. distillation) which gives a product 99.5% pure in 88% yield. In all methods involving the use of alkaline reagents the *m*-compound is also attacked unless H₂O is excluded, especially when NH₃ in MeOH is used.

J. W. BAKER.

Orientation effects in the diphenyl series. X. Quantitative nitration of 4:4'-dichloro- and 4:4'-dibromo-diphenyl and of 4-chloro-4'-bromodiphenyl. (MISS) F. R. SHAW and E. E. TURNER (J.C.S., 1932, 285—297).—Dinitration of 4:4'-dibromodiphenyl with 12 pts. of HNO₃ (*d* 1.52) gives 83.4±1.0% of 2:3'-dinitro-derivative (I), m. p. 152—153° (lit. 147—148°), the remainder being essentially (probably entirely) the 2:2'-dinitro-derivative (II), m. p. 150° (lit. 138°) (improved prep. given). Analysis of mixtures of (I) and (II) is carried out by determining the labile Br (piperidine method); (II) reacts with piperidine to a slight extent, thus necessitating a slight correction. Nitration of 4:4'-dibromo-2-nitrodiphenyl (various methods of prep. given) gives 81.2% of (I) and 18.8% of (II). (I) is nitrated further to a mixture of products containing 4:4'-dibromo-2:3':5'-trinitrodiphenyl; definite products could not be isolated by further nitration of (II). The mechanisms of mono- and di-nitration of 4:4'-dibromodiphenyl are discussed. 4:4'-Dichlorodiphenyl is dinitrated to a mixture of 81.3% of the 2:3'- (III), m. p. 141—142° (lit. 140°), and 18.7% of the 2:2'- (IV) -dinitro-derivatives; (III) and (IV) are produced in approx. the same ratio by nitration of 4:4'-dichloro-2-nitrodiphenyl. (IV) is also slightly

reactive towards piperidine. (III) is nitrated further to (mainly) 4:4'-dichloro-2:3':5'-trinitrodiphenyl, m. p. 166—167°, which reacts vigorously with piperidine, giving 4-chloro-2:3':5'-trinitro-4'-piperidinodiphenyl, m. p. 182°. 4-Chloro-4'-bromodiphenyl, prepared by brominating 4-chlorodiphenyl or by the method previously described (A., 1929, 561), has now been dinitrated (cf. *loc. cit.*) to a mixture of 2':3- (52.5%), 2:3'- (32.8%), and 2:2'- (14.7%) -dinitro-derivatives. Assuming that both intermediate mononitro-compounds are nitrated to give 3:2'- (or 2:3'-) and 2:2'-isomerides in the ratio 85:3:14:7, the proportions of 2- and 2'-mononitro-compounds first formed are 38.5 and 61.5%, respectively. These figures probably give a more accurate comparison of the relative directive effects of Cl and Br than the results of Holleman (A., 1915, i, 659) (using $p\text{-Cl}\cdot\text{C}_6\text{H}_4\text{Br}$).

H. BURTON.

Derivatives of triarylpropinenes, precursors of rubrenes, with special reference to the action of bases. J. ROBIN (Ann. Chim., 1931, [x], 16, 421—537).—Improved methods are given for the prep. of acetylenic carbinols of the type $\text{CAr}_2(\text{OH})\cdot\text{C}\cdot\text{CAr}$ (I), and their chlorides in accordance with the scheme $\text{ArC}\cdot\text{OMe} \xrightarrow{\text{PCl}_5} \text{ArCMeCl}_2 \rightarrow \text{CAr}\cdot\text{CH} \xrightarrow{\text{MgEt}} \text{CAr}\cdot\text{CMgBr} \xrightarrow{\text{COAr}_2} \text{(I)}$. Diphenyl- p -tolylethynyl, m. p. 72—73° (lit., m. p. 68—69°) (*Me*, m. p. 113—114°, and *Et*, m. p. 82—83°, ethers) (isomerised to p -tolyl β -phenylstyryl ketone, m. p. 74—75°, and a dimorphous form, m. p. 94—95°), and - β -naphthylethynyl-, m. p. 119—120° (*Et* ether, m. p. 79—80°), -carbinol are new. The spontaneous conversion of $\text{CPh}_2\text{Cl}\cdot\text{C}\cdot\text{CPh}$ (II) into $\text{CPh}_2\cdot\text{CHBz}$ (90—95%) and the rubrene (10—5%) (A., 1923, i, 922) is retarded by the absence of HCl and H_2O , the mechanism of the change involving the intermediate addition of HCl to the triple linking (cf. below), and unstable HCl additive compounds of α -chloro- α -diphenyl- γ - p -bromophenyl- Δ^8 -propinene, m. p. 95—100°, and of - γ - β -naphthyl- Δ^8 -propinene, m. p. about 155°, were isolated in dry Et_2O . Decomp. of (II) into rubrene and an intermediate substance, $\text{C}_{42}\text{H}_{29}\text{Cl}$ (III), m. p. 215—217° (cf. A., 1929, 922), occurs slowly in the dark at room temp. in Et_2O with rigid exclusion of H_2O . The same intermediate compound is obtained by the action of aq. NH_3 (either at room temp. in the dark or at 70°, the amount of rubrene formed increasing with time), NH_2Me , NHEt_2 , NMe_3 (50% yields), pyridine, piperidine, quinoline, styrene, and pinene (poor yields) in Et_2O , or by heating with 0.5 mol. of NaHCO_3 at 65—67°, and [with (II) only] by the action of NHEt_2 in EtOH at 50—60° (60% yield). (III) is converted readily and quantitatively into rubrene either in solution or by heating below 180°, and three alternative structures of the type



are suggested for it. With boiling EtOH (III) affords a substance, $\text{C}_{42}\text{H}_{29}\cdot\text{OEt}$, m. p. 214—215° (sol. in CS_2 , pptd. by COMe_2), and a substance, $\text{C}_{42}\text{H}_{29}\cdot\text{OH}$, m. p. 284—285° (insol. in CS_2). By the same methods α -chloro- α -diphenyl- γ - p -tolyl- Δ^8 -propinene is converted into a similar compound, m. p. 239—242°, - γ - β -naphthyl- Δ^8 -propinene into the compound, m. p. 257—260° (also a

yellow substance, not investigated), and - γ - p -bromophenyl- Δ^8 -propinene into a yellow substance, $(\text{C}_{21}\text{H}_{14}\text{BrCl})_2$, m. p. 234—236°, and two isomeric white compounds, $\text{C}_{42}\text{H}_{27}\cdot\text{Br}_2\text{Cl}$, m. p. 238—240° and m. p. 217—220°. By the action of NH_2Ph , o -, m -, and p -toluidines and anisidines on the ethynyl chlorides (type II) under various conditions are obtained intermediate colourless compounds of the type $\text{NHR}\cdot\text{CPh}_2\cdot\text{C}\cdot\text{CAr}$ (IV) [give no rubrene on heating, but their hydrochlorides give the rubrene and a little (V)], converted by heating with the base hydrochloride in EtOH at 70—80° into yellow isomerides of the type $\text{CPh}_2\cdot\text{CH}\cdot\text{CAr}\cdot\text{NR}$, the constitution of which is proved by hydrolysis to the ketones $\text{CPh}_2\cdot\text{CH}\cdot\text{COAr}$ from which they are also obtained by the action of the base and anhyd. ZnCl_2 . Thus from the appropriate components are obtained; α -anilino- (IV, $\text{Ar}=\text{R}=\text{Ph}$), m. p. 87—88° (hydrochloride, m. p. 158—160°); α - o -, m. p. 139—140°, α - m -, m. p. 117—118°, and α - p -, m. p. 115—116° (hydrochloride, m. p. 159—161°) -toluidino-, α - o -, m. p. 140—141° (hydrochloride, m. p. 140—141°), and α - p -, not crystalline, -anisidino- benzhydrylphenylacetylene; α -anilinobenzhydryl- p -tolyl-, m. p. 118—119° (hydrochloride, m. p. 127—130°), - β -naphthyl-, m. p. 146—147° (hydrochloride, m. p. 157—159°), and - p -bromophenyl-, m. p. 151—152° (hydrochloride, m. p. 125—127°), -acetylene, converted into the isomeric yellow anil of phenyl (V, $\text{Ar}=\text{R}=\text{Ph}$), m. p. 199—200°, p -tolyl, m. p. 162—163° (hydrochloride, m. p. 120°), β -naphthyl, m. p. 149—150° (hydrochloride, m. p. 156—159°), and p -bromophenyl, m. p. 138—139° (hydrochloride, m. p. 143—145°), β -phenylstyryl ketone: and the o -, m. p. 192—193°, m -, m. p. 139—140°, and p -, m. p. 174—175°, -methylanil, and o -, not cryst., and p -, m. p. 148—149°, -methoxyanil of phenyl β -phenylstyryl ketone. The conversion of (IV) \rightarrow (V) does not involve migration of a Ph group, since $\text{CPh}_2\cdot\text{NHPh}\cdot\text{C}\cdot\text{C}\cdot\text{C}_6\text{H}_4\text{Me} \rightarrow \text{CPh}_2\cdot\text{CH}\cdot\text{C}(\text{NPh})\cdot\text{C}_6\text{H}_4\text{Me}$ and not $\text{CPh}(\text{NPh})\cdot\text{CH}\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\text{Me}$, but is explained by initial addition of HCl to the triple linking (cf. above): $\text{CAr}_2\text{X}\cdot\text{CH}\cdot\text{CArCl} \xrightarrow{+} \text{CAr}_2\cdot\text{C}\cdot\text{CArBH} \rightarrow \text{CAr}_2\cdot\text{CH}\cdot\text{CAr}\cdot\text{B}$ ($\text{X}=\text{NHPh}$, $\text{BH}=\text{NHPh}$), which also applies to the similar conversion of the carbinols ($\text{X}=\text{OH}$), ethers ($\text{X}=\text{OR}$), and chlorides ($\text{X}=\text{Cl}$), and to the isomerisation of carbinols to ketones ($\text{X}=\text{BH}=\text{OH}$). Similar action of NH_3 on the ethynyl chlorides affords substances of the type $\text{NH}_2\cdot\text{CAr}_2\cdot\text{C}\cdot\text{CAr}$ together with products probably obtained by cyclisation of the side-chain, and thus are obtained α -aminobenzhydryl-phenyl-, m. p. 95—96° (hydrochloride, m. p. 166—167°, converted by heating at 200° into the hydrocarbon obtained by Moureu and others, A., 1930, 594) [together with a substance, m. p. 260° (hydrochloride)], - p -tolyl-, m. p. 108—109° (hydrochloride, m. p. 185—189°, converted by heating into NH_4Cl , the original substance, methylrubene, and the following compounds, m. p. 250° and 280°) (together with a substance, $\text{C}_{44}\text{H}_{35}\text{N}$, m. p. 250°, and an isomeric substance, m. p. 280°), - β -naphthyl-, m. p. 133—134° (hydrochloride, m. p. 157—159°), and - p -bromophenyl-, m. p. 111—112° [hydrochloride, m. p. 155—160° (decomp.)] [the other product in this case being the ether $\text{CPh}_2(\text{OEt})\cdot\text{C}\cdot\text{C}\cdot\text{C}_6\text{H}_4\text{Br}$], -acetylene. Unlike its action

on (II) (above) NHET_2 converts α -chloro- α -diphenyl-*p*-bromophenyl- Δ^2 -propinene into the corresponding α -diethylamino-derivative, m. p. 133—134° (*hydrochloride*, m. p. 147—150°). The bearing of these results on the mechanism of rubrene formation is discussed.

J. W. BAKER.

Catalytic dehalogenation by tetrahydronaphthalenes in presence of copper. (Miss) M. S. LESSLIE and E. E. TURNER (J.C.S., 1932, 281—285).—2-Iododiphenyl ether (I), m. p. 55—55.5° (prepared from the 2-NH₂ derivative by the usual method), and Cu-bronze at 200—220° give 2:2'-diphenoxydiphenyl ether, m. p. 100—101°. (I) and Et 2-chloro-3:5-dinitrobenzoate with Cu-bronze give an inseparable mixture of products, whilst (I) and Et 2-bromo-3:5-dinitrobenzoate at 180° afford Et 4:6:4':6'-tetranitrodiphenate as the only isolable product. 1-Iodo-tetrahydronaphthalene, b. p. 150°/17 mm., 279—280°/765 mm. (in small quantities only) (prepared from tetrahydro- α -naphthylamine), with Et 2-chloro-3:5-dinitrobenzoate (II) and Cu-bronze at 210—225° give (mainly) Et. 3:5-dinitrobenzoate, also formed from (II), tetrahydronaphthalene (III), and Cu-bronze at 200—215°. Picryl chloride, (III), and Cu-bronze at about 195° give $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ and C_{10}H_8 [formed by dehydrogenation of (III)]. (II) is unaffected by heating with Cu-bronze in cyclohexanol or decahydronaphthalene.

Ph_2 , $\text{CH}_2\text{Cl}\cdot\text{COCl}$, and AlCl_3 in CS_2 give 4:4'-di-(chloroacetyl)diphenyl, m. p. 226—227° which reacts vigorously with piperidine, but is unaffected by Cu-bronze in (III).

H. BURTON.

Preparation of trimethylnaphthalenes from 2:6-dimethylnaphthalene. V. VESELY and F. ŠTURSA (Coll. Czech. Chem. Comm., 1932, 4, 21—31).—2:6-Dimethylnaphthalene (I) with Br in CS_2 gives its 1-bromo- (II), m. p. 33—34°, b. p. 177—180°/8 mm., and 1:5(?)-dibromo-, m. p. 160—161°, derivatives. The Grignard compound of (II) with Me_2SO_4 gives 1:2:6-tri- together with some 2:6-di-methylnaphthalene. With 98% H_2SO_4 at 70—80° and then at 140—150° (I) affords its 7-sulphonic acid, from which 3:7-dimethyl- β -naphthol (III) is obtained. This with CH_2O (40%) in aq. $\text{AcOH}\text{--HCl}$ gives 7:7'-dihydroxy-2:2':6:6'-tetramethyl-8:8'-di-naphthylmethane, m. p. 231°, reduced by Zn and 4% NaOH to (III) and 1:3:7-trimethyl- β -naphthol, m. p. 106—107°, which, heated with Zn dust, gives 1:3:7-tri- and some 2:6-di-methylnaphthalene. When heated with 22% aq. $(\text{NH}_4)_2\text{SO}_3$ and aq. NH_3 at 250° (II) is converted into 3:7-dimethyl- β -naphthylamine, m. p. 134—135° (*Ac* derivative, m. p. 233—234°), converted by the Sandmeyer reaction into 2-bromo-3:7-dimethylnaphthalene, m. p. 138—139°, the Grignard compound of which with Me_2SO_4 gives only (I). 2:6-Dimethyl- α -naphthylamine (A., 1922, i, 999) is converted by diazotisation into 2:6-dimethyl- α -naphthol, m. p. 133°, and by nitration (of its *Ac* derivative) into its 4-nitro-derivative (IV), m. p. 194—195° (*Ac* derivative, m. p. 260°), similarly converted into 4-nitro-2:6-dimethyl- α -naphthol, m. p. 137—138°, oxidised by FeCl_3 to the quinone. Deamination of (IV) gives 4-nitro-2:6-dimethylnaphthalene, m. p. 84—85°, reduced by Fe and AcOH to the

4-amino-compound, m. p. 93—94° (*Ac* derivative, m. p. 207—208°), which by diazotisation affords the corresponding naphthol.

J. W. BAKER.

Electrochemical nitration of naphthalene. F. FICHTER and E. PLUSS (Helv. Chim. Acta, 1932, 15, 236—247).—In agreement with G.P. 100,417 (1897) the yield of 1-nitronaphthalene obtained by the action of HNO_3 (d 1.25) on C_{10}H_8 at 80° is increased by electrochemical procedure, but, contrary to the patent, C_{10}H_8 is attacked under ordinary conditions by HNO_3 (d 1.160) and a 92.5% yield of $\text{C}_{10}\text{H}_7\text{NO}_2$ is obtained with HNO_3 (d 1.200). The increased yield by the electrochemical method is not due to increased concn. of the HNO_3 resulting from electrolysis, which, in agreement with theory, is only 2.3%. The best yields are obtained with 40% HNO_3 and a c.d. of 0.3 amp. per sq. cm. for 1.5 hr., prolonged action increasing the amount of oxidation products formed. Determination of the CO_2 produced shows that the heat produced by such oxidation is sufficient to raise the temp. of the anode liquid from 80° to 100° and the increased yield by the electrochemical method is due to the higher temp. of nitration. In agreement with this even better yields are obtained by ordinary nitration of C_{10}H_8 with dil. HNO_3 at 95—98°, since by-product formation is almost excluded (*e.g.*, with 26.37% HNO_3 the yields by the electrochemical and ordinary nitration at 80°, and by ordinary nitration at 98° are 65.4, 23.5, and 92.8%, respectively).

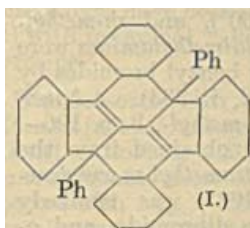
J. W. BAKER.

Rubrenes. L. ENDERLIN (Compt. rend., 1931, 193, 1432—1434).—Dimethylrubrene is converted by H_2SO_4 in C_6H_6 into colourless isomeric dimethyl- ψ -rubrenes, m. p. 293—294° and 271—272° ($+\text{C}_6\text{H}_6$, m. p. 220°), and by HNO_3 in C_6H_6 into a stable dimethylrubrene monoxide, m. p. 265° ($+\text{C}_6\text{H}_6$, m. p. 175°), which can be reduced to the hydrocarbon but cannot be further oxidised. The monoxide may also be obtained by partial reduction of the dissociable oxide, $\text{C}_{44}\text{H}_{32}[\text{O}_2]$.

F. R. SHAW.

Formula and constitution of a colourless hydrocarbon, $\text{C}_{42}\text{H}_{26}$, showing a violet fluorescence.

C. DUFRAISSE and L. ENDERLIN (Compt. rend., 1932, 194, 183—185).—A by-product in the prep. of rubrene without use of tert. bases is a colourless substance, (I), $\text{C}_{42}\text{H}_{26}$, m. p. about 430° (violet fluorescence), which is also formed by removal of H_2O from rubrene oxide with H_2SO_4 . It is considered to be formed



with two substances, $\text{C}_{42}\text{H}_{30}$, by disproportionation of rubrene.

R. S. CAHN.

Aminosulphonamides. M. BATTEGAY and J. MEYBECK (Compt. rend., 1932, 194, 186—187).—*N*-Chlorosulphonylacetanilide and NHMe_2 in dry Et_2O at -5° give NHMe_2HCl , NMe_2Ac , and dimethylaminosulphonanilide, $\text{NMe}_2\cdot\text{SO}_2\cdot\text{NHPh}$, m. p. 83—84°. Sulphondianilide, $\text{SO}_2(\text{NHPh})_2$, and aminosulphonanilide, $\text{NH}_2\cdot\text{SO}_2\cdot\text{NHPh}$, m. p. 108.5—109°, were similarly obtained.

R. S. CAHN.

Carbylamines. XIX. Reaction with aldehydic and ketonic acids. M. PASSERINI and G.

RAGNI (Gazzetta, 1931, 61, 964—969).—Phenylcarbylamine with phthalaldehydic acid gives the *phthalidecarboxylanilide*, m. p. 110°, with opianic acid a compound (I), m. p. 235°, which with alcoholic KOH loses 1 mol. of diphenylformamidine giving 5:6-dimethoxyphthalidecarboxylanilide (II), m. p. 182—185°, and with meconic acid gives *diphenylformamidine meconate*, m. p. 197°. (I) appears to be an additive compound of (II) and diphenylformamidine. E. E. J. MARLER.

Degradation of quaternary ammonium salts. IV. Relative migratory velocities of substituted benzyl radicals. V. Molecular rearrangement in related sulphur compounds. T. THOMSON and T. S. STEVENS (J.C.S., 1932, 55—69, 69—73; cf. A., 1930, 1585).—IV. The velocity of the change (I) $\text{COPh}\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})\text{Me}_2\text{Br} \rightarrow \text{COPh}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{NMe}_2$ (II), which takes place under the influence of alkalis, and is accompanied by 12—18% of by-products, is measured in a variety of solvents and for a series of substituted derivatives of (I). The reaction is approx. unimol. in regard to (I); its velocity increases, but not proportionately, with increase of alkoxide concn. over 1 mol., and is affected by medium in the order $\text{MeOH} < \text{EtOH} < \text{Pr}^i\text{OH} < \text{Pr}^t\text{OH}$: the temp. coeff. in MeOH is high, and the iodide corresponding with (I) rearranges at the same rate as the bromide. With aq. NaOH the (much smaller) initial velocities are proportional to the concn. both of alkali and of (I). Substitution in the $\cdot\text{CH}_2\text{Ph}$ radical affects the velocity of rearrangement in the order $\text{OMe} < \text{Me} < \text{halogens} < \text{NO}_2$, the effect of orientation being roughly $m < p < o$; in the *o*- and *p*-positions the common order of the halogens is reversed. Substitution of Br in the *p*-position of the $\text{COPh}\cdot\text{CH}_2\cdot$ residue does not alter the relative velocities of reaction in the benzyl, *p*-chloro- and *p*-bromo-benzyl series. *m*-Chloro- (*picrate*, m. p. 128—130°), *p*-chloro- (*picrate*, m. p. 125—126°), *o*-bromo- (*picrate*, m. p. 149—150°), *o*-iodo- (*picrate*, m. p. 134—136°), *m*-iodo- (*picrate*, m. p. 128—130°), *m*-nitro- [*picrate*, m. p. 209—211° (decomp.)], *o*-methyl- (*picrate*, m. p. 148—150°), and *m*-methyl- (*picrate*, m. p. 136—138°), -benzylidimethylamines were prepared from the corresponding benzyl bromides by the hexamine method (A., 1922, i, 333). *o*-Nitro- (*picrate*, m. p. 138—141°), and *p*-methyl-, b. p. 196—199°, -benzylidimethylamines were obtained from the benzyl bromides and NHMe_3 ; tetramethyl-*m*-xylylenediamine (*picrate*, m. p. 190—193°) was similarly prepared from crude *m*-xylylene dibromide, and *o*-methoxybenzylidimethylamine (hydrochloride, m. p. 149°) was obtained by the Eschweiler methylation of the primary amine. The following quaternary salts, prepared by combination of the appropriately substituted $\text{CH}_2\text{Ph}\cdot\text{NMe}_2$ with phenacyl or *p*-bromophenacyl bromide and subsequent double decomp., are described: phenacylbenzylidimethylammonium *picrate*, m. p. 132—134°, iodide, m. p. 174—176°; phenacyl-*o*- (bromide, m. p. 149—150°; *picrate*, m. p. 154—156°); -*m*- [bromide, m. p. 132—134°; *picrate*, m. p. 141—143° (decomp.)], and -*p*-chloro- [bromide, m. p. 186—187° (decomp.)]; *picrate*, m. p. 125—126°; -*o*- (bromide, m. p. 153—154°; *picrate*, m. p. 151—

153°); -*p*- (*picrate*, m. p. 130—131°), and -*m*-bromo-, (*picrate*, m. p. 132—134°); -*o*- (bromide, m. p. 174—176°; *picrate*, m. p. 149—151°), -*m*- [bromide, m. p. 176—177° (decomp.)]; *picrate*, m. p. 123—125°], and -*p*-iodo- (bromide, m. p. 183—185°; *picrate*, m. p. 139—141°); -*o*- (bromide, m. p. 142—144°; *picrate*, m. p. 155—158°), -*m*- (bromide, m. p. 174—175°; *picrate*, m. p. 154—156°), and -*p*-nitro- (*picrate*, m. p. 110—113°); -*m*-methoxy- (bromide, m. p. 150—152°; *picrate*, m. p. 111—112°); -*o*- (iodide, m. p. 160—162°; *picrate*, m. p. 131—133°), and -*m*-methyl-benzylidimethylammonium iodide, m. p. 134—135° (decomp.); *p*-bromophenacyl-*o*-methoxy- (bromide, m. p. 173—176°; *picrate*, m. p. 116—119°); -*p*-methyl- [bromide, m. p. 174—176° (decomp.)]; *picrate*, m. p. 128—130° (decomp.)]; -*p*-chloro- (bromide (m. p. 174—175°; *picrate*, m. p. 146—147°); -*p*- [bromide, m. p. 187—188° (decomp.)]; *picrate*, m. p. 157—158° (decomp.)], and -*m*-bromo- [bromide, m. p. 193° (decomp.)]; *picrate*, m. p. 136—137°]; and -*m*-nitro-benzylidimethylammonium bromide, m. p. 200—201° (decomp.), (*picrate*, m. p. 158—159°); *p*-bromophenacylbenzylidimethylammonium *picrate*, m. p. 159—160°; *s*-*m*- (dibromide), m. p. 205—206°, and *s*-*p*-xylylenebis-*p*-bromophenacyltetramethyldiammonium dibromide, m. p. 220—222° (decomp.). By treatment of these with alkali the following were prepared: ω -dimethylamino- ω -*o*-chloro-, m. p. 69—71°; -*m*-chloro-, m. p. 52—53°; -*p*-chloro-, m. p. 59—61°; -*o*-bromo-, m. p. 79—81°; -*o*-iodo-, m. p. 97—98°; -*m*-iodo-, m. p. 82—83°; -*p*-iodo-, m. p. 67—68°; -*o*-nitro-, m. p. 75—77°; -*m*-nitro-, m. p. 70—72°; -*m*-methoxy-, m. p. 61—63°; -*o*-methyl-, m. p. 62—63°; and -*m*-methyl-, m. p. 74—76°, -benzylacetophenones: *p*-bromo- ω -dimethylamino- ω -*o*-methoxy-, m. p. 82—83°; -*p*-methyl-, m. p. 91—93°, -*p*-chloro-, m. p. 75—76°; -*p*-bromo-, m. p. 77—78°; -*m*-bromo-, m. p. 68—70°; and -*m*-nitro-, m. p. 72—73°, -benzylacetophenones: 4:4'-dibromo- ω - ω' -bisdimethylamino- ω - ω' -*m*-, m. p. 143—144°, and -*p*-xylylenebisacetophenone, m. p. 138—140°.

V. A similar change to that of (I) \rightarrow (II) is realised with the corresponding sulphonium bromide, but not with phenacylbenzylsulphone. Phenacylbenzylmethylsulphonium bromide, m. p. 113—115° (decomp.) (*picrate*, m. p. 115—117°), prepared from benzyl methyl sulphide, b. p. 206—210°/751 mm., and phenacyl bromide, rearranges into ω -benzyl- ω -methylthiolacetophenone, m. p. 55—56°, when heated with an excess of NaOMe in MeOH. This product was identified by reduction of its oily sulphonium derivative (Me_2SO_4) with Zn and dil. H_2SO_4 to benzylacetophenone; the attempted synthesis from ω -bromo- ω -benzylacetophenone and Na methylmercaptide in EtOH gave only benzylacetophenone. Phenacylbenzylsulphone is unaffected by NaOMe in MeOH at the b. p., and at 120—140° hydrolysis to benzylmethylsulphone and BzOH occurs; boiling $\text{NMe}_2\cdot\text{CH}_2\text{Ph}$ is also without marked effect. Bromomethylphenylsulphone would not combine with $\text{NMe}_2\cdot\text{CH}_2\text{Ph}$ under any conditions, nor did it react with boiling piperidine. H. A. PIGGOTT.

dl- β -Amino- α -phenylpropanes. G. A. ALLES (J. Amer. Chem. Soc., 1932, 54, 271—274).— PhCHO (0.2 mol.), nitroethane (0.2 mol.), and *n*-amylamine

(0.2 mol.) give after 2 weeks in the dark β -nitro- α -phenyl- Δ^2 -propene, m. p. 65—66°; p -OMe·C₆H₄·CHO and veratraldehyde similarly yield the α -anisyl and α -3:4-dimethoxyphenyl derivatives. These are reduced electrolytically in EtOH-AcOH-12*N*-H₂SO₄ with a Hg cathode and a Pb anode at 30—40° to the corresponding β -amino- α -arylpropane. Demethylation of β -amino- α -anisylpropane with conc. HCl gives *dl*- β -amino- α -*p*-hydroxyphenylpropane hydrochloride, m. p. 171—172°; *dl*- β -amino- α -3:4-dihydroxyphenylpropane hydrochloride has m. p. 192°. The initial condensation does not occur with hydroxybenzaldehydes.

C. J. WEST (b).

Salts of trisulphonic acids. A. A. KUROTOSCHKIN (J. Gen. Chem. Russ., 1931, 1, 689—695).—The 1½ Ca salt of 1-nitronaphthalene-3:6:8-trisulphonic acid is reduced to the corresponding 1-NH₂-compound, various Ca and Na salts of which are described.

R. TRUSZKOWSKI.

Solubility relationships amongst optically isomeric salts. I. Malates of α -*p*-xenylethylamine. A. W. INGERSOLL and E. G. WHITE (J. Amer. Chem. Soc., 1932, 54, 274—281; cf. A., 1928, 1139).—An analysis of the solubility relationships amongst the salts resulting from inactive and partly active acids and bases is given, with particular reference to the problem of complete optical resolution. The original should be consulted for details. *p*-Phenylacetophenoneoxime, m. p. 186° (all m. p. are corr.), is reduced by Na-Hg and 95% EtOH (kept slightly acid by AcOH) to α -*p*-diphenylethylamine (α -*p*-xenylethylamine) (I), an oil, partial decomp. when distilled at 10 mm. (hydrochloride, m. p. 221°; *Bz* derivative, m. p. 179°), which gradually forms a carbonate on keeping. (I) is partly resolved by *l*-malic acid, giving *d*- α -*p*-xenylethylamine, $[\alpha]_D^{25} + 24.8^\circ$ in 95% EtOH (*l*-malate, m. p. 183°; hydrochloride, m. p. 230°, $[\alpha]_D^{25} + 12.8^\circ$ in H₂O). Details are given of the attempted completion of the resolution with *dl*-malic acid, and of its completion with partly active (*d*) malic acid. 1- α -*p*-Xenylethylamine hydrochloride has m. p. 230°, $[\alpha]_D^{25} - 12.2^\circ$ in H₂O. C. J. WEST (b).

Alkylation of amines as catalysed by nickel. C. F. WINANS and H. ADKINS.—See this vol., 236.

Salts of *o*-, *m*-, and *p*-phenylenediamines with organic acids. F. FEIGL and L. POPP-HALPERN (Monatsh., 1932, 59, 136—151).—Salts of *o*-, *m*-, and *p*-C₆H₄(NH₂)₂ with the following acids (the ratios in parentheses are quoted as the no. of mols. of diamine to no. of mols. of acid) are described; a solution of the base in Et₂O or EtOH is added to an excess of the acid (also in Et₂O or EtOH): CH₃Cl·CO₂H [*o*-(1:1), *p*-(1:2)]; CHCl₂·CO₂H [*o*-(1:1), *m*-(1:1), *p*-(1:2)]; CCl₃·CO₂H [*o*-(1:1), m. p. 150° (decomp.), *p*-(1:2)]; CH₂CN·CO₂H [*o*-(1:1), *p*-(1:2)]; CH₂Ph·CO₂H [*o*-(1:1), *p*-(1:2), m. p. about 105° (becomes coloured at 100°)]; phenoxyacetic acid [*o*-(1:1), m. p. 137°, *m*-(1:1), m. p. 125—126° (decomp.), *p*-(1:2), m. p. 148—149° (decomp.)]; ethoxyacetic acid [*o*-(1:1), *m*-(1:1), *p*-(1:1)]; picric acid [*o*-(1:1), m. p. 210—215° (decomp.), *m*-(1:1), *p*-(1:1), m. p. 210—215° (decomp.)]; PhSO₃H [*o*-(1:2), *m*-(1:2), *p*-(1:2)]; *o*-NO₂·C₆H₄·CO₂H [*o*-(1:1), *m*-(1:1), *p*-(1:1)]; *m*-NO₂·C₆H₄·CO₂H [*o*-(1:1), *p*-(1:1)]; oxanilic acid

[*o*-(1:2), *p*-(1:2)]; dibromosuccinic acid [*o*-(2:1), *m*-(2:1), *p*-(1:1)]; benzyldenemalonic acid [*o*-(2:1), *p*-(1:1)]; diphenic acid [*o*-(1:1), *p*-(1:1)]; *o*-C₆H₄(CO₂H)₂ [*o*-(2:1), *m*-(2:1), *p*-(1:1)]; H₂C₂O₄ [*o*-(1:1), *p*-(1:1)]. *p*-C₆H₄(NH₂)₂ generally gives neutral salts (1 CO₂H per 1 NH₂ group) (except with acids containing NO₂-groups), whilst *o*- and *m*-C₆H₄(NH₂)₂ often give basic salts (1 CO₂H per 2 NH₂ groups). The exceptions with *o*-C₆H₄(NH₂)₂ are with acids which cannot condense directly to the iminazoles. Salt formation is not related to the dissociation consts. of the acids. The basic *o*-C₆H₄(NH₂)₂ salts are formulated as C₆H₄ $\left\langle \begin{smallmatrix} \text{NH}_2 \\ \text{NH} \end{smallmatrix} \right\rangle$ HO·CO·R; they are considered to be intermediates in the production of iminazoles.

H. BURTON.

Heteropolarity. XV. Diphenyl-*p*-phenylenediamine and triphenylmethyl chloride. W. DILTHEY, W. SCHOMMER, and G. ESCHERICH (Ber., 1932, 65, [B], 95—97).—Titration of the salt obtained from CPh₃Cl and diphenyl-*p*-phenylenediamine (A., 1931, 955) with TiCl₃ or SnCl₂ shows it to be

[NHPPh·C₆H₄·NHPPh]⁺Cl, C₁₈H₁₆N₂. The extra mol. of diamine appears to be an integral portion of the solid salt. An analogous compound, m. p. 165—168°, is formed from CPh₃F and the diamine, whereas CPh₃Br gives a less well-defined substance. Since the colour of solutions of the chloride is intensified by addition of Br, FeCl₃, or diphenyl-*p*-phenylenediamine, the dissolved salt is decomposed into semiquinonoid salt and free amine.

H. WREN.

Stereoisomerism of dinaphthyl derivatives and preparation of optically active dyes. S. MURAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 17, 297—298).—2:2'-Dinitro-, +5H₂O, decomp. 310° (*Ba* salt of *d*-, $[\alpha]_D^{25} + 36.9^\circ$ in H₂O; *Ba* salt of *l*-, $[\alpha]_D^{25} - 35.5^\circ$), and 2:2'-diamino-1:1'-dinaphthyl-5:5'-disulphonic acid (I) (*Ba* salt of *d*-, $[\alpha]_D^{25} + 120.8^\circ$; *Ba* salt of *l*-, $[\alpha]_D^{25} - 122.0^\circ$), obtained by sulphonating the corresponding dinaphthyls, have been resolved using CH₂Ph·CH₂·NH₂ and bornylamine. Optically active dyes have been obtained by coupling diazotised (I) with resorcinol, salicylic acid, and *d*- and *l*-formyltyrosine.

F. R. SHAW.

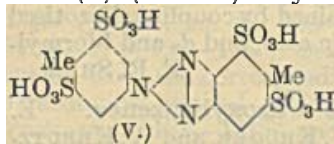
Stereoisomerism of azoxybenzenes. E. MÜLLER [with E. HORY, W. KRÜGER, and W. KREUTZMANN] (Annalen, 1932, 493, 166—173).—*cis*- and *trans*-stilbenes show similar ultra-violet absorption spectra with $\lambda_{\text{max}} = 2800$ and 3000 Å., respectively; the absorption strength of the *cis*- is about $\frac{1}{2}$ of that of the *trans*-form. *cis*- and *trans*-cinnamic acids show similar differences, as do the "normal" and *iso*-azoxybenzenes, *o*-azoxytoluenes, *o*-azoxyanisoles, and 2:2'-dichloroazoxybenzenes. The pairs of azoxybenzenes are probably *cis-trans*-isomerides.

H. BURTON.

Aliphatic diazo-compounds. Stable crystalline optically active diazo-compound. F. E. RAY (J. Amer. Chem. Soc., 1932, 54, 295—298).—The *d*- and *l*-forms of aminophenyl-2-hydroxy- α -naphthylmethane (cf. Betti, A., 1906, i, 950) have m. p. 137°, $[\alpha]_D^{25} \pm 60 \pm 0.2^\circ$ in Et₂O, and with HNO₂ in aq. pyridine give *d*- and *l*-diazophenyl-2-hydroxy- α -

naphthylmethane, m. p. 120° (decomp.), $[\alpha]^{20}_D +405^\circ$ and -420° in 95% EtOH-COMe₂ (4:1), which when heated at 125° pass into the unstable *ketazine*, m. p. 182°, of Ph 2-hydroxy- α -naphthyl ketone. Alkali does not racemise the *d*-diazo-compound, whilst a 1% solution of the *l*-isomeride in EtOH undergoes a 12% decrease in rotation after 4 hr. at 60–65°; boiling causes some decomp. to the *ketazine*. This result shows that a C atom attached to the diazo-group may retain its asymmetry. C. J. WEST (b).

Azo-dyes and their intermediates. VIII. *o*-Bisazo-dyes. P. RUGGLI, A. COURTIN, and (in part) E. MERZ. **IX. Comparison of absorption spectra of *o*-bisazo-dyes with the isomeric *p*-compounds.** F. BURKI, A. COURTIN, and P. RUGGLI. **X. *peri*-Bisazo dyes.** I. P. RUGGLI and A. COURTIN (Helv. Chim. Acta, 1932, 15, 75–108, 108–110, 110–119).—VIII. *o*-Bisazo-dyes are prepared: (a) by diazotisation and subsequent coupling from *o*-aminoazo-compounds; (b) by condensation of *o*-aminoazo-compounds with PhNO; and (c) by converting an *o*-hydroxyazo-compound by means of NaHSO₃ and NHPH-NH₂ into the corresponding *o*-phenylhydrazino-compound followed by oxidation. Derivatives without auxochromic groups are obtained by (b) and (c), and those containing such groups by (a) and (c). Evidence is discussed in support of the view that compounds obtained by all three methods have a true *o*-bisazo-structure rather than a cyclic tetrazine structure, e.g., the continuous sequence of colour change from deep red to orange in the series (XII) > (XVI) = (III) > (XIV) > (II) > (XVII) > (IX) > (XI) > (XIII) > (XV) > (VI) = (VII) > (VIII). The following are thus prepared: (a) The *bisazo-dyes* obtained by diazotisation of 2-amino-5:4'-dimethylazobenzene (I) (prep. from *p*-diazoaminotoluene described) and coupling with β -naphthol (II) and Na β -naphthol-6-sulphonate (III). Sulphonation of (I) at 85° gives a *disulphonic acid* (IV) and above 85° is obtained 2-*p*-tolyl-5-methylbenzotriazole-tetrasulphonic acid (V) (Ba salt). By diazotisation of (IV) and

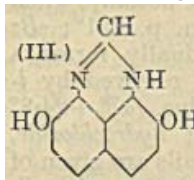


coupling is obtained the *o*-bisazo-dye with β -naphthol (VI) [reduced with alkaline hyposulphite in aq. EtOH to 1-amino- β -naphthol and its 4-sulphonic acid, and decomposed by hot HCl to the *triazole*-3':6-*disulphonic acid*, +H₂O, and 1:2-dihydroxynaphthalene, isolated as its Ac₂ derivative and as tetrahydroxydinaphthyl (Ac₄ derivative) formed from it by oxidation]. (b) (I) condenses with PhNO in alcoholic NaOAc at 100° to 4-benzeneazo-3-*p*-tolueneazotoluene, bordeaux-red, m. p. 85° (VII). (c) Treatment of Na benzeneazo- β -naphthol-4':6-disulphonate with NaHSO₃ and NHPH-NH₂ gives the corresponding 2- β -phenylhydrazino-derivative (as its NaHSO₃ additive compound), converted by air and NaOH into the *bisazo-dye* (VIII); similarly Na *o*-methoxybenzeneazo- β -naphthol-6-sulphonate gives the 2- β -phenylhydrazino-derivative oxidised to the *bisazo-dye* (IX); *p*-acetamidobenzeneazo- β -naphthol-6-sulphonate (X) gives the NaHSO₃ additive compound of the 2- β -phenylhydrazino-com-

pound, converted into the *bisazo-dye* (XI), in which hydrolysis of the Ac group is difficult. Hydrolysis of (X) gives the corresponding *p*-NH₂-compound (XII), converted into the NaHSO₃ additive compound, +3H₂O, of the 2- β -phenylhydrazino-derivative, converted by air and NaOH into the *p*-hydroxybisazo-dye (XIII) (replacement of NH₂ by OH) (*Ac* derivative), also obtained similarly from Na *p*-hydroxy- (XIV) or *p*-acetoxy- (XV) -benzeneazo- β -naphthol-6-sulphonate through the NaHSO₃ compound (*Ac* derivative) of the 2- β -phenylhydrazino-compound. Sulphonation of 4-amino-5:6'-dimethylazobenzene [4-azo- β -naphthol compound (XVI), m. p. 165–167°] with oleum (d^{20}_4 1.935) at 100° gives the 1:3'-*disulphonic acid* (Ba salt), from which, after diazotisation, the 4-azo- β -naphthol (XVII) is obtained.

IX. The absorption spectra of the two *o*-bisazo-dyes (II) and (VI) are, respectively, very similar (but slightly displaced in the direction of shorter wavelengths) to those of the isomeric *p*-compounds (XVI) and (XVII), thus confirming the bisazo-structure assigned.

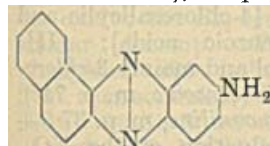
X. 2:7-Dihydroxynaphthalene (I) (prep. described) couples with 2 mols. of diazotised naphthionic acid to give the brownish-red 1:8-bisnaphthaleneazo-2:7-dihydroxynaphthalene-4':4'-disulphonic acid (II) (disodium salt) (converted in H₂O at 100° into a blue compound, possibly having an *o*-quinonehydrazone structure), the structure of which is proved by reduction with SnCl₂ and HCl in 85% HCO₂H to the hydrochloride of 2:7-dihydroxy-1:8-perimidine (III, brownish-orange crystals) (by condensation of the 1:8-diamine with the HCO₂H), oxidised by FeCl₃ or by air and NaOH to 7-hydroxyperimidine-quinone (red; intense blue solution in alkalis; decomp. with blue colour at 160°). With 1 mol. of diazotised naphthionic acid (I) affords 2:7-dihydroxyazonaphthalene-4'-sulphonic acid, which dyes wool red; similar coupling with diazotised sulphanilic acid gives 1-mono- and 1:8-bis-*p*-sulphobenzeneazo-2:7-dihydroxynaphthalene. The dyeing properties of these derivatives are discussed.



J. W. BAKER.

Action of salts of sulphurous acid on aromatic amino- and hydroxy-compounds. XIV. Rearrangements of azo-dyes, particularly into vat dyes. H. T. BUCHERER and M. RAUCH. **XV. Mechanism of rearrangement of azo- into vat dyes (naphthacarbazolequinones).** H. T. BUCHERER and F. HANUSCH. **XVI. Carbazoles and carbazolequinones (vat dyes of α -naphthaquinone series).** H. T. BUCHERER and M. HAYASHI (J. pr. Chem., 1931, [ii], 132, 227–273, 274–301, 302–320).—XIV. Condensation of *p*-sulphobenzeneazo- β -naphthol (I) with *p*-phenylenediamine or *p*-aminoacetanilide and NaHSO₃ gives, not the expected *p*-aminophenyl- β -naphthylamine derivatives, but bluish-violet dyes accompanied by sulphanilic acid and NH₃; the dyes can be vatted with Na₂S₂O₄ and evolve NH₃ with dil. alkalis. β -Naphthol-8- and -1-sulphonic acids, however, readily condense to Na *p*-aminophenyl- β -naphthylamine-8- (IV) (*Ac* derivative) and -1-sulphonate [*Ac* (also by Ac₂O), *Bz*, and *p*-

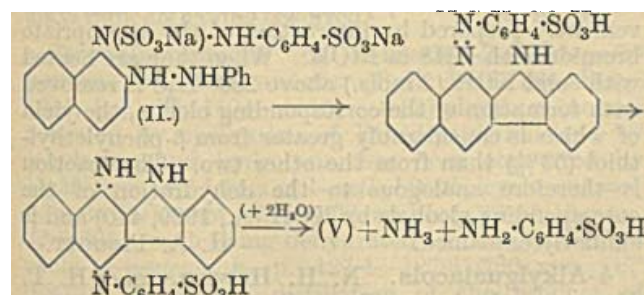
toluenesulphonyl derivatives]. The free amines do not interact with diazonium salts, but the Ac derivative of the -1-sulphonate readily couples with loss of the SO_3H group, which is also hydrolysed away by warm 7% aq. HCl. An acridine derivative appears to be formed by interaction of (IV) with CH_2O . *Na 4'-hydroxy-3'-carboxyphenyl- β -naphthylamine-sulphonate* is prepared from β -naphthol-1-sulphonic acid, 4-aminosalicylic acid, and NaHSO_3 , and does not couple. Red *azo-dyes* are prepared from the Ac and *p*-toluenesulphonyl derivatives of (IV) and *p*-diazobenzenesulphonic acid, and are converted by acids, and to some extent by alkalis, but best by 80% H_2SO_4 at 70° into 2-aminopheno- $\alpha\beta$ -naphthazine (annexed formula), m. p. 302° , and its acyl derivatives



[Ac derivative (Ac_2O), m. p. 292°]; the reaction proceeds more readily with the Ac compound. The action of cold conc. HCl on 1-sulphobenzeneazo-2-phenylhydr-

azinonaphthalene, "Red-I" ["III"] in A., 1925, i, 1338; the same designation is used in this abstract], gives, in addition to 4-aminopheno- $\alpha\beta$ -naphthazine, m. p. 156° ("Azine-I," *loc. cit.*) [acetate, m. p. 224° (warm Ac_2O)], and "Violet-I," $\text{C}_{44}\text{H}_{31}\text{O}_6\text{N}_7\text{S}_2$, Na phenyl-*p*-azoimidesulphonate; with warm dil. acid NH_3 is split off and the azine is not produced. "Yellow-IV" ["(II)," *loc. cit.*] is converted by 50% aq. H_2SO_4 into 2:3-benzcarbazole-1:4-quinone (V) (cf. A., 1880, 663) and a little 1-*p*-sulphobenzeneazo-2:3-benzcarbazole (VI); the latter is not formed if HCl (*d* 1.124) is used. By condensation of β -naphthol-1-sulphonic acid with NH_2NHPH and NaHSO_3 are formed, in addition to the carbazole derivatives (cf. A., 1910, i, 144), small amounts (<30%) of *o*-benzeneazonaphthalene, m. p. 84° , and its Na 1-sulphonate. The latter, but not the former, is converted into the carbazole derivatives by further action of NaHSO_3 , and these are therefore formed direct and not through the *N*- SO_3H as previously considered. 2:3-Benzcarbazole-1-sulphonic acid couples with *p*-sulphodiazobenzene in aq. NaHCO_3 or NaOAc to give (VI) (isolated as Na salt) by elimination of the 1- SO_3H group; (VI) with NaHSO_3 followed by hot HCl gives a small amount of (V).

XV. The formation of (V) from (II) on boiling with acids is accompanied by elimination of NH_3 and sulphanilic acid, but not of phenylhydrazine-*p*-sulphonic acid, and the following mechanism is therefore suggested for the rearrangement:



This explanation is supported by the formation of 2-anilino-1:4-naphthaquinone from benzeneazo- α -

naphthol and AcOH (A., 1892, 1476); the corresponding sulphonic acid is not formed from *p*-sulphobenzeneazo- α -naphthol and HCl, but with HCl and NH_2Ph 2-anilino-1:4-naphthaquinone is formed, whilst (I) or its NaHSO_3 compound readily yields 2-hydroxy-1:4-naphthaquinone and sulphanilic acid when heated with aq. HCl alone. The transformation of (II) into (V) is effected equally well by $\text{H}_2\text{C}_2\text{O}_4$ or AcOH, although in the latter case it is slow and is catalysed by $\text{H}_2\text{C}_2\text{O}_4$; with 10–50% aq. HNO_3 , however, a compound, $\text{C}_{16}\text{H}_{10}\text{O}_3\text{N}_4$, m. p. 233° , of unknown structure is formed in poor yield. A series of compounds [derivatives of (II)] is prepared by condensation of (I) with NaHSO_3 and *p*-chloro-, *p*-bromo-, *o*-methoxy-, and *p*-methoxy-phenylhydrazines, 4:4'-dihydrazinodiphenyl, and β -naphthylhydrazine-8-sulphonic acid; in the cases of *p*-chloro- and *o*-methoxy-phenylhydrazines, red *monoazo-dyes* of type (III) are prepared by warming with aq. alkali, and readily pass into disazo-dyes on air oxidation. By the action of HCl 6-chloro- [acetate, m. p. 250° (Zn, Ac_2O , and NaOAc)], 6-bromo-, 8-methoxy-, and 6-methoxy-2:3-benzcarbazole-1:4-quinone, and 2:3:6:7-dibenzcarbazole-1:4-quinone (?) are formed. 1-Hydrazinoanthraquinone-2-sulphonic acid is prepared by reduction of the corresponding diazonium sulphonate with SnCl_2 and HCl, but does not interact with (I) and NaHSO_3 . 2:3-Benzcarbazole-1:4-quinone-3'-sulphonic acid is obtained from crocein-orange and NH_2NHPH . 2-Hydroxy-1-benzeneazonaphthalene-3-carboxylic acid gives a compound with NH_2NHPH and NaHSO_3 , converted by warm alkali into the corresponding *azo-dye*, and by HCl into (V); the corresponding derivatives with *p*-chlorophenylhydrazine are also described. The phenylhydrazino-compound (Na salt) (and its *p*-chloro-derivative) from benzeneazo- β -naphthol-8-sulphonic acid is not converted into the carbazolequinone by conc. HCl or 50% H_2SO_4 .

XVI. 2:2'-Azonaphthalene-1:1'-disulphonic acid (Na_2 salt) is converted by warm dil. HCl into a red substance and β -naphthol, by $\text{Na}_2\text{S}_2\text{O}_4$ and AcOH into a substance, m. p. 280 – 290° , and by NaHSO_3 into Na 2:3:5:6-dibenzocarbazole-1-sulphonate (VII), which is desulphonated by Na-Hg in aq. EtOH to 2:3:5:6-dibenzocarbazole, m. p. 295 – 296° . The structure of the carbazole derivatives is inferred from the formation of (VII) by interaction of Na β -naphthylhydrazine-1-sulphonate with Na β -naphthol-1-sulphonate and aq. NaHSO_3 , the unsymmetrical (2:3:5:6-) structure being advanced to account for the elimination of one SO_3H group, and only one, during the reaction. This is confirmed by condensation of (I) with β -naphthylamine-4:8-disulphonic acid and NaHSO_3 , which gives a yellow compound (VIII) [of type (II)] containing four SO_3H groups which, nevertheless, gives Na 2:3:5:6-dibenzocarbazole-1:4-quinone(mono)sulphonate, which with Na-Hg gives 2:3:5:6-dibenzocarbazole-1:4-quinone, m. p. 377 – 378° . The last-named is also obtained from the compound (IX) from (I) and β -naphthylhydrazine-1-sulphonic acid. The condensation of *p*-sulphobenzeneazo-2:7-dihydroxynaphthalene and 7-methoxy-*p*-sulphobenzeneazo- β -naphthol with NH_2NHPH and NaHSO_3 to give the compounds (X) and (XI),

converted by HCl into 2'-hydroxy-, m. p. above 370°, and 2'-methoxy-, m. p. 299°, -2:3-benzocarbazole-1:4-quinones is described. The compounds (VIII), (IX), (X), and (XI) are converted by warm aq. NaOH into red azohydrazino-dyes [type (III)], which on oxidation in alkaline solution pass into disazo-dyes.

H. A. PIGGOTT.

Fluoran derivatives. IV. Azo-derivatives of dihydroxyfluorans. M. DOMINIKIEWICZ (Rocz. Chem., 1931, 11, 897—908).—o-3:5-Bisbenzeneazo-2:4-dihydroxybenzoylbenzoic acid (I), m. p. 235°, yields with resorcinol 2:4-bisbenzeneazo-3:6-dihydroxyfluoran, m. p. 260°, which on reduction gives 2:4-diamino-3:6-dihydroxyfluoran. With benzeneazoresorcinol in conc. H_2SO_4 (I) yields 1:6-dihydroxy-4-benzeneazofluoran, giving on reduction 4-amino-1:6-dihydroxyfluoran. 1:8-Dihydroxy-4:5-bisbenzeneazofluoran, prepared from phthalic anhydride and benzeneazoresorcinol, yields on reduction 4:5-diamino-1:8-dihydroxyfluoran, m. p. 195—196°. Certain of the above substances yield deep red solutions with intense orange fluorescence in the presence of alkalis.

R. TRUSZKOWSKI.

Preparation of phenols by direct dehydrogenation of hydroaromatic ketones. G. DARZENS and G. LÉVY (Compt. rend., 1932, 194, 181—183).—cycloHexanone with Ni at 240°, or with S in $C_{10}H_8$ at 200—240° yields PhOH. α -Ketotetrahydronaphthalene gives α -naphthol with S at 200—240° (yield 40%), or, better, with Se at 300—335° (yield 75%).

R. S. CAHN.

Replacement of bromine in bromophenols by the nitro-group. II. 3-Fluoro-2:4:6-tribromophenol. Some cases of group migration. H. H. HODGSON and J. NIXON (J.C.S., 1932, 273—275).—Dibromination of 3-fluoro-6-nitrophenol gives 3-fluoro-2:4-dibromo-6-nitrophenol (I), m. p. 76°, identified by conversion by aq. KOH into 2:4-dibromo-6-nitroresorcinol, m. p. 151°, which with Me_2SO_4 and alkali gives the 3-Me ether, m. p. 128°, also obtained by bromination of 6-nitroresorcinol 3-Me ether. The action of HNO_3 (d 1.42) on 3-fluoro-2:4:6-tribromophenol or bromination of 3-fluoro-2-nitrophenol also leads to (I), the Br in the 6-position being replaced by NO_2 in the former case (cf. 3-chloro-2:4:6-tribromophenol, A., 1931, 1287), and NO_2 migrating in the latter. 3-Fluorophenol with Br gives 3-fluoro-4:6-dibromophenol, m. p. 45°, which with HNO_3 (d 1.42) yields (normally) the 2- NO_2 -derivative, m. p. 74°, converted by aq. KOH into 4:6-dibromo-2-nitroresorcinol, m. p. 117°.

H. A. PIGGOTT.

Action of sodium methoxide on derivatives of m-dichlorobenzene. L. M. F. VAN DE LANDE (Rec. trav. chim., 1932, 51, 98—113).— $m-C_6H_4Cl_2$ and oleum (12% SO_3) at room temp. give 2:4-dichlorobenzenesulphonic acid, m. p. 86° [Ba (+ H_2O) salt]; the K salt and $SOCl_2$ at 180° afford 1:2:4-trichlorobenzene. 3-Chloro-4-fluoroaniline, prepared by reduction of the NO_2 -compound with $TiCl_3$, is converted by the usual method into 2:4-dichlorofluorobenzene (I), b. p. 172—174°, m. p. -13.8° to -13.2°. The Cannizzaro reaction with 2:4-dichlorobenzaldehyde gives 2:4-dichlorobenzoic acid (II) and

2:4-dichlorobenzyl alcohol, m. p. 59.5°. Reduction of 2:4-dichloronitrobenzene by the method of Lapworth *et al.* (J.C.S., 1921, 119, 765, 768) affords 2:4-dichlorophenylhydroxylamine, m. p. 43.5°, oxidised by $K_2Cr_2O_7$ and dil. H_2SO_4 to 2:4-dichloronitrosobenzene (III), m. p. 41.9° (not characterised), and converted by crystallisation from EtOH into 2:4:2':4'-tetrachloroazoxybenzene (IV), m. p. 126—127°. Improved methods of prep. of 2:4-dichlorobromobenzene (V) and 2:4-dichloriodobenzene (VI) are given. 2:4-Dichlorobenzophenone has m. p. 48° (lit. 52°).

The action of 2.98N-NaOMe at 183° on 14 2:4-dichlorobenzene derivatives, including the following, is studied; the products formed are given in brackets: (I) [2:4-dichlorophenol]; (II) [4-chlorosalicylic and (mainly) 2-chloro-4-hydroxybenzoic acids]; (III) [(IV)]; (V) [2:4-dichlorophenol and mainly 3-chloro-6-bromophenol, m. p. 62.5—63.5° (benzoate, m. p. 71°), synthesised from 3-chloro-6-bromoaniline, m. p. 37.8—38°, which is obtained by reduction of the NO_2 -derivative with Fe powder and dil. HCl]; (VI) [$m-C_6H_4Cl_2$, $m-ClC_6H_4OH$, 2:4-dichlorophenol, and a little (probably) 3-chloro-4-iodophenol]; 2:4-dichlorotoluene [2-chloro-*p*- and (mainly) 4-chloro-*o*-cresols]; 2:4-dichlorobenzonitrile, m. p. 60° [mainly (II)]; 1:2:4-trichlorobenzene [2:5-dichlorophenol]. The amount of Cl eliminated from the compound 2:4- $Cl_2C_6H_3R$ increases in the following order: $R=Me, I, H, Cl, Br, NO_2, CO_2H, SO_3H$.

3-Chloro-6-iodophenol, b. p. above 200° (decomp.) (benzoate, m. p. 87—87.7°) (not characterised), is prepared from 3-chloro-6-iodoaniline by the usual method.

H. BURTON.

Hexamethylenetetramine. III. Hexamethylenetetramine with naphthols and phenols. D. MAROTTA and E. ALESSANDRINI (Gazzetta, 1931, 61, 977—984).—Hexamethylenetetramine with α -naphthol gives in glacial AcOH a base $C_{33}H_{27}O_3N$ (acetate; hydrochloride; Br_3 -derivative), with β -naphthol a base, $C_{33}H_{27}O_3N$, m. p. about 230° (decomp.), and with PhOH, resorcinol, and phloroglucinol condensation products of trihydroxytrimethylamine with these phenols. These reactions are analogous to that between hexamethylenetetramine and H_2O_2 (A., 1930, 459).

E. E. J. MARLER.

"Desulphydration" of aralkyl mercaptans by potassium hydroxide. L. PALFRAY, S. SABETAY, and (MLLE.) D. SONTAG (Compt. rend., 1932, 194, 102—104).— β -Phenylethyl-, α -phenylethyl-, b. p. 83—84°/14 mm., and γ -phenylpropyl-thiols are conveniently prepared by interaction of the appropriate bromide with KHS in EtOH. When they are heated with solid KOH (2 mols.) above 230° H_2S is removed with formation of the corresponding olefine, the yield of which is considerably greater from β -phenylethyl-thiol (53%) than from the other two. The reaction is therefore analogous to the dehydration of the corresponding alcohols by KOH (A., 1929, 440) and is similarly explained.

H. A. PIGGOTT.

4-Alkylguaiaacols. N. H. HOWELLS and H. P. HOWELLS (J. Amer. Chem. Soc., 1932, 54, 401).—The prep. of alkylguaiaacols (see A., 1930, 468) by reduction of the corresponding acyl derivatives

is being studied. 4-*n*-Amylguaiacol has the max. PhOH-coeff. for the series. C. J. WEST (b).

Dimorphism of tetranitrodiphenyl derivatives. I. J. VAN ALPHEN (Rec. trav. chim., 1932, 51, 179—184; cf. A., 1931, 1048).—2:2'-Diethoxydiphenyl and abs. HNO₃ at -15° give 3:5:3':5'-tetranitro-2:2'-diethoxydiphenyl, m. p. 135.5° (from COMe₂), which when heated at 137—138° slowly solidifies and then melts at 148°; both forms react with NH₂Ph yielding 1:3:6:8-tetranitro-*N*-phenylcarbazole, m. p. (Maquenne block) 244°, immediately re-solidifying with m. p. 255°. The Ac₂ derivative, m. p. 179°, of 3:5:3':5'-tetranitro-2:2'-dihydroxydiphenyl when heated to 200—210° gives Ac₂O and the less fusible form of 1:3:6:8-tetranitrodiphenylene oxide; the Bz₂ derivative, m. p. 182°, undergoes a similar decomp. When 1:3:6:8-tetranitrodiphenylene oxide is heated (block) it melts at 239—240°, then solidifies, and re-melts at 255° (cf. A., 1917, i, 390). 3:5:3':5'-Tetranitro-2:2'-dimethoxydiphenyl and EtOH-NH₃ at 100° give 1:3:6:8-tetranitrocarbazole [*N*-Me derivative, m. p. (block) 277°, prepared similarly using NH₂Me; *N*-Et derivative, m. p. (tube) 216°, m. p. (block) 203°, immediately re-solidifying with m. p. 216°; *N*-Ph derivative (see above), prepared using NH₂Ph at 150°].

H. BURTON.

cycloPropane derivatives. J. HENRY (Bull. Soc. chim. Belg., 1931, 40, 647—656).—Since reduction of cyclopropyl alkyl ketones with Na and EtOH tends to give some open-chain alcohol by fission of the ring, the following secondary and *tert.* alcohols have been prepared by reduction of the appropriate ketone or ester with MgBu^δBr or MgPr^δBr, the latter giving only *tert.* alcohols: cyclopropyl-isopropylethyl-, b. p. 177—179°/767 mm.; -diisopropyl-, b. p. 76—77°/8 mm.; -methyl-, b. p. 123—124°/759 mm. (*Ac* derivative, b. p. 139.5—140.0°/759 mm.); -methylisobutyl-, b. p. 174—175°/759 mm.; -ethyl-, b. p. 138—139°/755 mm.; -*n*-propyl-, b. p. 158.5—159.5°/761 mm.; -*n*-butyl-, b. p. 178.5—179.5°/764 mm.; -*n*-butylisobutyl-, b. p. 110—111°/17 mm.; -isobutyl-, b. p. 75.5—74°(?) /17 mm.; and -di-isobutyl-, b. p. 102.5—103°/17 mm., -carbinol. In agreement with Bruylants (A., 1927, 653), the increase in *n* due to the cyclopropane ring is very small in the case of the *tert.* alcohols, but is marked in the case of the secondary alcohols, the val. varying with the nature of the alkyl groups present. In the reduction of cyclopropyl Bu^δ ketone with MgEtBr, cyclopropylethylcarbinol is obtained as a by-product, interchange of alkyl radicals having occurred. J. W. BAKER.

Stereoisomerides of 1-methyl-2-ethylcyclopentane. G. CHURDOGLU (Bull. Acad. roy. Belg., 1931, [v], 17, 1404—1415).—1-Ethylcyclopentanone, prepared by cyclisation of Et adipate, followed by ethylation and hydrolysis, has been converted by MgMeBr into 2 forms of 1-methyl-2-ethylcyclopentanol, b. p. 64.5°/13 mm., *d*₄²⁰ 0.8902, and b. p. 67.5°/13 mm., *d*₄²⁰ 0.9061, each being dehydrated to 1-methyl-2-ethylcyclo-Δ¹-pentene, b. p. 127.4—127.8°/760 mm., *d*₄²⁰ 0.8020. Fractional distillation of the product of hydrogenating the pentene gives two stereoisomerides of 1-methyl-2-ethylcyclopentane, (trans) b. p.

121.4—121.75°/760 mm., *d*₄²⁰ 0.7696, and (cis), b. p. 127.7—128°/760 mm., *d*₄²⁰ 0.7846. F. R. SHAW.

Configuration of ephedrine. K. FREUDENBERG, E. SCHOEFFEL, and E. BRAUN (J. Amer. Chem. Soc., 1932, 54, 234—236).—α-Mandelamide and MgMeI give *l*-acetylphenylcarbinol, converted by catalytic reduction (Pd-black) in EtOH-NH₃Me into *l*-ephedrine (30% yield); the configuration of the CH·OH group is thus established. *dl*-Ephedrine is prepared similarly from *dl*-mandelamide. C. J. WEST (b).

Rearrangement of *o*-tolyl triphenylmethyl ether. G. S. PARSONS and C. W. PORTER (J. Amer. Chem. Soc., 1932, 54, 363—365).—*o*-Tolyl CPh₃ ether and ZnCl₂ at 180° give βββ-triphenyl-α-*o*-hydroxyphenylethane (the Me ether, m. p. 172°, synthesised from *o*-OMe-C₆H₄·CHO and MgCPh₃Br, is oxidised to *o*-OMe-C₆H₄·CO₂H). The results of Schorigin (A., 1927, 54) and of van Alphen (*ibid.*, 660) are confirmed. C. J. WEST (b).

Montignie's ischolesterol. V. R. DE FAZI and F. MONFORTE (Gazzetta, 1931, 61, 882—885).—Montignie's "ischolesterol" (A., 1929, 1292), m. p. 137°, obtained by heating cholesterol with cinnamic acid is a mixture of these two substances with *meta*-cholesterol. E. E. J. MARLER.

Sterol group. XI. Formation of ethers of ergosterol and its derivatives. I. M. HEILBRON and J. C. E. SMIPSON (J.C.S., 1932, 268—273).—*Methoxyergostatriene*, m. p. 151—152°, [*α*]_D²⁰ -114°, is obtained (1) from ergosterol, MeI, "activated" Ag₂O, and a little NaOH, or (2) from K ergosteryl-oxide and MeI in C₆H₆. Its absorption spectrum and colour reactions are identical with those of ergosterol, but it does not acquire antirachitic properties on irradiation. It is converted by HCl in CHCl₃ at 0° into *methoxyisoergostatriene*, m. p. 116°, [*α*]_D²⁰ -66°, and by Hg(OAc)₂ in MeOH-EtOH-AcOH into *methoxydehydroergostatriene*, m. p. 106°. *Ethoxy*-, m. p. 123—124°, and *benzyloxy-ergostatriene*, m. p. 134—135°, are prepared by methods of type (1) and (2), respectively. *Methoxy-α-ergostadiene*, m. p. 148°, is obtained from α-dihydroergosterol, and *methoxy-α-ergostene*, m. p. 56°, from α-ergosterol by method (1); the latter is partly isomerised into *methoxy-β-ergostene*, m. p. 100°, by HCl in CHCl₃.

H. A. PIGGOTT.

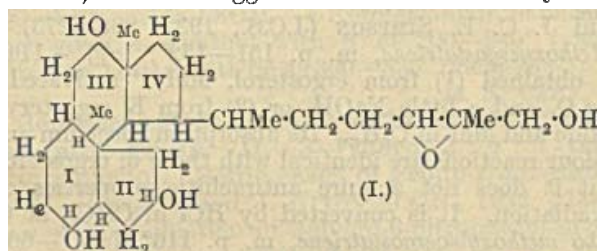
Action of ozone on ergosterol and its derivatives. F. REINDEL and H. KIPPAN (Annalen, 1932, 493, 181—190).—When ergosterol (or its acetate) is treated with 8—10% O₃ in CCl₄, 15—18 atoms of O per mol. are consumed. Ergosteryl acetate and 1.5—2.5% O₃ in hexane at 0° give a *triozonide*, m. p. about 100° (decomp.), which when treated with H₂ in presence of PtO₂ and Et₂O-AcOH and then steam-distilled, affords (cf. A., 1930, 1578) α-methylisovaleraldehyde (I) (*dinitrophenylhydrazone*, m. p. 124—125°), oxidised by Ag₂O to α-methylisovaleric acid [*Ag* salt; amide, m. p. 131.5° (corr.) (lit. 129°)]. (I) is considered to result from the group C:CH·CHMe·CHMe, present in the side-chain of the ergosterol mol.; the side-chain must, therefore, differ from that in cholesterol. (I) is not obtained from α-ergostenol (tetrahydroergosterol), indicating the

presence of a saturated side-chain. *allo-α-Ergosterol*, its acetate, and chloroergostane are practically unaffected by the above treatment. H. BURTON.

New isomeride of ergosterol, ergosterol-G. Z. NAKAMIYA (Z. physiol. Chem., 1932, 203, 255—258).—Ergosterol-*F* is probably a chemical individual. Treatment of the acetate with HCl gives a mixture containing *ergosteryl-G acetate*, m. p. 182°, $[\alpha]_D^{25}$ -62.5°, which yields on hydrolysis *ergosterol-G* (+ H₂O or MeOH), m. p. 149—150°, $[\alpha]_D^{25}$ -52.2°, containing 3, probably unconjugated, double linkings.

J. H. BIRKINSHAW.

Constitution of scymnol. R. TSCHESCHE (Z. physiol. Chem., 1931, 203, 263—271).—The triketo-acid (A., 1930, 1039) with HCl in MeOH gives a *Me chlorohydroxytriketocarboxylate*, m. p. 184—185°, which on catalytic hydrogenation yields a *Me chlorodihydroxydiketocarboxylate*, m. p. 196° (*dioxime*, m. p. 232°). With aq. HCl in AcOH the triketo-acid gives the Cl-derivative, which on CrO₃ oxidation yields the acid, C₂₄H₃₄O₅, m. p. 218—220° [*Me ester*, m. p. 232—233°; *Me ester trioxime*, m. p. 234° (decomp.)]. The triketo-acid on boiling with Zn-Hg in AcOH and HCl and esterification affords *Me 7:12-diketocholante*. Boiling conc. HNO₃ oxidises scymnol to a *tetracarboxylic acid*, C₂₂H₂₀O₁₀ (+H₂O), m. p. 295° (becoming brown) [*Me₄ ester*, m. p. 179—180°, $[\alpha]_D^{20}$ -24.2°]. In the suggested constitution for scymnol



(I) the positions of the OH in ring (I) and of the oxide ring are uncertain. J. H. BIRKINSHAW.

Prediction and verification of differences in colour [ultra-violet absorption spectra] of stereo-isomerides. (MME.) RAMART-LUCAS and (MLE.) BIQUARD (Compt. rend., 1932, 194, 187—189).—Since *cis* and *trans* isomerides have different absorption spectra, it is concluded theoretically that isomerides such as *dl*- and *meso*-forms, and cyclic *cis-trans* isomerides, will also differ in this respect. The following pairs of substances have one band in common and one different, the figures in parentheses being the extinction coeffs. of the resulting absorption min. between the bands: *dl*- and *l-s*-diphenylsuccinic acid (190 and 250, respectively); $\beta\gamma$ -diphenylbutane- $\beta\gamma$ -diol, m. p. 118° and 124° (140 and 110, respectively); $\beta\gamma$ -diphenylbutylene $\beta\gamma$ -oxide, m. p. 53° and 106° (110 and 260, respectively); β -phenyl- α -anisylbutane- $\alpha\beta$ -diol, m. p. 94° and 113° (250 and 500, respectively).

R. S. CAHN.

Catalytic action at high temperature and under high pressure. V. Catalytic hydrogenation of benzoic acid. S. KOMATSU and K. MITSUI (Mem. Coll. Sci. Kyoto, 1931, A, 14, 297—301).—BzOEt with Ni and H₂ at about 100 atm. (20°) and 115—200°, with or without EtOH, gives high yields of Et

hexahydrobenzoate. Similar treatment of BzOH-EtOH mixtures gives much BzOEt and little reduced ester. R. S. CAHN.

Action of potassium pyrosulphite on benzoyl chloride in presence of tertiary bases. I. GAZOPULOS (Praktika, 1931, 6, 154—162; Chem. Zentr., 1931, ii, 1700).—K₂S₂O₅ and BzCl in presence of C₅H₅N afford Bz₂O in 75% yield; the reaction is: C₅H₅N + BzCl = C₅H₅NCIBz; 2C₅H₅NCIBz + K₂S₂O₅ = O(SO₂Bz)₂ + 2C₅H₅N + 2KCl; O(SO₂Bz)₂ = 2SO₂ + Bz₂O. Denniger's statement that BzCl, Na₂CO₃, and C₅H₅N give Bz₂O when kept for 30 min. was not confirmed; Bz₂O is formed on heating, or by heating C₅H₅N, BzCl, and Na₂SO₃. A. A. ELDRIDGE.

Sulphophenylpropionic acids. II. C. H. K. MULDER (Rec. trav. chim., 1932, 51, 174—178; cf. A., 1931, 955).—K α -bromo- β -phenylpropionate and K₂SO₃ give after treatment with BaCl₂, *Ba α-sulpho-β-phenylpropionate* (+2H₂O). The *quinine salt* (+1.5H₂O), m. p. 228°, after 11 crystallisations from 50% EtOH affords the acid, [M]_D +73° [*Ba salt* (+4H₂O)], which is readily racemised. Valet's acid is β -sulpho- β -phenylpropionic acid. H. BURTON.

Reactivity of peri-substituted naphthalenes. I. Displacement of nitro-group in 8-nitro-1-naphthoic acid by thionyl halides to form 8-chloro- and 8-bromo-naphthoic acids. H. G. RULE and A. J. G. BARNETT (J.C.S., 1932, 175—179).—Interaction of SOCl₂ with 8-nitro-1-naphthoic acid, best in C₆H₆ at the b. p., gives 8-chloro-1-naphthoic acid, m. p. 167—168° (26% of theory), and 5:7(?)-dichloronaphthastyril, m. p. 269—270°. Similarly, SOBr₂ gives 8-bromo-1-naphthoic acid, m. p. 178° (*Me ester*, m. p. 33°; *amide*, m. p. 179—180°), in poor yield. Both the chloro- and the bromo-acids are best prepared by the action of the halogen on the chloromercuri-compound derived from naphthalic anhydride (cf. A., 1929, 1091).

H. A. PIGGOTT.

Action of hydrogen sulphide on acid chlorides. V. Naphthoyl chloride. L. SZPERL [with M. KIJEWSKA and W. LIPINSKI (Rocz. Chem., 1931, 11, 884—889)].—*Di-α*- and *di-β*-naphthoyl sulphides, m. p. 129—130° and 134—136°, are prepared by passing H₂S through boiling C₆H₆ solutions of the corresponding naphthoyl chlorides. R. TRUSZKOWSKI.

Mixed catalysts in the Friedel-Crafts reaction. W. A. RIDDELL and C. R. NOLLER.—See this vol., 235.

α -Alkylcinnamic acids and derivatives. M. T. BOGERT and D. DAVIDSON (J. Amer. Chem. Soc., 1932, 54, 334—338).— α -*n*-Propyl-, b. p. 142—143°/14 mm. (*oxime*, m. p. 70°), α -*n*-butyl-, b. p. 155—156°/15 mm. (*oxime*, m. p. 61°), and α -*n*-amyl-styryl *Me ketones*, b. p. 161—162°/14 mm. (*oxime*, m. p. 71°), are prepared from PhCHO (0.5 mol.), the appropriate *Me alkyl ketone* (1 mol.), and HCl (0.25 mol.) in the cold. These ketones are oxidised by NaOCl to *trans-α-n-propyl*-, m. p. 93° (*dibromide*, m. p. 149—150°), *n*-butyl- (*dibromide*, m. p. 109—110°), and *n*-amyl-cinnamic acids, m. p. 80° (*dibromide*, m. p. 143—144°); the *dibromide* of *trans-α*-ethylcinnamic acid has m. p. 99—100°. These dibromides are dehalogenated to the cinnamic

acids by KI in EtOH, converted by NaOAc in EtOH into β -bromo- β -alkylstyrenes, and by EtOH-KOH into phenylalkylacetylenes. The following are new: β -bromo- β -ethyl-, b. p. 126—128°/23 mm., -propyl-, b. p. 138—140°/22 mm., -butyl-, b. p. 148—150°/20 mm., and -amyl-styrenes, b. p. 161—162°/18 mm.; α -phenyl- β -propyl-, b. p. 102—103°/18.5 mm., -butyl-, b. p. 119—121°/18 mm., and -amyl-acetylenes, b. p. 126—127°/15 mm. C. J. WEST (b).

Metallic hydroxy-acid complexes. VI. Complexes of lead and zinc. (Miss) E. E. WARK (J.C.S., 1932, 41—43).—The following salts, of the general type Na_2MA_2 , are obtained by interaction of the normal heavy metal salt with NaOMe or NaOEt in MeOH or EtOH with complete exclusion of H_2O : *Na zincimandelate* (+1EtOH), *Na zincisalicylate* (+1MeOH), *Na zincilactate* (+2MeOH), *Na plumbimandelate* (+1EtOH), and *Na plumbisalicylate*.

H. A. PIGGOTT.
Resolution of *r*-phenylmethoxyacetic acid into optically active components. D. J. C. PIRIE and (Miss) I. A. SMITH (J.C.S., 1932, 338).—*d*-Phenylmethoxyacetic acid, m. p. 64—65°, $[\alpha]_D^{25} +151.5^\circ$, is readily prepared by resolution of the *r*-acid with quinine. H. A. PIGGOTT.

Configuration of cyclic α -hydroxy-acids [1-hydroxycycloalkane-1-carboxylic acids]. J. BOESEKEN and A. G. LUTGERHORST (Rec. trav. chim., 1932, 51, 159—167).—The conductivities of 1-hydroxy-cyclopentane-, -cyclohexane-, and -cycloheptane-1-carboxylic acids are increased by the addition of H_3BO_3 to about the same extent as the disubstituted glycollic acids, $\text{HO-CRR}'\text{-CO}_2\text{H}$. The spatial configuration of the OH and CO_2H groups is, therefore, the same in all these compounds, and is attributed to the angle between C_1 and the adjacent ring C atoms being about 109°. H_3BO_3 has no effect on the conductivity of 1-hydroxycyclobutane-1-carboxylic acid (prepared from the 1-Br-acid and a conc. aq. solution of AgNO_3), indicating the spatial separation of the OH and CO_2H groups. The above results also show that rings containing more than 5 C atoms are non-planar. The conductivity of 9-hydroxyfluorene-9-carboxylic acid is increased by H_3BO_3 , but not to the same extent as the C_5 — C_7 acids; the aromatic linkings probably cause a slight separation of the OH and CO_2H groups. H. BURTON.

Isomeric β -phenyl- α -*p*-nitrophenyl- δ -ketonic acids. S. AVERY, C. B. BISWELL, and E. E. LISTON (J. Amer. Chem. Soc., 1932, 54, 229—234).— $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{-CO}_2\text{Me}$ and Ph styryl ketone in MeOH-NaOMe give the *Me* ester, m. p. 182°, of "M" γ -benzoyl- β -phenyl- α -*p*-nitrophenylbutyric acid (I), m. p. 220—225° (decomp.) [*Et* ester (II), m. p. 141°, from (I) and EtOH-HCl; lactone, m. p. 162°, from (I) and AcCl at 60°; nitrile (A., 1925, i, 963), obtained free from its isomeride (see below) only with difficulty]. The ketone and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{-CO}_2\text{Et}$ in EtOH-NaOEt afford the *Et* ester (III), m. p. 188°, of "E" γ -benzoyl- β -phenyl- α -*p*-nitrophenylbutyric acid (IV), m. p. 220—225° (decomp.) [*Me* ester, m. p. 174°; lactone, m. p. 215°; nitrile (cf. loc. cit.)]. The "E" series is the more stable. (II) is converted into (III) by EtOH-NaOEt. The *Bu*^a ester, m. p. 152°, of (IV)

is obtained by interaction of Ph styryl ketone and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{-CO}_2\text{Bu}$ in BuOH-NaOBu. The cryst. forms of (I) and (IV) differ.

γ -Trimethylacetyl- β -phenyl- α -*p*-nitrophenylbutyric acid also exists in "M," m. p. 208—215° (*Me*, m. p. 178°, and *Et*, m. p. 147°, esters; lactone, m. p. 147°), and "E," m. p. 208—215° (*Me*, m. p. 163°, *Et*, m. p. 153°, and *Pr*, m. p. 165°, esters; nitrile, m. p. 145.5°; lactone, m. p. 168°), forms. EtOH-NaOEt again converts the "M"-Et into the "E"-Et ester.

C. J. WEST (b).

Synthesis of 5-hydroxy-2-methoxybenzoic acid. A. N. MELDRUM and M. S. SHAH (J. Indian Chem. Soc., 1931, 8, 575—580).—Contrary to Froelicher and Cohen (J.C.S., 1922, 121, 1652) nitration of $o\text{-MeO-C}_6\text{H}_4\text{-CO}_2\text{H}$ with mixed acids at 30—35° affords only the 5- (76%) and 3- (22%) -NO_2 -derivatives (separated as their Ca and Ba salts), the proportions being 73 and 25%, respectively, when nitration is effected at 75—100°. 5-Nitro-2-methoxybenzoic acid is smoothly reduced by FeSO_4 and NH_3 to the sulphate of the 5-NH₂-acid, converted by HNO_2 into the stable 5-diazosulphate, decomp. 150°. This could be converted into 5-hydroxy-2-methoxybenzoic acid, m. p. 172° (lit., m. p. 155—156°) (*Ba* + $3\text{H}_2\text{O}$ salt), only by heating with $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ at 145—155°. Subsequent methylation affords the 2 : 5-(OMe)₂-acid, m. p. 80° (lit., m. p. 76°). J. W. BAKER.

Hydrophthalides. VI. S. BERLINGOZZI (Gazzetta, 1931, 61, 886—897).— CH_2PhMgCl with $\Delta^{2:6}$ -dihydrophthalic anhydride gives dibenzyl- $\Delta^{2:6}$ -dihydrophthalide, m. p. 189°, and with Δ^2 -tetrahydrophthalic anhydride gives dibenzyl- Δ^2 -tetrahydrophthalide, m. p. 185°. Δ^2 -Tetrahydrophthalic anhydride condenses with phenylacetic acid giving benzylidenetetrahydrophthalide, m. p. 116°, which is hydrolysed to *o*-phenylacetyl-tetrahydrobenzoic acid, m. p. 119° (oxime, m. p. 159°). E. E. J. MARLER.

Dry distillation of copper phthalate does not yield fluoran. J. B. EKELEY (J. Amer. Chem. Soc., 1932, 54, 406).—The results previously reported (A., 1930, 1442) could not be repeated.

C. J. WEST (b).

New effect in solutions of optically active substances. R. KUHN (Ber., 1932, 65, [B], 49—51).—The observations of Pfeiffer and Quehl (this vol., 30) are exactly analogous to those of Kuhn and Albrecht (A., 1927, 876) on the behaviour of 4 : 4'-dinitrodiphenic acid towards quinine and cinchonidine. It is proposed to designate asymmetric transformations which can be detected only in the presence of optically active materials and in which the asymmetry ceases on removal of such materials as "asymmetric transformations of the first type." Transformations which persist after removal of the active assistant are to be known as "asymmetric transformations of the second type." H. WREN.

A case of *cis-trans*-isomerism in the hydrindene series. O. BLUM-BERGMANN (Annalen, 1932, 492, 277—283).—1-Lithio-3-phenylindene (I) (A., 1931, 208) and Me_2CO_3 in C_6H_6 give 3-phenylindene and *Me* 3-phenylindene-1-carboxylate (II), m. p. 93—94°, which is reduced catalytically (Pd-BaSO_4) in PrOH to *Me* 3-phenylhydrindene-1-carboxylate (III), m. p. 77—78°.

Successive treatment of (II) with NaCPh_3 and ClCO_2Me affords Me 3-phenylindene-1:1-dicarboxylate (IV), m. p. 105—107°, showing that in its production from (I) and ClCO_2Me (*loc. cit.*), the following changes occur (C^1 only shown): $>\text{CHLi} \longrightarrow >\text{CH}\cdot\text{CO}_2\text{Me} \longrightarrow >\text{C}(\text{CO}_2\text{Me})\cdot\text{OLi} \longrightarrow >\text{C}(\text{CO}_2\text{Me})_2$. The Me 3-phenylhydrindene-1-carboxylate (V), b. p. 197—198°/10 mm., obtained by successive reduction, hydrolysis, thermal decomp., and esterification of (IV) is converted by treatment with a little $\text{MeOH}\text{--}\text{NaOMe}$ at 100° (bath) into (III), thus showing that (III) and (V) are *cis-trans*-isomerides. (V) and a little $\text{EtOH}\text{--}\text{NaOEt}$ at 100° give Et 3-phenylhydrindene-1-carboxylate (VI), m. p. 69—70°. (I) and Et_2CO_3 in C_6H_6 afford 3-phenylindene, Et 3-phenylindene-1-carboxylate, b. p. 190—205°/10 mm. [reduced catalytically to (VI)], Et 3:3'-diphenyl-1:1'-di-indenyl-1:1'-dicarboxylate, m. p. 166—167°, and di-(3-phenyl-1-indenylene)methane, m. p. 205—206°. H. BURTON.

Optically active dinaphthylcarboxylic acids. J. MEISENHEIMER and O. BEISSWENGER (Ber., 1932, 65, [B], 32—42; cf. Stanley, A., 1931, 1155).—1:1'-Dinaphthyl-8:8'-dicarboxylic acid is readily resolved by brucine in MeOH ; the brucine salt of the *l*-acid (+ MeOH) has $[\alpha]_D^{25} = -400^\circ$ in CHCl_3 and that of the *d*-acid (+ $3\text{H}_2\text{O}$) +390°. Both salts are optically stable in EtOH , whereas the Na salts in dil. aq. solution have a half-life period of about 160 min. at 20° (max. observed $[\alpha]_D^{25}$ about 350°). Et H 1:1'-dinaphthyl-8:8'-dicarboxylate, m. p. 194—195°, prepared by partial hydrolysis of the Et_2 ester or, preferably, by the action of EtI on the Ag H salt, is readily resolved by brucine in AcOEt containing a little MeOH , whereby the acid is completely transformed into brucine Et 1:1'-dinaphthyl-8:8'-dicarboxylate (+ $3\text{H}_2\text{O}$), $[\alpha]_D^{25} = -350^\circ$ in CHCl_3 (highest observed val.), half-life period about 45 hr. in CHCl_3 at 20°. The acid has m. p. 199°, $[\alpha]_D^{25} = -525^\circ$ in dioxan, half-life period 35 hr., and the Na salt has $[\alpha]_D^{25} = +405.3^\circ$ in faintly alkaline solution, half-life period 28.2 hr. Et 8-chloronaphthoate, 1-bromonaphthalene, Cu powder, and a trace of I at 290° afford Et 1:1'-dinaphthyl-8:8'-dicarboxylate and Et 1:1'-dinaphthyl-8-carboxylate, m. p. 146°. The last-named compound is hydrolysed with difficulty to 1:1'-dinaphthyl-8-carboxylic acid, m. p. 242°, treatment of which with brucine in AcOEt yields the brucine salt of the *l*-acid (+ H_2O), $[\alpha]_D^{25} = -201^\circ$ in CHCl_3 , and of the *d*-acid, $[\alpha]_D^{25} = +106^\circ$ in CHCl_3 . The salts differ in cryst. form and never appear to separate simultaneously; seeding induces crystallisation of either form. Both salts are readily racemised, more rapidly in AcOEt than in CHCl_3 . The half-life period of the corresponding Na salts in H_2O is about 15 hr. Et chloronaphthoate, 2-bromonaphthalene, and Cu powder yield Et_2 1:2'-dinaphthyl-8:8'-dicarboxylate, Et 1:2'-dinaphthyl-8-carboxylate, m. p. 105°, and (?) Et 4-chloro-1:2'-dinaphthyl-4-carboxylate, m. p. 158°. 1:2'-Dinaphthyl-8-carboxylic acid, m. p. 189°, yields the following salts: strychnine, m. p. 207°, $[\alpha]_D^{25} = -50.8^\circ$ in CHCl_3 ; α -phenylethylamine, m. p. 207—208°, $[\alpha]_D^{25} = -10.0^\circ$ in MeOH ; quinine, m. p. 192—194°, $[\alpha]_D^{25} = +3.5^\circ$ in CHCl_3 ; coniine, m. p. 135° after softening at 119°, $[\alpha]_D^{25} = -27.5^\circ$ in CHCl_3 , +4.8° in pyridine. Since the salts crystallise well, the non-

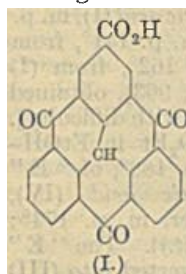
resolution of the acid is attributed to immediate, total racemisation in solution. H. WREN.

Dissociable organic oxides. Substances showing reversible oxidisability in aqueous solution. C. DUFRAISSE and N. DRISCH (Compt. rend., 1932, 194, 99—102).—Dibromorubrene is converted by prolonged action of Mg in the cold and subsequent addition of CO_2 into rubrenedicarboxylic acid. The acid, dissolved in org. media, and the salts in dil. aq. EtOH solution, have all the properties of the rubrenes, and form colourless oxides [acid (+ H_2O), Na salt (+1.5 EtOH)], which when heated alone or in solution dissociate with evolution of 54—55% of their oxidic oxygen; the Na salt is also partly dissociated by insolation in absence of air. The alkali salts of the rubrenedicarboxylic acid are only slightly sol. in H_2O and are easily pptd. by electrolytes, but those of the oxide dissolve more readily to soap-like solutions. H. A. PIGGOTT.

Derivatives of naphthalic acid. Synthesis of 3:4-dihydroxynaphthalic acid. K. DZIEWONSKI, Z. OLSZEWSKI, and W. KAHN (Rocz. Chem., 1931, 11, 870—883).—3-Hydroxynaphthalic anhydride yields with Br 4-bromo-3-hydroxynaphthalic anhydride, m. p. 286° (*imide*, m. p. 237—238°; 3-Bz, m. p. 247—248°, and 3-Ac derivative, m. p. 214°; 3-Me ether, m. p. 216—217°; phenylhydrazone, m. p. 283—284°; oxime, m. p. 303°), which on fusion with NaOH yields 3:4-dihydroxynaphthalic anhydride, m. p. 324—325° (phenylhydrazone, m. p. 317—318°; oxime, m. p. 312°; Bz, m. p. 222—223°, and Ac₂ derivatives, m. p. 217°; Me₂ ether, m. p. 226—228°). The same product is obtained from 4-nitro-3-hydroxynaphthalic anhydride, m. p. 235—236° (*imide*, m. p. 310°; Ac derivative, m. p. 167—168°), by reduction to 4-amino-3-hydroxynaphthalic anhydride (I), m. p. >360° (*imide*, m. p. 360°; Ac₂ derivative, m. p. 253°), which on hydrolysis yields 3:4-dihydroxynaphthalic acid. (I) can also be prepared by reduction of 4-nitroso-3-hydroxynaphthalic anhydride, m. p. 214° (decomp.), or by condensation of 3-hydroxynaphthalic anhydride with benzenediazonium chloride, and reduction of the product. 3:4-Dihydroxynaphthalic anhydride forms coloured lakes with Al, Cr, and Fe salts.

R. TRUSZKOWSKI.

Triphenylmethane derivatives with linked benzene nuclei. VI. Triketotrimethylenetriphenylmethane-4-carboxylic acid and its reduction. R. WEISS and F. MÜLLER (Monatsh., 1932, 59, 128—135; cf. A., 1929, 1445).—Mg *o*-tolyl bromide and *o*-2:4-dimethylbenzoylbenzoic acid give *o*-tolyl-m-4-xylylphthalide, m. p. 185°, reduced by 3% Na-Hg and EtOH to 2:2':4'-trimethyltriphenylmethane-2''-carboxylic acid, m. p. 222—223° (Me ester, m. p. 73—75°). Oxidation of this phthalide with KMnO_4 in aq. Na_2CO_3 affords triphenylmethane-2:4:2':2''-tetracarboxylic acid, m. p. (hydrated) 144° (Me₄ ester, m. p. 126°), converted by warm conc. H_2SO_4 into triketotrimethylenetriphenylmethane-4-carboxylic acid, dark blue (I), characterised as the NH_4 salt.

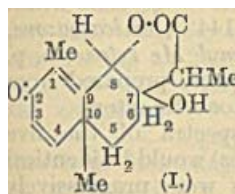


Reduction of (I) with Zn dust and 10% NaOH in H.

and subsequent treatment with BzCl gives a *keto-dibenzyloxytrimethylenetriphenylmethanecarboxylic acid*, yellowish-brown, which decomposes when heated (becoming blue).

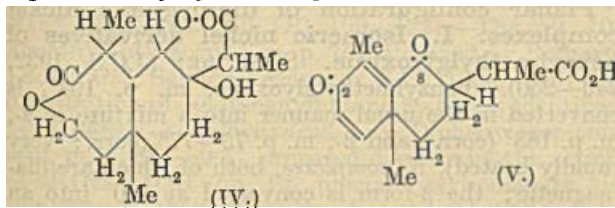
H. BURTON.

Santonin series. XVII. Constitution of artemisin. K. TETTWEILER, O. ENGEL, and E. WEDEKIND (Annalen, 1932, 492, 105—128).—Catalytic reduction (PdCl_2) of artemisin (I), b. p. $260^\circ/0.1$ mm., m. p. 203° , in MeOH gives small amounts of γ -, m. p. 224° (*oxime*, decomp. 256°), and δ -*tetrahydroartemisin*, m. p. 208° [*oxime* ($+ \text{H}_2\text{O}$), m. p. 137° , decomp. (anhyd.) 185°], in addition to α - (II) and β -*tetrahydroartemisin* (cf. Rimini and Jona, A., 1913, i, 1092); the existence of 4 stereoisomeric tetrahydro-



artemisins is in accordance with the structure now assigned to (I). Clemmensen reduction of (I) gives small amounts of two *deoxytetrahydroartemisins*, $\text{C}_{15}\text{H}_{24}\text{O}_3$, m. p. 205° and 228° , whilst catalytic reduction (PtO_2) of (I) in AcOH affords a mixture

(A) of two *hexahydroartemisins*, m. p. 208° (III) and 242° , which are probably stereoisomerides. (A) is dehydrogenated by Se at 270 — 300° to 1-methyl-7-ethylnaphthalene, indicating that (I) belongs to the eudesmol group of sesquiterpenes and that it contains the same C-skeleton as santonin and alantolactone. (I) does not contain a $\cdot\text{CO}\cdot\text{CH}_2\cdot$ group and is unaffected by Caro's acid; (II) is, however, similarly oxidised to the *dilactone* (IV), m. p. 224° . (I) is converted by boiling 10% NaOH into a diketomono-carboxylic acid (termed *artemionic acid*) (V), m. p. 208° (*Me* ester, m. p. 160°); the formation of (V) is explicable only by assuming that (I) contains a (*tert.*-)



OH group in the β -position to the $\cdot\text{CO}\cdot$ group of the lactone ring; the OH-lactone is first converted into a $\beta\gamma$ -dihydroxy-acid which passes (by loss of H_2O) into a $\beta\gamma$ -unsaturated γ -OH-acid, and thence into a γ -keto-acid. (V) must contain both the C:C linkings of (I); it is reduced catalytically (PdCl_2) in MeOH to *tetrahydroartemionic acid*, m. p. 192° [also obtained by the action of 10% NaOH on (II)]. Catalytic reduction (PtO_2) of (V) gives *hexahydroartemionic acid* (VI), m. p. 179° [also formed from (III) and 10% NaOH], in which the $>\text{C}_2\text{H}\cdot\text{OH}$ grouping exists. (VI) is reduced further by Na-Hg in dil. KOH to hexahydrosantonin. Treatment of (I) with HCO_2H and subsequent distillation at 0.1 mm. gives *artemesen* (VII), m. p. 182° (*oxime*, decomp. 244 — 245°), formed by loss of H_2O between C_7 and C_8 . (VII) does not contain a OH group (Zerevitinov), is reduced catalytically (PdCl_2) to *hexahydroartemesen*, m. p. 199° , and is converted by 10% NaOH into (V). Acetyl-artemisin (VIII) is reduced catalytically (PdCl_2) in MeOH to *tetrahydroacetylartemisin*, m. p. 166° (*oxime*,

decomp. 139°), also obtained from (II) and AcCl , which is hydrolysed by 5% NaOH to (II). (VIII) is also converted by 10% NaOH into (V) (cf. Bertolo, A., 1920, i, 444; 1923, i, 1108).

H. BURTON.

Ozonisation of benzaldehyde. II. E. BRINER, A. DEMOLIS, and H. PAILLARD.—See this vol., 235.

Oximes of β -bromocinnamaldehyde and related compounds. K. VON AUWERS and E. WOLTER (Annalen, 1932, 492, 283—292).—The β -bromocinnamaldoxime (I), m. p. 103 — 104° , previously described (A., 1931, 222), is the *anti*-form. (I) is converted by cold Ac_2O into *cis*- β -bromocinnamonitrile (II), b. p. 155 — $158^\circ/12$ mm., also formed by the action of POCl_3 and PCl_5 on *cis*- β -bromocinnamamide, m. p. 115 — 116° , which is prepared from the *cis*-acid by Stoermer's method (A., 1911, i, 295; 1913, i, 618). An Ac derivative of (I) cannot be prepared and the previously described (*loc. cit.*) Ac derivative, m. p. 68 — 69° , is that of *syn*- β -bromocinnamaldoxime (III), now obtained with m. p. 96 — 97° (instead of 63 — 66°). (III) and boiling Ac_2O give (II), but with PCl_5 in Et_2O , *trans*- β -bromocinnamonitrile, b. p. 161 — $163^\circ/12$ mm. (also prepared from *trans*- β -bromocinnamamide, m. p. 110 — 111°), results. (III) is converted by HCl in Et_2O into the hydrochloride of (I). The behaviour of (I) and (III) towards alkali (*loc. cit.*) is intelligible only by regarding the original β -bromocinnamaldehyde as a *cis*-compound; *cis*-addition of HBr to $\text{CPh}:\text{C}\cdot\text{CHO}$ occurs both in AcOH and CS_2 . Only one *hydrazone*, m. p. 81° , *phenylhydrazone*, m. p. 132 — 133° , *p*-nitrophenylhydrazone, m. p. 176 — 177° , *semicarbazone* ($+ \text{H}_2\text{O}$), m. p. 153 — 154° , m. p. (anhyd.) 195° , and *N*-carbethoxyhydrazone, m. p. 110.5 — 111.5° , of *cis*- β -bromocinnamaldehyde (IV) could be obtained. (IV) and $\text{NH}_2\cdot\text{NHMe}$ give 5-phenyl-1-methylpyrazole.

H. BURTON.

Nitration of oximes. W. CHARLTON, J. C. EARL, J. KENNER, and A. A. LUCIANO (J.C.S., 1932, 30—41).—The action of HNO_3 (d 1.46) on acetoxime in AcOH or CCl_4 at 50° gives a very small yield of dimethyl- ψ -nitrole; similarly dibenzylketoxime gives dibenzyl- ψ -nitrole (about 70%), converted by boiling EtOH into dibenzylidinitromethane, and by aniline and *m*-toluidine into *azo*-derivatives, $(\text{CH}_2\text{Ph})_2\text{C}(\text{NO}_2)\cdot\text{N}\cdot\text{NR}$, m. p. 108° and 109 — 110° , respectively. Camphoroxime gives *camphor*- ψ -nitrole, blue, m. p. 60° . Under the same conditions (in AcOH) benzoinoxime is decomposed into PhCHO and phenylmethylnitrolic acid; the *oxime*, m. p. 153 — 154° , of benzpiperoin similarly gives PhCHO and piperonylnitrolic acid, in confirmation of the structure assigned by Brass (A., 1930, 1589). Nitrolic acids are formed by nitration of *o*-, *m*-, and *p*-nitro-, *o*- and *m*-chloro-, and *o*-methoxy-benzaldoximes, and of *o*-tolualdoxime; dinitromethane derivatives are the main products from α -benzaldoxime, *m*- and *p*-tolualdoximes, *p*-chlorobenzaldoxime, anisaldoxime, and piperonaloxime. In many cases the free aldehyde and in some the oxime peroxide are also produced. *p*-Hydroxybenzaldoxime gives, however, 3-nitro-4-hydroxybenzaldehyde and its oxime. No definite products were isolated from the oximes of *m*-hydroxy- or *m*-methoxy-benzaldehydes, protocatechualdehyde, or 2-hydroxycyclohexanone (free ketone has m. p.

131—132°). The action of aq. (?) HBr on bromo-nitrosodimethylbutane in Et₂O gives tribromophenol and pinacolinoxime; similar results are obtained with an ethereal extract of the reaction product of KOBz and camphoroxime. The following are described: *m*-tolylidinitromethane, m. p. 53°; *o*-tolyl-, m. p. 64° (decomp.), *o*-chlorophenyl-, m. p. 72°, *m*-chlorophenyl-, m. p. 61°, and *o*-methoxyphenyl-, m. p. 68°, *m*-methylnitrolic acids; and *m*-chlorophenyl-benzaldoxime peroxide, m. p. 111°. H. A. PIGGOTT.

Dioximes. LXXXII. G. PONZIO (Gazzetta, 1931, 61, 943—951).—Phenylmethylglyoxime gives two peroxides regarded as phenylmethylglyoxadiazine, CMe.N·O $\xrightarrow{\text{CMe=N}}$ CPh.N·O, p. 62°, and a furoxan, CPh.N·O $\xrightarrow{\text{CPh=N}}$ CPh.N·O, p. 97°, respectively, whilst phenylcyanoglyoxime, obtained by the action of KCN on phenylchloroglyoxime (I), m. p. 150—151° (decomp.) (Ag, Ni salts; Ac₂, m. p. 134°, Bz₂, m. p. 182°, derivatives), gives only one peroxide, m. p. 75°, regarded as a dioxadiazine. The difference is ascribed to the positive and negative characters of Me and CN, respectively. Cyano-oximino-acetophenone, CPh.C(NOH)·CN (Ac, m. p. 89—90°, Bz, m. p. 110°, derivatives), with NH₂OH gives, not (I), but phenyloximinooxazalone, OH·N·C=CO $\xrightarrow{\text{CPh=N}}$ CPh.N·O. (I) with NH₂OH gives α -amino- $\alpha\beta$ -trioximino- γ -phenylpropane, m. p. 156—157° (decomp.). Reduction of (I) with SnCl₂ gives phenylcyanofurazan, Ph(C₂N₂O)CN, m. p. 40—41°. E. E. J. MARLER.

Ultra-violet absorption of lignin and chemically similar compounds. R. O. HERZOG (Zellstoff u. Papier, 1932, 12, 10).—The absorption phenomena of di- and tri-hydroxyphenyl compounds with CHO, Pr, allyl, and propenyl groups as side-chains have been examined. Lignosulphonic acid preps. of different origin show more strongly marked absorption max. after purification than do the raw products, and on dialysis the max. move towards the red. The former effect is attributable only to the removal of impurities. The absorption spectrum of pinewood lignin approximates to that given by diphenols and that of deciduous wood lignin to that of triphenols. The side-chains are saturated. B. P. RIDGE.

Constitution of so-called tetrahydropyrones. R. CORNUBERT and P. ROBINET (Compt. rend., 1932, 194, 107—109; cf. A., 1930, 343).—The product of condensation of PhCHO with 2-methylcyclohexanone in presence of HCl forms an oxime, m. p. 224—226° (corr.), and on reduction with Na and EtOH gives a sec.-alcohol, b. p. 127—128°, also obtained by action of KOH in EtOH or Bu^oOH. The pyrone structure is not revealed by action of NH₃ or amines. Oxidation with KMnO₄ in H₂O or COMe₂ gives BzOH, γ -aceto-butyric acid and degradation products, and a neutral compound, C₂₁H₂₂O₃ (?), m. p. 145—146°. HCl in AcOH at 160—180° gives chlorinated products, b. p. 230—250°/15 mm., but aq. HCl at 125—135° hydrolyses this "tetrahydropyrone" and also the product from benzaldehyde and 2-benzyl-2-methylcyclohexanone into their components. H. A. PIGGOTT.

Spatial configuration of molecules. Absorption by aldehydes, Ph·[CH₂]_n·CHMe·CHO, and

ketones, Ph·[CH₂]_n·CH₂·COMe, in the ultra-violet. (MME.) P. RAMART-LUCAS and L. LABAUNE (Ann. Chim., 1931, [x], 16, 276—307; cf. A., 1930, 1087).— γ -Phenyl- β -methyl- $\alpha\beta$ -propylene, b. p. 197°/757 mm., γ -*p*-tolyl- β -methyl- $\alpha\beta$ -propylene, b. p. 218°/759 mm., δ -phenyl- β -methyl- $\alpha\beta$ -butylene, b. p. 219°/760 mm., ϵ -phenyl- β -methyl- $\alpha\beta$ -amylene, b. p. 238°/760 mm., and ζ -phenyl- β -methyl- $\alpha\beta$ -hexylene, b. p. 255°, oxides were prepared from chloroacetone and the appropriate Grignard reagent. β -Phenyl- α -methylprop-, b. p. 90°/6 mm. (semicarbazone, m. p. 123°), β -*p*-tolyl- α -methylprop-, b. p. 163°/6 mm. (semicarbazone, m. p. 138°), ζ -phenyl- α -methylhex-aldehyde, b. p. 119°/8 mm. (semicarbazone, m. p. 57°), were prepared by isomerisation of the above oxides and also from the appropriate glycidic acids. ϵ -Phenyl-*n*-amyl Me ketone, b. p. 144° (semicarbazone, m. p. 115°), and δ -phenyl- Δ^2 -butenyl Me ketone, b. p. 131° (semicarbazone, m. p. 130°), were prepared from the appropriate derivatives of acetoacetic ester.

The ultra-violet absorption spectra of the five homologous aldehydes (and ketones) would be identical when $n > 2$ if the chromophores were progressively separated as each series is ascended; but, in passing from $n = 3$ to $n = 4$, variations are observed which indicate the spatial approach of the chromophores. Extinction coeffs. for EtOH and hexane solutions are given. J. G. A. GRIFFITHS.

Preparation of ketones from acid halides and the Grignard reagent. H. GILMAN and M. R. MAYHUE (Rec. trav. chim., 1932, 51, 47—50).—Rapid addition of 0.1 mol. of MgPhCl, MgPhBr, and MgPhI to 0.1 mol. of BzCl in Et₂O (10—15 c.c.) without cooling gives CPh₂ in yields of 48, 55, and 68.5%, respectively. CPh₂·OH is the main by-product.

H. BURTON.

Planar configuration of diamagnetic nickel complexes. I. Isomeric nickel derivatives of benzylmethylglyoxime. S. SUGDEN (J.C.S., 1932, 246—250).—Benzylmethylglyoxime, m. p. 194°, is converted in the usual manner into a mixture of α -, m. p. 168° (corr.), and β -, m. p. 75—77° (corr.; very rapidly heated), Ni-complexes, both of which are diamagnetic; the β -form is converted at 120° into an equilibrium mixture of α - and β -forms. Both regenerate the parent oxime with cold 15% HCl, and give its Ac derivative with Ac₂O and pyridine; the same form of the oxime is therefore present in each. The existence of two stable forms is not readily explained by stereoisomerism depending on a tetrahedral structure of the Ni atom, but is to be expected if the valency linkings of Ni are arranged at 90° to one another in a plane as required by Pauling's theory (A., 1931, 670). H. A. PIGGOTT.

Condensation of dibenzyl ketone with aromatic aldehydes and ketones. R. N. SEN and J. L. NANDI (J. Indian Chem. Soc., 1931, 8, 591—598).—By condensation of CO(CH₂Ph)₂ with the appropriate aldehyde or ketone with either 60% KOH in EtOH or with dry HCl in MeOH at room temp., the following derivatives are obtained: benzylidene, m. p. 86° (phenylhydrazone, m. p. 90—91°); cinnamylidene, m. p. 110° (phenylhydrazone, m. p. 120°; oxime, m. p. 150—151°); di-*o*-nitrobenzylidene, m. p. 226° (phenylhydrazone, m. p. 100°); di-*p*-hydroxybenzylidene,

m. p. 170° (*phenylhydrazone*, m. p. 120—122°; *oxime*, m. p. 131°; *Bz*₂ derivative, m. p. 158°); *diisopropylidene*, m. p. 91—92° (*phenylhydrazone*, m. p. 99°; *oxime*, m. p. 102°); *dibenzhydrylidene*, m. p. 91—92°, and *di-(α-phenylethylidene)*, m. p. 95° (*phenylhydrazone*, m. p. 106—107°). Condensation with salicylaldehyde affords the compound $\text{R} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CHPh} \cdot \text{CO} \\ \text{CH} = \text{CPh} \end{array}$ (R=H), m. p. 106° (*phenylhydrazone*, m. p. 50°), whilst resorcydaldehyde gives the analogous compound (R=OH), m. p. 151—152° (*phenylhydrazone*, m. p. 104—105°; *Bz* derivative, m. p. 110—111°); isatin gives the compound (?) $\text{C}_6\text{H}_4 \begin{array}{c} \text{C} - \text{CPh} - \text{CO} \\ | \\ \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{CHPh} \end{array}$, m. p. 255—257° (*oxime*, not melted at 280°; *dibromide*, not melting at 270°); and phenanthraquinone gives the compound $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH}) \cdot \text{CHPh} \\ | \\ \text{C} = \text{CPh} \end{array} > \text{CO}$, m. p. 102—103° (previous darkening) (*oxime*, m. p. 98°; *dibromide*, m. p. 148—150°). J. W. BAKER.

Fries reaction. F. F. BLICKE and O. J. WEINKAUFF (J. Amer. Chem. Soc., 1932, 54, 330—334).—*BzOPh* heated with AlCl_3 gives a quant. yield of *p-OH-C}_6\text{H}_4\text{Bz}*. *p*-Diphenyl benzoate gives 4-*p*-hydroxyphenylbenzophenone, m. p. 193—195° (Me ether, m. p. 168—169°, also prepared from 4-methoxydiphenyl, BzCl , and AlCl_3). *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Ph})_2$ and AlCl_3 in $\text{C}_6\text{H}_2\text{Cl}_4$ at 150° give 1-hydroxyanthraquinone and (mainly) phenolphthalein (formed also in quant. yield from Ph *o*-anisoylbenzoate and AlCl_3).

C. J. WEST (b).

Transitions from aromatically-substituted pinacols to indene hydrocarbons. O. BLUM-BERG-MANN (Ber., 1932, 65, [B], 109—122).—The “9:10-dimethylantracene,” m. p. 75°, obtained by Ramart-Lucas and Salmon-Legagneur (A., 1929, 815) by dehydration of β -*p*-diphenylbutane- β -diol is identified as 2-phenyl-3-methylindene. α - β -Diphenylpropionic acid, m. p. 88—89.5°, prepared directly by the action of KOH-EtOH on Et phenylbenzylmalonate, is transformed by cautious treatment with SOCl_2 into α -*p*-diphenylpropionyl chloride, b. p. 182—183°/17 mm., whilst when treated according to Auwers it gives (?) 2:3:5:6-tetraphenylcyclohexane-1:4-dione, m. p. 238°. The chloride is transformed by AlCl_3 in CS_2 under defined conditions into 2-phenylhydrindone, m. p. 75—77°, converted by MgMeI into 1-hydroxy-2-phenyl-1-methylhydrindene, m. p. 78—80.5° (decomp.), which passes by loss of H_2O into 2-phenyl-3-methylindene, m. p. 76—78°, the *oxime*, m. p. 184—185°, of which is not identical with 3-phenyl-2-methylindene-*oxime*, m. p. 198—199°. β -*p*-Diphenylbutyryl chloride, b. p. 193—194°/16 mm., is converted by AlCl_3 in CS_2 into 3-phenyl-3-methylhydrindone, b. p. 197—199°/16 mm., and thence by Br in CS_2 into 2-bromo-3-phenyl-3-methylhydrindone, m. p. 108—110°, which does not yield cryst. products when heated at 200—250° with S, P_4O_{10} , quinoline, pyridine, or NPhMe_2 . α -Phenylcinnamic acid is converted by SOCl_2 into (?) 2-phenyl-3- α -phenylcinnamoylindene, $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{CO} \cdot \text{CPh} \cdot \text{CHPh}) \cdot \text{CPh} \\ | \\ \text{CO} \end{array}$ m. p. 230—231°. 3-

Phenyl-2-methylindenehydrazone, m. p. 124—125° (corresponding *ketazine*, m. p. 203—204°), is transformed by NaOEt in EtOH at 145° into 3-phenyl-2-methylhydrindene, b. p. 181°/10 mm. The action of P_4O_{10} in C_6H_6 on α -diphenyl- β -methylpropane- α - β -diol and α - β -diphenylbutane- α - β -diol, respectively, causes pinacolin transformation with production of γ -diphenylbutan- β -one, m. p. 39—42°, b. p. 168—169°/11 mm., and Ph α -phenyl- α -methyl-ethyl ketone, m. p. 41—43°. The hydrocarbon obtained by Tiffeneau and Dorlencourt (A., 1907, i, 130) by the action of P_4O_{10} on α - β -diphenylpropane- α - β -diol is shown to be 2-phenylindene; the main product of the action is α -diphenylpropionaldehyde, b. p. 167.5—168°/11 mm. (semicarbazone, m. p. 193—193.5°), accompanied by a compound, $\text{C}_{30}\text{H}_{28}\text{O}_2$, m. p. 169—171°. α - β - γ -Tetraphenylbutane- β - γ -diol and AcBr afford 1:2-diphenyl-3-benzylindene, m. p. 118.5—119.5°, prepared synthetically by the action of CH_3PhCl on Li 2:3-diphenylindene. Reduction of 2:3-diphenyl-1-benzylideneindene by Al-Hg and H_2O in dioxan leads to 2:3-diphenyl-1-benzylindene, m. p. 118.5—120°, and 1:2-diphenyl-3-benzylindene, m. p. 117—119.5°. The production of substituted indenones from fatty-aromatic pinacols is not a general reaction, since α - β -diphenylbutane- α - β -diol and P_4O_{10} afford mainly α -*p*-diphenylbutaldehyde, b. p. 174—176°/11 mm. (semicarbazone, m. p. 175—176°), and a small amount of substance, $\text{C}_{32}\text{H}_{32}\text{O}_2$, m. p. 139—140°, and γ -phenyl- α - β -*p*-anisylpropane- α - β -diol yields β -phenyl- α -*p*-anisylpropionaldehyde, m. p. 139—140° (converted by EtOH-KOH at 125° into α -phenyl- β -*p*-anisylethane, m. p. 98—99°), and γ -phenyl- α -*p*-anisylpropan- β -one, m. p. 65—65.5° (converted by EtOH-KOH at 125—130° into *p*-anisylmethane, m. p. 50—52.5°, and $\text{CH}_2\text{Ph} \cdot \text{CO}_2\text{H}$, m. p. 72—75°).

H. WREN.

Synthesis and orientation of trichloroanthraquinones and aminodisulphonates of anthraquinone. II. A. A. GOLDBERG (J.C.S., 1932, 73—83; cf. A., 1931, 1062).—*K* 2-chloroanthraquinone-6- (chloride, m. p. 202—203°), and -7-sulphonate (chloride, m. p. 200—201°), are prepared by the action of KClO_3 and HCl on the corresponding anthraquinonedisulphonates. The former with 20% oleum at 155—160° yields *K* 2-chloroanthraquinone-3:6-disulphonate, converted by nascent Cl_2 into *K* 2:3-dichloroanthraquinone-6-sulphonate (chloride, m. p. 228—229°), the orientation of which is confirmed by its formation by sulphonation of 2:3-dichloroanthraquinone in absence of Hg. Sulphonation of 2:3-dichloroanthraquinone in presence of HgSO_4 yields 2:3-dichloroanthraquinone-5-sulphonic acid (*K* salt), since this with nascent Cl_2 gives 2:3:5-trichloroanthraquinone, m. p. 227—228°, which depresses the m. p. of 1:2:3-trichloroanthraquinone. Further sulphonation in presence of HgSO_4 gives 2:3-dichloroanthraquinone-1(or 4):5-disulphonic acid (*K* salt), converted as above into 1:2:3:5(or 8)-tetrachloroanthraquinone, m. p. 208°. 2:7-Dichloroanthraquinone gives on sulphonation the -3-sulphonic acid, m. p. above 300°, converted with difficulty into 2:3:6-trichloroanthraquinone, m. p. 245°, identified by difference and by its formation from 4:5:4'-trichloro-2-benzoylbenzoic acid (from PhCl , 4:5-di-

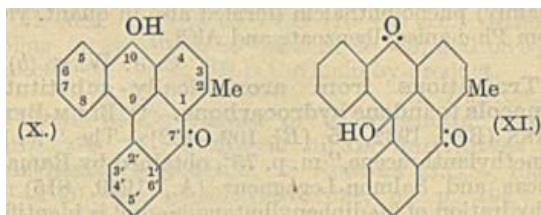
chlorophthalic anhydride, and AlCl_3 , m. p. 196—197°, by cyclisation with 5% oleum at 155—160°; 2:6-dichloroanthraquinone under the same conditions gives, most probably, the 3:7-disulphonic acid, the SO_3H groups of which are not removed by nascent Cl_2 . Sulphonation of K 2-chloroanthraquinone-7-sulphonate gives the 3:7-disulphonate, since this with Cl_2 gives K 2:3-dichloroanthraquinone-6-sulphonate, identified as its sulphonyl chloride (above), apparently accompanied by a higher chlorinated product. Sulphonation of 1:7-dichloroanthraquinone in presence of Hg gives the 8(?)sulphonic acid (K salt), readily converted into 1(?):2:8-trichloroanthraquinone, m. p. 190—192°. K 2-aminoanthraquinone-3:6- and -3:7-disulphonate are readily prepared from the corresponding chlorodisulphonates by heating with aq. NH_3 and CuSO_4 at 100°; both form intensely red aq. solutions. H. A. PIGGOTT.

Reduction of heteronuclear nitroanthraquinonesulphonates. A. A. GOLDBERG (J.C.S., 1932, 83—86).—Reduction of Na 1-nitroanthraquinone-5-sulphonate with aq. Na_2S at or below 0° gives Na 1-azoxyanthraquinone-5-sulphonate or Na 1-hydroxylaminoanthraquinone-5-sulphonate, according to the amount of Na_2S used; the latter is isomerised to Na 1-amino-4-hydroxyanthraquinone-5-sulphonate by conc. H_2SO_4 at 100°, and both are reduced to the aminoanthraquinone-5-sulphonate by Na_2S at 100°. Na 1-azoxy-, Na 1-hydroxylamino-, and Na 1-amino-4-hydroxy-anthraquinone-8-sulphonates are similarly prepared. H. A. PIGGOTT.

Tautomerism of anthraquinone-1-carboxyl chlorides and synthesis of compounds of the coeranthrene series. R. SCHOLL, H. DEHNERT, and L. WANKA (Annalen, 1932, 493, 56—96).—2-Methylanthraquinone-1-carboxyl chloride (1 mol.) heated with FeCl_3 (about 0.2 mol.) and an excess of C_6H_6 , gives 1-benzoyl-2-methylanthraquinone (1 pt.) and the lactone (I), m. p. 204° (7 pts.), of 9-hydroxy-9-phenyl-2-methyl-10-anthrone-1-carboxylic acid (II), converted into (I) above 100° or by short treatment with boiling AcOH. Reduction of (I) with Zn dust and AcOH affords the lactone (III), m. p. 173—174° (Ac derivative, m. p. 208—209°), of 9:10-dihydroxy-9-phenyl-2-methyl-9:10-dihydroanthracene-1-carboxylic acid (IV) and a little 9-phenyl-2-methylanthracene-1-carboxylic acid (V), m. p. 281—282° (becoming red), whilst reduction of (II) with Zn dust and aq. NH_3 gives (IV) and a considerable amount of (V). (IV) lactonises extremely readily. (III) is converted by EtOH-KOH into 10-hydroxy-9-phenyl-2-methylanthracene-1-carboxylic acid (+ H_2O) (VI), yellow, m. p. 225—250°, transformed by hot AcOH into 9-phenyl-2-methyl-10-anthrone-1-carboxylic acid (VII), colourless, m. p. 291—292°, also obtained from (I) and SnCl_2 in AcOH-HCl. (VII) is converted into (VI) by rapid dissolution in hot 10% NaOH and immediate acidification with HCl. (VII), Ac_2O , and NaOAc give the Ac derivative, decomp. 240°, of (VI). The lactone, m. p. 180—182° (becoming red), of 10-chloro-9-hydroxy-9-phenyl-2-methyl-9:10-dihydroanthracene-1-carboxylic acid is prepared from (III) and PCl_5 in CHCl_3 . (V) is also obtained by reduction of (III) with Zn dust and aq. NH_3 in EtOH or by reduction of (VI)

or (VII) with Zn dust and NaOH, AcOH, or aq. NH_3 . 9:9-Diphenyl-2-methyl-10-anthrone-1-carboxylic acid (VIII), m. p. 324—325°, is obtained from (I) and C_6H_6 in presence of AlCl_3 (see also below); the 9-Cl-9-Ph acid is probably an intermediate. Reduction of (I) with 2.5% Na-Hg and EtOH gives 9-phenyl-2-methyl-9:10-dihydroanthracene-1-carboxylic acid, m. p. 220—221°, which, like (V), is oxidised by CrO_3 in AcOH to (I). (VIII) is similarly oxidised (with loss of a Ph group) to (I). Oxidation of (I) with dil. HNO_3 at 185—195° gives 9-hydroxy-9-phenyl-10-anthrone-1:2-dicarboxylic acid (lactone, m. p. 203—204°), reduced by SnCl_2 and conc. HCl in AcOH to 9-phenyl-10-anthrone-1:2-dicarboxylic acid, m. p. 204.5—206.5°, and by Zn dust and aq. KOH to 9-phenylanthracene-1:2-dicarboxylic acid (IX) (+0.5MeOH) (anhydride, m. p. 208.5—209.5°). Treatment of (I) with Cl_2 at 205—220° in sunlight affords 2-dichloromethylanthraquinone-1-carboxylic acid, m. p. 212—213° (decomp.), converted by conc. H_2SO_4 at 130° into 2-aldehydeanthraquinone-1-carboxylic acid (not characterised).

When 9-phenyl-2-methyl-10-anthrone-1-carboxylic acid is shaken with conc. H_2SO_4 in CO_2 at room temp., 10-hydroxy-2-methylcoeranthrene(7') (X) [the unknown parent hydrocarbon (X, where Me and $\text{OH}=\text{H}$ and $\text{O}=\text{H}_2$) is designated coeranthrene], bluish-violet (Ac derivative, m. p. 208—209° after previous sintering), is formed, also obtained in a difficultly purifiable form from (VII) and AlCl_3 in PhNO_2 . (X), like anthranol, can be titrated with Br (2 equivs.)



and KMnO_4 (2 equivs. of O). The absorption spectrum of its dark green solution in conc. H_2SO_4 differs considerably from that of the similarly coloured solution of fur.-hydroxy-*p*-chlorophenylperihydrofurananthroxyl (A., 1931, 846). (X) is readily sol. in cold aq. NH_3 to a readily autoxidised greenish-blue solution, but is sparingly sol. in NaOH or KOH. (V) and conc. H_2SO_4 give 2-methylcoeranthrene-7', red, m. p. 175—176° [10- NO_2 -, m. p. 231—231.5° (decomp.) after previous darkening, and 10- NH_2 -derivatives (unstable)], which does not give a vat with alkaline $\text{Na}_2\text{S}_2\text{O}_4$ and is oxidised by CrO_3 in AcOH to the colourless 9-hydroxy-2-methyl-9:10-dihydrocoeranthra-10:7'-dione (XI) (cf. Weiss and Reichel, A., 1929, 1445), darkens at 195° and becomes black at 205°, which is readily reduced to (X). 9-Phenyl-2-methyl-9:10-dihydrocoeranthra-10:7'-dione (XII), m. p. 286—287°, and coeranthrene(7')-2-carboxylic acid, m. p. 264—266°, are prepared from (VIII) and (IX), respectively. 10-Hydroxycoeranthrene(7')-2-carboxylic acid is prepared but not characterised.

[With E. WEBER.] *p*-Tolyl, m. p. 198—199°, anisyl, m. p. 204°, and *p*-diphenyl, m. p. 231°, 2-methyl-1-anthraquinonyl ketones and 9-*p*-tolyl-, m.p.

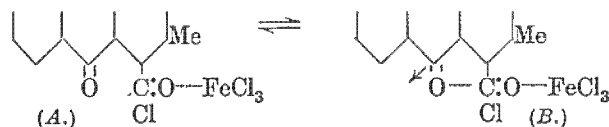
170°, -*p*-xylyl, m. p. 181—182°, -*anisyl*- (XIII), m. p. 156°, and -*p*-diphenyl-, m. p. 185—186°, -9-hydroxy-2-methyl-10-anthrone-1-carboxylic acid lactones are prepared from 2-methylanthraquinone-1-carboxyl chloride, the requisite ArH, and FeCl₃. When AlCl₃ is used in the prep. of (XIII), some 5'-methoxy-9-anisyl-2-methyl-9:10-dihydrocoeranthra-10:7'-dione (?), red, m. p. 252°, is produced.

[With H. von HOESSLE.] 2-Methylanthracene-1-carboxylic acid and SO₂Cl₂ in CHCl₃ give 9:10-dichloro-2-methylanthracene-1-carboxylic acid, m. p. 241—245° (decomp.) (sinters at 235°) [chloride, m. p. 237—242° (decomp.)].

[With K. STEPHANI.] Anthraquinone, PhOMe, and AlCl₃ after 2 days at room temp. and 1 hr. at 40—50° give 12—15% of *ms*-dianisylanthrone; condensation probably proceeds through the 9-hydroxy-9-anisyl- and 9-chloro-9-anisyl-anthrone.

[With O. HILLE.] Anthranol is obtained from anthraquinone, *m*-xylene, and AlCl₃ at 80—90°.

Prolonged interaction of 2-methylanthraquinone-1-carboxyl chloride, C₆H₆, and AlCl₃ at room temp. also gives (I); in boiling C₆H₆, (I) reacts further affording (VII), (VIII), (X), and (XI). The production of (I) and Ph 2-methyl-1-anthraquinonyl ketone (and related mixtures) is considered not to involve the existence of two forms of the carboxyl chloride or the conversion of the normal into the ψ -form by FeCl₃ (or AlCl₃) in solution. The production of dianisylanthrone and anthranol from anthraquinone shows that the C atom of the ketonic CO group can be activated (indirectly), and it is assumed that the equilibrium ($A \rightleftharpoons B$) first results. The amount of (I) produced is not influenced to any appreciable



extent by the amount of catalyst, but is affected by the solvent, and results from addition of C₆H₆ to (B) with subsequent loss of HCl. H. BURTON.

Manufacture of *p*-nitrosoamino-compounds or *p*-quinoneoxime-imino-compounds of the aromatic series. I. G. FARBENIND. A.-G.—See B., 1932, 95.

Manufacture of polycyclic compounds containing two CO groups [dibenzopyrenequinones]. I. G. FARBENIND. A.-G.—See B., 1932, 138.

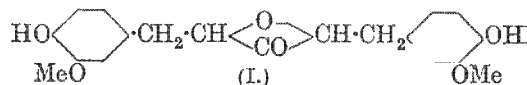
Lichen substances. VII, VIII. **Constitution of thamnolic acid.** II. Y. ASAHINA and S. IHARA. III. Y. ASAHINA and F. FUJIKAWA (Ber., 1932, 65, [B], 55—57, 58—60; cf. A., 1929, 818).—II. Methylation of the Me ether of orcinoldicarboxylic acid (from thamnolic acid) affords Me 3:5-dimethoxytoluene-2:4-dicarboxylate, m. p. 58—59°, doubtless identical with the synthetic product of Koller and Krakauer (A., 1929, 1459), hydrolysed to the corresponding acid, m. p. 212°. Thamnolic acid or its anil is transformed by diazomethane into a product, C₁₆H₈O₅(OMe)(OMe)₅, which gives unrecognisable compounds when heated with AcOH at 130—150°, but is hydrolysed by KOH to 3:5-dimethoxytoluene-

2:4-dicarboxylic acid, m. p. 212°. For the conversion of thamnolic acid into thamnol, *n*-nonoic acid can be replaced by stearic acid at 170°. *Tribenzoylthamnol*, prepared by means of Bz₂O in pyridine, has m. p. 158° (anil, m. p. 135—138°).

III. Thamnolic acid is converted by boiling 95% HCO₂H into thamnol and atranol is derived similarly from atranorin. The K derivative of nitroso-orcinol is transformed by boiling aq. Na₂S₂O₄ into 2:3:5-trihydroxytoluene, m. p. 148°, converted by Bz₂O in pyridine into the Bz₃ derivative, which could not be oxidised smoothly. *Tribenzoylthamnoloxime*, m. p. 176°, could not be transformed into the corresponding nitrile. Atranol is coupled with diazobenzene chloride to the azo-compound, C₁₄H₁₂O₃N₂, m. p. 190°, converted by Zn and AcOH into aminoatranol and thence by conc. KOH into thamnol. H. WREN.

New constituent of *Tsuga*-resin. J. KAWAMURA (Bull. Imp. Forestry Exp. Stat., Tokyo, 1932, No. 31, 73—76).—Extraction of the powdered wood of *Tsuga Sieboldii*, Carr., with Et₂O affords *tsugaresinol*,

(OH)₂(OMe)₂C₁₆H₁₂·C<sup>CO_O (I), m. p. 235—237° with slow evolution of CO₂, re-solidification and re-melting at 255° (Ac₂, m. p. 204—205°, and *di-p*-nitrobenzoyl, m. p. 257—258°, derivatives), converted by 1 mol. of 0.4*N*-KOH in EtOH into *tsugic acid*, C₁₆H₂₂O₇, m. p. 208—210°, resulting from fission of a β- or δ-lactone ring. Oxidation of this acid with HNO₃ affords a resin and H₂C₂O₄, but Me₂SO₄ and NaOH convert it into *dimethyltsugic acid*, m. p. 165—167°, oxidised by alkaline KMnO₄ to veratric acid. On the basis of



these results the structure (I) (or the corresponding δ-lactone) is suggested for *tsugaresinol*.

J. W. BAKER.

Modifications of gutta-percha hydrocarbon. A. W. K. DE JONG (Rec. trav. chim., 1932, 51, 61—66; cf. B., 1930, 1039).—The spongy variety of the hydrocarbon, which is generally obtained by crystallisation from a conc. solution in light petroleum, shows the same Röntgen diagram as the stable (α) form; it is compressed to a product which is much less sol. in C₆H₆ below 19° than the original material. Similar differences in solubility are found with the analogous products from sheet balata. When thin strips of the hydrocarbon are melted in H₂O at 100° and then cooled slowly, a product is obtained which gives a mixed (β + a little α) Röntgen diagram; the C₆H₆-insol. material (48%) consists of the α-form, some of which must have been formed from the β-modification during the treatment with C₆H₆. Fusion at 100° followed by rapid cooling in H₂O gives the β-form (Röntgen diagram), which when treated with C₆H₆ affords 27% as the insol. α-modification (also formed from the β-variety). The above β-forms probably contain some of the amorphous modification; both varieties are sol. in C₆H₆ and both may be transformed into the α-form. The product formed by fusion at 100° and cooling in ice shows the β-diagram; 40% is extracted by light petroleum at

21°, but the insol. material is entirely the β -modification. The solubilities of strips of the products obtained by fusion and cooling in C_6H_6 at 16° are lowered by cold pressing or stretching. The stretching of threads has little effect on their solubility in C_6H_6 .

H. BURTON.

Natural and synthetic rubber. VIII. Products of the destructive distillation of sodium rubber. T. MIDGLEY, jun., A. L. HENNE, and A. F. SHEPARD (J. Amer. Chem. Soc., 1932, 54, 381—386).—The pyrolysis products of Na rubber indicate that Na rubber is isomeric with natural rubber respecting the positions of its Me groups, and that the double linking of Na rubber differs from the true ethylenic linking of natural rubber. In the latter respect, Na rubber closely resembles over-vulcanised rubber. The compounds identified in the (destructive) distillate are: C_3H_6 and butenes (0.3%), $CHMe_2CH:CH_2$ (0.2%), $CH_2:CMcEt$ (2%), $CH_2:CMcEt:CH:CH_2$ (1.1%), $CMc_2:CHMe$ (4.2%), γ -methylpentenes (0.4%), C_6H_6 (0.1%), heptanes (0.03%), tetrahydrotoluene (0.4%), PhMe (0.1%), *m*- (0.1%) and *p*-xylenes (0.02%). Hexahydroxylene is probably formed. Compounds with 9 and 10 C atoms, similar to those from natural rubber, are also produced. C. J. WEST (b).

Synthesis of methyl- ψ -ionones of definite structure. E. CHERBULIEZ and A. HEGAR (Helv. Chim. Acta, 1932, 15, 191—201).—Condensation of $CHMeBrAc$ with citral in presence of Mg and $HgCl_2$ affords the *hydroxyketone*, dehydrated by $NaOEt$ to *methyl- ψ -ionone b*, $C_9H_{15}:CH:CMcAc$, b. p. 149—154°/13.5 mm. (*p*-bromophenylhydrazone, m. p. 156—158°; *picrate* of *aminoguanidine* derivative, m. p. 168°), whilst $CH_2Br:COEt$ similarly gives *methyl- ψ -ionone a*, $C_9H_{15}:CH:CH:COEt$, b. p. 159—162°/12.5 mm. (*p*-bromophenylhydrazone, m. p. 156—158°; *picrate* of *aminoguanidine* derivative, m. p. 151°) ($C_9H_{15}=CMc_2:CH:[CH]_2:CMc_2:CH$). In the course of unsuccessful syntheses the following results were obtained. Citral condenses with $CH_2Cl:CO_2Et$ to give the *OH-ester*, converted by distillation into Et citrylideneacetate, b. p. 150—153°/8.5 mm., hydrolysed by KOH in EtOH to the acid and a *substance*, b. p. 110—144°/8 mm., probably methylgeraniol obtained by decarboxylation of the hydroxy-acid: with $CMcBr(CO_2Et)_2$ is obtained the *ester* $C_9H_{14}:CH:CMc(CO_2Et)_2$, b. p. 184—197°/10 mm.

J. W. BAKER.

Menthylphosphorous acid. T. MIEOBEDZKI and A. RENO (Rocz. Chem., 1931, 11, 834—839).—*i*-Menthylphosphorous acid, m. p. 29°, is obtained, together with trimethyl phosphite and menthyl chloride, by hydrolysing $C_{10}H_{19}OPCl_2$, prepared by the action of excess of *i*-menthol on PCl_3 .

R. TRUSZKOWSKI.

Menthylphosphoric acids. T. MIEOBEDZKI and W. JANCZAK (Rocz. Chem., 1931, 11, 840—854).—The following substances have been prepared by hydrolysis of the products of interaction of menthol and $POCl_3$ in PhMe solution: *mono*-, m. p. 128—129° (*monohydrate*, m. p. 82.5°), *di*-, m. p. 105°, and *tri-i*-menthyl orthophosphates, m. p. 86°, and *di-i*-menthyl pyrophosphate, m. p. 198°.

R. TRUSZKOWSKI.

Dependence of optical rotatory power on chemical constitution. XIII. Naphthylene derivatives of stereoisomeric iminocamphors and methylenecamphors. B. K. SINGH and B. BHADURI (J. Indian Chem. Soc., 1931, 8, 623—632).—By condensation of camphorquinone and hydroxymethylenecamphor with 1:2- and 1:5-naphthylendiamine in EtOH in presence of anhyd. $NaOAc$, the following have been prepared: 1:2-*benzo-d*-, m. p. 116—117°, $[\alpha]_D +28.98^\circ$, -l-, m. p. 116—117°, $[\alpha]_D -29.42^\circ$, and -dl-, m. p. 123—124°, -*camphanoquin-oxaline*; 1:5-*naphthylenebisimino-d*-, not melting at 260°, $[\alpha]_D +740.9^\circ$, -l-, not melting at 260°, $[\alpha]_D -736.4^\circ$, and -dl-, not melting at 315°; 1-*amino-5-naphthylimino-d*-, m. p. 192—193°, $[\alpha]_D +565.0^\circ$ (*Ac* derivative, m. p. 173—174°, $[\alpha]_D +480.0^\circ$), -l-, m. p. 192—193°, $[\alpha]_D -482.6^\circ$ (*Ac* derivative, m. p. 173—174°, $[\alpha]_D -482.6^\circ$), and -dl-, m. p. 172—173°; 1:5-*naphthylenebisaminomethylene-d*-, m. p. 322—323°, $[\alpha]_D +435.4^\circ$, -l-, m. p. 322—323°, $[\alpha]_D -435.0^\circ$ (exhibits simple dispersion), and -dl-, m. p. 322—323°, -*camphor*. All the above rotation vals. are in $CHCl_3$; the vals. in other solvents and for other wave-lengths are tabulated and discussed in relation to the constitution of the various derivatives (cf. A., 1930, 1441).

J. W. BAKER.

Configuration of camphorquinoneoximes. J. MEISENHEIMER and W. THEILACKER (Annalen, 1932, 493, 33—56).—The various reactions of α - (I) and β - (II) -oximinocamphor recorded in the lit. indicate that (I) is the *anti*- and (II) the *syn*-form. (II) can be separated from a mixture of (I) and (II) by sublimation in a high vac. (I) is converted by PCl_5 in Et_2O at 0° into α -camphornitrilic acid, also formed together with α -camphoramidic acid by similar treatment of (II); in the last case (II) probably first rearranges into (I). The β -form (m. p. 183°) of $C_8H_{14}\begin{smallmatrix} CMe \\ \diagdown \\ C-N-OH \end{smallmatrix}$, described by Forster (J.C.S., 1905, 87, 236), is a mixture of the α - (III), m. p. 178°, and γ - (IV), m. p. 187° (now obtained with m. p. 195°, $[\alpha]_D +56.9^\circ$ in $CHCl_3$), forms; (III)+(IV) give mixed crystals which are identical with the supposed β -form. (I) and $MgMeI$ give (IV) (cf. *loc. cit.*), whilst (II) and $MgMeI$ afford (III) and (IV); in this last case, (II) is probably first converted (partly) into (I) and thence into (IV). (III) is dehydrated only with acids whilst dehydration of (IV) occurs with both acids and alkalis; in no case,

however, is the anhydride, $C_8H_{14}\begin{smallmatrix} CMe \\ \diagdown \\ C=N \end{smallmatrix}O$, described by Forster (*loc. cit.*), produced. (IV) is dehydrated by 10% H_2SO_4 at 100° (bath) to 3-*cyanol-1-acetyl-1:2:2-trimethylcyclopentane* (V), m. p. 38.5°, $[\alpha]_D +85.8^\circ$ in $CHCl_3$ [2:4-*dinitrophenylhydrazone*, m. p. 180°; *semicarbazone*, m. p. 242° (decomp.)], hydrolysed by 15% KOH to a mixture (A), m. p. 72°, of (mainly) α -, m. p. 85°, $[\alpha]_D +67.5^\circ$ in EtOH, and a little β -, m. p. 84°, -1-*acetyl-1:2:2-trimethylcyclopentane-3-carboxylic acids*, and by 10% EtOH-KOH to about 10% of (A) and 90% of the *imino*-compound (VI), $C_8H_{14}\begin{smallmatrix} CO \\ \diagdown \\ C(NH) \end{smallmatrix}CH_2$, m. p. 248° [deep violet *NO*-derivative, m. p. 239° (decomp.)], which, like the 4-iminobarbituric acids, is insol. in AcOH

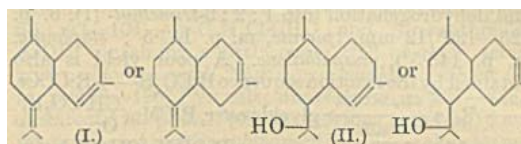
and sol. in dil. mineral acid. (VI) is hydrolysed by conc. HCl to the diketone, $C_8H_{14} \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH_2$, m. p. 223°, which is converted by MeOH-HCl into an oily Me ester, and by alkaline NaOBr into CBR_4 and *d*-camphoric acid. (III) and 10% H_2SO_4 at 100° (bath) give about 40% of (V) [resulting by partial conversion of (III) into (IV)], 10% of a compound, $C_{22}H_{38}O_4N_2$, m. p. 291°, and 50% of 1 : 2 : 2-trimethyl-1-(α -hydroxy- α -cyanoethyl)- Δ^3 -cyclopentene (VII), b. p. about 147°/12 mm., $[\alpha]_D^{25} +76.6^\circ$ in $CHCl_3$. (VII) is not hydrolysed by conc. H_2SO_4 or EtOH-KOH, but when distilled in vac. partly eliminates HCN to form 1-acetyl-1 : 2 : 2-trimethyl- Δ^3 -cyclopentene (2 : 4-dinitrophenylhydrazones, m. p. 166°), also obtained (in one case only) when a sample of (IV) which contained some (III) was treated with 10% H_2SO_4 at 100°, and the resulting oil hydrolysed with 15% EtOH-KOH. *d*-Camphor-2 : 4-dinitrophenylhydrazone has m. p. 174°. The configurations of the stereoisomeric oximinoepicamphors and camphorquinonedioximes (Forster, J.C.S., 1913, 103, 662) should be revised; the β - and γ -dioximes are *anti* and *syn*, respectively, whilst the α - and δ -dioximes have *amphi*-configurations.

H. BURTON.

Symmetrical methylcamphoric (4-methylcamphoric) acid from 4-methylcamphor. II. M. BREDT-SAVELSBERG (Ber., 1932, 65, [B], 1—11; cf. A., 1931, 625).—3-Methylcamphoric acid (I), $\begin{smallmatrix} OH \\ | \\ CH_2-CMe(CO_2H) \end{smallmatrix} > CMe_2$, m. p. 190.5—191.5° (decomp.), prepared by oxidation of methylisoborneol with $KMnO_4$, readily passes when heated or treated with $AcCl$, PCl_5 , or EtOH and acid into 3-methylcamphoric anhydride (II), m. p. 207—208°, also obtained by the energetic oxidation of 4-methylcamphor with HNO_3 (*d* 1-4) or by exposure to light of 4-methylcamphorquinone, m. p. 190—191°, in Et_2O ; the quinone is prepared by the successive action of $NaHSO_3$ in $AcOH$ and HCl on oximino-4-methylcamphor, m. p. 173—174° (decomp.) (*Na* salt), obtained by treatment of 4-methylcamphor with *Na* K amide in C_6H_6 and subsequently with amyl nitrite. (II) is transformed by conc. aq. NH_3 into 3-methylcamphoric acid, m. p. 162—163° (*Ca* salt monohydrate), and by NH_3 in MeOH at 160° into 3-methylcamphorimide, m. p. 256°. (I) and PCl_5 in light petroleum yield the anhydride and the unstable 3-methylcamphoryl dichloride, b. p. 155°/15 mm., m. p. 50°, whereas the acid and PCl_5 at 130—160° afford non-homogeneous methylchlorocamphoryl dichloride, transformed by $AcOH$ into methylchlorocamphoric anhydride, m. p. 209.5—210°. Esterification of (I) with EtOH and HCl or H_2SO_4 appears impossible on account of the ready anhydride formation and the *Et_2* ester, b. p. 123.8—124.2°/3 mm., $d_4^{25} 1.0250$, and *Et H* ester, m. p. 47°, are prepared by the action of EtI on the *Ag* salt in anhyd. Et_2O . The *Me_2* ester, and *Me H* ester have b. p. 101—104°/2 mm., m. p. 52—53° and m. p. 75.5—76.5°, respectively. Attempts to resolve (I) into its optical antipodes by cinchonidine in EtOH were unsuccessful (cinchonidine salt, m. p. 178.5—179.5°). Measurements of the first dissociation const. of apocamphoric, camphoric, 3-methyl- and phenyl-

camphoric acid in H_2O and 50% MeOH by the H_2 and quinhydrone electrodes are recorded. H. WREN.

Sesquiterpenes. II. Sesquiterpene and sesquiterpene alcohol from Japanese cedar oil (Cryptomeria Japonica or Sugi oil). S. KIMURA and S. MIZOSHITA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 273—286).—Japanese cedar oil contains kiganene (I), $C_{15}H_{24}$, b. p. 108—114°/4.5 mm., and kiganol (II), $C_{15}H_{25}OH$, b. p. 145—150°/9 mm. (I) with dry HCl gives cadinene dihydrochloride and with O_3 in CCl_4 gives $COMe_2$ and $AcOH$. (II) with S at 150—180° gives cadalene, and is dehydrated by phthalic anhydride at 120°; with colloidal Pd in $AcOH$ and H_2 at 1.6 atm. or with H_2 at 70 atm. and 170° in



presence of Ni it forms a hydrocarbon and dihydrokiganol, b. p. 124—128°/4.5 mm.; the latter is dehydrated by colloidal Pd in Ac_2O at 150° to a substance, $C_{15}H_{26}$, b. p. 102—108°/4 mm., which is oxidised by O_3 to $COMe_2$. (II) with Ac_2O at 150° affords a substance, $C_{15}H_{24}$, b. p. 108—114°/4.5 mm., which with Pd-asbestos at 320° in CO_2 gives cadalene and decahydrocadalene. (II) with O_3 gives $AcOH$. These results support either of the pairs of formulæ given above. R. S. CAHN.

New sesquiterpene alcohol. A. BLUMANN and F. HESSE (Ber., 1932, 65, [B], 90—92).—The sesquiterpene, $d^{15} 0.918$, $\alpha_D +9^\circ 50'$, from the volatile oil of *Pinus maritima* (Dupont, "Les essences de Térébenthine," p. 234) is converted by 50% H_2SO_4 at 35° into the sesquiterpene alcohol, $C_{15}H_{26}O$, m. p. 95.5—96.4°, b. p. 162—165°/20 mm., $d^{15} 0.936$, $[\alpha]_D^{25} -4.71^\circ$ in 25% EtOH (*Ac* derivative, m. p. 43—43.5°, b. p. 170—172°/19 mm., $d^{15} 0.992$, $[\alpha]_D^{25} +40.46^\circ$ in 25% EtOH), which is not oxidised by CrO_3 in $AcOH$ at 50—60° and is unchanged by HCO_2H , $H_2C_2O_4$, or HNO_3 at 100° or by 25% H_2SO_4 -EtOH. Its tert. nature is established by the isolation of the chromate, $(C_{15}H_{25})_2CrO_4$, m. p. 116—116.5°, when treated with CrO_3 in light petroleum. Dehydration with $ZnCl_2$ and P_2O_5 , respectively, gives products, b. p. 128—132°/19 mm., $d^{15} 0.923$, $\alpha_D -5^\circ 40'$, and b. p. 128—130°/17 mm., $d^{15} 0.929$, $\alpha_D +2^\circ 20'$. H. WREN.

Polyterpenes and polyterpenoids. LXIII. New synthesis of bisabolene. L. RUZICKA and M. LIGUORI (Helv. Chim. Acta, 1932, 15, 3—7).— β -Terpineol is converted by O_3 into 4-hydroxy-4-methylcyclohexyl methyl ketone, b. p. 88—89°/12 mm. (semicarbazone, m. p. 195—196°), which condenses with the Grignard compound from ϵ -bromo- β -methyl- Δ^3 -pentene, b. p. 75—78°/60 mm. [prepared by the action of KOBr on β - ϵ -dibromo- β -methylpentane, b. p. 82—85°/12 mm., which was obtained from the corresponding diol (A., 1907, i, 816)], to give bisabolol (trihydrochloride, m. p. 79—80°, identical with a specimen prepared from nerolidol). J. W. BAKER.

Polyterpenes and polyterpenoids. LXIV. Synthesis of sapotalin and other trimethyl-

naphthalenes. L. RUZICKA and L. EHMAN (Helv. Chim. Acta, 1932, 15, 140—162).—All the remaining trimethylnaphthalenes are synthesised, sapotalin (A., 1929, 1305) being the 1 : 2 : 7-derivative. Most pairs of picrates and styphnates give m. p. depressions, but in some cases no depression is obtained with isomeric compounds.

[With E. KELLER, H. SHUTZE, and P. PARODI-DELFINO.] Condensation of CH_2PhAc with Zn and $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$, dehydration, and reduction and hydrolysis of the unsaturated ester gives γ -phenyl- α - β -dimethyl- γ -butyric acid, the chloride of which with AlCl_3 affords 1-keto-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p. 125—130°/13 mm., converted by MgMeI and dehydrogenation into 1 : 2 : 3-trimethyl- (I), b. p. 125—130°/12 mm. (picrate, m. p. 142·5°; styphnate, m. p. 143·5°), -naphthalene. A poor yield is also obtained by the reaction sequence $\text{R}\cdot\text{CO}_2\text{H} \xrightarrow{\text{ZnMeI}} \text{R}\cdot\text{COCl} \xrightarrow{\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}} \text{R}\cdot\text{CH}(\text{CO}_2\text{Et})_2 \xrightarrow{\text{O}} \text{glycide ester, R}\cdot\text{CMe}(\text{CO}_2\text{Et})_2$

b. p. 162—163°/10 mm., $\rightarrow \text{R}\cdot\text{CHMe}\cdot\text{CHO}$, b. p. 130—140°/10 mm., $\rightarrow \text{R}\cdot\text{CHMe}\cdot\text{CO}_2\text{H} \rightarrow \text{C}_6\text{H}_4\langle \text{CHMe}\cdot\text{CHMe} \rangle \rightarrow \text{(I)}$ ($\text{R}=\text{CHMePh}\cdot\text{CHMe}$).

[With F. DES TOMBE and H. RAMONDT.] Similarly, Et $\alpha\beta$ -dimethylcinnamate (A., 1914, i, 281) is reduced (Bouveault) and converted into γ -phenyl- β -methyl-n-butyl bromide, b. p. 122°/12 mm.; the corresponding cyanide affords γ -phenyl- β -methylvaleric acid, b. p. 172°/12 mm., whence the chloride, b. p. 132—133°, affords 4-keto-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p. 141°/16 mm., converted by MgMeI into the 1 : 2 : 4-trimethyl-1 : 2-dihydro-, b. p. 109°/11 mm., and thence by Se into 1 : 2 : 4-trimethyl-, b. p. 146°/12 mm. (picrate, m. p. 147·5°; styphnate, m. p. 123·5°), -naphthalene.

[With J. CUENAT and S. BIASUTTI.] Similar reaction sequences convert Et β -(p-tolyl)- $\alpha\beta$ -dimethylacrylate into γ -(p-tolyl)- β -methylbutan- α -ol, b. p. 132—136°/12 mm., γ -(p-tolyl)- $\beta\gamma$ -dimethylpropyl bromide, b. p. 138—140°/13 mm., γ -(p-tolyl)- β -methyl-n-butyl acid, b. p. 188°/11 mm. (chloride, b. p. 144°/10 mm.), 4-keto-1 : 2 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p. 153°/10 mm. (reduced to the 4-hydroxy-compound, b. p. 133—134°/10 mm.), and 1 : 2 : 6-trimethyl-, b. p. 146°/10 mm. (styphnate, m. p. 148°), -naphthalene.

[With A. RENOLD.] β -p-Tolylethyl bromide, b. p. 116°/10 mm., condenses with $\text{CNaMe}(\text{CO}_2\text{Et})_2$ to give Et β -(p-tolylethyl)methylmalonate, b. p. 191—192°/16 mm., decarboxylated to the monocarboxylic acid, m. p. 50°, the chloride of which is cyclised to 1-keto-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p. 142°/13 mm. (semicarbazone, m. p. 218°), converted by MgMeI into 1 : 2 : 7-trimethyl-3 : 4-dihydro-, b. p. 130°/13 mm., dehydrogenated to 1 : 2 : 7-trimethyl-, b. p. 143°/13 mm. (picrate, m. p. 129°; styphnate, m. p. 156°), -naphthalene.

[With J. HARTNAGEL and W. HAUSSCHILD.] o-Tolyl methyl ketone with Zn and $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ gives Et β -(o-tolyl)- α -methylcrotonate, b. p. 128—132°/11 mm., reduced by Na and EtOH to γ -(o-tolyl)- β -methyl-n-butyl alcohol, b. p. 141—144°/15 mm., whence the bromide, b. p. 134—140°/14 mm., -valeric acid, b. p. 140·5—141°/0·7 mm. (chloride, b. p. 169°/15 mm.), 4-keto-1 : 2 : 8-trimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p.

162—166°/19 mm. [semicarbazone, m. p. 225—227° (decomp.)], and 1 : 2 : 8-trimethyl-, b. p. 152—155°/14 mm. (picrate, m. p. 133°; styphnate, m. p. 144·5°), -naphthalene are obtained.

[With R. WEBER.] 1 : 3 : 5-Trimethylnaphthalene is obtained by improvement of Heilbron and Wilkinson's method (A., 1931, 80).

[With H. ARNI and E. BERNASCONI.] p-Methylhydratropaldehyde (A., 1905, i, 116) similarly affords Et γ -(p-tolyl)- α -methyl- Δ^5 -pentenoate, b. p. 165—170°/12 mm., the acid, b. p. 139—140°/0·5 mm., being reduced to γ -(p-tolyl)- α -methylvaleric acid, b. p. 167—170°/10 mm. (chloride, b. p. 145—152°/11 mm.), 4-keto-1 : 3 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p. 145—150°/8 mm., and 1 : 3 : 6-trimethyl-, b. p. 140—144°/10 mm. (picrate, m. p. 115°; styphnate, m. p. 148°), -naphthalene.

[With P. PIRTH and R. THOMANN.] Et β -hydroxy- β -(p-tolyl)- α -methylpropionate, b. p. 159—160°/11 mm., by treatment with PBr_3 and then of the product with NPhMe_2 affords the corresponding cinnamic ester, b. p. 149°/12 mm., converted successively into β -(p-tolyl)- α -methyl-n-propyl alcohol, b. p. 129°/12 mm. (bromide, b. p. 125°/12 mm.), the butyric acid, b. p. 167—171°/8·5 mm. (chloride, b. p. 131—132°/9 mm.), and 1 : 3 : 7-trimethylnaphthalene, b. p. 131—133°/9 mm. (picrate, m. p. 142°; styphnate, m. p. 151·5°).

[With E. HEFTI and A. R. ALTUNA.] Similarly prepared Et 2 : 5 : β -trimethylcinnamate, b. p. 148—150°/12 mm., gives the saturated alcohol, b. p. 141°/12 mm. (bromide, b. p. 134—135°/12 mm.), γ -p-xylylvaleric acid, b. p. 170°/12 mm. (chloride, b. p. 144—145°/12 mm.), 8-keto-1 : 4 : 5-trimethyl-5 : 6 : 7 : 8-tetrahydro-, b. p. 138°/12 mm. (carbinol, b. p. 128°/12 mm.), and 1 : 4 : 5-trimethyl-, m. p. 63° (picrate, m. p. 144—145°; styphnate, m. p. 129—130°), -naphthalene.

[With W. H. ADDINK.] γ -(p-Tolyl)-n-butyl alcohol, b. p. 150°/15 mm. (by reduction of the crotonic ester) (bromide, b. p. 140°/20 mm.), gives γ -p-tolylvaleric acid, b. p. 155°/0·5 mm. (chloride, b. p. 145—147°/12 mm.), 4-keto-1 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p. 157—160°/15 mm., and 1 : 4 : 6-trimethyl-, b. p. 140—142°/15 mm. (picrate, m. p. 133°; styphnate, m. p. 114°), -naphthalene.

[With A. WEISZ.] Et γ -(o-tolyl)- $\alpha\beta$ -dimethyl-n-butyrate (Heilbron and Wilkinson, *loc. cit.*; here prepared by reduction of the Δ^5 -unsaturated ester, b. p. 130—145°/14 mm.), is similarly converted into 2 : 3 : 5-trimethylnaphthalene.

[With A. H. RIERINK.] p-MeC₆H₄·CHO and $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ afford the glycide ester, b. p. 148—152°/12 mm., converted into p-tolylacetone, b. p. 109—110°, condensed with $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ to give Et γ -(p-tolyl)- $\alpha\beta$ -dimethylcrotonate, b. p. 158—163°/13 mm., reduced (PtO_2 and H_2) to the butyric acid, b. p. 148—150°/0·6 mm., the chloride, b. p. 140°/12 mm., of which gives 4-keto-2 : 3 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydro-, b. p. 152—154°/12 mm., and 2 : 3 : 6-trimethyl-, b. p. 146—148°/14 mm. (picrate, m. p. 130°; styphnate, m. p. 165°), -naphthalene [a partial, unsuccessful, synthesis (with R. DELBES) is also described].

J. W. BAKER.

Furan Grignard reagents. H. GILMAN and A. P. HEWLETT (Rec. trav. chim., 1932, 51, 93—97).—

γ -2-Furylpropyl alcohol (A., 1927, 973) and SOCl_2 in Et_2O and pyridine give γ -2-furylpropyl chloride, b. p. $60^\circ/5$ mm., which could not be converted into a Grignard reagent. γ -Tetrahydro-2-furylpropyl chloride, b. p. $75^\circ/4$ mm., from the alcohol (*loc. cit.*) and SOCl_2 in C_6H_6 , forms a Grignard reagent with Mg and activated 12.5% Cu-Mg alloy, which is decomposed by CO_2 to γ -tetrahydro-2-furylbutyric acid, b. p. $145^\circ/5$ mm. H. BURTON.

β -Naphthylfurfurylamine. L. MUSAJO (Gazzetta, 1931, 61, 910-914).—Reduction of furfurylidene- β -naphthylamine with Mg in MeOH gives β -naphthylfurfurylamine, m. p. 46° (A., 1931, 237) (*hydrochloride*, m. p. 172°). E. E. J. MARLER.

Pentose reactions. I. Furfuraldehyde formation. C. D. HURD and L. L. ISENHOUR (J. Amer. Chem. Soc., 1932, 54, 317-330).—The conversion of xylose into furfuraldehyde is not effected by P_2O_5 or anhyd. ZnCl_2 , or by solutions of H_3PO_4 , $\text{CCl}_3\text{CO}_2\text{H}$, or HNO_3 . Distillation with HCl or H_2SO_4 gives the aldehyde, the yield depending on the acid concn., temp., and duration of the distillation; the reaction is of the first order. The behaviour of mineral acids at distillation temp. on furfuraldehyde, arabinose, rhamnose, tetramethylene glycol, ketoxylose, xylonic acid, glycerol, and erythritol is investigated; little or no reaction occurs in the last four cases. The significance of these results on the mechanism of the pentose \rightarrow furfuraldehyde reaction is discussed.

C. J. WEST (b).

Dihydro-1:4-pyrans. II. Degradation by use of the Beckmann rearrangement. T. Y. KAO and R. C. FUSON (J. Amer. Chem. Soc., 1932, 54, 313-317; cf. this vol., 63).—3-Cyano-6-benzoyl-2-phenyl-5:6-dihydro-1:4-pyran (I) gives two monoximes, m. p. 156.5 – 157° and 141 – 142° , both of which undergo the Beckmann rearrangement forming the anilide, m. p. 156 – 156.5° , of 3-cyano-2-phenyl-5:6-dihydro-1:4-pyran-6-carboxylic acid (II), m. p. 155 – 155.5° . Hydrolysis of (II) with 20% NaOH gives 2-phenyl-5:6-dihydro-1:4-pyran-3:6-dicarboxylic acid, m. p. 144 – 144.5° (decomp.); with boiling 50% H_2SO_4 , α -hydroxy-8-benzoylvaleric acid, m. p. 120 – 120.5° (88% yield) (oxime, m. p. 144 – 144.5°), results, thus establishing the structure of (I).

C. J. WEST (b).

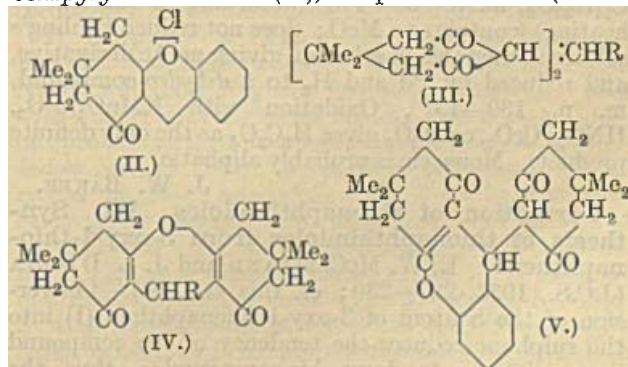
α -Esters of opianic acid, and opianic acid as a source of heterocyclic compounds. S. J. KANEVSKAJA and M. M. SCHEMJAKIN (J. pr. Chem., 1932, [ii], 132, 341-348).—Interaction of dry K opianate with chloroacetone at 100° gives opianoxyacetone, m. p. 105 – 106° [*disemicarbazone*, m. p. 205 – 206° (decomp.)], which with piperidine at 100° gives 3:4-dimethoxy-2-acetylisocoumarone, m. p. 151° . With $\text{CH}_2\text{ClCO}_2\text{Et}$ K opianate gives Et opianylglycollate, m. p. 87 – 88° (*semicarbazone*, m. p. 186°). These condensations proceed best with an excess of Cl-compound in absence of a solvent; in, e.g., EtOH as solvent Et ψ -opianate is produced under the influence of the K opianate. It is shown that the rearrangement of opianoxyacetone into Et ψ -opianate occurs with great rapidity in presence of org. or inorg. bases or of alkali salts of weak acids in EtOH solution; in *sec.*-amyl alcohol it is considerably

slower, and it is completely suppressed in *tert.*-amyl alcohol. H. A. PIGGOTT.

Synthesis of coumarins and chromones. D. CHAKRAVARTI (J. Indian Chem. Soc., 1931, 8, 619; cf. 1931, 1962).—Only those phenols which do not form coumarins by condensation with β -ketonic esters in the presence of H_2SO_4 give chromones with P_2O_5 as condensing agent, whilst those which readily give coumarins with H_2SO_4 give the same product with P_2O_5 . J. W. BAKER.

Condensation of aldehydes and phenols. VI. *p*-Chlorobenzylidenedi- β -naphthol [*p*-chlorophenyldi-2-hydroxy- α -naphthylmethane]. O. DISCHENDORFER and E. FRANSEVIĆ (Monatsh., 1932, 59, 93-104).— p - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ and β -naphthol in AcOH containing a little conc. HCl at room temp. give *p*-chlorophenyldi-2-hydroxy- α -naphthylmethane (I), m. p. 189 – 190° [*Na* salt; diacetate, m. p. 227 – 228° ; dibenzoate, m. p. 232° (slight previous sintering)], and *ms*-*p*-chlorophenyldinaphthopyran (9-*p*-chlorophenyl-1:2:7:8-dibenzoxanthene) (II), m. p. 293° ; (II) is the sole product when condensation is effected at 100° (bath). Oxidation of (I) with NaOBr in aq. EtOH gives *dehydro*-*p*-chlorobenzylidenedi- β -naphthol, m. p. 186° (slight previous sintering), whilst oxidation of (II) with MnO_2 and conc. HCl in AcOH and treatment of the resulting solution with FeCl_3 affords *ms*-*p*-chlorophenyldinaphthopyrylium chloride ferrichloride, m. p. 247° after previous sintering and darkening. This is converted by aq. COMe_2 into *ms*-*p*-chlorophenyldinaphthopyranol (9-*p*-chlorophenyl-1:2:7:8-dibenzoxanthihydrol), m. p. 241 – 243° [*chloride mercurichloride*, m. p. 247° (sinters at 238° and darkens from 224°); *perbromide*, $\text{C}_{27}\text{H}_{18}\text{OClBr}_3$, m. p. 193° (decomp.); *perchlorate*, m. p. 291° (decomp.) (darkens from 278°); *Et* ether, m. p. 239° (slight previous sintering); *Me* ether, m. p. 243 – 245°]. The ease of conversion of the isomeric chlorophenyldi-2-hydroxy- α -naphthylmethanes into the corresponding pyrans is in the order $p > o > m$. H. BURTON.

Reactivity of dimethyldihydroresorcinol. I. Condensation with aromatic aldehydes. G. P. CHAKRAVARTI, H. CHATTOPADHYAYA, and P. C. GHOSH (J. Indian Inst. Sci., 1931, 14A, 141-156).—Dimethyldihydroresorcinol (I) and salicylaldehyde with HCl in EtOH afford 2:2-dimethyl-4-ketotetrahydrobenzopyrylium chloride (II), m. p. above 290° (? free



base, m. p. above 290°), stable to KOH in hot EtOH. (I) condenses with aldehydes in presence of aq. or aq.-

alcoholic alkalis to give substances of type (III), which with boiling Ac_2O and a trace of pyridine yield xanthen derivatives (IV).

The following substances of type (III) were prepared, the radical named being the substituent R: *p*-hydroxyphenyl-, m. p. 184° (*Ac*-compound of the xanthen derivative, m. p. 208 — 209°); 3:4-dihydroxyphenyl-, m. p. 145° (decomp.); 3:4-methylenedioxyphenyl-, m. p. 136 — 137° ; phenyl-, m. p. 175 — 176° (xanthen derivative, m. p. 193°); *p*-methoxyphenyl-, m. p. 139 — 140° (*Br*₃- and *Br*₄-derivatives, m. p. 173° and 207° , respectively) (xanthen derivative, m. p. 243 — 246°); 4-hydroxy-3-methoxyphenyl-, m. p. 195° after softening at 189° (5-*Br*-derivative, m. p. 211 — 213° , also prepared from 5-bromovanillin (*Ac* compound of xanthen derivative, m. p. 148 — 149°); *p*-nitrophenyl-, m. p. 188 — 190° (xanthen derivative, m. p. 222°); *m*-nitrophenyl-, m. p. 186 — 188° ; styryl-, m. p. 202° [*Br*-derivative, m. p. 180 — 181° (decomp.)], giving in poor yield the xanthen derivative, m. p. 147 — 148° . (I) with piperonal and *m*-nitrobenzaldehyde in alcoholic HCl gives the xanthen derivatives (IV), m. p. 214° and 169° , respectively. When (I) is condensed with *o*-hydroxyaldehydes in presence of alkali, the products of type (IV) pass by loss of H_2O into anhydrides (V); *o*-hydroxybenzaldehyde and resorcyaldehyde thus give substances, m. p. 206° after sintering at 200° [*Ac* (m. p. 188°), *Bz* (m. p. 152 — 153°), *Br*- (decomp. 194°), and *NO*- (m. p. 100 — 103°) derivatives; phenylhydrazones, m. p. 237 — 241°] and 225 — 226° (decomp.), respectively. R. S. CAHN.

Plant colouring matter, robinin. C. E. SANDO (J. Biol. Chem., 1932, **94**, 675—680).—Robinin, m. p. 195 — 197° (anhyd.), from the flowers of the common locust (*Robinia pseudoacacia*), is $\text{C}_{33}\text{H}_{40}\text{O}_{19}$ when air-dried (+ $8\text{H}_2\text{O}$ when crystallised from H_2O). Crystallisation from EtOH gives a β -modification, m. p. 249 — 250° . The cryst. structure of the two forms is described. Hydrolysis of robinin yields 1 mol. of galactose, 2 mols. of rhamnose, and 1 mol. of kaempferol (cf. J.C.S., 1902, **81**, 473). F. O. HOWITT.

Plant colouring matters. XXXVIII. Colouring matter from "red" rice, monascin. H. SALOMON and P. KARRER (Helv. Chim. Acta, 1932, **15**, 18—22).—Crystallisation of the red pigment (not a single substance) obtained by extraction of *Monascus purpureus* with Et_2O gives monascin, $\text{C}_{24}\text{H}_{30}\text{O}_6$, m. p. 135 — 140° (according to the rate of heating) (contains no MeO; does not reduce Fehling's solution), unstable in solution, giving no *Ac* derivative, and reduced by Pd and H_2 to a dihydro-compound, m. p. 130 — 131° . Oxidation with KMnO_4 , O_3 , HNO_3 , CrO_3 , or H_2O_2 gives $\text{H}_2\text{C}_2\text{O}_4$ as the only definite product. Monascin is probably aliphatic.

J. W. BAKER.

Formation of thionaphthindoles. III. Synthesis of thionaphthindoles from 3-oxy-1-thionaphthens. E. W. McCLELLAND and J. L. D'SILVA (J.C.S., 1932, 227—230; cf. this vol., 64).—Conversion of the S atom of 3-oxy-1-thionaphthen (I) into the sulphone reduces the tendency of the compound to enolise or to form bis-compounds; thus the hydrazone of (I) yields indole derivatives, whereas that of the 1-dioxide is stable. The results are in

accord with Robinson's mechanism of the indole synthesis. Thionaphthindole and the following derivatives are obtained by heating the appropriate hydrazine and (I) in AcOH at 100° for 0.5—1 hr.: 6-, 2-, and 10-*Me*-, m. p. 172 — 174° , 257 — 258° , and 211° , respectively; 2-*Br*-, m. p. 262 — 264° . 3-Oxy-1-thionaphthen 1-dioxide phenylhydrazone has m. p. 245 — 246° (decomp.). Condensation of Et sodioacetate with 2-methylthiolbenzoyl chloride in boiling Et_2O , followed by hydrolysis with H_2SO_4 in EtOH, affords a product which, with hot aq. alkali, yields a little BzOH and 2-methylthiolacetophenone, m. p. 45 — 46° , which gives a stable phenylhydrazone, m. p. 117 — 118° ; the transformation of 2-thiolacetophenone into thionaphthindole by way of the phenylhydrazone is, therefore, assumed to be preceded by oxidation to (I). R. S. CAHN.

Application of calorimetry to pyrroles and pyrrole dyes. I. Calorimetric determinations with simple pyrroles. P. ROTHMUND and H. BEYER (Annalen, 1932, **492**, 292—299).—The heats of combustion of 11 pyrrole derivatives are determined, using a slightly modified form of the micro-calorimeter of Roth (A., 1924, ii, 748; 1925, ii, 591). The following nos. give the mol. heats of combustion (kg.-cal. at 15°) at const. vol. and pressure, respectively: Et 2:5-dimethylpyrrole-3-carboxylate, 1176.7, 1177.6; Et 2:4-dimethylpyrrole-3-, 1180.4, 1181.3, and -5-carboxylates, 1177.7, 1178.6; Et 2:3-dimethylpyrrole-4-, 1178.3, 1179.2, and -5-carboxylates, 1183.8, 1184.7; Et 2:4-dimethyl-3-ethylpyrrole-5-carboxylate, 1487.7, 1489.2; Et 2:4-dimethylpyrrole-3:5-dicarboxylate, 1491.5, 1492.5; Et 5-propionyl-2:4-dimethylpyrrole-3-carboxylate, 1596.6, 1597.8; Et 2:4-dimethyl-3- β -carboxyethylpyrrole-5-carboxylate, 1486.8, 1487.7; 5-aldehyde-2:4-dimethyl-3-ethylpyrrole, 1229.8, 1231.0; Et 3-acetyl-2:4-dimethylpyrrole-5-carboxylate, 1392.0, 1393.0. The heats of formation (kg.-cal.) of the above compounds are +117.1, 116.1, 115.5, 113.4, 110.0, 131.2, 222.4, 117.1, 227.2, 63.7, and 158.0, respectively. H. BURTON.

Reaction of organic halides with piperidine. II. α -Bromo- β -ketonic esters. B. W. HOWK and S. M. McELVAIN (J. Amer. Chem. Soc., 1932, **54**, 282—289; cf. A., 1931, 494).—Improved preps. of cyanodeoxybenzoin and Et α -benzoylphenylacetate are given. Et α -bromobenzoylacetate (I), b. p. 135 — $137^\circ/1$ mm.; Et α -dibromobenzoylacetate, b. p. 153 — $154^\circ/1$ mm.; Et α -bromo- α -benzoylpropionate (II), b. p. 148 — $150^\circ/1$ mm.; Et α -bromo- α -benzoylphenylacetate (III), b. p. 189 — $190^\circ/1$ mm., are prepared from the appropriate keto-esters and Br in boiling CCl_4 . (I) reacts rapidly with piperidine (IV) in dry Et_2O forming the hydrobromide of (IV) (90% yield), $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ (30% yield), and Et α -dipiperidinobenzoylacetate, m. p. 131 — 132° (39% yield) [also prepared from the *Br*₂-ester and (IV) in Et_2O]. (II) and (IV) give 28% of Et α -benzoyl- α - β -dipiperidinopropionate, m. p. 131 — 132° , and 35% of $\text{CHBzMe}\cdot\text{CO}_2\text{Et}$. The unbrominated ester arises from the action of the *Br*-ester on (IV) (whereby *N*-bromopiperidine results), whilst the formation of the piperidino-ester is best explained as a secondary reaction product resulting

from the action of *N*-bromopiperidine on the normal reaction product of (IV) and a *sec.*- or *tert.*-bromide. (III), a *tert.*-bromide which cannot lose HBr, reacts with (IV) only as a brominating agent, since the unbrominated ester and cleavage products were the only compounds isolated. C. J. WEST (b).

Preparation of quinolinic acid. W. STIX and S. A. BULGATSCH (Ber., 1932, 65, [B], 11—13).—Pyridine-2:3-dicarboxylic acid is obtained in 65—70% yield as the Cu salt by the oxidation of quinoline with 3% H₂O₂ at 70° in presence of H₂SO₄ and CuSO₄. The pyridine ring is shielded from further oxidation by the sparing solubility of the Cu salt. Replacement of CuSO₄ by FeSO₄ leads to much more rapid oxidation accompanied by rupture of the pyridine nucleus. Traces of Fe in the CuSO₄ greatly diminish the yield of pyridine-2:3-dicarboxylic acid.

H. WREN.

Quinoline compounds. V. U. N. BRAHMA-CHARI and T. BHATTACHARJEE (J. Indian Chem. Soc., 1931, 8, 571—573).—By condensation of the appropriate quinoline derivative with β -bromopropylphthalimide at 125—135° and subsequent fission of the phthalimido-derivative with N₂H₄ and HCl in the usual manner are obtained the *dihydrochlorides* of 8- β -aminoisopropylamino-, m. p. 235°, -6-methyl-, m. p. 255°, -6-methoxy-, m. p. 221°, and -6-ethoxy-, m. p. 231°, -quinoline. By similar methods are obtained the *dihydrochlorides* of 8- β -aminoethylamino-, m. p. 241°, and 8- γ -amino-*n*-propylamino-, m. p. 247°, -quinoline. J. W. BAKER.

Chemical-functional study of 2-phenylquinoline-4-carboxylic acid (atophan) and its determination. J. A. SANCHEZ (Rev. Centr. Estud. Farm. Bioquim., 1931, 20, 125—129; Chem. Zentr., 1932, ii, 1325).—A 1% solution of the NH₄ salt is pptd. by: Ag⁺, Hg²⁺, Pb²⁺, Bi³⁺, (UO₂)²⁺, Zn²⁺, Cd²⁺, Mn²⁺, Ni²⁺, Co²⁺, Cu²⁺, Al³⁺, Fe³⁺, Sn²⁺, and Au³⁺; after acidification with HCl, atophan solutions are pptd. by K₄Fe(CN)₆, K₂CrO₄, tannic acid, Folin's phosphotungstic reagent, Bertrand's silicotungstic reagent, and Sanchez' Mo reagent. 1% solutions of salts of quinine, brucine, sparteine, and cocaine also give cryst. ppts. For the determination of atophan 0.5 g. is dissolved in 80 c.c. of H₂O with 10 drops of conc. NH₃ solution; the excess of NH₃ is removed by boiling, and the liquid diluted to 100 c.c. Of this, 10 c.c. are treated with 20 c.c. of 0.1N-AgNO₃, diluted to 100 c.c., and filtered; 50 c.c. of the filtrate are treated with 10 c.c. of 0.1N-KCN, 10 c.c. of NH₃, and 20 drops of 20% KI solution, the excess of KCN being titrated with AgNO₃ (1 c.c. 0.1N-AgNO₃ = 0.0294 g. atophan). A. A. ELDRIDGE.

Coloured iodine compounds of an acridine derivative. D. KRÜGER (Ber., 1932, 65, [B], 13—18).—The colorations produced by the addition of I in aq. KI to solutions of 9-methyl-3:4-benzacridine methosulphate are invariably accompanied by the appearance of a coloured ppt. in conc. solution or of a distinct turbidity in dil. solution. If the separation of solid particles in the system acridine derivative-I is prevented by the addition of *p*-toluenesulphonate, the coloration is not observed. A similar effect is found with saponarin and α -naphthafavone,

but not with dextrin. The colour produced from the acridine derivative and I depends somewhat on experimental conditions; it does not disappear when the mixture is heated at 100° and is favoured by certain concn. relationships. The ability of compounds to yield colorations with I is considered to be due to slight constitutively-caused peculiarities in the structure of the colloidal particles of the adsorbent.

H. WREN.

Synthesis of pyrroles and their transformations. H. FISCHER and M. HUSSONG (Annalen, 1932, 492, 128—155).—Et (5-carbethoxy-2-methyl-3-pyrrolylmethyl)malonate (I), m. p. 72° (lit. 75°) (*Et* H ester, m. p. 119°), is obtained from Et 2-methylpyrrole-5-carboxylate, MeO·CH₂·CH(CO₂Et)₂, and SnCl₄ in CS₂; when the method previously described (A., 1928, 772) is used, a compound, C₁₇H₂₁O₅N, m. p. 202°, is also formed. (I) is converted by N₂H₄·H₂O in EtOH into a *dihydrazide*, C₁₂H₁₁O₄N₅, m. p. 212°, and reacts with AcCl in presence of SnCl₄ and CS₂ to give the 4-*Ac* derivative, m. p. 90°. (5-Carbomethoxy-, decomp. 188°, and (5-carbethoxy-, decomp. 175°, -2-methyl-3-pyrrolylmethyl)malonic acids pass when heated into the corresponding β -pyrrolylpropionic acids. (I) and Br (2 mols.) in CHCl₃ give *lit* (4-bromo-5-carbethoxy-2-bromomethyl-3-pyrrolylmethyl)malonate, m. p. 142°, also formed by further bromination of the previously described (*loc. cit.*) Br-derivative of (I). Et 3-aldehyde-2-methylpyrrole-5-carboxylate (II), CH₂(CO₂H)₂, and NH₂Ph in cold EtOH afford β -anilino- β -(5-carbethoxy-2-methyl-3-pyrrolyl)ethane- α -dicarboxylic acid (III), m. p. 155° (decomp.), converted by 10% NaOH into the *anil*, m. p. 155° (*hydrochloride*; *sulphate*), of (II); the *anil* and CH₂(CO₂H)₂ also give (III). When the reaction is carried out in hot EtOH, β -(5-carbethoxy-2-methyl-3-pyrrolyl)acrylic acid, m. p. 224°, results. This is reduced by Na-Hg to β -(5-carbethoxy-2-methyl-3-pyrrolyl)propionic acid (IV), m. p. 133° [4-*Ac*, m. p. 175°, and 4-*Br*, m. p. 185° (decomp.), derivatives], which with Br (4 mols.) in AcOH at 60° gives β -(4-bromo-5-carbethoxy-2-bromomethyl-3-pyrrolyl)propionic acid, m. p. 205° (decomp.). The last-named acid when boiled with H₂O eliminates CH₂O and HBr, forming *di*-(4-bromo-5-carbethoxy-3-carboxyethyl-2-pyrrolyl)methane, m. p. 225° (decomp.) (3:3'-*Me*₂ ester, m. p. 170°), in quant. yield. β -(5-Carboxy-2-methyl-3-pyrrolyl)propionic acid (V), decomp. 150°, and MeOH-HCl give the *Me*₂ ester, m. p. 77°, of (probably) 2:4-dimethyl-3:5-di- β -carboxyethylindole (VI), m. p. 196°; (VI) is also obtained from (V), HCO₂H, and HBr (*d* 1.49). Hydrolysis of (I) with NaOH affords a Na₃ salt (not characterised), which with MeOH-HCl furnishes the *Me*₄ ester, m. p. 144°, of (probably) 2:4-dimethyl-3:5-di- β -dicarboxyethylindole + H₂O (VII), m. p. 203° (decomp.); (VII) passes at 210° into (VI). Et 2-methylpyrrole-3-carboxylate and COCl₂ in PhMe give, after treatment with EtOH, *Et* 2-methylpyrrole-3:5-dicarboxylate, m. p. 132° (4-*Br*-derivative, m. p. 148°). (V) and Br (2.5 mols.) in CHCl₃ yield 4:5:3'-tribromo-5-methyl-3:4'-di- β -carboxyethylpyrromethene hydrobromide (free base), whilst (V), cryptopyrrolealdehyde, and HBr (*d* 1.49) in EtOH afford 3:5:5'-trimethyl-4-ethyl-4'- β -carboxyethylpyrromethene hydrobromide, m. p. 219° (decomp.). (IV), HCO₂H, and HBr give 5:5'-

dimethyl-4 : 4' carboxylethylpyrromethene hydrobromide, m. p. 195° (decomp. from 145°), brominated to 3 : 3'-dibromo-5 : 5'-dimethyl-4 : 4'-di- β -carboxylethylpyrromethene hydrobromide, not melted at 300° (decomp. 165°) (perbromide; free base). 4 : 5 : 4' : 5'-Tetrabromo-3 : 3'-di- β -carboxylethylpyrromethene hydrobromide, not melted at 300° (free base), is formed from di-(4-bromo-5-carboxy-3- β -carboxylethylpyrrol)methane(?) and Br in AcOH. Et 2-methylpyrrole-5-carboxylate (hydrazide, m. p. 213°), HCO₂H, and HBr give a compound, C₂₄H₃₃O₆N₃ or C₂₅H₃₁O₆N₃, m. p. 305°.

[With H. BERG.] Successive treatment of opso-pyrrolecarboxylic acid (VIII) [*Me* ester, b. p. 152°/11 mm., m. p. 29.5° (picrate, m. p. 104°)] with MgEtBr and ClCO₂Et gives the known carbethoxy-derivative (IX); the similarly prepared carbethoxy-derivative of hæmopyrrolecarboxylic acid has m. p. 149°. (VIII), anhyd. HCN, and HCl in Et₂O-CHCl₃ give the imine hydrochloride (X), C₉H₁₃O₂N₂Cl, decomp. 196°.

[With H. ROTH.] (IX) is also obtained from (VIII) in 7% yield by successive treatment with COCl₂ and EtOH in PhMe. Hydrolysis of (X) gives the corresponding aldehyde, which with CH₂(CO₂H)₂ and NH₂Ph in EtOH affords β -(5-carbethoxy-4-methyl-3- β -carboxylethyl-2-pyrrol)acrylic acid, m. p. 226°. This is reduced by Na-Hg to 4-methyl-2 : 3-di- β -carboxylethylpyrrole-5-carboxylic acid, m. p. 212° (*Me*₃ ester, m. p. 105°).

H. BURTON.

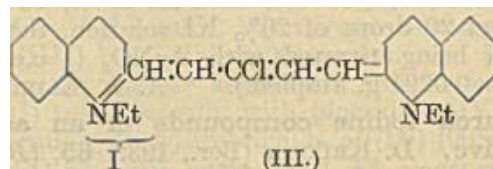
Cyanine dyes and related compounds. (Miss) F. M. HAMER, I. M. HEILBRON, J. H. READE, and H. N. WALLS (J.C.S., 1932, 251—260).—4 : 4'-Diphenyl-1 : 1'-diethyl-2 : 2'-carbocyanine iodide (I) is a much weaker photographic sensitiser than pinacyanol (II). The corresponding 1 : 1'-Me₂ compound and -quinazocarbocyanine have no sensitising action, but 1 : 1'-diisopropyl-2 : 2'-carbocyanine iodide (III) is more powerful than (II). The action of styrylquinoline methiodides is decreased by substitution by the Ph group. No parallelism exists between quinolinium and the corresponding benzopyrylium salts, and those of the latter class which are active are of no practical val. When virtual tautomerism is impossible, as in the divinyl and indolyl compounds described below, no sensitisation is observed. The figures in parentheses below are the max. of the absorption bands in m μ .

Addition of MgPhBr in Et₂O to 1 : 2-dimethyl-4-quinazolone in PhOMe, subsequent heating, and treatment of the resulting base with HI gives 4-phenyl-2-methylquinazoline methiodide (IV), m. p. 208° (decomp.), which with *p*- and *o*-dimethylaminobenzaldehyde and a little piperidine in boiling EtOH gives 4-phenyl-2-*p*- and -*o*-dimethylaminostyrylquinazoline methiodide, m. p. 202° (decomp.) (540) and 182° (decomp.), respectively. (IV) with CH(OEt)₃ in boiling pyridine gives 4 : 4'-diphenyl-1 : 1'-dimethylquinazocarbocyanine iodide, m. p. 270° (630 and secondary at 590), and with glyoxal in boiling pyridine gives 4 : 4'-diphenyl-2 : 2'-divinyldiquinazoline 1 : 1'-dimethiodide, m. p. 205° (decomp.). 4-Phenylquinaldine ethiodide (V) (m. p. 200—201°) with *p*-dimethylaminobenzaldehyde and a drop of piperidine in EtOH at 60° gives 4-phenyl-2-*p*-dimethylaminostyrylquinoline ethiodide (530) [corresponding methiodide, similarly prepared, m. p. 227° (decomp.) (530)], and

with *p*-methoxybenzaldehyde yields 4-phenyl-2-*p*-methoxystyrylquinoline ethiodide, m. p. 247°. 4-Phenyl-2-*p*-hydroxystyrylquinoline ethiodide, m. p. 220° (decomp.), and methiodide were similarly prepared. (V) and CH(OEt)₃ in boiling Ac₂O give (I) [corresponding 1 : 1'-Me₂ compound (625 and secondary at 575)]. 4-Phenylquinaldine alkiodides and glyoxal in boiling pyridine give 4 : 4'-diphenyl-2 : 2'-divinyldiquinoline 1 : 1'-dimethiodide and -diethiodide, whilst quinaldine ethiodide gives similarly 2 : 2'-divinylquinoline 1 : 1'-diethiodide (510). 2-Methylquinoline isopropiodide, m. p. 163—165° (decomp.), with CH(OEt)₃ in boiling Ac₂O gives (III) (605 and secondary at 560). 4-Phenylquinaldine methiodide, indole-3-aldehyde (VI), and a little piperidine in boiling EtOH give 4-phenyl-2-3'-indolylvinylquinoline methiodide, m. p. 252° (decomp.). 4-Phenyl-2-3'-indolylvinylquinazoline methiodide, similarly prepared, has m. p. 238° (decomp.). 7-Methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride and (VI) in boiling EtOH give 7-methoxy-2-phenyl-3-methyl-4-3'-indolylvinylbenzopyrylium chloride (dyes wool bright purplish-blue). 4-Phenyl-2 : 6-dimethylpyrylium perchlorate was converted into the chloride (an oil), which, when warmed with *p*-NMe₂-C₆H₄-CHO in EtOH and subsequently treated with FeCl₃ gives 4-phenyl-2 : 6-pp'-tetramethyldiaminodistyrylpyrylium ferrichloride (550 and 435). The absorption bands are also recorded for many known styrylbenzopyrylium salts. R. S. CAHN.

Dicarbocyanines. New series of cyanine dyes. S. BEATTIE, I. M. HEILBRON, and F. IRVING (J.C.S., 1932, 260—268).—In accordance with analogy, increase in length of the polymethine chain to 5 members shifts the absorption and sensitising max. of cyanine dyes towards the red. The new substances, particularly those containing quinoline nuclei, are excellent photographic sensitisers. A Ph group in the quinoline nucleus largely, and a NO₂-group in the aliphatic chain completely, destroys the sensitising action. The figures in parentheses and brackets below are the max. of the absorption bands and sensitising action, respectively, in m μ .

The prep. of mucochloric acid is modified. α -Bromo- β -anilinoacetaldehyde (I) has m. p. 164° (lit. 184°). Quinaldine methiodide and α -chloro- β -anilinoacetaldehyde anil (II) in boiling pyridine with (but not without) a little piperidine give 11-chloro-1 : 1'-diethyl-2 : 2'-dicarbocyanine iodide (III), m. p. 228—230° (decomp.); the 11-Br-compound (700)

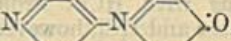


[755] is similarly obtained from the anil (IV) of (II). (IV), 1 : 2 : 3 : 3-tetramethylindoleninium iodide (V), and the free methylene base in hot EtOH give 10-bromo-1 : 1' : 3 : 3' : 3'-hexamethylindodicarbocyanine iodide, deep blue (645), also prepared from (V) and (I) or mucobromic acid; the corresponding 11-Cl-compound, m. p. 240—241° (decomp.), was similarly prepared, but better in Ac₂O, and also by boiling an alcoholic

solution of (IV), the hydrochloride of (II), and anhyd. KOAc. Boiling 2:3:3-trimethyl-1-ethyl-indoleninium iodide or the free base, the hydrochloride of (II), and anhyd. KOAc in Ac_2O gives 10-chloro-3:3:3'-tetramethyl-1:1'-diethylindodicarbocyanine iodide and chloride, respectively. (V), the corresponding methylene base, and α -nitro- β -anilinoacetaldehyde anil (VI) in boiling EtOH give 10-nitro-1:1':3:3'-hexamethylindodicarbocyanine iodide. Quinaldine ethiodide, (VI), and a little piperidine in boiling pyridine afford 11-nitro-1:1'-diethyl-2:2'-dicarbocyanine iodide (490 and 580). Addition of 1-methylbenzoxazole ethiodide to (II) and anhyd. KOAc in boiling Ac_2O gives 10-chloro-1:1'-diethyl-oxadicarbocyanine iodide, m. p. 214—215° (decomp.) (580) [615 and, less markedly, 580], and the 10-Br-compound was similarly prepared. 1-Methylbenzthiazole ethiodide gives similarly 10-chloro-1:1'-diethylthiodicarbocyanine iodide, m. p. 233—234° (decomp.), and the corresponding 10-Br-compound (645) [690]. 4-Phenylquinaldine ethiodide gives similarly 11-chloro-4:4'-diphenyl-1:1'-diethyl-2:2'-dicarbocyanine iodide, and the corresponding 10-Br-compound (730) [700] was prepared in pyridine in presence of piperidine. Lepidine ethiodide gives 11-chloro-1:1'-diethyl-4:4'-dicarbocyanine iodide by the Ac_2O method, and the corresponding 11-Br-compound (800) [840] by the pyridine-piperidine (excess) method (not obtained in Ac_2O). The dicyanines are highly coloured dyes.

R. S. CAHN.

N-4'-Pyridyl-4-pyridone. F. ARNDT (Ber., 1932, 65, [B], 92—93°).—The compound described as "pyridyl ether" (A., 1930, 615) is shown to be N-4'-

pyridyl-4-pyridone, , since it is converted by P_2S_5 in PhMe into N-4'-pyridyl-4-thiopyridone, m. p. 200°, which gives coloured salts with 1 equiv. and colourless salts with 2 equivs. of acid. The diperchlorate, m. p. 189—190° (slight decomp.), is described.

H. WREN.

Reactions of dihalogenobarbituric acids. D. NIGHTINGALE and A. E. SCHAEFFER (J. Amer. Chem. Soc., 1932, 54, 236—239).—5:5-Dibromobarbituric acid (I) and NH_2Et (2 mols.) in dil. EtOH give 57% of 5-bromo-7-ethyluramil (α -bromo-5-ethylaminobarbituric acid), m. p. 185° (decomp.). The following 5-bromo-5-alkylamino- and -dialkylamino-barbituric acids are prepared similarly: methylamino-, m. p. 175—176° (decomp.); butylamino-, m. p. 178° (decomp.); allylamino-, m. p. 179—180° (decomp.); benzylamino-, m. p. 186° (decomp.); β -hydroxyethylamino-, m. p. 159° (decomp.); diethylamino-, m. p. 167—168° (decomp.); di-n-propylamino-, m. p. 216° (decomp.); di-n-amylamino-, chars at 273°; diisoamylamino-, m. p. 304° (decomp.), and dibenzylamino-, m. p. 242° (decomp.). 5:5-Dichlorobarbituric acid (II) is less reactive than (I), reacting readily only with benzylamines. (I) or (II) and $\alpha\text{-C}_{10}\text{H}_7\text{-NH-NH}_2$ in AcOH give 85% of alloxan- α -naphthylhydrazone, m. p. 264°, whilst (I) and $\text{NPh}_2\text{-CO-NH-NH}_2$ afford alloxan-4:4-diphenylsemicarbazone, m. p. 267° (decomp.). (I) also reacts with H-CO-NH_2 , H-CO-NHPh , and $\text{H-CO}_2\text{CH}_2\text{Ph}$, but the results could not be interpreted satisfactorily.

C. J. WEST (b).

NN'-Substituted pyrimidine and purine derivatives. I. NN'-Substituted barbituric acids. B. HEPNER and S. FRENKENBERG (Ber., 1932, 65, [B], 123—126).—1-Phenyl-3-methylbarbituric acid, m. p. 118—122°, is prepared in 70% yield by slowly warming phenylmethylcarbamide with malonic acid and Ac_2O , removing the solvent in vac., and heating the product with Ac_2O at 70°. The following mono-C-alkylated derivatives are prepared by condensing phenylmethylcarbamide with the requisite mono-substituted malonic ester in presence of NaOEt-EtOH and heating the residue left after removal of the solvent for several hr. at 120—130°: 5-n-propyl-, m. p. 106°; 5-ethyl-, m. p. 81°; 5-allyl-, m. p. 107—108°; 5-isopropyl-, m. p. 91°, 1-phenyl-3-methylbarbituric acid. Condensation of phenylmethylcarbamide with disubstituted malonyl chlorides leads to the following disubstituted 1-phenyl-3-methylbarbituric acids: di-ethyl-, m. p. 87°; dipropyl-, m. p. 89°; diallyl-, m. p. 96.5°; phenylethyl-, m. p. 104.5°; propylallyl-, m. p. 97°. 1-Phenyl-3-methyl-5:5-diethyl-2-thiobarbituric acid has m. p. 110°.

H. WREN.

Colorimetric determination of allantoin. H. W. LARSON (J. Biol. Chem., 1932, 94, 727—738).—Urine is treated successively with phosphotungstic acid, basic $\text{Pb}(\text{OAc})_2$, and 5% H_2SO_4 . An aliquot of the final filtrate is reduced at 100° with the Folin ammoniacal Cu reagent (A., 1926, 1282). The colour produced on adding acid molybdate reagent is compared with suitable standards. Human urine yielded 0.0025—0.0030% of allantoin, which, when isolated by pptn. with Hg salts, had m. p. 236—237° (cf. A., 1931, 976, 1080).

F. O. HOWITT.

1:3-Diphenyl-5-methyl- and 3-phenyl-1-(p-hydroxy-m-carboxyphenyl)-5-methyl-pyrazoline. J. S. TURSKI, W. STEPROWSKI, and F. ZYGMUND (Rocz. Chem., 1931, 11, 909—914).—1:3-Diphenyl-5-methyl-pyrazoline has been prepared from NHPh-NH_2 and benzylideneacetone, whilst with 4-hydroxyphenylhydrazine-3-carboxylic acid, 5-(or 3)-phenyl-1-(p-hydroxy-m-carboxyphenyl)-3(or o)-methylpyrazoline, m. p. 212°, is obtained; this, on heating with AcOH yields a product, m. p. 248°, which does not give the pyrazoline reaction.

R. TRUSZKOWSKI.

Condensation of butyl chloral hydrate with arylhydrazines. F. D. CHATTAWAY and H. IRVING (J. Amer. Chem. Soc., 1932, 54, 263—271; cf. A., 1930, 324; 1931, 722).—2:5-Dichlorophenylhydrazine hydrochloride (I) and butyl chloral hydrate (II) in warm EtOH, give β -chloro- α -ketobutaldehyde-2:5-dichlorophenylhydrazone (III), m. p. 142—143°; the 3:5-dichloro-, m. p. 118.5—120° (decomp.), and the 4:5-dibromo-phenylhydrazones, m. p. 195—196° (decomp.), are similarly prepared. (I) and (III) in boiling MeOH give α -keto- β -methoxybutaldehyde-2:5-dichlorophenylhydrazone (IV), m. p. 220° (decomp.); in EtOH, the β -ethoxy-osazone, m. p. 190° (slight decomp.), results. (I) and (II) in MeOH give a mixture of (III) and (IV). (III) and EtOH-NaOEt give 4-hydroxy-1-(2':5'-dichlorophenyl)-5-methylpyrazole, m. p. 162—163° (benzoate, m. p. 133—134°); the 3':5'-dichloro-isomeride, m. p. 180—181°, and the 3':4'-dibromo-analogue, m. p. 132—133°, are prepared. 2:4:6-Trichlorophenylhydrazine hydro-

chloride and (II) in H_2O at 60° give $\alpha\beta$ -dichlorocrotonaldehyde-2:4:6-trichlorophenylhydrazone (V), m. p. $156-157^\circ$, reduced by Zn and AcOH to 2:4:6-trichloroaniline. (V) and Cl in AcOH give $\alpha\beta\beta\omega$ -pentachlorobutaldehyde-2:4:6-trichlorophenylhydrazone, whilst with Ac_2O and a little conc. H_2SO_4 $\alpha\beta$ -dichlorocrotonaldehyde-N-acetyl-2:4:6-trichlorophenylhydrazone, m. p. $91-92^\circ$ (decomp.), results. If the above reaction is carried out in warm EtOH, (V) and (mainly) chloro- α -ketobutaldehyde-2:4:6-trichlorophenylhydrazone (VI), m. p. $107-109^\circ$ (reduced to 2:4:6- $Cl_3C_6H_2\cdot NH_2$) [N-Ac derivative, m. p. $136-137^\circ$, also obtained by the action of Ac_2O on the 2:4:6-trichlorophenylhydrazone of (II)]. (VI) and NaOEt give 4-hydroxy-1-(2':4':6'-trichlorophenyl)-5-methylpyrazole, m. p. $152-153^\circ$ [hydrochloride, m. p. 175° (decomp.); Na salt; benzoate, m. p. 113°]. $\alpha\beta$ -Dichlorocrotonaldehyde-2:4:6-tribromophenylhydrazone, m. p. 157° [N-Ac derivative, m. p. $113-114^\circ$ (decomp.)]; β -chloro- α -ketobutaldehyde-2:4:6-tribromophenylhydrazone, m. p. $122-123^\circ$ (decomp.) (N-Ac derivative, m. p. $171-172^\circ$), and 4-hydroxy-1-(2':4':6'-tribromophenyl)-5-methylpyrazole, m. p. $177.5-178^\circ$ (benzoate, m. p. $128-130^\circ$), are also described. C. J. WEST (b).

Action of potassium hypobromite on amides of β -benzoylamino-acids. Preparation of iminazoline derivatives. S. J. KANEVSKAJA (J. pr. Chem., 1932, [ii], 132, 335-340).— β -Benzamido- β -phenylpropionamide, m. p. $239-240^\circ$, prepared by successive action of $SOCl_2$ and NH_3 on benzoyl- β -phenylalanine, is converted by KOBBr in alkaline solution into 2-keto-4-phenyltetrahydroiminoazole (2-keto-4-phenyliminazolidine), $CO < \begin{array}{c} NH \cdot CHPh \\ NH \cdot CH_2 \end{array}$ m. p. $160-161^\circ$,

and BzOH; the former is identified by its hydrolysis by boiling conc. HCl to $\alpha\beta$ -diamino- α -phenylethane, b. p. $156-157^\circ/42$ mm. (dihydrochloride, decomp. above 260°), and CO_2 . H. A. PIGGOTT.

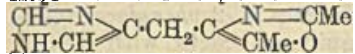
New reaction of certain diazosulphonates derived from β -naphthol-1-sulphonic acid. VIII. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from 2-chloro-4-nitroaniline. F. M. ROWE and C. DUNBAR (J.C.S., 1932, 11-19; cf. A., 1931, 1169).—Phthalazine, phthalazone, and phthalimidine derivatives of 2-chloro-4-nitroaniline are usually, but not always, intermediate in character between the corresponding unchlorinated and 2:6- Cl_2 -compounds, thus supporting the constitutions previously assigned to the latter. 2'-Chloro-4'-nitrobenzeneazo- β -naphthol-1-sulphonate (modified prep.) with Na_2CO_3 and NaOH gives Na 1-(2'-chloro-4'-nitrobenzeneazo)- β -naphthaquinone-1-sulphonate, 2'-chloro-4'-nitrobenzeneazo- β -naphthol, and Na H 3-(2'-chloro-4'-nitrophenyl)-1:3-dihydrophthalazine-1-sulphonate-4-acetate (a yellow acid dye), whence 1-hydroxy-3-(2'-chloro-4'-nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid (I), m. p. $(+0.25PhMe)$ $110-130^\circ$, (dry) 204° [*Me* ester, m. p. $(+0.5C_6H_5)$ $135-145^\circ$ after softening at 120° , (dry) 166° ; Et ester, m. p. $(+0.5C_6H_5)$ 168° after softening at 100° , (dry) 169° ; Ac derivative, m. p. $(+0.5EtOH)$ 118° after softening at 110° , (dry) 153° ; anilide, m. p. 195°], was obtained. With $Na_2S_2O_4$ and NaOH at

90° , or with $SnCl_2$ in boiling, conc. HCl (I) gives 1-hydroxy-3-(2'-chloro-4'-aminophenyl)tetrahydrophthalazine-4-acetic acid (II), m. p. $236-237^\circ$ (decomp.) (Ac derivative, m. p. 277°), which led by two methods to 2'-chloro-4'-amino-3-phenylphthalaz-1-one, m. p. 240° (decomp.) [Ac derivative, m. p. 321° (decomp.) after darkening at 290°], which with hot alkaline $Na_2S_2O_4$ gives 1-keto-3-(2'-chloro-4'-aminophenyl)tetrahydrophthalazine, m. p. $220-223^\circ$ (hydrochloride; Ac derivative, m. p. $217-219^\circ$), and with Zn dust and boiling conc. HCl yields a mixture of the same 1-keto-compound and 2'-chloro-4'-amino-N-phenylphthalimidine, $+0.25EtOH$, m. p. $188-189^\circ$ (Ac derivative, m. p. 234°). (I) and somewhat diluted H_2SO_4 at 130° give a resin, m. p. $130-150^\circ$, containing some 2-chloro-4'-nitro-3-phenylphthalaz-1-one, since reduction by aq. Na_2S affords some 2'-chloro-4'-amino-3-phenylphthalaz-1-one, although methylation of the resin furnished impure products. With cold, dil. H_2SO_4 and $K_2Cr_2O_7$ (I) yields 2'-chloro-4'-nitro-3-phenyl-4-methylphthalaz-1-one (III), m. p. 201° (picrate, m. p. $204-205^\circ$), which with Me_2SO_4 in $PhNO_2$ gives 2'-chloro-4'-nitro-1-methoxy-3-phenyl-4-methylene-3:4-dihydrophthalazine, m. p. 133° . 2'-Chloro-4'-amino-3-phenyl-4-methylphthalaz-1-one (IV), m. p. 285° [hydrochloride; Ac derivative, m. p. 308° (decomp.)], is best prepared by similar oxidation of (II), reduction of (III) by Na_2S affording also some 1-keto-3-(2'-chloro-4'-aminophenyl)-4-methyltetrahydrophthalazine, m. p. $220-223^\circ$ (hydrochloride; Ac derivative, m. p. $218-220^\circ$). The last compound is better prepared from (IV) by an excess of $Na_2S_2O_4$ or by Zn dust and dil. HCl; it is oxidised to the phthalaz-1-one on prolonged boiling with HCl. Prolonged reduction of (IV) by Zn dust and HCl, however, yields 2'-chloro-4'-amino-N-phenyl-3-methylphthalimidine, m. p. 212° (Ac derivative, m. p. 253°). R. S. CAHN.

Dehydrogenation of pyridine by anhydrous ferric chloride. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1932, 20-30).—Dehydrogenation of pyridine by anhyd. $FeCl_3$ in steel autoclaves, possibly modified by impurities in the steel, affords $FeCl_2$, Fe, and mainly 2:2'-dipyridyl (A., 1928, 1262) together with (a) the same gases as are obtained by berginisation (A., 1931, 362), (b) monocyclic pyridines, mostly 3-ethylpyridine, but including 2- and 4-ethyl-, 3- and 4-methyl-, 2:3- and 3:4-dimethyl-, 2-isopropyl-, and 2-amino-pyridine, (c) 3:4', 2:3', 2:4', and (in one experiment) 3:3'-dipyridyl, 2:2'- and 3:4'-dipiperidyl, and unidentified alkylidipyridyls, (d) 2:2':2'-tripyridyl (2:6-bis-2'-pyridylpyridine) (I), m. p. $88-89^\circ$, b. p. 370° (picrate, m. p. 210°), and a 2:2':tripyridyl (II), m. p. $84-85^\circ$ (picrate, m. p. 206°), (e) resins, including a base, m. p. 214° , (f) a non-basic, nitrogenous oil, b. p. $90-310^\circ$, and (g) an insoluble residue. The picrate, m. p. $159-160^\circ$, of a base (? a diethylpyridine) is described. (I) functions as a tridentate group, forming a very stable ferrous bromide, $C_{30}H_{22}N_6Br_2Fe \cdot 1.5H_2O$, and similar co-ordination compounds with Ni and Ag salts. (II) forms similar compounds. Dyeings with these substances are not fast. R. S. CAHN.

Constitution of bases prepared from protein. II. $C_5H_{11}ON$ and $C_9H_{11}ON_3$. F. WREDE and W.

KEIL (Z. physiol. Chem., 1931, 203, 279—286; cf. A., 1931, 1430).—The base $C_5H_{11}ON$ is identical with α -hydroxymethylpyrrolidine obtained by reduction of proline ester with Na in EtOH (A., 1923, i, 1224). The chloroaurate has m. p. 174° (lit. 152°). Histidine when heated with AcOH and AcCl and then with Ac_2O and NaOAc yields the base $C_9H_{11}ON_3$, probably



identical with the product from protein. It forms a Me_3 derivative, isolated as the chloroaurate, $C_9H_8ON_3Me_3\cdot 2HAuCl_4$, m. p. 172°. With histamine, AcCl and Ac_2O produce *N*-acetylhistamine (chloroaurate, m. p. 203°). In the previous paper 3:5- should read 3:6-diketopiperazine.

J. H. BIRKINSHAW.

Ring structure of adenosine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1932, 94, 809—819).—Adenosine hydrate was acetylated and then simultaneously deacetylated and methylated by refluxing with Me_2SO_4 and NaOH in $COMe_2$ solution. The product with gaseous HCl in Et_2O -MeOH at 0° gave trimethyl-*N*-methyladenosine, decomp. 210°, $[\alpha]_D^{25} -21.2^\circ$ in H_2O . This on hydrolysis yielded monomethyladenine and syrupy trimethylribofuranose, b. p. 90—92°/0.02 mm., which with $Br\cdot H_2O$ gave a γ -lactone and with HNO_3 inactive dimethoxysuccinic acid. These facts indicate a furanoside ring structure for adenosine and inosinic acid (cf. Robinson, A., 1927, 960, 1225).

F. O. HOWITT.

Tetrapyrrolethanes, dipyrrol diketones, and pyrrol pyrrolmethyl ketones. H. FISCHER, H. BAUMGARTNER, and E. PLOTZ (Annalen, 1932, 493, 1—19).—The substance, m. p. 275°, previously obtained (A., 1927, 1206) as a by-product in the bromination of β -5-carbethoxy-2:4-dimethyl-3-pyrrolpropionic acid (I) is *s*-tetra-(5-carbethoxy-4-methyl-3- β -carboxyethyl-2-pyrrol)ethane (II), m. p. 275° (corr.) [*Et*₄ ester, m. p. 132° (corr.)], also formed from di-(5-carbethoxy-4-methyl-3- β -carboxyethyl-2-pyrrol)methane (III) (A., 1926, 1261) and conc. aq. $FeCl_3$ in AcOH at 60°. *s*-Tetra-(5-carbethoxy-3-methyl-4-ethylpyrrol)ethane, m. p. 164° (corr.), is prepared similarly from di-(5-carbethoxy-3-methyl-4-ethylpyrrol)methane.

[With E. THURNHER.] *s*-Tetra-(5-carbethoxy-4-methyl-3-ethylpyrrol)ethane, m. p. 175°, is obtained from the corresponding dipyrrolmethane and aq.-alcoholic $FeCl_3$.

The formation of (II) from (I) probably occurs by way of (III), which is now shown to be produced by the prolonged action of Br (0.5 mol.) on (I) in AcOH. (II) could not, however, be isolated from the reaction product of (III) and Br in AcOH, whereby a *perbromide*, $C_{23}H_{29}O_8N_4Br_3$, m. p. 108° [hydrolysed by H_2O at 30° to a substance, $C_{23}H_{29}O_8N_4Br$, m. p. 170° (corr.)], results. The dipyrrolmethane system appears to be stabilised by the introduction of 5:5'-di(carbethoxy)-groups; 5:5'-dialkylated dipyrrolmethanes show a marked tendency to pass into pyrromethenes. Thus, cryptopyrrole (2:4-dimethyl-3-ethylpyrrole) [5-benzeneazo-derivative, m. p. 91° (*Cu* salt, decomp. about 171°)] condensed with $[CH(OMe)_2]_2$ in presence of conc. HCl gives 3:5:3':5'-tetramethyl-4:4'-diethylpyrromethene (IV) and not the tetrapyrrolethane. *Mg* cryptopyrrol bromide (V), prepared from

MgEtBr and cryptopyrrole, is decomposed by dry O_2 to (IV) and a compound (VI), $C_{16}H_{24}ON_2$, m. p. 222° which is probably an ether. (VI) is converted by HI (*d* 1.96) in AcOH at 100° (bath) into cryptopyrrole, also formed, together with a substance, m. p. 195°, by the action of conc. HCl, and is oxidised by $FeCl_3$ to tetra-(3:5-dimethyl-4-ethyl-2-pyrrol)ethylene(?), m. p. 250° (corr.).

Cryptopyrrole, $(CO_2Et)_2$, and EtOH-NaOEt give 2:4-dimethyl-3-ethyl-5-pyrrolglyoxylic acid; the *Et* ester and (V) afford di-(3:5-dimethyl-4-ethyl-2-pyrrol) diketone (VI), m. p. 193° (corr.), also formed from (V) and $(CO_2Et)_2$ or, better, $(COCl)_2$. Di-(4:5-dimethyl-3-ethyl-2-pyrrol) and di-(3:5-dimethyl-2-pyrrol) diketones, m. p. 215° (corr.) and 245°, respectively, are prepared from $(CO_2Et)_2$ and the appropriate *Mg* pyrrol bromide. (VI) is reduced by Zn dust and 10% HCl in AcOH to 3:5-dimethyl-4-ethyl-2-pyrrol 3:5-dimethyl-4-ethyl-2-pyrrolmethyl ketone (VII) (A., 1930, 1298). Oxidation of (VII) with O_2 in MeOH-KOH gives a yellow compound (VIII), $C_{36}H_{44}O_3N_4$, m. p. 229°, which appears to contain 4 pyrrol groups, since it gives a positive Gmelin's reaction. (VIII) is reduced by HI in AcOH to cryptopyrrole, is converted by boiling with AcOH into a red dye, $C_{36}H_{44}O_3N_4$, m. p. 263° (positive Gmelin's reaction), and is oxidised by $FeCl_3$ in EtOH to a yellowish-brown substance, m. p. 273°, which shows no Gmelin's reaction and is reduced by Zn dust and AcOH to a compound, m. p. 230°, not identical with (VIII). 3:5-Dimethyl-2-pyrrol 3:5-dimethyl-2-pyrrolmethyl ketone (not described) and O_2 in MeOH-KOH give a colourless compound, $C_{28}H_{34}(or\ 36)O_3N_4$, m. p. 230°, converted by boiling with AcOH into a red dye, $C_{28}H_{32}O_3N_4$ (?), m. p. 245°. H. BURTON.

Porphyrins. XXVIII. isoUroporphyrin II, and the Curtius degradation in the pyrrole series. H. FISCHER and E. THURNHER. XXIX. Uroporphyrins from mussel shells. H. FISCHER and E. HAARER (Z. physiol. Chem., 1932, 204, 68—80, 101—104; cf. A., 1931, 633).—XXVIII. Reduction of Et 2:4-dimethyl-3-(ω -cyano- ω -carbethoxy)vinylpyrrole-5-carboxylate with Na-Hg in EtOH-AcOH gives the corresponding substituted *Et* compound, m. p. 133°, yielding the 3-(ω -cyano- ω -hydrazido)ethyl derivative, m. p. 192°. With HNO_2 , the latter forms an azide which gives the urethane, m. p. 226°, in boiling EtOH. Et 3-($\beta\beta$ -dicarbethoxy)ethyl-2:4-dimethylpyrrole-5-carboxylate by similar stages gives the dihydrazidoethyl derivative, m. p. 222° (forming Et 2:4-dimethylpyrrole-5-carboxylate at the m. p.) (diazide; diurethane, m. p. 172°). The Me_8 ester of isouroporphyrin gives a K_1 salt, *Ag* salt, m. p. 315° (containing an active H by Zerevitinov), phyllin, m. p. 239°, *Ni* salt, m. p. not below 300°, *Zn* salt, m. p. not below 300°, nitro-derivative, m. p. 240° (*Fe* salt, m. p. 279°; *Cu* salt, m. p. 280°; *Ag* salt), chlorin (identified spectroscopically), octahydrazide, m. p. not below 300°, octa-azide. 5:5'-Dicarbethoxy-3:3'-di-($\beta\beta$ -dicarbethoxyethyl)-4:4'-dimethylpyrromethane yields the corresponding 3:3'-di-($\beta\beta$ -di-hydrazido)-derivative, m. p. 155°, tetra-azide, and tetraurethane, m. p. 266°.

XXIX. Uroporphyrin was isolated from mussel

shells (*Pteria vulgaris*) from the Indian Ocean as the Me₈ ester. It was degraded to coproporphyrin.

J. H. BIRKINSHAW.

Optical properties of chlorophyll. I. Absorption of light by solutions and suspensions of chlorophyll- α and - β , and of their mixtures. J. C. GHOSH and S. B. SEN-GUPTA (J. Indian Chem. Soc., 1931, 8, 581—589).—The absorption spectra of pure chlorophyll- α and - β and of mixtures in solution in COMe₂ and in suspension in 1% aq. COMe₂ and in *M*/32,000 lecithin (after dialysis) have been plotted. In general, for $\lambda=6400$ —6300 Å., chlorophyll- α has a larger extinction coeff. than has chlorophyll- β , the reverse being true for shorter wave-lengths. The total mol. concn. of any chlorophyll ($\alpha+\beta$) solutions in COMe₂ is determined by dividing the mol. extinction coeff. by the observed extinction coeff. at $\lambda=6500$ Å. (the point where the curves for various mixtures coincide), the ratio α/β then being determined by graphical interpolation from the observed mol. extinction coeff. at $\lambda=4600$ Å. (where small changes in the ratio result in large changes in the val. of ϵ).

J. W. BAKER.

Copper phyllocyanate. A. TSCHIRCH (Pharm. Zentr., 1932, 73, 33—35).—The Cu compound of phyllocyanic acid (phæophytin), formed in the preservation of colour in green vegetables by Cu, is different in character from the green Zn compound obtained by the action of Zn powder on the brownish-green pigment of dead leaves, since, unlike the latter, its colour is stable to acids and alkali and it exhibits no fluorescence in solution, whilst the Cu is not detectable by ordinary reagents. J. W. BAKER.

Acetylene and its isooxazolic derivatives. VIII. 5-isoOxazoleamine. A. QUILICO (Gazzetta, 1931, 61, 970—976).—5-isoOxazolediazoidime (A., 1931, 1169) and SnCl₂ give the hydrochloride of 5-isooxazoleamine (I), which with HNO₂ gives 5-diazoaminoisooxazole (II), m. p. 140° (decomp.); this is reduced by SnCl₂ to 5-isooxazolehydrazine (A., 1930, 449) and (I). Treatment of (I) with HNO₂ in a large excess of HCl gives 5-isooxazolediazonium chloride, which couples with β -naphthol, giving 5-isooxazolylazo- β -naphthol, m. p. 155°. (II) also couples with NH₂Ph in presence of NaOAc. The free base could not be isolated from (I).

E. E. J. MARLER.

Acenaphthenequinone series. A. C. SIRCAR and S. C. SEN (J. Indian Chem. Soc., 1931, 8, 605—612).—Condensation of acenaphthenequinone with *o*- (I) and *p*- (II) -chloro-, *o*- (III) and *p*- (IV) -nitro-, *m*- (V) and *p*- (VI) -hydroxy-, *p*-dimethylamino- (VII), and *p*-acetamido- (VIII) -benzaldehyde, resorcy- (IX), salicyl- (X), anis- (XI), and *p*-bromosalicyl- (XII) -aldehyde, and vanillin (XIII) in presence of NH₃ affords oxazoles (A) or iminazoles (B), according to the conditions. Thus (II), (III), and (VII)—(IX) give exclusively (A) at 0°, and (B) at higher temp.: (I), (V), and (X) give inseparable mixtures of (A) and (B) at 0°, but exclusively (B) at higher temp.; (IV), (VI), and (XI) give only (B) even at 0°, whilst (XII) and (XIII) do not react at 0° and give only (B) at higher temp. The following are described: 2'-, not melting at 290°, and 4'-chloro-, 3'- and 4'-, not melting at 290°, -hydroxy-, 3' : 5'-dihydroxy-, not melting at 300°;

4'-hydroxy-3'-methoxy-, 2'-, m. p. 150° (decomp.), and 4'-, m. p. 185° (decomp.), -nitro-, 4'-acetamido-, m. p. 255° (decomp.); 4'-dimethylamino-, m. p. 223° (decomp.); 2'-hydroxy-4'-bromo-, 3-nitro-4'-acetamido-, 3 : 4-dinitro-4'-acetamido-, 3-nitro-4'-chloro-, and 3-nitro-4'-hydroxy-3'-methoxy-2-phenylacenaphth-iminazole; 4'-chloro-, m. p. 245° (decomp.), and 4'-acetamido-, m. p. 288° (decomp.), -2-phenylacenaphth-oxazole. Acenaphthenequinone reacts with (X) in C₆H₆ in sunlight to give the monosalicyloyl derivative, m. p. 192° (decomp.) (Ac derivative, m. p. 248°), of acenaphthenequinol, the cinnamoyl, m. p. 246° (decomp.) Bz, m. p. 230° (decomp.), and anisoyl, m. p. 193° (decomp.), derivatives being obtained similarly. Condensation with COMe₂ gives the compound, C₁₀H₁₆ $\begin{smallmatrix} \text{C(OH)CH}_2\text{Ac} \\ \text{CO} \end{smallmatrix}$, m. p. 117° (decomp.).

The tinctorial properties of these derivatives are described. J. W. BAKER.

Condensation of aldehydes and ketones with *o*-aminothiophenols, benzthiazolines, and benzthiazoles. II. H. P. LANKELMA and P. X. SHARNOFF (J. Amer. Chem. Soc., 1932, 54, 379—381; cf. A., 1931, 1075).—The following substituted 5-chlorobenzthiazolines are prepared from 4-chloro-2-aminothiophenol hydrochloride (I) and the appropriate aldehyde or ketone in pyridine: 2-*Pr*, m. p. 49°; 2-*Pr* ^{β} , m. p. 45°; 2-*Bu*, m. p. 78°; 2-*Bu* ^{β} , m. p. 69°; 2-*benzyl*, m. p. 89°; 2 : 2-dimethyl-, m. p. 37°; 2-phenyl-2-methyl-, m. p. 71°. 5'-Chlorospiro-1-cyclohexane-2'-, m. p. 93°, and 5'-chlorospiro-1-cyclopentane-2'-, m. p. 47°, -benzthiazolines are obtained from (I) and cyclo-hexanone and -pentanone, respectively.

The following substituted 5-chlorobenzthiazoles are prepared similarly from (I) and the appropriate Ar·CHO: 2-furyl-, m. p. 122°; 2-*m*-nitrophenyl-, m. p. 146°; 2-*o*-hydroxyphenyl-, m. p. 201°; 2-*p*-hydroxy-*m*-methoxyphenyl-, m. p. 173°; 2-3' : 4'-methylenedioxyphenyl-, m. p. 173°, and 2-styryl-, m. p. 134°.

C. J. WEST (b).

Alkaloids of the *Senecio* species. I. Necines and necic acids from *S. retrorsus* and *S. jacobaea*. R. F. H. MANSKE (Canad. J. Res., 1931, 5, 651—659).—The names "necine" and "necic acid" are proposed for the basic and acidic products, respectively, obtained on hydrolysis of alkaloids present in the *Senecio* species. *S. aureus* yields to MeOH a small amount of basic and neutral material. *S. retrorsus* of S. African origin contains a substance, C₁₂H₁₆O₇, m. p. 190° after sintering at 175°, and retrorsine (I), C₁₈H₂₅O₆N, m. p. indef. about 214—215° (decomp.) (methiodide, decomp. 266°). Hydrolysis of (I) with KOH in EtOH gives retronecine, C₈H₁₃O₂N [hydrochloride, m. p. 164°; Bz derivative (hydrochloride, m. p. 151°; methochloride, m. p. 128°); probably contains a CH₂·CO group], and retronecic acid, C₁₀H₁₆O₆ (K₂ salt; lactone, C₁₀H₁₄O₆, m. p. 186°; di-*p*-phenylphenacyl ester, m. p. 155°). *S. jacobaea* contains a substance, C₇H₉O₃ (phenylhydrazone, m. p. 178°), glucose, and jacobine, C₁₈H₂₃O₅N, m. p. 223—224° (decomp.) after previous decomp. (methiodide, decomp. 252° after darkening at 238°). Hydrolysis of the last-mentioned

substance affords retronecine and *jaconecic acid*, (?) $C_{10}H_{16}O_6$, m. p. 178—179° R. S. CAHN.

Identity of *neonicotine* and the alkaloid *anabasine*. C. R. SMITH (J. Amer. Chem. Soc., 1932, 54, 397—399).—Anabasine (Orekhov and Men-shikov, A., 1931, 498) is identical with *neonicotine* (3-pyridyl-2'-piperidine) (*ibid.*, 367). Crude anabasine sulphate also contains *methylanabasine* [*picrate*, m. p. 222—223° (corr.)], also obtained by methylating anabasine. C. J. WEST (b).

Synthesis of alkeine derivatives of methoxy-acids. J. BRAUN and E. PŁAZEK (Rocz. Chem., 1931, 11, 890—896).—O-Methylmandeloyl and O-methyltropoyl chlorides are condensed with tropine to yield *methylhomotropine*, b. p. 144—146°/0.3 mm. (*monohydrate*, m. p. 50—55°; *picrate*, m. p. 238°; *picrolonate*, m. p. 226°; *MeI* derivative, m. p. 251°), and O-methyltropine, b. p. 162—164° (*picrate*, m. p. 203°; *MeI* derivative, m. p. 231°), respectively, with $NMe_2 \cdot [CH_2]_2 \cdot OH$ to yield, respectively, *dimethylaminoethyl O-methylmandelate*, b. p. 120—122°/0.3 mm. (*MeI* derivative, m. p. 259°; *picrate* of *MeI* derivative, m. p. 165°), and O-methyltropate, b. p. 124—126°/0.3 mm. (*MeI* derivative, m. p. 256°; *picrate* of *MeI* derivative, m. p. 102°), and with γ -(N-piperidyl)propyl alcohol to yield the corresponding O-methylmandelate, b. p. 160—162°/0.35 mm. (*MeI* derivative, m. p. 140°), and O-methyltropate, b. p. 168—170°/0.3 mm. (*MeI* derivative, m. p. 137°). R. TRUSZKOWSKI.

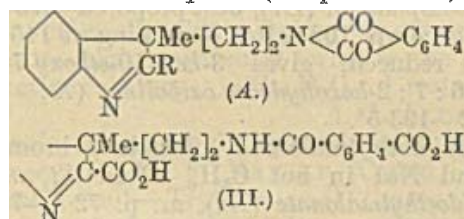
Synthesis of physostigmine (*eserine*). I. Some indolenine derivatives. II. Synthesis of a base which is believed to be *dl*-noreserethole. R. ROBINSON and H. SUGINOME. III. Synthesis of de-ethoxydehydroeseretholemethine. H. S. BOYD-BARRETT and R. ROBINSON. IV. Plancher rearrangement of indole derivatives. H. S. BOYD-BARRETT. V. Synthesis of dehydroesermetholemethine. F. E. KING and R. ROBINSON (J.C.S., 1932, 298—304, 304—317, 317—321, 321—325, 326—336).—1. The product of the reaction of Et isopropyl-acetoacetate and benzenediazonium chloride in aq. EtOH, when heated with NaOH in EtOH, gives α -keto- β -methylbutyric acid phenylhydrazone (I), m. p. 146—147° (cf. A., 1896, i, 169), which with hot alcoholic H_2SO_4 affords Et 3:3-dimethylindolenine-2-carboxylate, $C_6H_4 \cdot \begin{smallmatrix} CMe_2 \\ \diagup \quad \diagdown \\ N \end{smallmatrix} \cdot C \cdot CO_2Et$, (II), m.

79—80°, 2:3-dimethylindole (III), and 3:3-dimethylindolenine-2-carboxyphenylhydrazide (IV), m. p. 155—156° (cf. *loc. cit.*). Use of abs. alcoholic H_2SO_4 gives relatively more (II). (I) with HCl in hot, dry EtOH gives 3:3-dimethylindolenine-2-carboxylic acid (V), m. p. 132—133° (decomp.), and 3:3-dimethylindolenine (VI), m. p. 214—215° [*picrate*, m. p. 146—147° (lit. 135°)], also formed by loss of CO_2 from (V) at 135—140°. The hypotheses that, in the above prep., $C_6H_4 \cdot \begin{smallmatrix} CMe_2 \\ \diagup \quad \diagdown \\ N \end{smallmatrix} \cdot C \cdot CON_2H_2Ph$ (IV) is formed from (II)

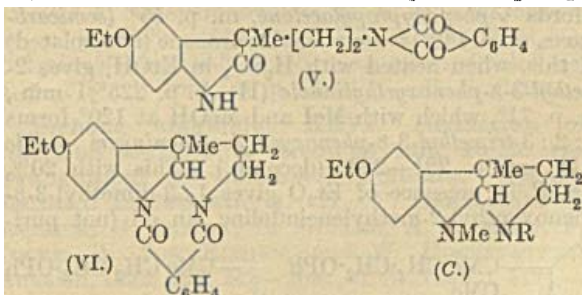
and $NH_2 \cdot NHPh$ liberated by hydrolysis, and (III) by the action of the alcoholic H_2SO_4 on the initial product (VI), are confirmed by experiment. Diazotised *p*-phenetidine led similarly to α -keto- β -methylbutyric acid *p*-ethoxyphenylhydrazone, m. p. 128—129°, 5-ethoxy-3:3-dimethylindolenine-2-carboxylic

acid, m. p. 161—162° (decomp.), and 5-ethoxy-3:3-dimethylindolenine, m. p. 96—98° (*picrate*, m. p. 145—146.5°; *hydrochloride*, m. p. 92—93°; *chloroplatinate*, decomp. 270° after darkening at 160°).

II. A base, believed to be *dl*-noreserethole, is synthesised. Reduction of acetaldoxime (modified prep.) by amalgamated Al and H_2O gives γ -hydroxy-n-butylamine, b. p. 172°/755 mm. [*chloroplatinate*, m. p. 206° (decomp.); *picrate*, m. p. 122°], the *phthalo*-derivative (m. p. 47—48°) of which with an excess of hot saturated aq. HBr forms *phthalo*- γ -bromobutylimide (I), m. p. 56.5—57°; with less HBr some methyl- β -phthalimidoethylcarbinyl hydrogen *phthalate*, $C_6H_4 \cdot \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ N \end{smallmatrix} \cdot [CH_2]_2 \cdot CHMe \cdot O \cdot CO \cdot C_6H_4 \cdot CO_2H$, m. p. 101°, is also formed, which with hot 80% HBr gives (I) and phthalic acid. (I) with NaI and Et potassioacetoacetate in EtOH forms Et δ -phthalimido- α -acetyl- β -methylvalerate, b. p. 215—217°/1 mm., which with diazotised *p*-phenetidine, best in presence of alcoholic NaOEt, yields Et δ -phthalimido- α -keto- β -methylvalerate *p*-ethoxyphenylhydrazone, m. p. 108—109°, which with HCl in hot EtOH affords Et 5-ethoxy-3-methyl-3-(β -phthalimidoethyl)indolenine-2-carboxylate (II; A, R=CO₂Et), m. p. 132—133°. An attempt to oxidise the *methosulphate* (m. p. 50—60°) of (II)

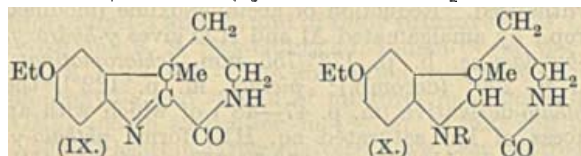


with alkaline $K_3Fe(CN)_6$ gave the *methohydroxide* (?), m. p. 116° (decomp.). (II) with KOH in cold EtOH gives a small amount of an acid, m. p. 270° (decomp.), with much 5-ethoxy-3-methyl-3-(β -o-carboxybenzamidoethyl)indolenine-2-carboxylic acid (III), decomp. 90—150° (K_2 salt, + H_2O , m. p. 290° after softening at 283°). (III), when heated in xylene, loses CO_2 to yield 5-ethoxy-3-methyl-3-(β -phthalimidoethyl)indolenine (IV; A, R=H), m. p. 123—124° (*picrate*, m. p. 156—157°; *methosulphate*, m. p. 153—154°), an acid, decomp. 170°, and a neutral substance, $C_{21}H_{22}O_3N_2$, m. p. 218—219°; the neutral substance with boiling AcOH and HCl affords a base and 5-ethoxy-3-methyl-3-(β -phthalimidoethyl)indolinone (V), m. p. 169—170°. (III) at 190°, or at 210° in vac., gives CO_2 , H_2O ,



phthalic anhydride, NN'-diphthaloyldinoreserethole (VI), m. p. 218—219°, (V), and (IV). (III) with Ac_2O gives phthalic anhydride quantitatively and unidentified products, and with Ac_2O in boiling C_6H_6

gives a small yield of neutral substance, m. p. 228°. The methosulphate of (IV) with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in boiling EtOH gives phthalhydrazide and a cryst. salt, from which KOH liberates dl-noreserethole (VII; C , $\text{R}=\text{H}$), an oil (hydrochloride, m. p. 191—192°;



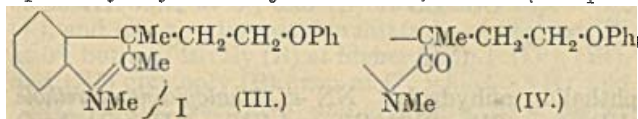
chloroplatinate, $+1.5\text{H}_2\text{O}$, decomp. from 185°; picrate, m. p. 180—181°; this with Me_2SO_4 in EtOAc- C_6H_6 led to a base, $\text{C}_{15}\text{H}_{22}\text{ON}_2$, b. p. about 200°/1 mm., probably dl-eserethole (VIII; C , $\text{R}=\text{Me}$), probably obtained also from (VII), aq. CH_2O , and HCO_2H at 135—165°.

(II) with an excess of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in boiling EtOH gives a substance, m. p. 111—112°, but with 1 mol. of the reagent affords 3-keto-10-ethoxy-7-methyl-3:4:5:6-tetrahydro-4-psi-carboline (IX), m. p. 194—195°, which with Zn dust and HCl (d 1.16) yields 3-keto-10-ethoxy-1:7-dimethyl-3:4:5:6:7:2-hexahydro-4-carboline (X; $\text{R}=\text{Me}$), m. p. 148—149°. The methosulphate of (IX), best prepared with Me_2SO_4 in C_6H_6 , decomp. 162° after darkening at 145°, when similarly reduced, gives 3-keto-10-ethoxy-7-methyl-3:4:5:6:7:2-hexahydro-4-carboline (X; $\text{R}=\text{H}$), m. p. 192—193.5°.

Et sodiomethylmalonate, phthalo- β -bromoethyl-imide, and NaI in hot C_6H_6 afford Et₂ methyl- β -phthalimidoethylmalonate (XI), m. p. 72.5—73° (corresponding Me₂ ester, m. p. 85—85.5°), which with boiling HCl gives the corresponding acid, decomp. at 170—180° to γ -phthalimido- α -methylbutyric acid, m. p. 112—113°. The last-mentioned condensation, when carried out in EtOH, gives a poor yield of (XI) and Et β -aminoethyl phthalate, an oil (picrate, m. p. 155—156°; hydrochloride, m. p. 113°), hydrolysed by boiling 5% NaOH. Most of the above substances give low analyses for C unless burnt very slowly in a long, hot PbCrO₄ tube.

III. De-ethoxydehydroeserolemethine,

$\text{NMe} \langle \text{C}_6\text{H}_4 \rangle \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$ (I) (cf. A., 1925, i, 292), is synthesised. β -Phenoxyethyl bromide and Et acetoacetate in presence of NaOEt in boiling EtOH give a product which with hot 5% aq. NaOH affords γ -phenoxypropylacetone, m. p. 55° (semicarbazone, m. p. 140°); the phenylhydrazone (not isolated) of this, when heated with H_2SO_4 in EtOH, gives 2-methyl-3- β -phenoxyethylindole (II), b. p. 225°/1 mm., m. p. 71°, which with MeI and MeOH at 120° forms 1:2:3-trimethyl-3- β -phenoxyethylindoleninium iodide (III), m. p. 221—223° (decomp.). This with 20% NaOH in presence of Et₂O gives 1:3-dimethyl-3- β -phenoxyethyl-2-methyleneindoline, an oil (not puri-

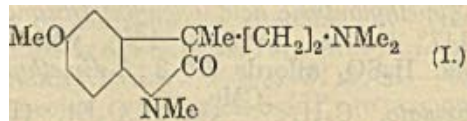


fied), which is oxidised by KMnO_4 in cold COMe_2 to 1:3-dimethyl-3- β -phenoxyethyl-2-indolinone (IV), b. p.

190—195/1 mm. [$(\text{NO}_2)_2$ -derivative, m. p. 169—171°], whence by means of boiling HBr 1:3-dimethyl-3- β -bromoethyl-2-indolinone, b. p. 155—160°, is obtained. This with NHMe_2 in aq. MeOH at 170—180° forms (I) (1:3-dimethyl-3- β -dimethylamino-2-indolinone), an oil [quaternary picrate, m. p. 153—155°; 6- NO_2 -derivative, an oil (picrate, m. p. 222°; methiodide, m. p. 167—169°)], and with NH_2Me similarly gives 1:3-dimethyl-3- β -methylaminoethyl-2-indolinone, an oil [H oxalate, m. p. 204° (decomp.)]. The product (II) is proved to have the constitution assigned to it rather than that of 2- γ -phenoxypropylindole by its colour reactions and by analysis of the products obtained from it.

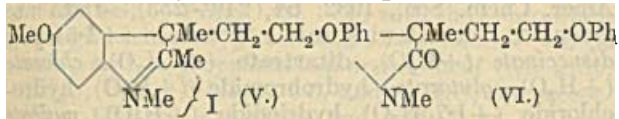
IV. The migration of the Ph group in the reaction of 2-phenylindole with MeI to yield 3-phenyl-1:2:3-trimethylindoleninium iodide, m. p. 227° (decomp.) [chloroplatinate, m. p. 224° (decomp.); zincichloride, m. p. 275° (decomp.)] [previously formulated as a methyleneindoline hydriodide (cf. A., 1899, i, 452)], is confirmed by oxidation of the chloride (I), m. p. 94°, by KMnO_4 in cold COMe_2 to 3-phenyl-1:3-dimethylindolinone (II), b. p. 150—160°/2 mm., m. p. about 50° (NO_2 -derivative, m. p. 138°). (I) and (II) are synthesised by independent methods. Phenylacetonitrile and NaNH_2 give the sodio-derivative, which with MeI in dry Et₂O gives α -phenylpropionitrile, b. p. 229—233°, the phenylmethylhydrazide of which, m. p. 128°, when heated with CaO at 200° in an atm. of H_2 , affords (II). α -Phenyl- α -methylacetone (best purified through the semicarbazone), b. p. 212—214°, gives a phenylmethylhydrazone, which, when heated with ZnCl_2 in EtOH, gives the zincichloride obtained from (I). (I) and diphenylformamidine in Ac_2O yield 3:3'-diphenyl-1:3:1':3'-tetramethyl-2:2'-indocarbocyanine chloride, m. p. 255—258° (decomp.), thus proving the occurrence of a Me group in position 2 in (I). The migration of groups from position 2 to 3 is not due to the tendency to form salts of a strong base, since Ph, Et, and Pr^β migrate more readily than Me.

V. dl-Dehydroesermetholemethine (I) has been synthesised and resolved. The l-base is identical with



the product obtained by degradation of physostigmine, thus confirming the constitution of the alkaloid. C-Alkylation of indole derivatives is considered to be effected in nature by CH_2O . γ -Phenoxypropylacetone- p -methoxyphenylhydrazone with H_2SO_4 in EtOH gives 5-methoxy-2-methyl-3- β -phenoxyethylindole (II), m. p. 113—114°. Et α -acetyl- δ -phenoxyvalerate, b. p. 198—203°/15 mm., with p -methoxybenzenediazonium chloride gives a p -methoxyphenylhydrazone, which with H_2SO_4 in hot EtOH forms Et 5-methoxy-3- β -phenoxyethylindole-2-carboxylate (III), m. p. 179°; the corresponding acid, m. p. 179—180°, loses CO_2 at 200° in vac. to yield 5-methoxy-3- β -phenoxyethylindole (IV), m. p. 89°. The alternative constitution, 5-methoxy-2- γ -phenoxypropylindole, for (II) is excluded because (IV) (which has a free position in the pyrrole nucleus), but not (II) or (III),

gives a colour with Ehrlich's reagent in the cold, and because of the constitution of the products obtained on methylation. Methylation of (IV) gives only impure products, but (II) with MeI and MeOH at 120° yields 5-methoxy-1:2:3-trimethyl-3- β -phenoxyethylindoleninium iodide (V), m. p. 200° (corresponding chloride, hygroscopic, and picrate, m. p. 128—130°), which with 20% NaOH and Et₂O forms 5-methoxy-

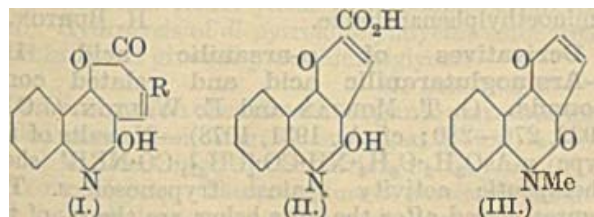


1:3-dimethyl-3- β -phenoxyethyl-2-methyleneindoline, m. p. 65°, oxidised by KMnO₄ in cold COMe₂ to 5-methoxy-1:3-dimethyl-3- β -phenoxyethyl-2-indolinone (VI), b. p. 238—243°/1 mm. [(NO₂)₃-derivative, m. p. 192—193°]. This with HBr (d 1.7) at 150° gives 5-hydroxy-1:3-dimethyl-3- β -bromoethyl-2-indolinone, m. p. 199—200° (Ac derivative, m. p. 71—72°, b. p. 190—192°/1 mm.), converted by Me₂SO₄ and 5% NaOH at 15° into the Me ether, b. p. 170—175°/1 mm., which with NHMe₂ in MeOH at 150° affords dl-5-methoxy-1:3-dimethyl-3- β -dimethylamino-2-indolinone (Ia), an oil (methiodide, m. p. 130—135° when heated rapidly, 157—158° after being dried in vac.; quaternary picrate, m. p. 193—195°). Physostigmine, when treated with NaOEt in dry EtOH in N₂, and then with Me p-toluenesulphonate, gives esermethole, b. p. 164—167°/12 mm. (methiodide, m. p. 169—170°; quaternary picrate, m. p. 194°), the methochloride of which with K₃Fe(CN)₆ and KOH in H₂O yields the l-base (Ib) (methiodide, m. p. 142° when heated rapidly, 186—187° after being dried in vac.; quaternary picrate, m. p. 132—133°; d-bromocamphorsulphonate, m. p. 245—248°, [α]_D²⁰ +28.0° in EtOH). The synthetic dl-base (Ia) gives a d-bromocamphorsulphonate, a syrup, which by fractional crystallisation gives the salts of the d- and l-bases, from which the d- and l-methopicates were prepared; the l-picrate yields a l-methochloride, a gum, which decomposes at 150—200°, and at 260—300° affords the l-base, identical with (Ib).

Colour reactions are described for many of the substances recorded in the above memoirs.

R. S. CAHN.

Syntheses of a substance isomeric with dictamnine. Y. ASAHINA and M. INUBUSE (Ber., 1932, 65, [B], 61—63; cf. A., 1930, 1454).—Dictamnine is converted by O₃ in CHCl₃ and decomp. of the ozonide with boiling H₂O into dictamnol, m. p. 260°, transformed by HBr in AcOH or by EtOH-KOH into nordictamnol [2:4-dihydroxyquinoline-3-aldehyde], not molten below 350° (phenylhydrazone, m. p. 235°),



obtained synthetically from 2:4-dihydroxyquinoline, CHCl₃, and 15% NaOH. With CN·CH₂·CO₂H and

KOH nordictamnol affords nordictamnylideneacetic acid, m. p. 275° (decomp.), hydrolysed by conc. H₂SO₄ to the compound (I) (+H₂O) (R=CO₂H), m. p. 305—310° (decomp.), which loses CO₂ when heated with formation of the lactone (I, R=H), m. p. 335°, transformed by Br in AcOH into the Br-derivative (I, R=Br) gradual decomp. above 300°. The last-named compound is converted by 10% KOH into the substance (II), m. p. 310° (decomp.), transformed by successive methylation and dry distillation into ψ -dictamnine (III), m. p. 225°. H. WREN.

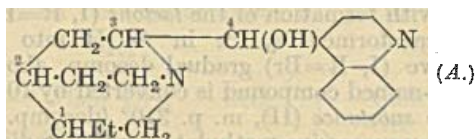
Determination of narcotine in morphine-narcotine mixtures and in opium preparations. J. LEVY and O. GAUDIN (Bull. Sci. pharmacol., 1930, 37, 407—414, 478—500; Chem. Zentr., 1931, ii, 1725).—The action of morphine, codeine, thebaine, narcotine, papaverine, narceine, dionine, heroine, dilaudide, dicodide, and "lukodal" on the surviving guinea-pig intestine was studied. In small doses the phenanthrene derivatives diminish, and the isoquinoline derivatives increase, the peristaltic action; in large doses all produce a lowering of muscular tone of differing intensity. Narcotine is 200 times as active as morphine. All the above alkaloids can thus be determined, and narcotine can be determined in presence of other alkaloids. Opium extracts give vals. which are too high, apparently owing to the presence of other active substances in the H₂O-sol. resin.

A. A. ELDRIDGE.

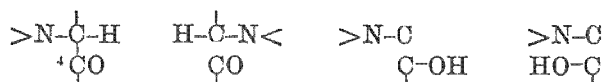
Synthesis of methyltryptamines and some derivatives. R. H. F. MANSKE (Canad. J. Res., 1931, 5, 592—600).—Tryptamine (I) (improved prep. from acraldehyde by way of β -bromoacetal, β -cyano-propionacetal, and γ -aminobutyroacetal) with MeI in cold CHCl₃ gives the methiodide, unchanged (I), NN'-dimethyltryptamine (II), m. p. 47° (hydrochloride, a resin; picrate, m. p. 168°), and N-methyltryptamine (III) (phenylcarbamido-derivative, m. p. 153°; hydrochloride, m. p. 180°; picrate, m. p. 191°), identical with that obtained from calycanthine. The methochloride of (III), m. p. 193°, when distilled below 1 mm., gives a poor yield of (II). (I), when heated with MeI and COMe₂, affords 3-benzoyl-2:2-dimethyl-2:3:4:5-tetrahydrocarboline, m. p. 285°, and a little methiodide. (III) gives a phthalyl derivative, m. p. 177.5°, whence it is regenerated by N₂H₄ and then has b. p. 154°/1 mm. (hydrochloride, m. p. 198°); its Bz derivative with POCl₃ in hot CHCl₃ yields 2-phenyl-1-methyl-4:5-dihydrocarboline, m. p. 94° (hydrochloride, m. p. 237°), oxidised by CrO₃ in hot dil. H₂SO₄ to 2-phenyl-1-methyl-3-carboline, an oil (hydrochloride, m. p. 278°; picrate, m. p. 234°). R. S. CAHN.

Cinchona alkaloids. XXVI. Reduction of Cinchona ketones to alcohols and steric rearrangement of Cinchona alkaloids. Stereochemical investigations. II. P. RABE [with A. IRSCHICK, G. SUSZKA, E. MULLER, A. NIELSEN, F. KOLBE, W. VON RIEGEN, and W. HOCHSTATTER] (Annalen, 1932, 492, 242—266; cf. A., 1910, i, 417).—Reduction of hydrocinchoninone (I) (4, where CH·OH=CO) with Al in EtOH-NaOEt or catalytically (Pd-black) gives a mixture of epihydrocinchonine (II), m. p. 126°, [α]_D²⁰ +88.4° in 99% EtOH, epihydrocinchonidine (III), m. p. 106° [α]_D²⁰ +48.3° in 99%

EtOH, hydrocinchonine (IV), and hydrocinchonidine (V); (II) and (III) are separable from (IV) and (V) through their ready solubilities in Et₂O. (II)—(V) are all represented by (A) (see below) and are all



convertible into hydrocinchotoxin. The production of (II)—(V) is explained by the conversion of (I) (in solution) into a mixture of two keto- and two enol forms (partial structures given below); subsequent addition of 2H gives four stereoisomeric alcohols.



The production of similar series of stereoisomerides from quinine (or quinidine) and cinchonine by treatment with amyl-alcoholic KOH (cf. Koenigs and Husmann, A., 1896, i, 707) shows that racemisation of C¹ and C² does not occur to any appreciable extent, and from the rotatory powers of (II)—(V) and of derivatives (see below) the configurations of C³ and C⁴ in (II), (III), (IV), and (V) are +, −, +, +, and −, respectively (in these and other compounds, the first sign is C³, the second C⁴). (II) and PCl₅ give a *chloride*, an oil, [α]_D²⁰ +105.8° in EtOH (all rotations in abs. EtOH unless stated otherwise) [*dipicrate*, m. p. 193° (decomp.)], reduced by Fe and H₂SO₄ to *deoxyhydrocinchonine* (VI) (A, where CH·OH=CH₂), m. p. (+2H₂O) 60—61°, m. p. (anhyd.) 74—75°, [α]_D²⁰ +147°. The *chloride*, m. p. 109—110°, [α]_D²⁰ −61.7°, from (III) is similarly reduced to *deoxyhydrocinchonidine* (VII) (A, where CH·OH=CH₂), m. p. 52° (also given as m. p. 42—44°), [α]_D²⁰ −21.2° [*H dianisoyl-d-tartrate*, m. p. 177° (corr.) (decomp.)]. (VI) and (VII) are stereoisomerides having C³ + and −, respectively (the configurations of C¹ and C² being the same in all the cases quoted), and are both produced, together with 4-methylquinoline, from hydrocinchoninehydrazone (not characterised) and powdered KOH at 180°.

Quinine (or quinidine) is converted by amyl-alcoholic KOH into a mixture of quinine (−), epiquinine (−+), an oil, [α]_D²⁰ +43.3° in 99% EtOH [*dibenzoyl-d-tartrate*, m. p. 159° (corr.) (decomp.)]; *dihydrochloride*, m. p. 196° (decomp.) (reduced catalytically to *epihydroquinine*), quinidine (+), and *epiquinidine* (+), m. p. 113°, [α]_D²⁰ +102.4° [*dibenzoyl-d-tartrate*, m. p. 167° (decomp.)]; *dihydrochloride*, m. p. 195—196° (decomp.) (reduced catalytically to *epihydroquinidine*). Cinchonine similarly gives a mixture of cinchonidine (−), *epicinchonidine* (−+), m. p. 103—104°, [α]_D²⁰ +62.8° [*dianisoyl-d-tartrate*, m. p. 180° (corr.) (decomp.)] [reduced catalytically to (III)], cinchonine (+), and *epicinchonine* (+), m. p. 82—83°, [α]_D²⁰ +120.3° [*dianisoyl-d-tartrate*, m. p. 172° (corr.) (decomp.)] [reduced catalytically to (II)]. The series *hydroquinine* (−), *epihydroquinine* (−+), an oil, [α]_D²⁰ +32.5° [*chloride*, m. p. 123°, [α]_D²⁰ −40°]; *dibenzoyl-d-tartrate*, m. p. 151° (decomp.)], *hydroquinidine* (+), and *epihydroquinidine* (+), m. p. 122°, [α]_D²⁰ +73.7° [*chloride*, an oil, [α]_D²⁰ +101.7°;

dibenzoyl-d-tartrate, m. p. 156—157° (decomp.)], is also studied.

[By H. MEYER.] *Dianisoyl-d-tartaric acid*, m. p. 186°, [α]_D²⁰ −162.8° in 99% EtOH, is prepared from *d-tartaric acid* and *p-OMe-C₆H₄-COCl* at 120°.

H. BURTON.

Optical crystallographic data for some salts of strychnine. C. F. POE and J. E. SELLERS (J. Amer. Chem. Soc., 1932, 54, 249—253).—Data are given for the following salts: *dioxalate* (+1.5H₂O), *disuccinate* (+H₂O), *ditartrate* (+3H₂O), *chlorate* (+H₂O), *glutarate*, *hydrobromide* (+H₂O), *hydrochloride* (+1.75H₂O), *hydriodide* (+H₂O), *maleate* (+H₂O), *malonate* (+6H₂O), *nitrate*, *oxalate* (+4.5H₂O), *perchlorate* (+H₂O), *phosphate* (+2H₂O), *selenate* (+4.5H₂O), *sulphate* (+5H₂O), *sulphate* (+6H₂O), *thiocyanate* (+H₂O). C. J. WEST (b).

Optical identification of strychnine. C. F. POE and J. E. SELLERS (Ind. Eng. Chem. [Anal.], 1932, 4, 69).—The salts of strychnine with HClO₄, HCl, HBr, and HI may be used for their optical detection (see preceding abstract). E. S. HEDGES.

Partial syntheses in the morphine series. II. (−)-Bromosinomeninone from dihydrothebainone. C. SCHOFF, T. PFEIFER, and H. HIRSCH (Annalen, 1932, 492, 213—225).—During the formation of 1-bromodihydrocodeinone (I) from crude dibromodihydrothebainone and alkali (A., 1931, 104), small amounts of 1-bromodihydrothebainone and (−)-*bromosinomeninone* (II), m. p. 226—227° (decomp.), [α]_D²⁰ −52.3° in 2N-AcOH [*methiodide* (+H₂O), m. p. 243° (decomp.)]; *dioxime*, m. p. 187—189° (decomp.) (sinters at 184°), accompanied (in one case) by a *substance*, m. p. 203° (decomp.) (sinters at 201°), are produced; (II) is racemised by (+)-*bromosinomeninone*, [α]_D²⁰ +53.7° in 2N-AcOH. (II) is also obtained in about 60% yield when dihydrothebainone is brominated with 3 mols. of Br and the resulting (1:5:7)-Br₃-derivative (III) (not characterised) treated with dil. NaOH, or from (I) and Br (1 mol.) in presence of K₂CO₃ and cold MeOH. The formation of (II) from (III) is analogous to the production of *buchucamphor* (*diosphenol*) from *dibromo-menthone* and *-carvomenthone* (Wallach, A., 1918, i, 442). (II) is converted by boiling with Ac₂O and NaOAc into 1-bromo-4:6-diacetoxy-3-methoxyphenanthrene (IV), m. p. 184—185°, and 1-bromotriacetylisothebenine (V), m. p. 168—170°. Catalytic reduction (Pd-BaSO₄+PdCl₂) of (IV) in AcOH-NaOAc gives 4:6-diacetoxy-3-methoxyphenanthrene (converted by successive demethylation and acetylation into 3:4:6-triacetoxyphenanthrene), whilst (V) similarly affords *triacetylisothebenine*, m. p. 182—183°. *isoThebenine* is probably 4:6(or 7)-dihydroxy-3-methoxy-5-β-methylaminoethylphenanthrene. H. BURTON.

Derivatives of *p*-arsanilic acid. III. *p*-Arsinoglutaranilic acid and related compounds. G. T. MORGAN and E. WALTON (J.C.S., 1932, 276—280; cf. A., 1931, 1078).—Na salts of the type *p*-AsO₃H₂·C₆H₄·NH·CO·[CH₂]₃·CO·NRR' show therapeutic activity against trypanosomes. The figures placed after the salts below are the *p_H* of the aq. solutions. Me H and Et H glutarate (b. p. 158°/27 mm. and 170°/34 mm., respectively) with SOCl₂ give

γ-carbomethoxy- [(I), b. p. 110°/30 mm.] and -carboethoxy- [(II), b. p. 110°/20 mm.] -butyryl chloride, respectively. (I) and (II) with atoxyl (III) in cold *N*-NaOH give *Me* (IV) and *Et* (V) *p*-arsinoglutaranilate (*Na* salts, 7.5 and 8), respectively. (IV) with cold aq. NH_3 slowly gives NH_4 glutaranilamide-*p*-arsinate, $+\text{H}_2\text{O}$ deliquescent, 5, and with aq. NH_2Me at 80° yields glutaranilomethylamide-*p*-arsinic acid (*Na* salt, $+\text{1.5H}_2\text{O}$, 6). (V) with the appropriate amine gives similarly glutaranilo-dimethylamide-, -ethylamide-, and -*n*-propylamide-*p*-arsinic acid (*Na* salts, $+\text{2H}_2\text{O}$, 6.5, $+\text{3.5H}_2\text{O}$, 6.5, and $+\text{H}_2\text{O}$, 8, respectively). Glutaric anhydride and NH_2Ph at 15° give glutaranilic acid, which with *p*-arsanilic acid at 180° gives glutaranilide and glutaranilide-*p*-arsinic acid (*Na* salt, $+\text{2H}_2\text{O}$, 7.5). Glutaric acid and (III) at 180° give a small yield of glutaranilide-*pp'*-diarsinic acid (*Na*₂ salt, $+\text{H}_2\text{O}$, 7.5) [not obtained from glutaryl chloride and (III) in dil. alkali]. (V) with SO_2 and a trace of KI in conc. HCl at 0° gives *p*-dichloroarsinoglutaranilic acid, m. p. 156—158°, which with hot NaOH affords *p*-arsinoglutaranilic acid, and with cold Na_2CO_3 gives *Et* *p*-arsinoglutaranilate. Alkaline hydrolysis of (V) and subsequent reduction also gives the dichloride. The last-mentioned acid with H_2O_2 gives *p*-arsinoglutaranilic acid. The determination of As in these org. compounds is modified. R. S. CAHN.

[Path to optically active germanium compounds.] R. SCHWARZ (Ber., 1932, 65, [B], 130; cf. A., 1931, 1435).—A reply to Krause (this vol., 181).

H. WREN.

Action of magnesium alkyl iodides on triphenylphosphine dichloride. B. K. BLOUNT (J.C.S., 1932, 377).— MgMeI and PPh_3Cl_2 in C_6H_6 give triphenylmethylphosphonium iodide. The substance, m. p. 162—163° (A., 1931, 1173), is impure triphenylethylphosphonium iodide. R. S. CAHN.

Peptides of glutamic acid. III. Preparation of *γ*-glutamylpeptides. W. VOSS and R. GUTTMANN (Z. physiol. Chem., 1932, 204, 1—12; cf. A., 1930, 1170).—Thionyl chloride and monoammonium *d*-glutamate give a mixture of NH_4Cl and *d*-glutamyl monochloride (I) together with *l*-pyrrolidonyl chloride, since treatment with NH_2Ph gives *d*-glutamylanilide (II), m. p. 209° (decomp.) [hydrochloride, m. p. 176—177°, $[\alpha]_D^{25} +26.06^\circ$ (in 50% EtOH)], and *l*-pyrrolidonylanilide, m. p. 185—187°, $[\alpha]_D^{25} +17.43^\circ$ in 80% EtOH (*α*-naphthylcarbimido-derivative, not melted at 240°, phenylcarbimido-derivative, m. p. 204.5—205.5°). Oxidation of (II) with H_2O_2 or Br gives succinil. With glycine *Et* ester (I) gives *γ*-glutamylglycine ester (contaminated with NH_4Cl), which on hydrolysis with KOH or HCl in EtOH yields *l*-pyrrolidonecarboxylic acid. Hydrolysis of *dl*-pyrrolidonylglycine ester with KOH in EtOH gives *dl*-pyrrolidonylglycine.

J. H. BIRKINSHAW.

Determination of carbon in organic compounds. A. CHALMERS (Ind. Eng. Chem. [Anal.], 1932, 4, 1—2).—C is determined by oxidation to CO_2 by CrO_3 and conc. H_2SO_4 . The procedure is particularly suitable for cellulose compounds and is unsuitable for compounds containing the halogens, N, or S.

E. S. HEDGES.

Wet micro-combustion of organic compounds with particular reference to cellulose derivatives. A. CHALMERS (Ind. Eng. Chem. [Anal.], 1932, 4, 143—144).—The oxidising mixture consists of CrO_3 and H_3PO_4 (1:9). A special apparatus is described. E. S. HEDGES.

Micro-analysis of gases in relation to organic and physiological chemistry. D. BURK and R. T. MILNER (Ind. Eng. Chem. [Anal.], 1932, 4, 3—7).—A review of methods of micro-analysis of gases with particular reference to org. compounds. Applications of the Warburg apparatus to org. and physiological chemical problems are described. E. S. HEDGES.

Micro-Dumas method for determination of nitrogen. R. T. K. CORNWELL (Ind. Eng. Chem. [Anal.], 1932, 4, 42).—Improvements in manipulation are suggested. E. S. HEDGES.

Determination of sulphur in organic substances by combustion in an air stream. J. SIELISCH and R. SANDKE (Angew. Chem., 1932, 45, 130—132).—The products of combustion are collected in 3% H_2O_2 and the H_2SO_4 thus formed is titrated with 0.05*N*-KOH. Certain org. substances containing N in addition to S also produce HNO_3 in the absorption vessel. In such a case the H_2SO_4 is determined gravimetrically. Two arrangements of the combustion apparatus are described, according to whether the org. substance is liquid or solid. Typical results are compared with those obtained by other methods.

E. S. HEDGES.

Determination of bromine in organic substances. F. SCHULZ (Coll. Czech. Chem. Comm., 1932, 4, 20).—A question of priority.

E. S. HEDGES.

Micro-analytical determination of methoxyl and methylimide groups. K. H. SLOTTA and G. HABERLAND (Ber., 1932, 65, [B], 127—129).—The apparatus employed is a slight modification of that of Edlbacher (A., 1918, ii, 336), the joint between quartz and glass being rendered gas-tight by picein. The substance, mixed with NH_4I , a little PhOH, and red P and HI (*d* 1.7) is heated and the vapours are passed through 1.5% $\text{Na}_2\text{S}_2\text{O}_3$ solution containing 0.5% of Na_2CO_3 . Subsequent treatment is effected according to Viebock (A., 1931, 107, 246) except that 0.02*N*- $\text{Na}_2\text{S}_2\text{O}_3$ is used. After 30 min. the evolution of Me from OMe is complete. After renewal of the wash liquid the heating is resumed slowly and the temp. kept at 350° for 1 hr. after the HI has distilled off. After cooling to 200°, titration is effected. During the cooling the HI is sucked back. The mixture is again heated at 350° for 30 min. and titrated. After a third heating only 1—2 drops of 0.02*N*- $\text{Na}_2\text{S}_2\text{O}_3$ are usually required and are without influence on the result. H. WREN.

Preparing a picrolonate from a picrate as a means of identification. L. KLEIN and J. F. WILKINSON (Analyst, 1932, 57, 27—28).—The picrate is dissolved in a large vol. of H_2O containing a little H_2SO_4 , and, after cooling, a slight excess of nitron in 5% AcOH is added. Picrolonic acid is added to the filtrate from the insol. nitron picrate and after a time the clear solution is evaporated to small vol. in vac.

below 40°, cooled, and the picrolonate recryst. from hot H₂O. T. McLACHLAN.

Analysis of resorcinol. D. O. JONES, M. A. PRAHL, and J. R. TAYLOR (Ind. Eng. Chem. [Anal.], 1932, 4, 84—88).—Two methods for determining the crystallising point of resorcinol are described. The pure substance crystallises at 109.80°. Traces of H₂O lower the crystallising point and increase the

degree of supercooling; the lowering effect of PhOH has also been determined. A method is described for determining PhOH in commercial resorcinol by fractional steam-distillation. The reaction between pyrocatechol and Pb(OAc)₂ is quant., but Pb(OAc)₂ gives no ppt. with pure resorcinol. The test may be used to determine pyrocatechol in technical resorcinol, but some oxidation products of resorcinol also give a ppt. E. S. HEDGES.

Biochemistry.

Respiration in the larvæ of certain parasitic Hymenoptera. W. H. THORPE (Proc. Roy. Soc., 1932, B, 109, 450—471).—The CO₂ output of the larva isolated between microscope slide and cover slip may be followed by observing the change in colour with a suitable indicator added to the medium, whilst the O₂ consumption may be examined by the use of a biological indicator, e.g., by the introduction of flagellate protozoa such as *Polytoma uvella*, which collect in the regions of highest O₂ tension, or of luminous bacteria (*B. phosphorescens*) which emit light only in the presence of sufficient dissolved O₂. The tail of caudate ichneumonids does not function as a respiratory organ. When large, and supplied with a good blood circulation, the caudal vesicle of braconids plays a part in respiration but is not of outstanding importance, gas exchange taking place over the whole body surface. W. O. KERMAK.

Comparison of normal iron content of the blood of tropical and temperate peoples. G. M. STREEF (Arch. néerland. Physiol., 1931, 16, 552—565; cf. Parjono, A., 1930, 629).—Determinations of the Fe and hæmoglobin contents, and the O₂ capacities, of samples of blood show that these vals. are identical for tropical and temperate peoples. H. DAVSON.

α-, β-, and γ-Hæmoglobin. T. TADOKORO, M. ABE, and K. YOSHIMURA (J. Biochem. Japan, 1931, 14, 145—161).—Oxyhæmoglobin from horse's blood is treated with HCl, hæmin is removed by Et₂O, and globin "isomerides" (α, β, and γ) are fractionally pptd. by gradual addition of NH₃. The fractions thus obtained exhibit graded differences in isoelectric point, S content, N distribution, and Pt content of the PtCl₄ ppt. F. O. HOWITT.

[Determination of hæmoglobin.] C. E. JENKINS and C. S. D. DON (Brit. J. Exp. Path., 1931, 12, 212—217).—The hæmoglobinometer and O₂-capacity methods are compared.

CHEMICAL ABSTRACTS.

Hæmin of the respiratory oxygen-carrying enzyme, artificial hæmoglobins, and Spirographis-porphyrin. O. WARBURG and E. NEGELEIN (Biochem. Z., 1932, 244, 9—32).—When globin is coupled with hæmin, the absorption bands are displaced towards those of the respiratory enzyme. Phæohæmin-*b* and Spirographis-hæmin on coupling with globin also give bands displaced towards those of the respiratory enzyme. The prep. of Spirographis-porphyrin and the optical properties of Spirographis-

hæmoglobin and chlorocruorin are described. In faintly alkaline solutions of phæohæmin-*b* and Spirographis-hæmin the respiratory enzyme bands disappear and bands similar to those of blood-hæmin are obtained, the change being reversed on acidification. P. W. CLUTTERBUCK.

Spirographis-hæmin. O. WARBURG and E. NEGELEIN (Biochem. Z., 1932, 244, 239—242).—The prep. and properties of the oxime and Me₂ ester, m. p. 285° (corr.), of Spirographis-porphyrin are described. Hydrogenation of the porphyrin gives a product which forms a Me₂ ester, C₃₄H₃₈O₄N₄, m. p. 246° (corr.). P. W. CLUTTERBUCK.

Reagent for the preparation of hæmin crystals from blood. G. BERTRAND (Bull. Soc. Chim. biol., 1931, 13, 1263—1267).—A reagent containing cryst. MgCl₂ 1 g., glycerol 5 g., H₂O 1 g., glacial AcOH 20 g., has many advantages over aq. NaCl and AcOH for use in the detection of blood. The suspected material should be heated with a small quantity of the reagent on a glass slide until the glass can no longer be touched at the point of contact with the flame. A. LAWSON.

Enzymes of leucocytes. VI. Amylases of leucocytes. VII. Desmo- and lyo-trypsin of leucocytes. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1931, 203, 189—240; 1932, 204, 181—196; cf. A., 1930, 942).—VI. The glycogenolysis is followed by the determination of glucose in experiments with leucocytes and of maltose with glycerol extracts (which do not contain maltase). Leucocytes act more rapidly than glycerol extracts. The optimum *p*_H (usually about 6.2—6.4) is somewhat variable, but is unaltered by addition of NaCl.

Leucocytes after treatment with glycerol contain a system of three desmoamylases (β, γ, and δ) not requiring phosphate for activation. They are stable and are inhibited by glycerol. β-Desmoamylase is dissolved by Na₂HPO₄. Papain at *p*_H 5.9 dissolves from the residue the γ-amylase, which now resembles the β-component in the buffer. The residues contain δ-amylase. During the fractionation inhibitors are removed, since the fractions are individually more active than the mixture. There is evidence for an α-desmoamylase active only in presence of phosphate.

The unstable glycerol-sol. α-lyoamylase requires a phosphate (or arsenate) buffer (about 0.05*M*). With arsenate and very dil. phosphate the enzyme is activated by Ca⁺⁺. It differs from pancreatic amylase chiefly in its phosphate requirements. β-Lyoamylase,

which strongly resembles the pancreatic amylase, is obtained from leucocytes by glycerol extraction.

VII. A method of obtaining leucocyte trypsin involving less autolysis consists in extracting the COM₂-treated cells with 100% glycerol and cooling during dilution and centrifuging. In the isolation of the leucocytes, they are washed only once with physiological salt solution. Under these conditions the glycerol-sol. trypsin is reduced to 7–11%.

J. H. BIRKINSHAW.

Proteins of blood-plasma. I. W. BERGER and L. PETSCHACHER. II, III. L. PETSCHACHER (*Folia Hæmatol.*, 1930, 40, 81–164, 225–369; *Chem. Zentr.*, 1931, ii, 1154).

Serum-proteins. B. LUSTIG (*Biochem. Z.*, 1932, 244, 165–166).—A reply to Schmitz (cf. A., 1931, 1440). P. W. CLUTTERBUCK.

Neutralisation curves of biological systems with special reference to serum. M. GEX (*Compt. rend.*, 1932, 194, 316–318).—The quantity $I - dq/dp_H$ (where q is the amount of normal acid required to bring the biological system to a given p_H) has been determined for various body-fluids, including normal and pathological sera. The sera curves may be classified into 4 main types, of which examples are given.

W. O. KERMACK.

Optical rotation of blood-glucose. J. THOMAS (*Bull. Soc. Chim. biol.*, 1931, 13, 1223–1227).—Blood-plasma (rabbit) is dialysed, neutralised, and treated with yeast, the NH₂-N and optical rotation at p_H 7.5 and 1.5 being measured before and after fermentation. The results indicate that NH₂-acids have an almost negligible effect on the rotation of blood-sugar, which is considered to be due to another form of glucose besides the α - and β -forms.

A. LAWSON.

Micro-determination of blood-urea. II. L. CUNY and J. ROBERT (*Bull. Soc. Chim. biol.*, 1931, 13, 1167–1177, and *J. Pharm. Chim.*, 1932, [viii], 15, 7–17).—The method is a modification of that of Allen and Luck (A., 1929, 962). Tanret's reagent is used for the pptn., and $N/3\text{-K}_2\text{Cr}_2\text{O}_7$ for the oxidation, the excess of the latter being determined iodometrically.

A. LAWSON.

Asbestos filters for the micro-determination of urea. J. ROBERT (*Bull. Soc. Chim. biol.*, 1931, 13, 1178–1186).—An asbestos filter suitable for the separation of the dioxanthylcarbamide in the urea determination by the method of Cuny and Robert (cf. preceding abstract) is described. Porous glass micro-filters are unsuitable.

A. LAWSON.

Determination of blood-calcium. E. J. BIGWOOD and G. ROOST (*Bull. Soc. Chim. biol.*, 1931, 13, 1214–1222).—A technique for the determination of serum-Ca by pptn. as CaC_2O_4 and subsequent titration with KMnO_4 is described. Comparison is made of results obtained using the serum before and after ashing, and the best results using the serum directly are obtained by pptg. from the serum diluted three times with H_2O and keeping the ppt. for 12–15 hr. before filtering.

A. LAWSON.

Determination of calcium in serum. M. L. TAMAYO (*Anal. Fis. Quím.*, 1931, 29, 706–709).—

Direct pptn. is unsatisfactory. The Ca-protein system should first be destroyed, and pptn. effected from simple, non-colloidal solution. The best conditions for pptn. are discussed.

H. F. GILLBE.

Blood-phosphorus and phosphatæmia. M. JAVILLIER and M. FABRYKANT (*Bull. Soc. Chim. biol.*, 1931, 13, 1253–1262).—Ingestion of glucose and injection of adrenaline or insulin have no effect on the total and lipin-P of the human blood; a slight decrease of inorg. P, however, takes place. Parallel results are obtained after the ingestion of a vol. of H_2O equal to the vol. of the glucose solution. Determination of phosphatæmia is therefore of no val. in diagnosis.

A. LAWSON.

Influence of bile acids on phosphorus metabolism. I. Blood-phosphate following administration of cholic acid. T. KIMURA (*J. Biochem. Japan*, 1931, 14, 51–60).—The inorg. and org. PO_4''' of the blood of dogs are increased by intravenous injection of Na cholate, a max. being reached in 2–3 hr., after which the vals. fall to subnormal levels within 5 hr.

F. O. HOWITT.

Effect of glucose on production and action of hæmolytic antibodies. G. MAROTTA (*Mem. R. Accad. Italia*, 1931, 2, Biol. No. 2, 13 pp.).—The hæmolytic power of rabbit serum on ox erythrocytes is developed more rapidly and reaches twice the val. when the erythrocytes are injected suspended in glucose instead of NaCl solution. Preliminary glucose injections increase the normal hæmolytic power on sheep corpuscles and stimulate the formation of anti-bovine hæmolysins on subsequent injection. The hæmolytic potency of sera *in vitro* has in glucose solution twice the val. that it has in NaCl solution.

R. K. CALLOW.

Does invertase occur in blood after injection of sucrose? G. BERG (*Arch. exp. Path. Pharm.*, 1932, 163, 713–725).—No invertase or lactase was detected in the blood of the rabbit or dog following injections of sucrose.

C. C. N. VASS.

Blood-coagulation. XXIV. Inhibition of blood-coagulation by "liquoid." B. STUBER and K. LANG (*Biochem. Z.*, 1932, 244, 214–221).—The inhibition of blood coagulation by "liquoid" (Na polyanetholesulphonate; cf. A., 1931, 379) is due to its physico-chemical action. Small additions of "liquoid" stabilise and large amounts form stable liquoid-protein salts. Protein solutions can thereby be made resistant to heat-coagulation.

P. W. CLUTTERBUCK.

Occurrence of dihydrocholesterol in human brain. I. H. PAGE and E. MÜLLER (*Z. physiol. Chem.*, 1932, 204, 13–14).—The new sterol from brain (A., 1930, 1608) is a mol. compound of cholesterol and dihydrocholesterol.

J. H. BIRKINSHAW.

Basic amino-acids from neurokeratin. Is neurokeratin a true keratin? R. J. BLOCK (*J. Biol. Chem.*, 1932, 94, 647–651).—Pig brains were extracted with org. solvents, digested with trypsin and pepsin, and the residue was washed free from inorg. salts and dried by EtOH and Et₂O. The mol. proportions of histidine, lysine, and arginine in the neurokeratin (cf. A., 1917, i, 61) thus prepared were

approx. 1:2:2 and hence, despite the keratin-like solubilities of the material, neurokeratin is not a true keratin (cf. A., 1931, 1317). F. O. HOWITT.

So-called unsaponifiable fraction of mammalian liver. II. Lignoceryl sphingosine. S. J. THANNHAUSER and E. FRANKEL (Z. physiol. Chem., 1931, 203, 183—188; cf. A., 1930, 632).—From the Et₂O-sol. portion of the unsaponifiable fraction of pig's liver there was isolated *lignoceryl sphingosine*, m. p. 90—90.5°, which on hydrolysis with MeOH containing aq. H₂SO₄ gave lignoceric acid and sphingosine. J. H. BIRKINSHAW.

***Haliotis indigo*.** F. N. SCHULZ and M. BECKER (Z. physiol. Chem., 1931, 203, 157—161).—Evidence is advanced indicating that the pigment, contrary to Lemberg's view (A., 1931, 1321), is a simple indigo derivative. J. H. BIRKINSHAW.

Arcaine. F. KUTSCHER and D. ACKERMANN (Z. physiol. Chem., 1931, 203, 132—134; cf. A., 1931, 1178).—Arcaine was isolated as sulphate from freshly-collected *Arca noae* by pptn. with MeOH from the mixed sulphates of the arginine fraction. None was obtained from *Mytilus edulis*. J. H. BIRKINSHAW.

Basic extractives of octopus muscle. T. ISEKI (Z. physiol. Chem., 1931, 203, 259—262).—From the arginine fraction of the muscle extract there was isolated by picric acid pptn. a substance, m. p. 235—238°, probably methylagmatine dipicrate. The lysine fraction gave much betaine and a *chloroplatinate*, C₂₇H₃₄O₈N₅H₂PtCl₆, m. p. 187°. J. H. BIRKINSHAW.

Physical and chemical properties of synovial mucin. C. A. CHARD and M. PIETRE (Compt. rend., 1932, 194, 221—224).—Mucin separated from the synovial fluid of the ox resembles salivary mucin in respect of pptn. by dil. acid, but is rather more sol. in dil. AcOH. When hydrolysed it yields approx. 8% of reducing material calc. as glucose. When injected into a rabbit it produces an antiserum with which it reacts *in vitro* forming a ppt. containing approx. 15% of mucin and 85% of serum-protein. W. O. KERMACK.

Vitellin of hen's egg. H. O. CALVERY and A. WHITE (J. Biol. Chem., 1932, 94, 635—639).—The prep. of vitellin and its analysis for H₂O, ash, N, P, S, N-distribution, and the principal NH₂-acids are described. The following results were obtained on a H₂O- and ash-free basis: cystine, 1.19; arginine, 7.77; histidine, 1.22; lysine, 5.38; tyrosine, 5.01, and tryptophan, 1.24%. F. O. HOWITT.

Crystallised ovalbumin. H. O. CALVERY (J. Biol. Chem., 1932, 94, 613—634).—Cryst. ovalbumin was heat-coagulated, washed with H₂O, digested with boiling EtOH followed by cold Et₂O, and dried. Elementary analysis and a complete determination of the constituent NH₂-acids were carried out on the material, comparison being made with the results of other investigators. The mol. wt. of the protein based on the proportions of the NH₂-acids is discussed. F. O. HOWITT.

Permeability of egg shell. W. A. OSBORNE (Austral. J. Exp. Biol., 1931, 8, 239—240).—The yolk of an intact hen's egg is slowly dehydrated by im-

mersion in glycerol or saturated (NH₄)₂SO₄. CHCl₃ penetrates the shell in a few hr. and coagulates the albumin. Et₂O enters the egg slowly and is absorbed by the yolk without affecting the white. The shell is very impervious to EtOH, immersion in which does not cause coagulation of the albumin in 3—6 months, although traces of EtOH are found in the yolk. A. COHEN.

Lead content of human bones. E. BARTH (Arch. path. Anat. Physiol., 1931, 281, 146—151; Chem. Zentr., 1931, ii, 731).—The subjects had not been in Pb works, neither had they suffered from Pb poisoning. The ash of bones contained: infants 0.0—0.04, young adults 0.02—0.065, older adults 0.06—0.19 mg. of Pb per 3.0 g.; the accuracy of the method, however, is estimated to be 0.03—0.04 mg. per 3 g. A. A. ELDRIDGE.

Gold in biological material. B. BERTRAND (Compt. rend., 1932, 194, 409—413).—No Au was found in brain tissue. P. G. MARSHALL.

Histospectrography. A. POLICARD and A. MOREL (Compt. rend., 1932, 194, 491—493).—Spectrographic methods can be applied successfully to the detection and approx. determination of elements in a section of biological material <0.5 sq. mm. and 50—100 μ in thickness. P. G. MARSHALL.

Physical nature of "cytotropism" and allied phenomena and their bearing on the physics of organic form. N. RASHEVSKY (J. Gen. Physiol., 1932, 15, 289—306).—The case of a drop suspended in a non-uniform solution is examined thermodynamically with a view to the explanation of the phenomena of "cytotropism" and "induction." Forces may exist between two such drops, larger than those due to possible charges, if the drops are seats of chemical reactions which produce substances diffusing into the medium. A possible experimental method of examining these forces is suggested. H. DAVSON.

Picro-Congo-red staining. G. P. GNANAMUTHU (J. Roy. Microscop. Soc., 1931, 51, 401—402).—Ehrlich's haematoxylin is preferable to gentian-violet or alcoholic borax-carmin as a primary stain in the histological study of the tongue muscles of Reptilia. Good differentiation of the tissues is obtained when this is followed by a picro-Congo-red stain of varying composition. P. G. MARSHALL.

Effect of fixatives and other reagents on cell-size and tissue bulk. A. A. TARKHAN (J. Roy. Microscop. Soc., 1931, 51, 387—400).—Abs. EtOH produces the greatest shrinkage (chiefly on connective tissue) and exerts most of its effect in 2—3 hr. K₂Cr₂O₇ produces shrinkage in conc. solutions (4%), but swelling in a dilution of 0.02—1.0%. Picric acid behaves similarly. Saturated HgCl₂ shrinks both cellular and fibrous tissue. CH₂O (5—10%) does not cause any swelling in 2 days. A slight shrinkage is sometimes observed and toughening of the tissues occurs after >3 days' immersion. C₆H₆ shrinks tissues less than PhMe or xylene and penetrates rapidly; cedar oil produces the least shrinkage. The time of paraffin embedding should be minimal and the temp. > 2—3° above the m. p. of the wax in order to reduce shrinkage to a min. P. G. MARSHALL.

Vital staining and permeability. III. E. GELLHORN (Protoplasma, 1931, 14, 28—35; cf. A., 1931, 649).—The velocity of staining of sea-urchin eggs in standard buffer solutions is affected by previous exposure to neutral salt solutions, being increased by treatment with univalent and Mg chlorides and decreased by CaCl_2 and, to a smaller extent, by BaCl_2 . SrCl_2 has little effect. Ion antagonism previously recorded is based on the effects of ions on permeability. A. G. POLLARD.

Intramolecular rearrangement and the electric charges of dye. H. SULLMANN (Protoplasma, 1931, 13, 509—515).—The penetration and deposition of stains in living tissues is discussed in relation to solubility in electrolyte solutions, salting out, distribution of electric charges, and the internal rearrangement of the dye mol. A. G. POLLARD.

Kaijo of cocoons and their sericin particles. II. H. KANEKO (Bull. Sericult., Japan, 1931, 4, (2), 3—5; cf. A., 1931, 1322).—Measurements of viscosity, η , and electrophoresis have been made with sericin solution. R. CUTMILL.

Salivary lipase. H. KOEBNER (Z. ges. exp. Med., 1931, 76, 792—803; Chem. Zentr., 1931, ii, 863).—The saliva of a tortoise contained a lipase having max. activity at p_H 8.2. During human pregnancy the salivary lipase increases and remains high during lactation. A. A. ELDRIDGE.

Indoxyl (indican) in cow's and goat's milk. C. PORCHER and A. TAPERNOUX (Compt. rend., 1932, 194, 416—418).—Indoxyl is not present in goat's or cow's milk after administration of indole. Hervieux' positive results are shown to be due to the action of Obermayer's reagent on thymol in the colour test used by him. P. G. MARSHALL.

Protein and pseudoprotein in urine. H. PECKER (J. Pharm. Chim., 1932, [viii], 15, 18—21).—The presence of pseudoprotein is shown by an opalescence given by conc. aq. citric acid. Urine is filtered, NaCl added, heated to b. p., and AcOH added, whereby protein and pseudoprotein are pptd., removed by centrifuging, and weighed. True protein is determined by the "ring-test" with HNO_3 , the difference giving the pseudoprotein content, the pathological significance of which is discussed. F. O. HOWITT.

Composition of urine and blood of *Echidna aculeata*. M. L. MITCHELL (Austral. J. Exp. Biol., 1931, 8, 237—238).—The faeces-free urine is acid, has a normal mammalian P : N ratio, and a variable urea content, 7.8% being the max. val. found. The mean distribution of the total urinary N is : urea-82.0, NH_3 -6.4, creatinine-4.3, and uric acid-N 0.19%. A. COHEN.

Determination of sugar in urine. D. J. DE JONG (Pharm. Weekblad, 1932, 69, 41—43).—Examination of the Burman glycometer method led to the prep. of a stable solution by addition of KCNS and glycerol to Fehling's solution, by means of which rapid determinations may be made. S. I. LEVY.

Determination of uric acid and hydroxypurines in urine. A. E. COSTA (Anal. Fis. Quim., 1931, 29, 659—662).—The Kayser-le Breton method is satis-

factory, but double pptn. is essential; with single pptn. the results are high and erratic.

H. F. GILLBE.

Is blood-protein amide-nitrogen a source of urinary ammonia? T. P. NASH, jun., and E. F. WILLIAMS, jun. (J. Biol. Chem., 1932, 94, 783—808).—Protein is pptd. from blood or plasma by H_2WO_4 and the total and amide-N determined by the method of Bliss (A., 1929, 339), whose hypothesis (A., 1931, 110) of the NH_3 -providing function of the amide-N of the blood-proteins is criticised. Thus the increase in protein amide-N of the femoral venous blood following injection of $(\text{NH}_4)_2\text{CO}_3$ into the companion femoral artery, in the amide level following administration of HCl, and in the urinary NH_3 after work could not be substantiated. The non-increase in the blood-amide-N in the anuric dog also contradicts the theory.

F. O. HOWITT.

Determination of sulphur in urine. Photometric method. P. W. BOUTWELL and E. W. TOEPFER (Ind. Eng. Chem. [Anal.], 1932, 4, 117—119).—Inorg. SO_4^{--} in urine can be determined nephelometrically as BaSO_4 , and total SO_4^{--} can be determined similarly after hydrolysis with HCl. Total S may be determined by oxidising urine with HNO_3 and HClO_4 and then determining SO_4^{--} as BaSO_4 either nephelometrically or gravimetrically.

E. S. HEDGES.

Origin of aromatic intestinal poisons and urinary pigments. E. BECHER (Med. Welt, 1931, 5, 873—875; Chem. Zentr., 1931, ii, 1312).—Indole, cresol, and PhOH disappear from the urine of dogs surviving excision of the intestine. The urine then becomes pale in colour. Apparently urinary pigments, like aromatic intestinal poisons, arise from bacterial action in the intestine. A. A. ELDRIDGE.

Scattering of light in urines. S. RANGANATHAN (Indian J. Physics, 1931, 6, 463—466).—Wide variations are shown under pathological conditions, whilst normal urines vary over a comparatively small range. E. S. HEDGES.

Participation of metabolic processes in the formation of faeces. E. VOIT (Z. Biol., 1932, 92, 169—190).—In dogs the quantity of faeces excreted in the fasting condition is approx. proportional to the surface area of the animal. Foods appear to stimulate the intestinal mucous membrane and to increase the secretion of the material which ultimately goes to form a considerable proportion of the faeces, the rest coming from food residues. When animals are fed with fat, starch, or muscle-protein the faeces excreted per unit area is a linear function of the quantity of food ingested. Similar results have also been obtained with man. W. O. KERMAK.

Determination of fat in faeces. A. ALLODI and G. PALOMBA (Clin. Med. Ital., 1929, 60, 15 pp.; Chem. Zentr., 1931, ii, 603).—The faeces are dried to const. wt. at 45—50°, and 2—5 g. are extracted 3 times with 25 c.c. of abs. EtOH at 60—70°, then several times with aq. Et_2O , the united extracts being evaporated and the residue dissolved in 50 c.c. of Et_2O . 10 c.c. of the filtrate are titrated with 0.05N-alcoholic NaOH. The remaining 40 c.c. are treated with NaOH and neutralised with HCl; the residue from the

ethereal liquid consists of neutral fat, fatty acids, and unsaponifiable matter. Soaps may be present in the residue from the first treatment with EtOH.

A. A. ELDRIDGE.

Stercobilin and porphyrins from faeces. I. C. J. WATSON (*Z. physiol. Chem.*, 1932, 204, 57—67).—Cryst. *stercobilin hydrochloride* (I), m. p. 136—150°, probably $C_{33}H_{45}O_8N_4Cl$, was isolated from normal and pathological faeces. Elimination of HCl gave a semi-cryst. product, m. p. 116—148°. Reduction of (I) with AcOH-HI gave a cryst. acid, m. p. 159°, probably impure bilirubic acid. Deutero- and copro-porphyrin are both present in normal human faeces. The deutero-porphyrin probably arises normally from meat ingested, but was present in a case of haemolytic icterus on a meat-free diet. Coproporphyrin is found in larger than normal amounts in pernicious anaemia.

J. H. BIRKINSHAW.

Albuminuria. H. S. DIEHL and C. A. MCKINLAY (*Arch. Int. Med.*, 1932, 49, 45—55).—A correlation between albuminuria and various clinical data in adolescents is attempted.

H. DAVSON.

Tests for protein, especially Bence-Jones protein, in urine. E. E. OSGOOD and H. D. HASKINS (*J. Lab. Clin. Med.*, 1931, 16, 575—582).—Bence-Jones protein is detected by heating the urine with 0.2 vol. of 50% AcOH and 0.6 vol. of saturated NaCl solution. A ppt. appears at 40—65°, dissolves at 75—100°, and reappears on cooling to 70—90° or below.

CHEMICAL ABSTRACTS.

(a) **Determination of homogentisic acid in blood-serum and in the milk of the alcaptonuric.** F. LANYAR and H. LIEB. (b) **Iodometric determination of homogentisic acid in urine.** H. LIEB and F. LANYAR (*Z. physiol. Chem.*, 1931, 203, 135—141, 141—142).—(a) The protein is pptd. with a mixture of 10% Na_2WO_4 and 0.67N- H_2SO_4 . Phosphotungstic acid and borax are added to the filtrate, and the blue colour is observed in a colorimeter. The homogentisic acid present is then destroyed and a known quantity added. This observation gives the blank. The average homogentisic acid content of blood is 3—4 mg. per 100 c.c.

(b) A reply to Metz (*A.*, 1931, 113).

J. H. BIRKINSHAW.

Potency of liver extract. J. P. MCGOWAN (*Arch. Int. Med.*, 1932, 49, 26—44).—A biological assay of the strength of liver extract in pernicious anaemia is described.

H. DAVSON.

Calcium and magnesium in the human aorta and their variations in atheroma. A. POLICARD, A. MOREL, and P. P. RAVAUULT (*Compt. rend.*, 1932, 194, 201—203).—There is no parallelism between the variations in the amounts of Ca and Mg in the human aorta during the course of arterial sclerosis. The mineral impregnations consist mainly of Ca, the Mg taking no part, and it seems that the amounts of Mg diminish in the course of the formation of aortic lesions.

A. LAWSON.

X-Ray diffraction studies of calculi. S. RANGANATHAN (*Indian J. Physics*, 1931, 6, 433—444).—Uric acid in human calculi and $CaCO_3$ in cattle calculi exist in the cryst. state. In pigmented gall-

stones, cholesterol is deposited in a micro-cryst. state.

E. S. HEDGES.

Cholesterol content of the blood of healthy rats and of rats with Jensen sarcoma. F. DANNENBERG (*Biochem. Z.*, 1932, 244, 128—132).—The cholesterol contents of the blood of healthy male rats are very const., the mean val. with 15 animals being 96 mg. per 100 c.c. (76.1 free, 19.9 combined with fatty acid). Of 10 vals. for the blood of rats with sarcoma, 4 showed considerable increase (28%) and 2 considerable decrease (14.4%). The free and esterified cholesterol vals. are proportionally affected, but a relationship between the size and age of the tumour and the amount of disturbance is not detectable.

P. W. CLUTTERBUCK.

Vitamin-A in horse melanoma. S. V. GUDJOUSSEN [with G. OPPENHEIM] (*Z. Krebsforsch.*, 1930, 33, 155—157; *Chem. Zentr.*, 1931, ii, 1161).—Vitamin-A was not detected in the sarcoma or the musculature.

A. A. ELDRIDGE.

Biological effects of radioactive substances.

I. **Effects on a transplantable mouse carcinoma.**

II. **Effects on the normal rabbit.** J. W. SPIES (*Amer. J. Cancer*, 1931, 15, 2173—2181).—I. Small quantities of U and Th, when injected into tumour-bearing mice, accelerated the increase in vol. of the neoplasms and shortened life. Large doses sometimes produced acute nephritis.

II. Repeated intravenous injection of small quantities of a U-Th mixture into rabbits causes only doubtful temporary changes in blood-cholesterol and non-protein-N; hypoglycaemia may occur.

CHEMICAL ABSTRACTS.

Significance of the phosphorus intake in the diet and blood-phosphorus concentration in the experimental production of caries immunity and caries susceptibility in the rat. H. KLEIN and E. V. MCCOLLUM (*Science*, 1931, 74, 662—664).—The P-level in the diet is an important factor in producing caries susceptibility or immunity in the rat. Diets containing 0.4802 g. of P or less per 100 g. tend to induce caries when the Ca intake is 0.3424%. Diets reported (*A.*, 1931, 1083) to produce immunity contain 0.5282 g. or more of P per 100 g., and 0.4012 g. or less of Ca %. Caries arises in rats when blood-P falls below a crit. level (approx. 10.5+5 mg. of P per 100 g. of serum); this level appears to depend on the level of P, Ca, and vitamin ingested in the diet. Particle size does not appear to be the controlling factor.

L. S. THEOBALD.

Oral treatment of diabetes. I. **Bile acids as resorption agents for insulin.** E. WAHNCAU and F. BERTRAM (*Klin. Woch.*, 1931, 10, 486—488; *Chem. Zentr.*, 1931, i, 2493).—Insulin pills had no effect on the condition or metabolism in diabetes; large doses of "cholosulin" were also without effect on the blood-sugar, except that when given before sugar it somewhat delayed (but did not reduce) the hyperglycaemia. The effect is due to the bile acids.

A. A. ELDRIDGE.

Oral treatment of diabetes. IV. **Liver extract as resorption agent of insulin.** F. BERTRAM, S. HORWITZ, and E. WAHNCAU (*Klin. Woch.*, 1931, 10, 1214—1217; *Chem. Zentr.*, 1931, ii, 1310).—In only

one case (fasting) was orally administered insulin effective.

A. A. ELDRIDGE.

Determination of creatinine in diabetic blood. G. V. RUDD (Austral. J. Exp. Biol., 1931, 8, 203—208).—Myers' method ("Practical Chemical Analysis of Blood," 1924, 69) gives high results due (a) to a high glucose content of the blood causing darkening of the solution used for colour comparison, and (b) to an unknown chromogen in the blood. The first error is eliminated by removal of glucose by fermentation, but the results are still higher than those of the Folin-Wu method (A., 1919, ii, 308), which is only slightly affected by a high blood-sugar, and gives accurate vals. for tungstic acid blood-filtrates.

A. COHEN.

Diastase and skin. Effect of cutaneous administration of diastase on carbohydrate metabolism. B. OTTENSTEIN (Klin. Woch., 1931, 10, 1114—1116; Chem. Zentr., 1931, ii, 1013).—Capillary blood in skin disease had a diastase val. of 90—110 mg. per 100 c.c.; in diabetes the val. was 20—70, and normally 130—170. Cutaneous administration of diastase leads normally to a fall in the blood-sugar and a rise in the diastase; in diabetes there is first a rise in the blood-sugar, and then a fall to a lower val.

A. A. ELDRIDGE.

Functional psychoses and dispersion. H. B. LANG and J. A. PATERSON (J. Physical Chem., 1931, 35, 3425—3451; cf. Bancroft, A., 1931, 872, 1084).—Na amytal (a coagulating agent) and NaCNS (a peptising agent) were administered to 46 cases showing mental disorders. The results indicate that in dementia præcox and catatonia the nerve colloids are in a state of over-dispersion, and in maniacal-depressive psychoses, epilepsy, and benign stupor reactions they are in a state of decreased dispersion. The condition of the majority of cases in the first group was improved by the coagulating agent and aggravated by the peptising agent. The condition of a majority of those in the second group was improved by the peptising agent and aggravated by the coagulating agent.

C. T. SNELL (b).

Colloid chemistry of insanity. II. W. D. BANCROFT and J. E. RUTZLER, jun. (J. Physical Chem., 1931, 35, 3452—3479; cf. A., 1931, 1084).—The work of Lang and Paterson (see preceding abstract) supports the view that insanity is a physical disorder of the brain. Administration of Na amytal and NaCNS is indicated as a fundamental diagnostic test in cases of mental disorders.

C. T. SNELL (b).

Acidosis of nephritis. A. P. BRIGGS (Arch. Int. Med., 1932, 49, 56—76).—Acidosis in renal deficiency is associated with waste of fixed base due to the increased velocity of the fluids through the tubules preventing adequate reabsorption. NH_3 formation, which is depressed in nephritics, prevents excess acidity in the genito-urinary tract.

H. DAVSON.

Food intake in pregnancy, lactation, and reproductive rest in the human mother. C. F. SHUKERS, I. G. MACY, E. DONELSON, B. NIMS, and H. HUNSCHER (J. Nutrition, 1931, 4, 399—410).—The food ingested by rats increased by 19% in pregnancy, 111% in lactation, and 21% in post-lactation.

The intakes of energy, protein, fat, carbohydrate, Ca, and P for a reproductive cycle were determined for 3 women. Lactation increases the food demand by about 60% over that in pregnancy.

CHEMICAL ABSTRACTS.

Bones in experimental scurvy. G. BAYER (Beitr. path. Anat. allg. Path., 1931, 87, 204—208; Chem. Zentr., 1931, ii, 737).—The wt. and % composition scarcely differ from the normal.

A. A. ELDRIDGE.

Chlorine in experimental scurvy. A. MICHAUX (Bull. Soc. sci. Hyg. aliment., 1931, 19, 117—131; Chem. Zentr., 1931, ii, 737—738).—Lack of vitamin-C caused considerable retention of Cl owing to its effect on blood-sugar and muscular tissue. Administration of vitamin-C, even when much salt is given, leads to normal excretion.

A. A. ELDRIDGE.

Applications of colloid chemistry in the serum diagnosis of syphilis. H. EAGLE (J. Physical Chem., 1932, 36, 259—267).—The aggregation of an aq. suspension of antigen by syphilitic serum is wholly analogous to the aggregation of bacteria, red cells, or a dissolved antigen by the homologous antiserum. An explanation of the mechanism is given. Of the numerous sensitising substances found, sitosterol and the sterols from maize germ and wool are of practical importance. Their use as adjuncts to cholesterol causes a significant increase in the sensitivity of the Wassermann antigen, whilst the physical properties of the maize sterol have led to the development of a new simple and sensitive flocculation test for syphilis.

F. SAUNDERS (b).

Chemotherapeutic activities of indium in trypanosomiasis and syphilis. C. LEVADITI, J. BARDET, A. TCHAKIRIAN, and A. VAISMAN (Compt. rend., 1932, 194, 325—327).—In tartrate has a preventive and curative action against *T. evansi* in mice, but its action is uncertain against experimental syphilis in the rabbit and it is without either preventive or curative action on *T. brucei*, *Sp. duttoni*, or *Sp. gallinarum*.

W. O. KERMACK.

Experimental hyperindicanæmia and its relation to uræmia. M. S. S. EARLAM and A. BOLLIGER (Austral. J. Exp. Biol., 1931, 8, 209—216).—Following intravenous or rectal injection, indican is rapidly excreted through the kidneys by normal dogs, and more slowly by dogs with impaired renal function. In the latter cases toxic effects are not observed, although the plasma-indican vals. greatly exceed those found in uræmia. Large doses do not hasten the death of dogs previously subjected to the equiv. of bilateral nephrectomy. The toxic action of a massive and fatal dose of indican is attributed to the K content of the drug. Indican retention is therefore not a contributing factor in uræmia.

A. COHEN.

Oxidation-reduction potential of living tissue. D. OKUYAMA (J. Biochem. Japan, 1931, 14, 69—78).—The val. of E_h for living muscle tissue of frog and rat was 0.15 and for liver 0.10 volt. Death of the animal, ligation of the principal blood-vessels, or presence of narcotics resulted in a decrease of the potential.

F. O. HOWITT.

Oxidation-reduction potential in the snail, *Agriolimax agrestis*. E. AUBEL and R. LÉVY (Compt. rend. Soc. Biol., 1930, 105, 358—359; Chem. Zentr., 1931, i, 2488).

Lipschitz' nitro-reduction. K. HIKIJI and T. HASEGAWA (Arch. exp. Path. Pharm., 1932, 163, 672—686).—The reduction of $\text{o-C}_6\text{H}_4(\text{NO}_2)_2$ to $\text{NO}_2\text{-C}_6\text{H}_4\text{-NH-OH}$ by living cells is measured colorimetrically. Fresh muscle-tissue (frog, rabbit) kept at the physiological temp. loses in a few min. the greater part of its reducing power; this loss is equally great in N_2 or O_2 . Inhibition of reduction by NaCN is less in rabbit's muscle than in frog's and is greater in air or O_2 than in N_2 . The surface area between the reaction mixture with or without addition of NaCN determines the extent of reduction. Whereas frog's muscle loses the whole of its reducing power on treatment with air at 0° for 20 min., rabbit's muscle retains 50% of its reducing power. Short exposure to ultra-violet radiation diminishes the reducing power either in presence or absence of NaCN. The nitro-reduction power in different isotonic salt solutions conforms with the typical ionic series. Caffeine and thyroxine exert no effect on the reducing power, but EtOH (1 : 1000) causes an increase of 33%. C. C. N. VASS.

Energy metabolism and acid-base regulation. D. JAHN [with A. BÜRESCH and J. KIRCHBACH] (Deut. Arch. klin. Med., 1931, 170, 387—435; Chem. Zentr., 1931, ii, 871).—By the method described the O_2 demand and the processes of acid-base regulation can be observed together after work, oral administration of sugar, or treatment with histamine, adrenaline, or insulin. A. A. ELDRIDGE.

Measurement of growth of tissue *in vitro* by determination of the increase in metabolism. F. LIPMANN (Biochem. Z., 1932, 244, 177—186).—A method is described for determination of the increase in mass of a tissue from the increase in its metabolism. The O_2 -utilisation of growing heart fibroblasts is measured in plasma- $\text{PO}_4^{'''}$ solution and the increased metabolism accompanying the increase in tissue is determined manometrically in terms of the aerobic formation of acid. P. W. CLUTTERBUCK.

Proliferation of tissue cells *in vitro* and their metabolism. F. LIPMANN and A. FISCHER (Biochem. Z., 1932, 244, 187—189).—In 9 days the mass of heart fibroblasts as determined by the method of the preceding abstract increased by 12 times. P. W. CLUTTERBUCK.

Embryochemical investigations with the injection method. V. Behaviour of glycogen in the incubated hen's egg on sugar injection. E. KATAOKA (Z. physiol. Chem., 1931, 203, 272—278; cf. A., 1930, 952).—Glucose, fructose, mannose, galactose, maltose, and lactose, but not arabinose, xylose, or glucosamine, give rise to glycogen in the hen's egg during incubation. The action of hydroxymethylfurfuraldehyde is indefinite. The glycogen content of fresh and incubated eggs is less during the summer months than in winter. J. H. BIRKINSHAW.

Glycogen formation and respiratory quotients in rats fed exclusively on fat. D. E. GREGG (J.

Nutrition, 1931, 4, 385—398).—Rats fed on butter-fat exhibit a gradual formation of liver-glycogen averaging 3—4 times the concn. in control animals. The total glycogen content of fat-fed rats exceeds the controls by 22%. The amount of glycogen deposited is equiv. to about 2% of the ingested glycerol, and probably originates from this. The urinary N is generally depressed. No evidence of the conversion of fatty acids into carbohydrates was obtained.

CHEMICAL ABSTRACTS.

Glycogen and fat formation in rats. V. Carbohydrate-free diets. E. M. GREISHEIMER (J. Nutrition, 1931, 4, 411—418).—With rats fed on lard, caseinogen free from lactose, and salt mixture 185, increase in the % of lard increases the liver-lipins and decreases the -glycogen. The liver-wt. was greatest with diets low in lard.

CHEMICAL ABSTRACTS.

Glycogen formation in denervated muscle. J. BAUM (Klin. Woch., 1931, 10, 987; Chem. Zentr., 1931, ii, 1159).—Denervated extremity muscles have a high glycogen content, especially after 1—4 days. The increased glycogen content was observed with dehepatised, but not with depancreatized, frogs.

A. A. ELDRIDGE.

Lactic acid fermentation of warm-blooded tissue. V. Activation of anaerobic fermentation in the liver by pyruvic acid, acetaldehyde, and methylene-blue. O. ROSENTHAL (Biochem. Z., 1932, 244, 133—156).—Activation of anaerobic fermentation in the liver on addition of pyruvic acid is compared with the extra fermentation obtained when asphyxiation occurs some time after removal (cf. A., 1931, 765). The occurrence of the pyruvic acid effect and of extra-fermentation depends on the presence of a similar factor, and the supposed fermentation activator cannot be identical with pyruvic acid. Activation of fermentation to a similar extent is also obtained by addition of MeCHO and of methylene-blue.

P. W. CLUTTERBUCK.

Muscular contraction without formation of lactic acid. E. MARTINI (Klin. Woch., 1931, 10, 1031—1032; Chem. Zentr., 1931, ii, 1159—1160).—Frog's muscles poisoned with $\text{CH}_2\text{I-CO}_2\text{H}$ exhibit contraction at $30\text{--}35^\circ$ (normal $40\text{--}42^\circ$). Poisoned muscles contract in acidified Ringer solution at a higher temp. than in neutral solution. KCl, quinine, and caffeine cause contraction in poisoned muscle.

A. A. ELDRIDGE.

Swelling of normal muscle and of muscle poisoned with iodoacetic acid in rest and after work. S. L. ØRSKOV (Biochem. Z., 1932, 244, 33—41).—The vol. of centrifuged muscle-protein obtained from 1 g. of frog's muscle after freezing, pulverising, treating with H_2SO_4 , and keeping at 0° for 2—24 hr. is greater with active than with resting muscle.

P. W. CLUTTERBUCK.

Fate of glyoxals in the animal body. F. SAKUMA (J. Biochem. Japan, 1931, 13, 423—440).—The susceptibilities of glyoxals to alkaline hydrolysis or to glyoxalase action in decreasing order are as follows: methyl-, phenyl-, and hydroxymethyl-glyoxal, glucosone, and glyoxal. The subcutaneous and intravenous lethal doses of these compounds are determined. Examination of the blood and urine for the contents

of glyoxals, lactic acid, and sugar following administration shows a rather prolonged retention of the glyoxals in the blood, accompanied in most cases by an increase in the blood-sugar and lactic acid levels.

F. O. HOWITT.

Bile acids and carbohydrate metabolism. XI. Synthesis and fission of hexosephosphoric acid. Z. URAKI (J. Biochem. Japan, 1931, 14, 123—144).—The phosphorylation of fructose in liver-, kidney-, or muscle-tissue is increased by presence of Na cholate, inhibited by NaCl, and is dependent on the $[H^+]$ of the system. Na cholate inhibits the hydrolysis of fructose di- and mono-phosphoric acids, differences in the inhibitory effect being shown by different tissues according to which ester functions as substrate. The role of bile acids in glycogen formation is discussed.

F. O. HOWITT.

Action of ions on ageing in heart press-juices. H. WASSERMAYER (Z. physiol. Chem., 1931, 203, 241—254).—Heart and skeletal muscle show similar ageing phenomena, particularly in regard to the influence of ions, but heart muscle ages more slowly, and the press-juice is less sensitive to alkali. The buffering of the press-juices is similar; the lactic acid content does not explain the course of ageing. The formation of phosphagen on addition of $NaHCO_3$ occurs only slowly. On addition of adenosinephosphoric acid there is in both types of muscles a synthesis of $H_4P_2O_7$ which slowly reaches a max.

J. H. BIRKINSHAW.

Thyroid gland and carbohydrate metabolism. I. H. L. POPPER and S. HIRSCHHORN (Klin. Woch., 1931, 10, 1071—1072; Chem. Zentr., 1931, ii, 1017).—A relationship between the carbohydrate metabolism and the size of the struma is indicated.

A. A. ELDRIDGE.

Protein nutrition of the chick. I. Influence of different protein concentrates on growth. W. D. McFARLANE, W. R. GRAHAM, jun., and G. E. HALL (J. Nutrition, 1931, 4, 331—349).—Equal amounts of crude protein from buttermilk powder, fish meal, or meat meal (with marmite 15, cod-liver oil 3, bone ash to make total ash 4.36, white rice to 100%) had practically the same effect on growth. Mortality was high with fish and meat. The protein of cod-liver meal is biologically inferior for growth. Vegetable protein appears necessary for chicks.

CHEMICAL ABSTRACTS.

Relative values of proteins of linseed and cottonseed meals in nutrition of growing rats. W. W. BRAMAN (J. Nutrition, 1931, 4, 249—259).—A ration containing approx. 8% of linseed meal proteins was superior in promoting growth to one containing cottonseed meal. In each case the biological val. of the N was 78. The digestibility of cottonseed N was 9% less than that of linseed N, probably owing to the inclusion of hulls in the former.

CHEMICAL ABSTRACTS.

Physiological effect of rations restricted principally or solely to lucerne. II. J. R. HAAG (J. Nutrition, 1931, 4, 363—370).—The crude proteins are deficient in cystine.

CHEMICAL ABSTRACTS.

Influence of temperature on protein metabolism. I. Nitrogenous extractives of toad's liver

during summer. S. SIBUYA (J. Biochem. Japan, 1931, 14, 111—122).—The NH_2 -acid and purine content are increased during summer when the nature of the food ingested demands an increased protein metabolism to maintain the requirements of fat and carbohydrate. The marked increase in the liver-tyrosine is discussed with reference to the formation of melanin and thyroxine. F. O. HOWITT.

Function of the intestinal wall and the liver in absorption of the products of protein digestion. R. MARTENS (Bull. Soc. Chim. biol., 1931, 13, 1187—1198).—Following ingestion of peptone by dogs, larger increases of polypeptide-N in the portal vein than in the carotid are obtained, showing the possibility of the passage of peptide mols. through the intestinal walls. Increases of the polypeptide-N in the hepatic over that in the portal vein after (a) ingestion and (b) direct injection into the portal vein of NH_2 -acids confirm the results of previous workers, viz., that the intestinal wall and the liver are capable of synthetic action. A comparison of the vals. obtained for the NH_2 - and polypeptide-N in the portal, splenic, and renal veins of dogs, fasting, and after injection of NH_2 -acids into the portal vein, show that these vals. increase after injection in all cases.

A. LAWSON.

Blood-amino-acids. Changes following ingestion of protein or milk. C. GIAUME (La Pediatria-Arch., 1931, 3, 17 pp.; Chem. Zentr., 1931, ii, 867).—The blood- NH_2 -N curve of dogs and the distribution between serum and corpuscles after ingestion of protein have been studied. When young animals are fed with mother's milk there is no marked rise in blood- NH_2 -N, but a rise was observed on feeding with cow's milk. It is concluded that foreign proteins undergo more rapid combustion and absorption.

A. A. ELDRIDGE.

Causes of the specific dynamic action of food-stuffs. I, II. E. LUNDGAARD (Skand. Arch. Physiol., 1931, 62, 223—242, 243—281; Chem. Zentr., 1931, ii, 1444—1445).—I. The actions of various NH_2 -acids and N-free org. acids on rabbits and cats have been compared. The action of NH_4 salts is similar to that of NH_2 -acids.

II. Glycine, alanine, glutamic acid, aspartic acid, and tyrosine are active for the dog. NH_4 glycollate and lactate act similarly to NH_2 -acids. The sp. dynamic action of N-free foods is attributed to the increased availability of oxidisable material, whilst that of proteins is preferably explained by the irritation theory.

A. A. ELDRIDGE.

Tryptophan metabolism. II. Growth-promoting ability of *dl*-tryptophan. C. P. BERG and M. POTGIETER (J. Biol. Chem., 1932, 94, 661—673).—The addition of 0.05% *l*-tryptophan is necessary for maintenance of wt. in rats fed on a tryptophan-deficient diet, whilst a supplement of 0.2% permits a normal rate of growth. Replacement of the *l*-isomeride by double the amount of the *dl*-form results in an increase of rate of growth, indicating that more than the naturally occurring component is utilised. Replacement by the same amount of *dl*-tryptophan results in no significant difference in growth. Hence

tryptophan deficiency is remedied by the *dl*-form with approx. the same facility as by the *l*-isomeride.

F. O. HOWITT.

Behaviour of a homologue of creatine in the animal body. F. TECHNER (Ber. Sachs. Ges. Wiss., math.-physikal. Kl., 1930, 82, 219—226; Chem. Zentr., 1931, ii, 1447).—On subcutaneous injection of ϵ -methylguanido-hexoic acid into dogs, 54.7 (or on taking into account blank experiments 72%) or on oral administration 6.5% was found in the urine. Degradation products were not found. Creatine may be formed immediately. Data concerning the solubility of picrolonic acid and its compounds with methylguanido-butyric and -hexoic acids and creatinine are recorded.

A. A. ELDRIDGE.

Origin of uric acid in birds. G. PUPILLI (Biochim. Terap. sperim., 1930, 17, 113—127; Chem. Zentr., 1931, ii, 466).—Oral administration of org. compounds containing a three-C chain (lactic, formylglyoxylic, glyceric, and tartaric acids) simultaneously with intramuscular administration of urea increases the excretion of uric acid proportionally to the quantity of urea given. The same action is shown by urea alone. Urea and tartaric acid (which may originate from lactic acid through glyceric and hydroxypyruvic acids) participate in the formation of uric acid; mesoxalic and malonic acids do not.

A. A. ELDRIDGE.

Factors which determine renal weight. XII. Nitrogen intake as varied by the addition of urea to the diet. L. L. MACKAY, E. MACKAY, and T. ADDIS (J. Nutrition, 1931, 4, 379—383).—The increase in wt. of the kidneys of rats is less than that produced by consumption of the same amount of N as protein.

CHEMICAL ABSTRACTS.

Influence of diets containing excess of acid on the amount of nitrogen excretion. E. F. TERROINE and M. CHAMPAGNE (Compt. rend., 1932, 194, 203—206).—The addition of excess of acid (H_3PO_4 and HCl) to a carbohydrate diet which reduces the N excretion of pigs to the min., causes large increases in the amount of total N excreted, in accordance with the amount of added acid. Whilst the urea excretion diminishes, that of NH_3 and NH_2-N always increases, creatinine and allantoin vals. remaining const. The protein metabolism only is affected.

A. LAWSON.

Mineral exchange of man. I. S. H. BASSETT, C. A. ELDEN, and W. S. McCANN (J. Nutrition, 1931, 4, 235—248).—The organisation and methods of award for the study of metabolism are described. Analysis of complete diets for Ca gave results lower than those calc. from composition tables; results for N, P, K, Mg, and Fe were only slightly low, whilst those for Na were consistently high. Methods are described.

CHEMICAL ABSTRACTS.

Retention of calcium in the growing and adult organism. E. HESSE (Klin. Woch., 1931, 10, 1067—1068; Chem. Zentr., 1931, ii, 1158).—When young, but not older, rats are fed for 6—8 weeks on a $K-PO_4$ prep. there is a marked storage of K and PO_4 .

A. A. ELDRIDGE.

Influence of bile acids on calcium metabolism. IV. Faecal calcium following administration of

bile acids. K. FUZIWARA (J. Biochem. Japan, 1931, 13, 465—471).—The faecal Ca, which is normally dependent on the diet, is decreased following subcutaneous administration of Na cholate to dogs.

F. O. HOWITT.

Calcium and phosphorus supply of dairy cows. R. G. LINTON (Agric. and Live Stock, India, 1931, 1, 673—687).—The divergence of opinion as to the % utilisation by milch cows of ingested Ca and P is discussed, and the significance of the use of high-ash hay and of the effect of vitamin-D in increasing Ca and P absorption is emphasised.

A. G. POLLARD.

Magnesium and the growth of the rat. Magnesium in the absence of vitamin-A. J. LAVOLLEY (Bull. Soc. Chim. biol., 1931, 13, 1205—1209, 1210—1213).—To a diet containing caseinogen 17 g., dextrin 5 g., starch 28 g., sucrose 20 g., arachis oil 15 g., filter-paper 7 g., Ca lactate 2.6 g., salts 4 g., and preps. of vitamin- B_1 , $-B_2$, $-A$, and $-D$ and found by analysis to contain 3 mg. Mg per 100 g., successive quantities of $MgCl_2$ were added. Rats fed on this diet required a min. of 30—50 mg. of Mg per 100 g. for normal growth as compared with controls fed on the same diet containing supplements of 73 and 52 mg. of Mg per 100 g. Below this min. the growth decreased greatly. The growth of rats fed on the above diet, but containing in addition 4 g. of dried yeast, and no vitamin-A, is unaffected by progressive increase of the Mg content from 30 to 118 mg. per 100 g.

A. LAWSON.

Metabolism of sulphur. XVIII. Distribution of urinary sulphur in the rabbit following administration of bromobenzene. S. A. LOUGH and H. B. LEWIS (J. Biol. Chem., 1932, 94, 739—747).—Oral administration of PhBr (0.4—0.7 g. per kg.) results in an increased excretion of ethereal SO_4 and org. S and in a decreased excretion of inorg. SO_4 . These changes indicate a metabolism of halogen derivatives of C_6H_6 in rabbits similar to that occurring in dogs, i.e., there is a limited synthesis of phenylmercapturic acids.

F. O. HOWITT.

Detection of carbon monoxide in exhumed cadavers. W. WEIMANN (Deut. Z. ges. gerichtl. Med., 1931, 17, 48—50; Chem. Zentr., 1931, ii, 1035).—CO was detected chemically and spectroscopically after 50 (summer) days in the liquid expressed from internal organs, particularly the lungs and spleen.

A. A. ELDRIDGE.

Solubility coefficients of ethyl chloride in water and in water containing dissolved hæmoglobin or one of its derivatives. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1931, 106, 222—224; Chem. Zentr., 1931, ii, 260).—Addition of hæmoglobin, reduced hæmoglobin, or methæmoglobin increases the solubility of $EtCl$. This corresponds with the action of serum or blood.

A. A. ELDRIDGE.

Effect of denatured hæmoglobin on the solubility of ethyl chloride in water. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1931, 106, 224—226; Chem. Zentr., 1931, ii, 260).—Hæmoglobin denatured by heat or boiling $EtOH$ has the same effect as normal hæmoglobin.

A. A. ELDRIDGE.

Determination of the solubility of ethyl chloride in solutions of hæmatin. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1931, 106, 226—229; Chem. Zentr., 1931, ii, 260).—The solubility of EtCl in 0.5% hæmatin solution is higher than that in H₂O or 0.1N-NaOH and of the same order as in blood or hæmoglobin solutions. A. A. ELDRIDGE.

Effect of anæsthesia on blood-sugar. E. C. MECKIE (Surgery, Gyn., Obstet., 1931, 53, 329—337).—Et₂O anæsthesia is associated with hyperglycæmia owing to mobilisation of liver-glycogen.

CHEMICAL ABSTRACTS.

Determination of "avertin" in blood. E. ENDREJET (Arch. exp. Path. Pharm., 1932, 163, 708—712).—The Et₂O extract of blood is treated with 5% KOH in EtOH and the Et₂O removed at 40°; the residue is refluxed for 2 hr. at 50° and the Br determined. By this method, 95—99% of "avertin" dissolved in blood is determined. C. C. N. VASS.

Test of a new local anæsthetic group. Pharmacology of aminoethoxybenzthiazole. K. BALLOWITZ (Arch. exp. Path. Pharm., 1932, 163, 687—699).—2-Amino-6-ethoxybenzthiazole is insol. in H₂O and is not decomposed in acid, neutral, or alkaline aq. media. Its chloride (solubility 1 : 9) is a typically active local anæsthetic comparable with cocaine. Either intravenously or subcutaneously its toxicity is comparable with that of novocaine, particularly in warm-blooded animals. C. C. N. VASS.

Determination of the activity of hypnotics by means of body position and labyrinth reflexes.

I. Relative activities of "novonal," "neodorm," and "veronal." O. GÜRNT (Arch. exp. Path. Pharm., 1932, 164, 118—157).—The method for evaluating hypnotic activity shows that novonal is approx. 1.1—1.3 times as active as veronal and that the activity of neodorm relative to that of veronal varies with the depth of narcosis, neodorm being more active with light and veronal with deep narcosis. Observations have also been made on the "narcotic range," the time of reaching max. activity, and on the duration of narcosis. W. O. KERMAK.

Therapeutic activity of various compounds of the adrenaline series. A. RUHL (Arch. exp. Path. Pharm., 1932, 164, 8—32).—The comparative activities of derivatives of CH₂Ph·CH₂·NH₂ tested on experimental animals or surviving organs agree with those found by clinical tests in man. The action of the compounds on the heart and coronary circulation and on the blood-vessels in mild and severe collapse has been determined. Adrenaline remains relatively potent in severe collapse, the other compounds becoming relatively weaker with increasing severity of impairment of the circulation. W. O. KERMAK.

New class of choline esters. H. KREITMAIR (Arch. exp. Path. Pharm., 1932, 164, 346—356).—Carbamylcholine chloride, NMe₃Cl·CH₂·CH₂·O·CO·NH₂, a relatively stable compound, the aq. solutions of which are unaltered on boiling, closely resembles acetylcholine in its toxic and pharmacological actions, but is quantitatively considerably more powerful. W. O. KERMAK.

Peptide-nitrogen during serum and histamine shocks. R. MARTENS (Bull. Soc. Chim. biol., 1931, 13, 1199—1204).—In the course of shocks caused by the injection of horse serum and of histamine into dogs, there is no appreciable difference in the amount of free polypeptide in the arterial blood. Both the urea and the NH₂-acid content, however, increase. A. LAWSON.

Action of some pyridine derivatives on uric acid excretion. R. CIUSA and L. MUSAJO (Annali Chim. Appl., 1931, 21, 553—558).—2-Phenylpyridine-4-carboxylic acid increases uric acid in the urinary secretion. O. F. LUBATTI.

Colloid osmotic (onkotic) pressure. XVIII. Action of various diuretics on the colloid osmotic pressure. E. KYLIN (Arch. exp. Path. Pharm., 1932, 164, 33—39).—"Salyrgan," "diuretin," and caffeine tend to lower the colloid osmotic pressure of the serum of rabbits, whilst "euphyllin" tends to raise it. W. O. KERMAK.

Quinotoxine. I. Detection of quinotoxine in presence of quinine. M. BACHSTEZ. **II. Toxicity of quinotoxine.** L. DE CARO (Arch. exp. Path. Pharm., 1932, 164, 314—323).—I. Small quantities of quinotoxine may be detected in presence of quinine by addition to 1 c.c. of the aq. solution of the hydrochloride of 2 drops of 5% Na nitroprusside and 5 drops of 30% Na₂CO₃·10H₂O. A characteristic red colour within 4 min. indicates the presence of quinotoxine, which may be detected when 0.125 mg. is present in 1 c.c. of a solution containing 1% of quinine.

II. The toxic action of quinine and quinotoxine on mice and white rats is not a simple additive function of the toxicities of the two components.

W. O. KERMAK.

[Pharmacological] action of synthetic papaverine derivatives. **I.** B. VON ISSEKUTZ, M. LEINZINGER, and Z. DIRNER. **II.** B. VON ISSEKUTZ, A. NYARY, and E. BOTZ (Arch. exp. Path. Pharm., 1932, 164, 158—172, 173—187).—I. Of the three compounds, 6 : 7-dimethoxy-1-(3 : 4-diethoxybenzyl)-, 6 : 7-diethoxy-1-(3 : 4-dimethoxybenzyl)-, and 6 : 7-diethoxy-1-(3 : 4-diethoxybenzyl)-isoquinoline, the last, "perparin," is the most active pharmacologically and least toxic, being superior to both papaverine and "eupaverin," 3-methyl-6 : 7-methylenedioxy-1-(3' : 4'-methylenedioxybenzyl)-isoquinoline.

II. Perparin is more powerful than papaverine or eupaverin in weakening heart action, decreasing pulse frequency and amplitude, and in bringing about vaso-dilatation, and preventing constriction by adrenaline in the perfused rabbit's ear. Perparin and papaverine also lower the blood-pressure and increase the frequency and depth of breathing.

W. O. KERMAK.

Detection of strychnine in cases of poisoning. A. W. NUNN (Pharm. J., 1932, 128, 145).—The organs are digested for 2—3 hr. in warm 2% aq. HCl and the digest is dialysed for 24 hr. in distilled H₂O several times. The H₂O is evaporated to half its bulk and tested with Mayer's reagent. If the test is positive it is evaporated to small vol., made alkaline with aq. NH₃, and extracted with CHCl₃. The CHCl₃ is

removed and the residue tested with $K_2Cr_2O_7$ and H_2SO_4 .
H. DAVSON.

Mechanism of the antiglycosuric action of santonin. A. LEULIER and (MME.) A. ROCHE (Bull. Soc. Chim. biol., 1931, 13, 1268—1277).—A more detailed account of work already noted (A., 1931, 1087).

[Pharmacological] action of *Pinellia tuberifera*. P. ROBOZ (Arch. exp. Path. Pharm., 1932, 164, 1—7).—Extracts made from the root nodules of *P. tuberifera* decreased the activity of mice and the vomiting in dogs produced by apomorphine.

W. O. KERMAK.

Blood and urine following bromide injection. A. B. HASTINGS, H. N. HARKINS, and S. K. LIU (J. Biol. Chem., 1932, 94, 681—695).—Injections of NaCl and NaBr in dogs is followed by distribution ratios of Br concn. between erythrocytes and serum uniformly greater than those of Cl. Presence of Br' lowers the Cl' ratios, confirming the stronger attraction of the red blood-cells for Br' than for Cl'. The kidneys appear to excrete Cl' more readily than Br', an injection of NaBr causing practically as great an excretion of Cl' as an equal injection of NaCl. The two salts also produce a marked change in the blood- H_2O balance and in the CO_2 level, accompanied by a moderate hyperpnoea.

F. O. HOWITT.

Method of action of calcium. II. Antagonistic heart actions of calcium and magnesium in normal calves. III. In oxen with abnormal mineral metabolism. B. SJOLLEMA, L. SEEKLES, and F. C. VAN DER KAAJ. IV. Calcium-magnesium antagonism in magnesium narcosis in young calves. L. SEEKLES and B. SJOLLEMA (Biochem. Z., 1932, 244, 1—4, 5—8, 167—176).—II. Intravenous injection of $CaCl_2$ or $MgCl_2$ causes similar heart disturbances in young calves, whereas injection of a mixture in the correct proportions (4 parts $CaCl_2 \cdot 6H_2O$ and 1.5 parts $MgCl_2 \cdot 6H_2O$) has a much less injurious effect.

III. The decrease of toxicity of $CaCl_2$ by mixing with $MgCl_2$ is proved experimentally in 30 cows with abnormal mineral metabolism.

IV. After intravenous injection of Mg salts into calves (3—5 days old) narcosis is not obtained in spite of the lowering of the serum-Ca/Mg ratio to 1 or even to 0.58. After previous decrease of the serum-Ca by intravenous injection of oxalate, intravenous injection of Mg brings about narcosis lasting only a few min., the Ca/Mg ratio then being 0.8—0.9. The duration of narcosis may be increased by injecting $MgSO_4$ simultaneously with MgC_2O_4 , the ratio then being 1.1—1.27. Narcosis is also produced by subcutaneous injection of $MgSO_4$ without previous injection of MgC_2O_4 , the ratio then being 1.32.

P. W. CLUTTERBUCK.

Absorption and excretion of gold thio-compounds. A. LUMIERE and JULLIARD (Compt. rend. Soc. Biol., 1930, 105, 396—398; Chem. Zentr., 1931, ii, 267).—24 hr. after the injection of "allochrysin" into guinea-pigs most of the Au has disappeared from the blood, but Au is detectable for 5—7 days. The Au is dissolved in the plasma. A. A. ELDRIDGE.

Effect of the antagonism of sodium and calcium on the biological action of ultra-violet

rays. G. TEICHLER (Pflüger's Arch. Physiol., 1931, 227, 558—570; Chem. Zentr., 1931, ii, 1446—1447).—The coagulability of albumin by ultra-violet light is less in NaCl or CaCl₂ solution than in a mixture. The change in fluorescing power after ultra-violet irradiation is independent of the salt medium. Hence cation antagonism has no effect on the primary photochemical processes in the irradiated protein mol. Irradiated euglobulin solutions show a much higher fluorescing power than non-irradiated, but no greater coagulation. With progressive acidification the irradiated solutions are much more sensitive to coagulation than non-irradiated. Similar effects of the salt medium are observed in the irradiation of yeast and catalase.
A. A. ELDRIDGE.

Selective action of living tissue to homogeneous radiation. W. MORPETT (Nature, 1932, 129, 133).—The formula connecting biological response with wave-length max. (A., 1931, 122) may be associated with a series of nuclear energy levels in one of the light atoms which form the main bulk of living tissues.

L. S. THEOBALD.

Mechanism of oxidation processes. XXIX. Dehydrogenating enzymes of milk. IV. H. WIELAND and W. MITCHELL (Annalen, 1932, 492, 156—182).—The dehydrogenation reaction with methylene-blue in the system enzyme-xanthine+MeCHO is studied further (cf. A., 1931, 389), with particular reference to the amount of uric acid formed. With more xanthine (or hypoxanthine) than is necessary for the hydrogenation of the methylene-blue and a large excess of MeCHO, the whole of the dye is used for the dehydrogenation of the purine to uric acid; increase in the concn. of MeCHO raises the time of decolorisation and decreases the no. of enzyme units (cf. A., 1930, 248). With less xanthine than is necessary for the hydrogenation of the dye and the same concns. of MeCHO, the whole of the base is again converted into uric acid; decolorisation is slower in these cases than with MeCHO alone. The enzymic dehydrogenation of MeCHO with *p*-benzoquinone (freshly-prepared solutions in air-free H_2O must be used) at pH 6.8 occurs more rapidly than with methylene-blue; reaction is, however, soon retarded (with small amounts of the enzyme) (owing to its destruction). With xanthine (or hypoxanthine), the velocity is slower than with MeCHO, but with mixtures of xanthine and MeCHO reaction occurs more readily than with either constituent alone, and the increase in velocity is more marked with diminished MeCHO concns. in the mixtures. In all these experiments with the quinone the velocities are measured by the rate of disappearance of the quinone, which is used mainly for the dehydrogenation of the MeCHO. These results again indicate (cf. *loc. cit.*) that xanthine- and aldehyde-dehydrogenases are different enzymes. The amount of O_2 absorbed (from air) by a mixture of hypoxanthine and enzyme is increased by the addition of methylene-blue; *p*-benzoquinone has a strong inhibitory action on the similar uptake of O_2 by xanthine + enzyme.

$CuSO_4$, $HgCl_2$, $AgNO_3$, $Pb(OAc)_2$, $FeSO_4$, $ZnSO_4$, and As_2O_3 all retard (to varying extents) the enzymic dehydrogenation of xanthine in presence of methylene-

blue; Cr, Ni, Co, Mn, Cd, and Tl salts cause practically no retardation. The retardation caused by HgCl_2 , HAuCl_4 , or AgNO_3 is completely inhibited by KCN (if sufficient is used for the formation of complex cyanides). KCN has, however, no effect on the retardation caused by Fe, Pb, and Zn salts. Metal ions are responsible for the retarding effects. Pptn. of the enzyme by CuSO_4 or HgCl_2 causes inactivation, whilst preliminary treatment of the enzyme solution with H_2S causes a loss in activity towards xanthine + methylene-blue of about 50%.

Bz·CHO can be dehydrogenated with milk enzyme in presence of methylene-blue. H. BURTON.

Mechanism of oxidation processes. XXX. Dehydrogenating enzyme-system of yeast. H. WIELAND and O. B. CLAREN (Annalen, 1932, 492, 183—212).—Suspensions of 2 g. of fresh, well-washed yeast (pure bottom yeast is used for all the experiments) in 35 c.c. of half-saturated buffered PhMe- H_2O are shaken in O_2 in Barcroft-Warburg vessels for 15 hr. at 30° , the evolved CO_2 being removed with KOH. The resulting suspension of "impoverished" yeast (I) ferments glucose as readily as fresh yeast; the spontaneous fermentation and self-respiration of (I) are minimal. PhMe, unlike thymol and CHCl_3 , has little effect on the O_2 -consumption of yeast suspensions at p_H 6.8. The O_2 -consumption of mixtures of (I) and EtOH is a linear function of time at all the concns. ($M/4$ — $M/120$) of EtOH studied; the reaction velocity is the same whether O_2 or air is used, and phosphate buffer (optimum concn. $M/20$) accelerates slightly the O_2 -uptake. EtOH is also dehydrogenated by (I) + methylene-blue in N_2 ; the reaction velocity is much slower than with O_2 , probably due to the difficulty of the large mols. of the dye in penetrating the yeast-cells. Experiments on the O_2 - and methylene-blue-consumption of fresh and dry yeasts (same stock) in absence and presence of EtOH (concn. $M/40$) indicate that the dehydrogenations with O_2 and the dye could occur through different enzymes. It is very improbable that two enzymes do exist, and the fact that methylene-blue is decolorised by dry yeast 7 times as fast as by fresh yeast (for the same O_2 -consumptions) is explicable by a loss of 80% of the enzyme on drying and a seven-fold increase of the active surface accessible to the dye.

The absorption of O_2 by mixtures of (I) and MeCHO increases with diminished concn. of MeCHO and is optimal at $M/120$ — $M/180$; reaction is slower than for EtOH, and the use of air for O_2 definitely decreases the velocity. The O_2 -consumption of fresh yeast is decreased slightly by Ac·CHO in concn. of $M/40$, whilst the CO_2 -production increases; with (I), the same concn. of Ac·CHO increases the O_2 -consumption to about the same val. as for EtOH, but the amount of CO_2 produced increases only slightly. The amounts of methylene-blue consumed and CO_2 evolved in the dehydrogenation of Ac·CHO with the dye (M) and (I) in N_2 indicate that the following changes occur: $\text{Ac}\cdot\text{CH}(\text{OH})_2 + \text{M} \rightarrow \text{Ac}\cdot\text{CO}_2\text{H} + \text{MH}_2$; $\text{Ac}\cdot\text{CO}_2\text{H} \rightarrow \text{MeCHO} + \text{CO}_2$. The same enzyme is responsible for the dehydrogenation of EtOH, MeCHO, and Ac·CHO. Preliminary work on the dehydrogenation of lactic acid by (I) + O_2 is reported.

The above aerobic dehydrogenation of EtOH gives AcOH as the sole product. MeCHO and (I) in N_2 give AcOH and EtOH by a Cannizzaro reaction; in O_2 , EtOH and a larger quantity of AcOH are produced. In this case some MeCHO is dehydrogenated directly to AcOH and some of the AcOH is oxidised further [it is shown that $M/30$ -NaOAc admixed with (I) absorbs O_2 at about the same rate as EtOH]. H. BURTON.

Aldehydease of liver. L. REICHEL and H. BERCZELY (Z. physiol. Chem., 1931, 203, 178—182).—Aldehydease from horse's or hog's liver was purified by extraction of the crude product with glycerol and pptn. from the latter by COMe_2 and H_2O . This product showed an activity 20 times that of the original. J. H. BIRKINSHAW.

Amylases in resting and germinating seeds. I. Barley. G. NORDH and E. OHLSSON (Z. physiol. Chem., 1932, 204, 89—100).—The amylase of ungerminated barley is pure saccharogenamylase (β -amylase), the amount of which increases steadily during germination. Dextrinogenamylase (α -amylase) first arises during germination about the end of the first week and its production proceeds with great rapidity. The formation and amount of each enzyme present are completely independent of the other.

J. H. BIRKINSHAW.

Vegetable amylases. Diastase action in absence of maltose. A. S. SCHULTZ and Q. LANDIS (J. Amer. Chem. Soc., 1932, 54, 211—220).—Diastatic action of certain vegetable amylases in absence of inhibitive agencies such as maltose, irreversible adsorption on interfaces due to shaking, or on diatomaceous earth or filter-paper pulp, is a linear function of time and enzyme concn. throughout large variations in substrate concn. Adsorptive agents such as extended liquid-vapour surface films caused by continued shaking, diatomaceous earth, or filter-paper pulp have marked inhibitive effects. The initial presence of small amounts of saponin, gelatin, albumin, caseinogen, or peptone, however, prevents this inhibition. Glycine and agar have no effect. Unpurified, ground soya-bean diastase, unlike the enzymes of wheat flour and malt syrup, does not appear to be subject to adsorption at extended liquid-vapour surface films caused by shaking. The Michaelis const. for a flour diastase is about 0.25 in terms of percentage substrate concn. A convenient method for the determination of diastatic activity is described; the sugars are fermented by yeast as rapidly as they are formed, and the resulting CO_2 is measured.

C. J. WEST (b).

Pancreatic enzymes. XVIII. Chemical nature of pancreatic amylase. E. WALDSCHMIDT-LEITZ and M. REICHEL (Z. physiol. Chem., 1932, 204, 197—203; cf. A., 1925, i, 741).—Pancreatic amylase is freed from other enzymes by one treatment with $\text{Al}(\text{OH})_3$ followed by three treatments with kaolin. In this way the impurities are removed, the purified amylase not being adsorbed. Three treatments of this product with $\text{Al}(\text{OH})_3$ C_7 at neutral reaction (the third with addition of EtOH), one treatment with $\text{Fe}(\text{OH})_3$ at p_H 5, and pptn. of the mother-liquor from the Fe adsorption with 2 vols. of COMe_2 yields a product which is free from protein. J. H. BIRKINSHAW.

Action of tetramethylammonium hydroxide, choline, and their hydrochlorides on the activity of amylolytic enzymes. F. CAUJOLLE and J. MOLINIER (Compt. rend. Soc. Biol., 1930, 104, 294—295; Chem. Zentr., 1931, ii, 584).—The bases depress the amylolytic activity of saliva, pancreas, and aq. malt extract; the hydrochlorides, however, have a favourable influence on the amylolytic action of the saliva and pancreas, but not on that of aq. malt extract.

A. A. ELDRIDGE.

Enzymic amylolysis. II. Amylokinase, a natural activator of starch degradation in germinating barley. E. WALDSCHMIDT-LEITZ and A. PURR (Z. physiol. Chem., 1931, 203, 117—131; cf. this vol., 193).—Germinating barley shows proteolytic before amylolytic activity. A peptidase is formed showing max. activity at the same time as the proteinase. Amylokinase remains after adsorption of amylase with $\text{Al}(\text{OH})_3 \text{ C}_7$ at p_{H} 5. The kinase accelerates the action of barley amylase; the course of the reaction becomes linear. The activation is independent of reaction and of time; in this respect amylokinase is contrasted with enterokinase. Zooamylase (from pancreas) is activated little at p_{H} 6.8, but strongly at acid reaction by amylokinase. The unit of the latter is defined; the activator is most stable at p_{H} 5, is inactivated in 30 min. at 100° , is non-dialysable, and adsorbed by $\text{Al}(\text{OH})_3 \text{ C}_7$ at neutrality and by $\text{Fe}(\text{OH})_3$.

J. H. BIRKINSHAW.

Glutathione in metabolism. H. PRINGSHEIM, H. BORCHARDT, and H. HUPFER (Naturwiss., 1932, 20, 64).—Oxidised glutathione, $[\alpha]_D -100^\circ$, behaves as an activator of amylase, whilst dithioglycollic acid, m. p. 105° , is inactive.

P. G. MARSHALL.

Action of enzymes of the gastric juice of *Helix pomatia* and of barley-malt on cellulose glycol ether. W. ZIESE (Z. physiol. Chem., 1931, 203, 87—116).—The gastric juice of *H. pomatia* quickly degrades, but does not completely hydrolyse, H_2O -sol. hydroxyethylcellulose (prepared from cellulose and ethylene oxide). The change is detected by the fall in viscosity. Dil. solutions of the enzyme resist heating for 5—10 min. at 100° . Cu^{++} shows some inhibitory action; the Cu-HCN complex is more powerful. Cysteine and glutathione are strongly inhibitory, $\text{Na}_2\text{S}_2\text{O}_3$ and H_2S inactive. The poisoning effect of the active substances is much less with a citrate than with a phosphate buffer.

Barley malt similarly degrades hydroxyethylcellulose and shows greater resistance to the inhibitors of *Helix* juice. In a mixture of *Helix* (1 : 2000) and malt (1 : 5) enzymes the *Helix* enzyme is still inactivated by the inhibitors, whilst the malt enzyme is unaffected.

J. H. BIRKINSHAW.

Enzymic histochemistry. II. Peptidase distribution in the root and leaf-germ of the malt grain. K. LINDERSTRÖM-LANG and H. HOLTER (Z. physiol. Chem., 1932, 204, 15—53; cf. A., 1931, 1455).—The dipeptidase activity of small sections of the primordial roots and leaf-germs of germinating barley was examined by transfer of the sections (cut after embedding the organ in paraffin wax) to a peptidase solution and micro-titration of the NH_2 groups. The enzyme was not transferred to the substrate, but

the rate of diffusion of the substrate through the cell-walls was fully sufficient for the purpose. There was a considerable variation of activity along the root, which showed a sharp max. at 0.8 mm. from the tip; the leaf-germ showed little variation along its length. The ratio of rate of hydrolysis of alanyl-glycine to that of leucyl-glycine is least in the growth zone of the root tip and greatest in the remainder of the root.

J. H. BIRKINSHAW.

Constitution of polypeptides and of proteolytic enzymes. Y. MIYANOKI (J. Biochem. Japan, 1931, 13, 389—421).—Erepsin caused hydrolysis of glycyl-asparagine (84%), glycyldiaminopropionic acid (15.8%), diglycyldiaminopropionic acid (28.6%), glycylososerine (21.7%), asparagylasparagine (28.6%), and asparagylhistidine (12.9%); pepsin hydrolysed none of these. Trypsin and trypsin-kinase hydrolysed 8.4 and 11.4%, respectively, of diglycyldiaminopropionic acid. Papain hydrolysed 11.6% of diglycyldiaminopropionic acid and 13.1% of asparagyl-asparagine.

CHEMICAL ABSTRACTS.

Mechanism of enzyme reactions. III. Action of trypsin on a mixture of two proteins. H. G. K. WESTENBRINK (Arch. neerland. Physiol., 1931, 16, 528—541).—The conclusion by Northrop (A., 1922, i, 693) that trypsin is saturated with 3% caseinogen and 4% gelatin and that hydrolysis of one is uninfluenced by saturation of the enzyme with the other is incorrect. The almost equal rates of hydrolysis of 3% and 7% caseinogen during the first 40 min. are ascribed to the influence of rapidly decomposed peptides produced from the protein.

H. DAVSON.

Isolation of methionine by enzymic hydrolysis. V. DU VIGNEAUD and C. E. MEYER (J. Biol. Chem., 1932, 94, 641—645).—Caseinogen is hydrolysed by incubation at 37° with pancreatic extract. Tyrosine is filtered off and tryptophan pptd. by HgSO_4 to yield a filtrate which is treated with $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ and then neutralised by NaOH . The ppt. thus formed is washed with H_2O and the pptn. repeated twice on the combined filtrates. The three ppts. are treated with aq. $\text{Ba}(\text{OH})_2$ and the filtered solution is freed from methionine by HgCl_2 . Regeneration of the NH_2 -acid is followed by concn. of the solution almost to dryness in a vac. and methionine is crystallised from 95% EtOH in presence of NH_2Ph with a yield of 0.1—0.2%.

F. O. HOWITT.

Specificity of the urease of the amoebocytes of *Limulus* and the behaviour of warmed and dialysed extracts of the tissue of amoebocytes. L. LOEB and I. LORBERBLATT (Biochem. Z., 1932, 244, 222—238).—The salt effect with amoebocyte urease of *Limulus* is sp. for this urease and is not obtained with the urease of muscle and serum of *Limulus*.

P. W. CLUTTERBUCK.

Phytase and specificity of phosphatase. K. HORIUCHI (J. Biochem. Japan, 1931, 14, 163—189).—Phytase from rice-bran but not takaphosphatase hydrolyses phytin, the optimum reaction being p_{H} 4.3. Kidney-phosphatases acting on glycerophosphates include one with an optimum at p_{H} 9 and another with one at p_{H} 3.1, only the latter attacking phytin when the optimum is at p_{H} 4.3. cycloHexanolphos-

phoric acid is hydrolysed by takaphosphatase (optimum p_H 3.1), phytase (5.6), and kidney-phosphatase (3.1 and 5.6); hence there is no enzymic relationship between this acid and phytin. Inositol-monophosphoric acid behaves similarly to phytin, excepting that the optima for hydrolysis by rice-bran and kidney enzymes are p_H 5.6 and 3.1, respectively, for the former and 4.3 in both cases for the latter. The specificity of these phosphatases is discussed.

F. O. HOWITT.

Influence of bile acids on glycerophosphatase. H. TAKATA (J. Biochem. Japan, 1931, 14, 61—67).—Hydrolysis of glycerophosphoric acid by liver- or kidney-phosphatase is inhibited by cholic acid.

F. O. HOWITT.

Enzymic fission of diphenylpyrophosphoric acid. K. KURATA (J. Biochem. Japan, 1931, 14, 25—50).—The action of phosphatases of various origins with PhH_2PO_4 , $H_4P_2O_7$, and $Ph_2H_2P_2O_7$ as substrates was investigated. Enzymic preps. containing phosphatase and pyrophosphatase do not always hydrolyse $Ph_2H_2P_2O_7$ and hence another factor is necessary. By adsorption methods the enzymes responsible for the fission of PhH_2PO_4 and $H_4P_2O_7$ and the activating agent for that of $Ph_2H_2P_2O_7$ may be separated.

F. O. HOWITT.

Pyrophosphatase of malt and yeast. H. LUERS, B. VON ZYCHLINSKI, and K. BENGTSSON (Woch. Brau., 1932, 48, 519—522, 529—533).—Aq. extracts of green malt and of malt rootlets contain a pyrophosphatase; plasmolysed yeast yields a similar enzyme. The p_H optima for malt and yeast pyrophosphatases are 5.5 and 6.4—6.8, and the temp. optima 37—42° and 42—47°, respectively. Above 50° the action of both is markedly checked. With neither is there direct proportionality between amount of enzyme and rate of reaction; the latter is retarded by the orthophosphate produced. The time-reaction curve for malt pyrophosphates falls off in a normal manner; the reaction is not unimol. Yeast pyrophosphatase acts slowly at first, the velocity of reaction increasing greatly after an "induction period." This is attributed to impurities, and the enzyme prepared from yeast which has been kept neutral during plasmolysis by the careful addition of NH_3 gives a time-reaction curve of normal form. When EtOH is added to the aq. extracts, that from malt yields an active ppt. only with >50 vol.-% EtOH; from yeast plasmolysate the enzyme is completely pptd. at this concn. The EtOH ppts. yield dry active preps.

F. E. DAY.

Degradation of sugars by fermentation. C. NEUBERG (Bull. Soc. Chim. biol., 1931, 13, 1294—1309).—A lecture.

Chemical nature of cozymase. K. MYRBACK and H. VON EULER (Z. physiol. Chem., 1931, 203, 143—153).—From dry wt. measurements in diffusion experiments (cf. A., 1927, 902) with highly active preps. the mol. wt. of cozymase is about 370. Activity measurements are less accurate and give higher vals. Inosic acid was isolated (as Ba salt) from the deamination products of cozymase. J. H. BIRKINSHAW.

Cozymase and adenosinetriphosphate. R. NILSSON and H. VON EULER (Z. physiol. Chem., 1932,

204, 204—210).—The cozymase action of adenosine-phosphoric acid varies so much with different preps. that the view that the acid activates glucose fermentation is not supported. In methylene-blue experiments similar differences were observed.

J. H. BIRKINSHAW.

Cocarboxylase, a new co-enzyme of alcoholic fermentation. E. AUHAGEN (Z. physiol. Chem., 1932, 204, 149—167).—When dried bottom-yeast is washed with a buffered phosphate solution at p_H 7.8, the whole co-enzyme system is removed, but the fermentative power of this "ætiozymase" is restored by boiled juice, which cannot be replaced by a mixture of purified cozymase + Mg + hexosediphosphate + inorg. phosphate, but requires a further co-enzyme. This cocarboxylase is prepared by pptn. from dialysed boiled juice by neutral $Pb(OAc)_2$ and removal of Pb with H_2S . A further purification is attained by pptn. with $Ba(OAc)_2$. The less sol. fraction of the ppt. is highly active. Cocarboxylase becomes inactive in a few hr. at 100°; it is relatively stable at slightly acid reactions and up to p_H 10. In addition to cocarboxylase, $MeCHO$ (or $AcCO_2H$ or $AcCHO$) must be added to restore completely the fermentation by ætiozymase. Ætiozymase decarboxylates $AcCO_2H$ only after addition of cocarboxylase. Fresh muscle does not contain cocarboxylase, which may account for the different course of muscle from that of yeast fermentation. Cocarboxylase is necessary to phosphoric ester production, but does not activate methylene-blue decolorisation in presence of hexosediphosphate as donator.

J. H. BIRKINSHAW.

Liberation of invertase from yeast. II. W. GRASSMANN and T. PETERS (Z. physiol. Chem., 1932, 204, 135—148; cf. A., 1929, 352).—By extraction of malt extract, or malt after 5—8 days' germination, a mixture of amylase and proteinase is obtained from which the proteinase is eliminated by adsorption on $Al(OH)_3$ prep. C_2 or $Fe(OH)_3$. The purified amylase is able to liberate considerable amounts of invertase from yeast "injured" by treatment with $EtOAc$ at 40° for 1 hr. Amylase from *Aspergillus oryzae* has the same action, but that of animal origin has no effect. Amylase liberates from treated yeast only about half the amount of N set free by papain.

J. H. BIRKINSHAW.

Conditions for the transformation of acetoacetic acid by yeast. E. FRIEDMANN (Biochem. Z., 1932, 244, 42—56).—The optimum conditions for the conversion of acetoacetic acid into $d(+)$ - β -hydroxybutyric acid (this vol., 194) are investigated and curves show the dependence of the reaction on medium, p_H , and concn. of reactants (sugar, acetoacetic acid, and yeast).

P. W. CLUTTERBUCK.

Quantitative investigation of acetoacetic acid transformation and β -hydroxybutyric acid formation by yeast. E. FRIEDMANN (Biochem. Z., 1932, 244, 57—68).—The disappearance of acetoacetic acid and the formation of β -hydroxybutyric acid under the action of yeast in presence and absence of sugar are quantitatively investigated. In presence of sugar, hydroxybutyric acid is readily formed, its formation ceasing after 8 hrs. fermentation. The reaction then proceeds more slowly and does not give

this product. In absence of sugar, the reaction is much slower. Hydroxybutyric acid does not appear during the first 8 hr. and is produced, but to a smaller extent and more slowly, in the later stages.

P. W. CLUTTERBUCK.

Transformation of acetoacetic acid and formation of β -hydroxybutyric acid by fermenting yeast. Hydroxybutyric acid content as determined by oxidation. E. FRIEDMANN (Biochem. Z., 1932, 244, 69—75).—In duplicate experiments the amount of β -hydroxybutyric acid as determined by oxidation is much greater than the amount as determined polarimetrically. Part of this difference is accounted for by the fact that in centrifuging to obtain a clear filtrate for polarisation, the pptd. yeast carries down some of the acid. Even after deproteinisation, however, the oxidation val. of the filtrate is much larger than the polarisation val. During fermentation, about 60% of the acetoacetic acid disappearing is transformed into $d(+)$ - β -hydroxybutyric acid (rapid reaction finishing in 8 hr.); the remaining 40% is converted by a slow reaction into some other substance (not l -hydroxybutyric acid) which is not detected by the polarimetric determination but gives rise to ketones with $K_2Cr_2O_7-H_2SO_4$ and is therefore determined as hydroxybutyric acid.

P. W. CLUTTERBUCK.

Accessory food substances for osmophilic yeasts. I. Bioactivator in honey stimulating fermentation. II. Comparison of honey bioactivator with bios. A. G. LOCHHEAD and L. FARRELL (Canad. J. Res., 1931, 5, 529—538, 539—543).—I. Addition of 1% honey solution to a synthetic nutrient medium diminishes the time required for onset of fermentation by *Zygosaccharomyces mellis*. The activator is distinct from fructose. It resists boiling, is non-volatile, insol. in Et_2O and $COMe_2$, but sol. in 85% $EtOH$. There exist two factors which act in conjunction but are inactive singly; one of them is adsorbed on blood-charcoal at p_H 4.2 and can be eluted by 95% $EtOH$, whilst the other is unadsorbed.

II. The non-adsorbed factor differs from inositol although the latter is present in the charcoal filtrate. The adsorbed factor is present in crude bios II but is not an essential part.

P. G. MARSHALL.

Nutritional physiology of a cultivated top-yeast. W. SCHWARTZ and R. KAUTZMANN (Arch. Mikrobiol., 1931, 2, 537—567).—The yield of yeast on malt wort is independent of $[H^+]$ within the range p_H 3.5—6.5, but in artificial media there is a slight increase towards the alkaline side. The effect of PO_4^{4-} on yeast growth depends mainly on its buffer effect, the amount required as nutrient being small. Amounts $>0.4M$ per litre have little effect on the yield. A min. of 0.01% N is required in synthetic media. Increasing the glucose content beyond 10% does not improve the yield. Among numerous N sources examined, NH_2 -acids produced highest yields, followed by NH_4 tartrate, succinate, malate, phosphate, sulphate, and other inorg. salts. A mixed source of N has no greater effect than that anticipated by the sum of the individual constituents. Beer wort, molasses, and yeast water contain a thermolabile growth factor which stimulates the growth of yeast in artificial media. Treatment with activated C

removes this factor from wort, which is thus decolorised and rendered free from N.

A. G. POLLARD.

Effect of rhizopin on the growth of *Aspergillus niger*. N. NIELSEN (Compt. rend. Lab. Carlsberg, 1931, 19, No. 5, 1—10).—Rhizopin solution (culture media on which *Rhizopus suinus* has been grown), previously shown to stimulate the growth of *Avena*-coleoptiles, has a marked effect during the first few days on the growth of *A. niger*. Under optimum conditions a yield 9 times as great as in the absence of rhizopin is obtained. After a longer time the difference is less marked and ultimately the growth in the presence of rhizopin may be inferior to that in its absence. Rhizopin also stimulates the formation of conidia. It is not certain that the *A. niger*-stimulating substance is identical with that which stimulates the growth of coleoptiles.

W. O. KERMACK.

Mannitol as substrate for growth of *Aspergillus niger*. M. OBATON (Compt. rend., 1932, 194, 302—304).—*A. niger*, after having been cultivated to a suitable stage of growth for 48 hr. on a medium containing sucrose, grows well when transferred to a medium containing mannitol.

W. O. KERMACK.

Multiplication of bacteria. J. RÉGNIER and A. KAPLAN (Compt. rend., 1932, 194, 397—399).—Whilst bacteria in small nos. multiply at a const. and rapid rate, those in large nos. multiply at a const. rate but more slowly. The fact that this rate is const. from the beginning of the logarithmic period is believed to indicate that bacteria have within themselves the factors which determine the decrease in the rate of their multiplication.

A. LAWSON.

Bacterial growth. Existence of latent phase. J. RÉGNIER, R. DAVID, and A. KAPLAN (Compt. rend., 1932, 194, 323—325).—*B. pyocyaneus* grown in a liquid medium does not show a latent phase when the no. present is determined by microscopic counting, but when enumeration is by plating on a solid medium, a latent phase of about 2 hr. is observed.

W. O. KERMACK.

Variability of [bacterial] growth rate. O. RAHN (J. Gen. Physiol., 1932, 15, 257—277).—On the assumption that the doubling of genes is a chemical process following mass-action laws, curves are calc. for the division of cells with time. The shape of these curves agrees with the experimentally determined curves for *B. aerogenes* and *Saccharomyces ellipsoideus*.

H. DAYSON.

Stability of bacterial emulsions at 80°. P. LASSEUR, A. DUPAIX, and M. GROJEAN (Compt. rend., 1932, 194, 495—497).—Suspensions of bacteria were made in distilled H_2O ($\kappa=1.2 \times 10^{-6}$), 0.02% aq. NaCl, and physiological saline. In each case a fall in γ followed heating to 80°, together with a slight rise in η and a considerable increase in κ . The p_H rose but was still in the region favourable to agglutination. The following bacteria were used: *B. caryocyaneus*, *B. chlororaphis*, *B. prodigiosus*, and *B. balticus*.

P. G. MARSHALL.

Assimilation of atmospheric nitrogen by certain bacteria. M. SCHRODER (Zentr. Bakt. Par., 1932, II, 85, 177—212).—Contrary to the views of Beijerinck, *Spirillum lipoferum* was unable to utilise

atm. N₂ in synthetic media even in the presence of peat extract, humates, small amount of N salts, or sterile garden soil. Prolonged subculturing of *Azotobacter* in artificial media gradually destroyed its N-fixing power. Fixation of N by *Azotobacter* occurred only when, in addition to sugars, KH₂PO₄, MgSO₄, and CaCO₃, the nutrient contained small amounts of Fe, Zn, Cu, W, Mo, and Si. Nutrients prepared with "conductivity" H₂O in place of distilled H₂O gave evidence of the lack of Si and W. NaCl is not essential for growth and N-fixation and Ca is unnecessary for growth in N-containing media. Growth of *Azotobacter* and *Chlorella* in double cultures occurs in nutrients free from N and inorg. material and is accompanied by N accumulation. A. G. POLLARD.

X-Ray spectrum of the cellulose of *Acetobacter xylinum*. Y. KHOUVINE, G. CHAMPETIER, and R. SUTRA (Compt. rend., 1932, 194, 208—209).—Cultures of *A. xylinum* grown on glycerol, sorbitol, and α -glucoheptitol form membranes of cellulose, more resistant to chemicals than cotton, but identical in X-ray spectrum. The membranes mercerised with Na₂CO₃ or nitrated with HNO₃ show X-ray spectra identical with that of mercerised cotton and nitro-cotton, respectively. *A. xylinum* is therefore capable of synthesising cellulose from widely differing alcohols. A. LAWSON.

New species of cellulose-decomposing bacteria, *Cellvibrio calida*, n. sp. A. ITANO and S. ARAKAWA (Proc. Imp. Acad. Tokyo, 1931, 7, 367—368).—The organism was isolated from dry farm soil. F. R. SHAW.

Action of thermophilic bacteria on coal. R. LIESKE (Ges. Abhandl. Kennt. Kohle, 1930, 9, 35—40; Chem. Zentr., 1931, ii, 1657).—CO₂ is evolved from brown coal at 55° in a current of N₂ when thermophilic bacteria are present. A new bacterial species, apparently growing specifically on coal, was found. Brown or bituminous coal causes vigorous evolution of CO₂, N₂, and H₂ from fermenting sugar solutions, apparently owing to catalytic influence on a fermentation process. A. A. ELDRIDGE.

Formation of chymase by *B. prodigiosus*. C. GORINI (Milchwirt. Forsch., 1931, 12, 199—200; Chem. Zentr., 1931, ii, 459).—A review. The optimum temp. is 40°, not 50° (Wahlin, 1928). A. A. ELDRIDGE.

Ketone-aldehyde mutase and glycolase of lactic acid bacteria. E. SIMON (Zentr. Bakt. Par., 1932, II, 85, 269—276).—*Streptobact. casei* and *B. casei* produce lactic acid from methylglyoxal in 0.1—0.2% solution. In greater concn. (1%) methylglyoxal is toxic to the organisms. The optical activity of the acid produced differed according to the organism used. The enzyme activity was increased by the addition of the co-enzyme from yeast. Similar changes were produced with MeCHO and phenylglyoxal. Prods. from the organisms by EtOH—Et₂O also converted Mg hexosediphosphate into methylglyoxal and lactic acid. A. G. POLLARD.

Difference in fermentation of the *coli-typhosus* group under aerobic and anaerobic conditions. B. I. BLANKOV and Z. L. GRINGOT (Mikrobiol. J., Russia, 1929, 9, 248—251; Chem. Zentr., 1931, ii,

1588).—Lactose and maltose were attacked by *B. coli* only under anaerobic, glucose and galactose under aerobic or anaerobic, conditions. *B. typhosus* abd. attacks maltose and mannitol under anaerobic, and glucose and galactose under both, conditions; sucrose and lactose are not attacked. *B. paratyphosus*-A and -B and *B. typhosus* differ. A. A. ELDRIDGE.

Effect of bacterial toxin on the secretion of adrenaline. S. ONO (Z. ges. exp. Med., 1931, 76, 689—693; Chem. Zentr., 1931, ii, 1308).—Intravenous injection of 1—4 mg. of coli-toxin per kg. into rabbits causes an increase in the secretion of adrenaline; the effect is not observed with smaller or larger doses. 5 mg. cause toxic symptoms unaccompanied by hyperglycemia. A. A. ELDRIDGE.

Lipins of tubercle bacilli. XXVI. Separation of lipin fractions from leprosy bacillus. N. UYEI and R. J. ANDERSON (J. Biol. Chem., 1932, 94, 653—666).—The following fractions were isolated from *Mycobacterium leprae* by extraction with EtOH—Et₂O and CHCl₃ at room temp.: phosphatides, COMe₂-sol. fat, CHCl₃-sol. wax, total lipins, and polysaccharides. Comparison is made of these fractions with those corresponding with human tubercle bacillus (A., 1927, 1114). The former organism, which has a total lipin content exceeding 30%, exhibits a lower phosphatide and wax content than the latter. F. O. HOWITT.

Manganese bacteria in waters of Texas. F. W. JESSEN (J. Amer. Water Works Assoc., 1932, 24, 78—87).—Examination of 150 samples of H₂O from various localities showed that 16 contained Mn in concns. of 0.01—3.6 p.p.m. Mn is not a food requirement of organisms which can oxidise it, this property being apparently an independent one. Some cultural characteristics of several bacteria capable of oxidising Mn are given. C. JEPSON.

Oxidation of manganese by bacteria. O. B. WILLIAMS and F. W. JESSEN (J. Amer. Water Works Assoc., 1932, 24, 88—92).—The organisms which oxidise Mn are strict aerobes, but lose this power after being obtained in pure culture and re-inoculated twice. An attempt to determine the actual e.m.f. in bacterial colonies oxidising Mn and to calculate therefrom the probable state of oxidation was only partly successful. C. JEPSON.

Transmissible lysozyme of bacteria. R. LEGROUX (Compt. rend., 1932, 194, 210—212).—Essences of mustard, rosemary, and cinnamon capable of killing staphylococci and spores of *B. subtilis* have no effect on the transmissible lysozyme of bacteria, which in this respect behaves like an enzyme, and should therefore not be called a bacteriophage. A. LAWSON.

Transmissible lysozyme. R. LEGROUX and K. DJEMIL (Compt. rend., 1932, 194, 319—320).—By the use of formol an anabacteriophage may be prepared analogous to anatoxin, capable of producing antibacteriophage when injected into a rabbit, but not exerting the characteristic lytic action. Bacteriophage resembles enzymes in being highly adsorbed on colloidal Al(OH)₃ and in being eluted with NaH₂PO₄ solution. These analogies with non-living material

support the view that bacteriophage is enzymic in nature. W. O. KERMACK.

Intracellular bacteriophage in lysis of staphylococci. J. H. NORTHROP and A. P. KRUEGER (J. Gen. Physiol., 1932, 15, 329—332).—Lysis is determined by the internal concn. of phage in the bacterial cell or the total concn. of phage per c.c. of dispersion medium.

H. DAVSON.

Peroxidase. I. Potentiometric studies. II. Effect on bactericidal action of phenols. S. KOJIMA (J. Biochem. Japan, 1931, 14, 79—93, 95—109).—I. The oxidation potential of H_2O_2 in presence of peroxidase is not greater than that of H_2O_2 alone, indicating absence of activation of the peroxide. The potentials of various systems of peroxidase with *o*-, *m*-, and *p*-cresol, benzidine, etc. with and without H_2O_2 are determined and the possibility of quinone formation is discussed.

II. The coagulation of proteins by phenols is not related to the bactericidal power of the latter. In presence of H_2O_2 and peroxidase phenols exhibit a bactericidal activity greater than normal, the high oxidation potential and the transitory nature of the system indicating formation of a quinone. The increased activity with aerobiosis is therefore assumed to be due to formation of H_2O_2 , which together with bacterial peroxidase results in the production of a quinone. F. O. HOWITT.

Bactericidal properties of mono-ethers of dihydric phenols. II. Mono-ethers of quinol. E. KLARMANN, L. W. GATYAS, and V. A. SHTERNOV (J. Amer. Chem. Soc., 1932, 54, 298—305; cf. A., 1931, 1289).—The bactericidal potency of quinol alkyl ethers towards *B. typhosus* reaches a max. at C_5 and then decreases; with *S. aureus* it increases with length of the C chain. Compounds containing more than 8 C atoms in the alkyl group could not be used owing to their sparing solubility. The *n*-alkyl derivatives are more active than the *sec*-alkyl compounds. Aryl ethers are also powerful germicides; the Ph ether is most effective against *B. typhosus*, the $CH_2Ph \cdot CH_3$ ether against *S. aureus*. Alternation is observed with the aralkyl ethers. The following monoethers of quinol are new: *Pr*, m. p. 56—57°; *Pr^s*, b. p. 117°/4 mm.; *Bu*, m. p. 64—65°; *amyl*, m. p. 49—50°; *sec-amyl*, m. p. 48—49°; *hexyl*, m. p. 48°; *heptyl*, m. p. 60°; *octyl*, m. p. 60—61°; *nonyl*, m. p. 68.5°; β -phenylethyl, b. p. 183°/4 mm.; γ -phenylpropyl, m. p. 75—76°. Most of these were obtained by condensation of quinol with the alkyl halide, either directly, or with K_2CO_3 or KOH; the Ph ether was prepared from *p*- $C_6H_4Br \cdot OH$ and PhOH, since PhBr did not react. The bactericidal concns. are tabulated. C. J. WEST (b).

Killing of colon bacilli by ultra-violet light. R. W. G. WYCKOFF (J. Gen. Physiol., 1932, 15, 351—361).—Colon bacilli under ultra-violet irradiation die at a semi-logarithmically linear rate. H. DAVSON.

Has the pancreas an effect on the resorption of fatty acids? M. NOTHMANN and H. WENDT (Arch. exp. Path. Pharm., 1932, 164, 266—270).—Oleic acid fed to depancreatized dogs is absorbed from the intestinal tract up to approx. 90% of that admini-

stered. In a normal dog 98% was absorbed and the slightly lower vals. in the depancreatized animals are probably due to the trapping of the acid in the undigested foodstuffs. These results do not support the view that the pancreas aids the absorption of fat by means of a hypothetical internal secretion (cf. A., 1931, 1450). W. O. KERMACK.

Action of hypophysin on water metabolism. P. ROBOZ (Klin. Woch., 1931, 10, 456; Chem. Zentr., 1931, i, 2492).

Action of so-called anterior pituitary growth hormone. A. DRIELS and G. MOSBERG (Klin. Woch., 1931, 10, 1504—1505; Chem. Zentr., 1931, ii, 1590).—Experiments on rats are described.

A. A. ELDRIDGE.

Hormones of the corpus luteum. Separation and purification of three active substances. H. L. FEVOLD, F. L. HISAW, and S. L. LEONARD (J. Amer. Chem. Soc., 1932, 54, 254—263; cf. A., 1930, 1320).—The corpus luteum of the sow secretes three active principles, relaxin (I), corporin (II), and a mucifying hormone (III), which are best extracted by acidulated EtOH (20 c.c. conc. HCl per litre). (I) is first separated from the mixture by its insolubility in 99% EtOH; (III) is insol. in Et₂O or light petroleum, whilst (II) is sol. The yield of (II) is increased by extracting the tissue with hot EtOH-HCl, but (I) is thereby destroyed completely (heat-labile) (cf. *loc. cit.*). (III) is not affected by pepsin or trypsin; it is, however, completely inactivated by CH_2O , HNO_2 , or $BzCl$ (probably owing to the action on a free NH_2 group). (II) is a fat-sol. substance and resembles the follicular hormone of the ovary, except in its instability to alkalis. (I) has a sp. action on the pelvic ligaments, (II) is concerned with the physiology of the uterus, whilst (III) acts on the vaginal mucosa. (II) is probably identical with the progestin of Corner and Allen (Amer. J. Physiol., 1929, 88, 326). C. J. WEST (b).

Resistance of the follicular hormone to ageing. M. M. MAINO (Arch. Ist. biochim. Ital., 1931, 3, 352—358).—Estrin, both cryst. and in neutral aq. solution, has been kept unchanged for 2 years in sealed tubes. R. K. CALLOW.

Hormonal pregnancy reaction. Ether-sugar method. B. ZONDEK (Klin. Woch., 1931, 10, 1484—1488; Chem. Zentr., 1931, ii, 1590).—The urine is preferably extracted with Et₂O which removes toxic substances and female sexual hormone from male urine; it also removes an inhibitor of the anterior pituitary hormone. Addition of glucose to urine of pregnancy detoxicates it and facilitates the anterior hormone reaction. A combination of the methods is specially advantageous. A. A. ELDRIDGE.

Quantitative action of male sexual hormone. M. ARON (Endokrinol., 1931, 9, 8—17; Chem. Zentr., 1931, ii, 1307).—The hormone causes a biological effect in proportion to its quantity. Each sexual characteristic of the same individual exhibits its own sensitivity towards the hormone. A. A. ELDRIDGE.

Determination of the male sexual hormone. E. GLASER and O. HAEMPEL (Naturwiss., 1931, 51, 1021).—The method depends on the development in

the fins and body of the castrated fish *Rhodeus amarus* of the intense red and black colorations which appear normally only at spawning time. The unit is taken as the smallest amount which produces, after intra-peritoneal injection of 0.2 c.c. in at least 3 or 4 equally heavy 3-year-old fish, a coloration lasting 4–5 hr. 0.0002 g. of yohimbine hydrochloride produces the same result. A. LAWSON.

Male sexual hormone from urine and its effect on birds. J. M. KABAK (Endokrinol., 1931, 9, 84–98; Chem. Zentr., 1931, ii, 1589).—Male or female urine extracts caused growth of the contracted comb of castrated cocks. A. A. ELDRIDGE.

Determination of vitamins in foods. P. REYHER (Z. Ernähr., 1931, 1, 81–91; Chem. Zentr., 1931, i, 2498).—For the determination of vitamin-B young pigeons, and for that of -D young guinea-pigs, were employed for the prophylactic method. The method and precautions employed are described. The vitamin contents of various foods are recorded. A. A. ELDRIDGE.

Vitamin content of edible fungi. A. SCHEUNERT and J. RESCHKE (Deut. med. Woch., 1931, 57, 349–351; Chem. Zentr., 1931, i, 2498).—Various relative contents of vitamins-A, -B₂, and -D are recorded; vitamin-C was not detected. A. A. ELDRIDGE.

Characterisation of vitamin-A. I. Spectroscopic evidence. I. M. HEILBRON and R. A. MORTON. II. Biological experiments. B. AHMAD and J. C. DRUMMOND (J.S.C.I., 1931, 50, 183–184T, 184–186T).—I. In fish-liver oils and concentrates of varying degrees of freshness the substance absorbing maximally at 328 m μ (vitamin-A) is probably identical with that responsible for the band at 572 m μ in concentrates in the SbCl₃ colour test. The chromogen giving rise to the band at 606 m μ with SbCl₃ is a separate, although probably related, entity. The following criteria, partly fulfilled by "dihydrocarotene," are given for vitamin-A: a colourless substance with max. absorption at 320–330 m μ , giving with SbCl₃ a blue colour with max. absorption at 583 m μ , the intensities of these bands being equal for equal wts. of vitamin.

II. The absorption of ingested carotene by rats was low unless the diet contained fat (10%). Although the presence of vitamin-A was suggested by spectroscopic examination of the caecum fat, bacterial cultures from the caecum gave mainly negative results when tested for ability to convert carotene into vitamin-A. Following administration of carotene to rats, vitamin-A was stored in the liver, the fat from which contained a pigment, probably a degradation product of carotene. Vitamin-A was not formed in similar experiments with cats on a vitamin-A-deficient diet, nor after perfusion of their livers with carotene, although the latter was destroyed. "Dihydrocarotene" fed to vitamin-A-deficient rats failed to promote growth or gave irregular results. A. COHEN.

Dose of vitamin-A administered as carotene. A. POLAK and J. A. STOKVIS (Arch. neerland. Physiol., 1931, 16, 542–551).—A dose of 0.5–1 $\times 10^{-6}$ g. per day, fed *per os*, is sufficient to cure and prevent xerophthalmia in rats fed on varying vitamin-A-free basal diets. H. DAVSON.

Chlorophyll as vitamin-A. E. BURGI (Klin. Woch., 1931, 10, 1313; Chem. Zentr., 1931, ii, 1446).—The growth-vitamin-A is present in rhodin; the effects observed are not due to the presence of carotene. A. A. ELDRIDGE.

Oxidisability of substances containing vitamin-A. H. VON EULER and L. AHLSTROM (Z. physiol. Chem., 1931, 204, 168–180).—The O-absorption of various liver-oils is approx. parallel with their growth activity. The absorption figures are particularly high for vitamin-A preps. of high activity. Liver sections from rats on a complete diet show much greater absorption in blood or serum than in Ringer solution. Haemin also increases the O-absorption. J. H. BIRKINSHAW.

Effect of light on the synthesis of vitamins. V. G. HELLER and R. R. ST. JOHN (J. Nutrition, 1931, 4, 227–233).—The vitamin potency of green leaves is not destroyed by blanching. The vitamin seems to be stored in that portion of the plant most exposed to sunshine. The most actively growing portion, if etiolated, may be devoid of vitamin-A. Neither wave-length nor heat is solely responsible for the formation of vitamin. No relationship between vitamin-A potency and colour of beans, carrots, and beets was observed. Vegetables, in general, are a poor source of vitamin-D.

CHEMICAL ABSTRACTS.

Fat-soluble vitamins. XXXII. Distribution of vitamin-A in tomato and the stability of added vitamin-D. H. STEENBOCK, I. M. SCHRADER, B. M. RISING, and A. M. WIRICK (J. Nutrition, 1931, 4, 267–279).—Tomato pulp, free from skin and seeds, contains about 32 times as much vitamin-A as the serum. Irradiated ergosterol, when added to tomato pulp, maintained its activity for at least 13 months after sterilisation. CHEMICAL ABSTRACTS.

Stability of vitamins-A and -D in cod-liver oil. Biological evaluation of vitamin-D. E. POULSSON (Arch. Int. Pharmacodyn. Ther., 1930, 38, 200–208; Chem. Zentr., 1931, ii, 735).—A sample 31 years old retained half, and a 26-year-old sample retained all, of its probable original vitamin-A content. The great stability is attributed to the presence of highly unsaturated and easily oxidisable fatty acids, which protect the vitamin from the destructive action of O₂. Determination of vitamin-D activity is described. A. A. ELDRIDGE.

Antineuritic vitamin. I. Method of assay, concentration, and solubility in organic solvents. R. J. BLOCK, G. R. COWGILL, and B. H. KLOTZ (J. Biol. Chem., 1932, 94, 765–782).—The assay of the vitamin (B₁) by a combination of wt.-maintenance and curative techniques in pigeons on a diet of polished rice, meat residue, salt mixture, and cod-liver oil is recommended. Polished rice alone as a diet leads to irregular results in wt.-maintenance. Importance is assigned to anorexia as characteristic of B₁-avitaminosis. In the investigation of the concn. of the vitamin by pptn. with Ag, rice polishings were extracted with acidulated aq. EtOH, the extract was concn. in vac., the vitamin adsorbed on Lloyd's reagent and eluted with NaOH. The alkaline solution was neutralised with H₂SO₄, Na₂SO₄ pptd. by EtOH, and

the solution conc. to a syrup. This syrup was treated with various combinations of acids and bases in presence of AgNO_3 or Ag lactate, the vitamin being regenerated from the Ag ppt. thus formed. Concn. factors thus obtained were 4–23 with a recovery of 5–50%. The solubility of the vitamin in the binary and ternary mixtures of H_2O , EtOH , and other org. solvents was studied and its solubility in abs. EtOH confirmed.

F. O. HOWITT.

Preparation of crystalline antineuritic vitamin from yeast. A. WINDAUS, R. TSCHESCHE, H. RUHKOPF, F. LAQUER, and F. SCHULTZ (Z. physiol. Chem., 1932, 204, 123–128).—Vitamin- B_1 was obtained as an unstable cryst. *chloroaurate* from a yeast extract which had undergone preliminary purification (adsorption on fuller's earth, removal of impurities with HgSO_4 and AgNO_3 and by benzylation). It was converted into the *picrolonate*, m. p. 229° (decomp.), analysis of which indicates that the probable formula of the vitamin is $\text{C}_{12}\text{H}_{17}\text{ON}_3\text{S}$. The *hydrochloride*, m. p. 245° (decomp.), shows an absorption max. at 250–260 $\text{m}\mu$ similar to active yeast extracts and an antineuritic activity of 1.4–3.3 γ in the pigeon test.

J. H. BIRKINSHAW.

Vitamin- B_1 and vitamin- B_2 content of cereals. R. A. HETLER, C. R. MEYER, and D. HUSSEMAN (Illinois Agric. Exp. Sta. Bull., 1931, No. 369, 167–211).—Diets containing 50% of oats or oat products, maize, wheat, rice polishings, or tiki-tiki produced sufficient heat-stable vitamin- B_2 for the growth of rats. Sufficient vitamin- B_1 was obtained with 25% of these foods. Vitamin- B_1 is distributed throughout the oat grain, but is more conc. in the embryo than in the endosperm. A diet containing 50% of oats (to supply vitamin- B_1) produced normal lactation, but oats are insufficient as a sole source of vitamin- B_2 for this purpose.

A. G. POLLARD.

Tentative method of assaying foods for vitamin- B_2 . H. E. MUNSELL (J. Nutrition, 1931, 4, 203–210).—30% of white maize in the Sherman and Spohn vitamin- B -free diet does not supply sufficient vitamin- B_2 to promote growth or prevent symptoms of pellagra, but normal growth occurs when autolysed yeast is added. An 80 wt.-% EtOH extract of white maize fed at a level of 3% supplies sufficient vitamin- B_1 for normal growth, and contains little vitamin- B_2 .

CHEMICAL ABSTRACTS.

Reduction-capacity of plant foodstuffs and its relation to vitamin-C. I. Reducing substances of lemon-juice. J. TILMANS, P. HIRSCH, and W. HIRSCH. II. Reducing substance of lemon-juice as a stabiliser for the true vitamin. J. TILMANS, P. HIRSCH, and F. SIEBERT (Z. Unters. Lebensm., 1932, 63, 1–20, 21–30).—I. The juice from 300 lemons was decitrated by treatment with H_2SO_4 , neutralised with CaCO_3 , and then shaken four times with COMe_2 in presence of H_3PO_4 at 0° , the solvent being removed by distillation each time and the ppt. dissolved in $\text{H}_2\text{O} + \text{MeOH}$ and repptd. with COMe_2 . A solution of this product was pptd. with $\text{Ba}(\text{OH})_2$ and H_2SO_4 and then with $\text{Pb}(\text{OAc})_2$, and an extract of the resulting liquid in $\text{AcOH} + \text{Et}_2\text{O}$ evaporated and the residue extracted with COMe_2 . The operations were carried

out as far as possible in an atm. of inert gas and in the absence of catalytic metals. The final prep. gave positive xanthoprotein and carbohydrate (Molisch and reduction) reactions and contained a small amount of N, but tannin, phenol, and other protein reactions were negative. It was acidic, sol. in H_2O , MeOH , EtOH , and COMe_2 , but insol. in Et_2O , C_6H_6 , or CHCl_3 , and gave a pale blue colour in ultra-violet light similar to that of the original juice. The reducing power of the product at all stages of separation was controlled by titration with a solution of 2 : 6-dichloroindophenol, in presence of AcOH and sufficient NaOAc to bring the from 5 (red) to 7 (blue), the end-point being given by the production of a blue colour permanent for 1 min. The final substance had an apparent equiv. wt. of 500. Experiments with guinea-pigs showed antiscorbutic power for daily doses corresponding with 1 c.c. of fresh juice, and confirm the conclusion that the reducing substance is the carrier of vitamin-C. This effect is destroyed by oxidation of the juice or of the final prep. with Cl_2 solution, H_2O_2 being less effective.

II. Experiments with decitrated lemon-juice confirm the conclusion that the antiscorbutic effect and reduction capacity towards 2 : 6-dichloroindophenol of the juice are correlated (cf. A., 1927, 487, 702; 1928, 801). Since decitrated lemon-juice oxidised with an equiv. quantity of 2 : 6-dichloroindophenol still possessed its antiscorbutic effect if administered immediately, and since this effect is usually destroyed by oxidising agents and disappears after 1 day in air or 7 days in CO_2 (but not after 1 day in CO_2), it is concluded that the effect of vitamin-C is due to the reducing substance and its primary oxidation product, and that the first stage of oxidation is probably reversible.

J. GRANT.

Antiscorbutic vitamin. I. O. RYGH, A. RYGH, and P. LALAND. II. Narcotine and its derivatives as antiscorbutics. O. RYGH and A. RYGH (Z. physiol. Chem., 1932, 204, 105–111, 114–122).—I. Et_2O extracts of neutralised orange-juice showing a high antiscorbutic activity consisted of a syrup and cryst. narcotine. The crystals were obtained in highest yield from unripe fruit. Narcotine is inactive against scurvy, but is weakly activated by ultra-violet irradiation, since although the test animals receiving 0.5 mg. per day of irradiated product died, they showed no signs of scurvy.

II. Daily doses of 0.1–2 mg. of irradiated narcotine protect guinea-pigs against scurvy. An increase above 2 mg. weakens the protection. Of derivatives of narcotine tested, only dimethylnor-, methylnor-, and nor-narcotine had definite antiscorbutic action. Methylnornarcotine (the o-diphenol), obtained by heating narcotine with conc. HCl for 8 days at 100° , was highly active, 0.02–0.03 mg. daily giving protection to guinea-pigs. Although the experimental animals died in 5 weeks they were quite free from scurvy. An addition of vitamin-C-free juice (obtained by heating orange-juice for 3 hr. at 100° with air bubbling through) to the diet maintained the animals' health and wt. The activity shown by the other two nornarcotines may be due to contamination with methylnornarcotine.

J. H. BIRKINSHAW.

Isolation of narcotine from various vegetables. P. LALAND (Z. physiol. Chem., 1932, 204, 112—114).—Narcotine was isolated from unripe tomatoes, cabbages, and potatoes, but was not found in cranberries. Milk contained a trace. J. H. BIRKINSHAW.

Crystalline vitamin-D. F. A. ASKEW, R. B. BOURDILLON, H. M. BRUCE, R. K. CALLOW, J. ST. L. PHILPOT, and T. A. WEBSTER (Proc. Roy. Soc., 1932, B, 109, 488—506).—Calciferyl 3 : 5-dinitrobenzoate, lemon-coloured crystals, m. p. 147—149°, $[\alpha]_{5461}^{20} + 69^\circ$ in C_6H_6 (cf. A., 1931, 1464), is prepared by extracting irradiated ergosterol with cold 90% EtOH, pptg. the unchanged ergosterol in the extract with digitonin, and treating the resin obtained by evaporation of the EtOH with pyridine and 3 : 5-dinitrobenzoyl chloride. When hydrolysed it yields calciferol, $C_{27}H_{42}O$, m. p. 114.5—117°, $[\alpha]_{5461}^{20} + 122^\circ$, $[\alpha]_{5461}^{20} + 102.5^\circ$ in EtOH. The best yields (about 40%) were obtained by irradiation with light from a Hg-vapour lamp, filtered through 1% xylene in EtOH to exclude wave-lengths below 275 μ . The exclusion of O_2 during the manipulations is not necessary after the irradiation is completed. Ultra-violet irradiation of calciferol with wave-lengths of 210—280 μ or longer rapidly converts calciferol into products showing little absorption at wave-lengths greater than 260 μ . The activity of calciferol equals approx. 40,000 International units per mg., whilst the toxic dose to mice is 0.1 mg. Calciferyl p-nitrobenzoate, m. p. 90—93°, $[\alpha]_{5461}^{20} + 65^\circ$ in C_6H_6 , yields unchanged calciferol on hydrolysis. Pyrocalciferyl 3 : 5-dinitrobenzoate, orange prisms from $COMe_2$ (from C_6H_6 -EtOH, light yellow needles containing 1 mol. C_6H_6), m. p. 166—169°, $[\alpha]_{5461}^{20} + 250^\circ$ in C_6H_6 , prepared from the crude irradiation product by distillation at 150°, followed by esterification with 3 : 5-dinitrobenzoyl chloride and fractional crystallisation, yields on hydrolysis pyrocalciferol, $C_{27}H_{42}O$, m. p. 93—95°, $[\alpha]_{5461}^{20} + 624^\circ$, $[\alpha]_{5461}^{20} + 502^\circ$ in EtOH. Vitamin- D_1 of Windaus, Lüttringhaus, and Deppe (A., 1931, 1464) prepared by the citraconic anhydride method was esterified with 3 : 5-dinitrobenzoyl chloride and the product fractionated into the less sol. calciferyl 3 : 5-dinitrobenzoate and the more sol. dinitrobenzoate, m. p. 139—141°, $[\alpha]_{5461}^{20} + 24^\circ$ in C_6H_6 , of a third sterol, which has been named sterol X ("lumisterol"). Sterol X obtained by hydrolysis of the dinitrobenzoyl derivative has m. p. 116.5—118.5°, $[\alpha]_{5461}^{20} + 220^\circ$, $[\alpha]_{5461}^{20} + 176^\circ$ in EtOH (not quite pure) and shows max. absorption (ϵ 22.5 at 273 μ). Vitamin- D_2 of Windaus and others (A., 1931, 1464) is apparently identical with calciferol. Chemical, spectroscopic, and polarimetric data confirm the view that vitamin- D_1 is a mixture of calciferol (vitamin- D_2) and sterol X in approx. equimol. proportions. Various samples of impure calciferol previously obtained by distillation were apparently mixtures of the three sterols in varying proportions, probably consisting of solid solutions of the association compound (vitamin- D_1) of calciferol and sterol X in a second association compound of calciferol and pyrocalciferol. There is no evidence that pyrocalciferol or sterol X possesses any antirachitic activity and the activity and toxicity of various purified irradiation products are accounted for by their

content of calciferol. There is no evidence that any active product other than calciferol is formed by irradiation of ergosterol. W. O. KERMAK.

Crystalline vitamin- D_2 . A. WINDAUS, O. LINSERT, A. LUTTRINGHAUS, and G. WEIDLICH (Annalen, 1932, 492, 226—241).—Vitamin- D_2 (I), $C_{27}H_{42}O$, m. p. 115—116°, $[\alpha]_{5461}^{20} + 103^\circ$, $[\alpha]_{5461}^{20} + 124^\circ$ in EtOH, $[\alpha]_{5461}^{20} + 82.6^\circ$, $[\alpha]_{5461}^{20} + 98.6^\circ$ in $COMe_2$, $[\alpha]_{5461}^{20} + 91.2^\circ$, $[\alpha]_{5461}^{20} + 106.3^\circ$ in Et₂O [3 : 5-dinitrobenzoate, m. p. 148—149°, $[\alpha]_{5461}^{20} + 55^\circ$, $[\alpha]_{5461}^{20} + 71^\circ$ in C_6H_6 , $[\alpha]_{5461}^{20} + 79.5^\circ$, $[\alpha]_{5461}^{20} + 102^\circ$ in $COMe_2$, hydrolysed by EtOH-KOH in N_2 to (I)], is obtained by irradiating ergosterol in C_6H_6 with the unfiltered light from a Mg arc in absence of O_2 ; the irradiated mixture is freed from ergosterol by crystallisation and with digitonin, the residue treated with citraconic anhydride [with which (I) reacts only slowly] in Et₂O-light petroleum at room temp., the reaction mixture hydrolysed with 10% MeOH-KOH at room temp., and the vitamin then extracted with light petroleum (all these operations are carried out in absence of O_2). (I) sublimes undecomposed in a high vac., absorbs approx. 30 when titrated with BzO_2H , shows a characteristic absorption max. at 265 μ , is only slowly attacked by O_2 , and when over-irradiated yields suprasterols I and II. Active daily doses of (I) per rat are 0.015 and 0.027; (I) is about twice as active as vitamin- D_1 (Windaus *et al.*, A., 1931, 1464). (I) is identical with the calciferol of Askew *et al.* (A., 1931, 1464).

[With FERNHOLZ.] Reduction of (I) with Na and PrOH and treatment of the product formed with HNCO gives the allophanate (II), m. p. 184—186°, $[\alpha]_{5461}^{20} + 14.1^\circ$ in $CHCl_3$, of dihydrovitamin- D_2 , m. p. 65°, $[\alpha]_{5461}^{20} + 8.02^\circ$ in $CHCl_3$, $+11.9^\circ$ in Et₂O (benzoate, m. p. 72°, $[\alpha]_{5461}^{20} + 28.5^\circ$ in EtOH).

Catalytic reduction (Pt-black) of (II) in AcOH affords the allophanate, m. p. 211°, $[\alpha]_{5461}^{20} + 36.9^\circ$ and $+37.6^\circ$ in $CHCl_3$, of hexahydrovitamin- D_2 (not yet obtained cryst.). When (I) is heated at 188°/vac. a mixture of a substance (III), m. p. 122—124°, $[\alpha]_{5461}^{20} + 256^\circ$, $[\alpha]_{5461}^{20} + 320^\circ$ in $CHCl_3$, and a compound (IV), $C_{27}H_{42}O$, m. p. 93—94°, $[\alpha]_{5461}^{20} + 508^\circ$, $[\alpha]_{5461}^{20} + 625^\circ$ in EtOH (3 : 5-dinitrobenzoate, m. p. 170—171°, $[\alpha]_{5461}^{20} + 213^\circ$, $[\alpha]_{5461}^{20} + 269^\circ$ in C_6H_6), is produced. (IV) is identical with the pyrocalciferol of Askew *et al.* (*loc. cit.*), whilst (III) is an additive (1 : 1) compound of (IV) and an isomeric alcohol.

The "substance L" of Reerink and van Wijk (A., 1930, 256; 1931, 1197) is impure vitamin- D_1 . When vitamin- D_1 is heated at 140°/vac., substances of higher rotatory power are produced. The calciferol of Angus *et al.* (A., 1931, 881) is considered to be a thermal rearrangement product of the vitamin. It is reported that vitamin- D_1 is an additive (1 : 1) compound of vitamin- D_2 and an inactive sterol (designated lumisterol). H. BURTON.

Supposed non-toxicity of filtered irradiated ergosterol preparations. F. LAQUER (Klin. Woch., 1931, 10, 1072—1074; Chem. Zentr., 1931, ii, 735).—The filtered preps. (not exposed to radiation $\lambda < 280 \mu$) are as toxic as unfiltered (totally) irradiated preps. The alleged non-toxicity is attributed to inactivity due to inadequate irradiation.

A. A. ELDRIDGE.

Pharmacological significance of sterols. H. HANDOVSKY (Klin. Woch., 1931, 10, 1158—1159; Chem. Zentr., 1931, ii, 869—870).—Administration to rabbits of vitamin-D or saponin markedly increases oxidation in the liver without affecting the R.Q. Continuation leads also to an increase in glycolysis.

A. A. ELDRIDGE.

Effect of ingestion of irradiated ergosterol on bones. A. WISKOTT (Z. Kinderheilk., 1930, 49, 79—89; Chem. Zentr., 1931, i, 2497).—Young rats became deficient in the dry substance, ash, P, and Ca of the bones; feeding Ca had no effect. In acute vigantol poisoning of adult rats the ash was not diminished, but it was reduced after relatively small doses extending over 6 months.

A. A. ELDRIDGE.

Irradiated milk: energy requirements for antirachitic activation. G. C. SUPPLEE, M. J. DORCAS, and A. F. HESS (J. Biol. Chem., 1932, 94, 749—763).—The character and amount of radiant energy required for the antirachitic activation of cow's milk and the biological activity of the irradiated product were investigated. Suitable radiations from C and Hg-vapour lamps conferred well-marked antirachitic and calcifying properties on milk within a few sec. Such milk retained its healing properties on drying.

F. O. HOWITT.

Vitamin-E. IV. Vitamin content of faeces. A. JOHÁSZ-SCHÄFFER (Arch. path. Anat. Physiol., 1931, 281, 53—65; cf. *ibid.*, 3, 35, 46; Chem. Zentr., 1931, ii, 736).—Orally administered vitamin-E is partly excreted in the faeces of rats. It does not originate in the intestinal tract as a result of bacterial activity.

A. A. ELDRIDGE.

Modern agricultural chemistry as related to the nutrition of the higher plants. K. SCHARRER (Ernähr. Pflanze, 1932, 28, 6—11, 25—29).—A discussion of recent work in plant nutrition with bibliography.

A. G. POLLARD.

Oxygen metabolism of succulent *Crassulaceae*. J. WOLF (Planta [Z. wiss. Biol.], 1931, 15, 572—644).—Relationships between acid formation and carbohydrate metabolism are examined. The balance between carbohydrate utilised and malic acid and CO₂ produced is not exact, there being, in most cases, a deficit on the carbohydrate side. There is no evidence that malic acid is derived from non-fermentable carbohydrates. Exclusion of O₂ or treatment with HCN retards malic acid formation. Narcotics have a similar effect even in concns. which do not affect oxidative processes to an appreciable extent. Variations in the malic acid content of leaves of different ages and at varying temp. are recorded. The assimilation process favours the decomp. of malic acid in part because of the increased O₂ content of the tissues, but more especially as a result of the lowered CO₂ pressure. High concn. of CO₂ may reduce acid decomp. by inhibiting the first stage of oxidation (oxalacetic acid formation), and also, by restricting oxidative processes, cause an accumulation of MeCHO, which in turn inhibits the decomp. of intermediate α -ketonic acids by carboxylase.

A. G. POLLARD.

Malic acid formation in *Crassulaceae*. K. WETZEL and W. RUHLAND (Planta [Z. wiss. Biol.], 1931, 15, 567—571).—Malic acid is produced in *Crassulaceae* and probably in other plants from pyruvic acid. Its formation is related to the reduced carboxylase activity brought about by an accumulation of MeCHO.

A. G. POLLARD.

Respiration of carrot tissue in buffer solutions. L. A. THOMAS (Austral. J. Exp. Biol., 1931, 8, 225—236).—The CO₂ output of carrot tissue in various buffer solutions is determined. The increased respiration rate observed with increasing [H⁺] may be due to the direct effect of the latter or to the [HCO₃⁻] dependent on [H⁺].

A. COHEN.

Formation of anthocyanin in fruit harvested unripe, and the relation between its formation and the activity of the chloroplasts. J. C. POLITIS (Praktika, 1928, 3, 440—441; Chem. Zentr., 1931, ii, 588).—Plasmolysis, coloration of the protoplasm, and degeneration of the nucleus are observed; after separation of the fruit the epicarpal cells die, formation of anthocyanin pigment afterwards occurring. In green fruit during chlorophyll assimilation, when oxidation processes apparently prevail, the formation of anthocyanin is retarded owing to the formation of anthocyanidins by reduction of the corresponding oxyflavones. Flavone compounds are converted in harvested unripe fruit into anthocyanins, reduction processes prevailing.

Changes in barley proteins on storage and sprouting. E. TAKAHASHI and K. SHIRAHAMA (J. Fac. Agric. Hokkaido, 1931, 30, 119—161; Chem. Zentr., 1931, ii, 1505).—The protein of *Hordeum sativum*, Jess., var. Marumi, except that sol. in NaCl solution, showed marked changes. The quantity, composition, and physical nature of the hordein are altered. In 1 year the protein mol. becomes more complex, the hordein increasing in quantity and containing more humin- and sec. NH₂-N. In 1—3 years or on sprouting, the barley contains less complex protein. Bynin is regarded as a denatured hordein produced during germination.

A. A. ELDRIDGE.

Non-protein-nitrogen of the Alaska pea: chemical nature of humin-nitrogen. S. L. JODIDI (J. Agric. Res., 1931, 43, 811—825).—Non-protein-N of Alaska pea seeds contains approx. 7.6% of acid amide-N, 10.5% of humin-N formed on hydrolysis of the acid amides; 8.4% of NH₂-N, 41.8% of peptide-N, and 11.7% of humin-N formed on hydrolysis of the polypeptides, the corresponding figures for peas grown on K₂O-treated soil being approx. 11.4%, 6.7%, 6.0%, 37.6%, and 21.5%, respectively. Humin-N resulting from hydrolysis of the acid amides is split by hydrolysis with 37% HCl into a sol. portion containing 61% of the total humin-N and an insol. portion with 41.4% residual humin-N. Since the sol. portion contained only 52.4% NH₂-N corresponding with 32% of the total humin-N the actual NH₂-N is probably higher. Inasmuch as the humins gave NH₂-N on hydrolysis, they probably contain peptide linkings.

W. G. EGGLETON.

Formation and biological significance of alkaloids. A. GUILLAUME (Bull. Soc. Chim. biol.,

1931, 13, 1243—1247).—Experiments are described showing the formation of alkaloids in young shoots of *Lupinus mutabilis*—facts which are not in agreement with the view that alkaloids are assimilated during seed germination. Evidence is also given of the ability of seeds to lose considerable quantities of alkaloids to the soil. A. LAWSON.

Fertilisers and the growth and alkaloid content of *Lobelia inflata*, L. M. MASCRÉ and H. GÉNOT (Compt. rend., 1932, 194, 384—386).—The effect on the growth and alkaloid content of *L. inflata* of fertilisers containing 6% of H_3PO_4 and K in the form of superphosphate [in one case $Ca_3(PO_4)_2$] and KCl, respectively, containing in addition separate supplements of 6% N as $NaNO_3$, $(NH_4)_2SO_4$, dried blood, and 6% K as KCl is studied. The results show that whilst K decreases, and P has little effect on, the growth, both increase the alkaloid content. The effect of $(NH_4)_2SO_4$, $NaNO_3$, and dried blood on growth decreases in this order, the reverse being the case for the alkaloid content. A. LAWSON.

Urea and ureides in higher plants. II. Appearance and disappearance of urea in plants. G. KLEIN and K. TAUBOCK (Jahrb. wiss. Bot., 1931, 74, 429—458; Chem. Zentr., 1931, ii, 256—257).—Urea does not appear in or disappear from plants of the same kind at the same time.

A. A. ELDRIDGE.

Coloration of plants during desiccation. A glucoside hydrolysable by emulsin in *Bergenia cordifolia*. M. BRAECKE (Bull. Soc. Chim. biol., 1931, 13, 1228—1242).—Determinations of the optical rotation and reducing sugar content of the EtOH extract of the leaves and stems of *B. cordifolia* before and after partial and complete removal of material with basic Pb acetate and again before and after separate treatment with emulsin and invertase, show that sucrose, and a considerable amount of one or more glucosides, hydrolysable by emulsin and pptd. by basic Pb acetate, are present. These glucosides are probably the cause of the blackening of the leaves of *B. cordifolia*, since they are hydrolysed by emulsin to form yellow crystals sol. in Et_2O which become reddish-violet on exposure to air or under the action of oxidases. A. LAWSON.

Colorimetric determination of *Digitalis* glucosides based on Baljet's reaction. J. A. C. VAN PINXTEREN (Pharm. Weekblad, 1932, 69, 4—8).—Determinations based on comparison of the colorations in alkaline picrate solution with those of known ouabain solutions show no relationship with the physiological effect of *Digitalis* extracts.

S. I. LEVY.

Sweet principle of kaà-he-e (*Stevia Rebaudiana*, Bertoni). IV. Stevioside. M. POMARET and R. LAVIEILLE (Bull. Soc. Chim. biol., 1931, 13, 1248—1252; cf. this vol., 46).—Stevioside cannot be classed as a saponin, since it has no haemolytic action. It is non-toxic when administered to guinea-pigs, rabbits, and cocks in amounts up to 2 g., and is rapidly eliminated, to a large extent unchanged.

A. LAWSON.

Distribution of the saponins in *Agrostemma githago* and *Saponaria officinalis*. F. G. DE

WILDE (Pharm. Weekblad, 1932, 69, 65—78).—From determinations of saponin and sugar in the various parts of *A. githago* at all stages of growth, it is concluded that saponin is an intermediate reserve material, used for the building up, when the plant is full grown, of more complicated, unknown food reserve substances, and formed by the break-up of these during germination. In the case of *S. officinalis* the determinations support the same conclusion, but the influence of assimilation on formation of saponin is much clearer. S. I. LEVY.

Grape-seed oil. I. J. MIKŠIĆ and A. REZEK (Glasn. Hem. Društva Kralj. Jugoslavije, 1930, 15 pp.; Chem. Zentr., 1931, i, 2490—2491).—The seeds of a cross between *Vitis riparia* and *V. labrusca* contained 10.7% of an oil, d^{20}_D 0.9221, I val. 135.1. Saponification afforded 68.5% of unsaturated liquid acids (I val. 140.3), 8.84% of solid acids (apparently containing erucic acid), and 0.664% of unsaponifiable matter containing about 50% of phytosterol (sitosterol). The seeds of *V. vinifera* contain larger amounts of phytosterol and liquid fatty acids.

A. A. ELDRIDGE.

Chemical composition of oil of *Ruvettus pretiosus*, the "castor-oil fish." W. M. COX, jun., and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 220—229).—Two samples of the oil showed the following consts.: d^{25}_D 0.8697, 0.8700; I val. (Wijs) 83.9, 74.4; sap. val. 115.4, 124.0; n^{25}_D 1.4633, 1.4628; acid val. and Reichert-Meissl val., each 0. The oil is best classified as a liquid wax. The fatty acids (54.4%) consist of stearic (1.5%), oleic (40%), gadoleic (1.3%), erucic (0.3%), $C_{24}H_{48}O_2$ (trace), $C_{26}H_{50}O_2$ (trace), hydroxyoleic (7%). The unsaponifiable portion (48.5%) contains oleyl (14.3%), tetradecyl (trace), cetyl (16.2%), and octadecyl alcohols (2.1%), cholesterol (0.15%), squalene, and glycerol (traces). Extraction with liquid SO_2 is a satisfactory method for the separation of the saturated and unsaturated constituents of the unsaponifiable fraction. The oil is a mild laxative. C. J. WEST (b).

Dibasic acids in Japan wax. M. TSUJIMOTO (Bull. Chem. Soc. Japan, 1931, 6, 325—337).—Samples of Japan wax (from the berries of *Rhus succedanea*, L.) contain about 5—6% of dibasic acids (determined by means of their insolubility in light petroleum), their separation being best effected either by fractional pptn. with $Pb(OAc)_2$ in 95% EtOH, or by esterification and hydrolysis of the residue after distilling off the more volatile esters. Separation of the constituents of the dibasic acids was attempted by fractional crystallisation and fractional distillation of their esters, the analyses, physical consts., and sap. val. of the fractions being recorded. The main constituent is probably the acid $C_{23}H_{44}O_4$, m. p. 122—123.5° (*Me* ester, m. p. 57.8°), but the acid $C_{22}H_{42}O_4$ also appears to be present in considerable proportions (cf. "japanic acid," A., 1900, i, 271). Addition of small amounts of these dibasic acids to fatty acids increases the coherency, tenacity, and opacity of the structure. J. W. BAKER.

Dibasic acids in some sumach-berry waxes. M. TSUJIMOTO (Bull. Chem. Soc. Japan, 1931, 6, 337—341).—By the methods described above (pre-

ceding abstract) the dibasic acids in the waxes obtained from *Rhus vernicifera*, DC. (I), *R. sylvestris*, S. and L. (II), *R. trichocarpa*, Miq. (III), and *R. toxicodendron*, L. (IV), have been examined. The fatty acids from (I) contain 6.3% of dibasic acids, mainly $C_{22}H_{42}O_4$: (II) and (IV) contain 1.6 and 6.3%, respectively, mainly $C_{23}H_{44}O_4$, whilst (III) gives only a small amount of a substance, m. p. 102° , the nature of which was not ascertained. J. W. BAKER.

Chemical composition of spores of the higher fungi. W. FRIESE (Z. Unters. Lebensm., 1932, 63, 72—77).—Washed, air-dried spores contained H_2O 5.19%, ash 2.99%, comprising 48% K_2O , 2.4% Na_2O , 24.7% P_2O_5 , with 1.44% Fe and 0.07% Mn, and in certain potato moulds traces of Ca and Mg (mean of 15 types), 3.67% N, and 3.46% of fat (n_D^{20} 1.478). The ash (especially of *Amanita*) and H_2O contents were less, and the Fe (especially in *Amanita*) and Mn contents greater, than those of the corresponding air-dried fungi (cf. A., 1929, 1346). Washed spores from four varieties of *Amanita* dried at 105° had a mean ash content of 1.9%, whilst that of similarly-treated spores of the other varieties was 3.48%. J. GRANT.

Nitrate storage in higher marine algæ. S. SUNESON (Z. physiol. Chem., 1932, 204, 81—88).—Several species of marine algæ were examined for NO_3^- . The amount varied considerably with the species and the part of the organism studied. *Laminaria digitata* (stipes) contained 3% on dry wt.

J. H. BIRKINSHAW.

Catalase and sugar determinations in chlorophyll-defective plants. H. VON EULER, U. GARD, and G. RISLUND (Z. physiol. Chem., 1931, 203, 165—177).—The catalase ratio between yellow and white barley mutants differs little for germination at 6° and 19° , respectively. The ratio is much higher for plants grown in the light than for unilluminated plants. The ratio for green and white mutants reaches a min. at the 8th day of germination. Four mutants showed little variation in glucose content, the max. difference being about 25% at the 7th—8th day. In the case of *Pelargonium zonale*, chlorophyll-defective portions of plants grown in glucose solution had a higher catalase content than in H_2O . In *Antirrhinum* leaves and in old leaves of *Abutilon striatum* with A-chlorosis the green/white catalase ratio was high. The green portions of *Abutilon* contain 0.76% of tryptophan (on dry wt.). J. H. BIRKINSHAW.

Buffer systems of *Kleinia articulata*. D. THODAY and H. EVANS (Protoplasma, 1931, 14, 64—74).—The form of the titration curve of the juices of old stems of *K. articulata* is similar to that of malic acid containing small amounts of Al, and that of young stems to malic acid containing Ca phosphate. The presence of Al^{+++} , Ca^{++} , and PO_4^{---} in the juices is demonstrated. A. G. POLLARD.

Urea permeability of stomata cells of various ages. F. WEBER (Protoplasma, 1931, 14, 75—82).—The guard cells of *Ranunculus ficaria* stomata are highly permeable to urea during their active stages, but have low permeability in the embryonic stage and in old yellowed leaves. A. G. POLLARD.

Specificity of the precipitin reaction in tobacco mosaic disease. H. P. BEALE (Contr. Boyce Thompson Inst., 1931, 3, 529—539).—Evidence favours the view that the sp. antigenic substance in virus extract of tobacco mosaic disease is foreign antigenic material, possibly virus itself, rather than altered host-protein. A. G. POLLARD.

Feulgen's reaction: application to botanical material. L. A. MARGOLENA (Stain Tech., 1932, 7, 9—16).—Feulgen's reaction (A., 1924, i, 905) is excellent for nuclear staining and has been applied to normally treated sections of many vegetable tissues. It is positive with lignin, suberin, and cutin and is useful for their detection. Several yeasts were tested. All reacted positively, with a fusiform purple nucleus. Results with bacteria are so far inconclusive. H. W. DUDLEY.

New method of differentiating gentian-violet when used as a somatic chromosome stain. D. A. JOHANSEN (Stain Tech., 1932, 7, 17—20).—The addition of 0.5% of picric acid to the dehydrating alcohols makes possible a better differentiation than has previously been obtainable. The method is specially applicable to root-tips of plants of arid regions. H. W. DUDLEY.

Reduction [processes]. K. SPIRO (Z. Hyg., 1931, 113, 39—47).—Applications of the Mo-blue reaction to determinations of reducing substances and for the examination of biological oxidation-reduction actions are described. A. G. POLLARD.

Determination of sodium in organic substances having high potassium content. B. SJOLLEMA and J. W. DIENSKE (Biochem. Z., 1931, 243, 396—400).—In the procedure of Barber and Kolthoff (A., 1928, 859) if the ratio K:Na exceeds 20:1 part of the K must be removed before pptn. of the Na. In the method described this is done with tartaric acid and good results are obtained even when the ratio is 60:1. W. MCCARTNEY.

Iodometric and manometric determination of nitrogen with hypobromite. A. FUJITA and S. KASAHARA (Biochem. Z., 1931, 243, 256—268).—N in biological material can be determined, with accuracy equal to that obtained in the micro-Kjeldahl method, by oxidising the substance (0.2—0.55 mg. N for iodometric, 0.06—0.25 mg. for manometric) with hot H_2SO_4 in the presence of K_2SO_4 and H_2O_2 , making the resulting solution feebly alkaline, adding alkaline NaOBr solution, and either measuring the N_2 liberated by Warburg's method or determining the excess of NaOBr used by adding KI and HCl and titrating with 0.01N- $Na_2S_2O_3$. W. MCCARTNEY.

Van Slyke's method for determination of amino-groups. K. L. ZIRM (Biochem. Z., 1931, 243, 310—311).—In the Van Slyke apparatus foaming (e.g., of liquids containing up to 1% of serum) can be counteracted by the introduction of a roll of metallic gauze (Pt, Cu, or steel) or, alternatively, by means of octyl alcohol added from a special tap-funnel attached to the reaction vessel. W. MCCARTNEY.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1932.

General, Physical, and Inorganic Chemistry.

Relations between corresponding quadruplets of N I, O II, S II, and Cl III. J. GILLIES (Compt. rend., 1932, 194, 606—607). C. A. SILBERRAD.

Light intensities of neon discharges. P. JOHNSON (Phil. Mag., 1932, [vii], 13, 487—494).—Light intensities in the visible and ultra-violet spectrum of a d.c. discharge in Ne were measured and correlated with the pressure and current. H. J. EMELÉUS.

Study of a neon discharge by use of collectors. C. G. FOUNT and I. LANGMUIR (Physical Rev., 1932, [ii], 39, 237—253).—Resonance radiation from a Ne arc can travel 20—30 cm. through non-ionised Ne; absorption by normal gives excited Ne atoms, which, in the metastable state, diffuse to the walls and metal electrodes and there liberate secondary electrons.

N. M. BLIGH.

Profile of the magnesium line at 5183 Å. in the solar spectrum. G. RIGHINI (Atti R. Accad. Lincei, 1931, 14, 285—287). H. F. GILLBE.

Arc spectrum of magnesium, Mg I. F. PASCHEN (Sitzungsber. preuss. Akad. Wiss., 1931, 32, 9 pp.).—The spectrum is described and analysed.

A. J. MEE.

Zeeman effect and A-type and spin doubling in the CaH bands. W. W. WATSON (Physical Rev., 1932, [ii], 39, 278—288; cf. A., 1930, 1075).

N. M. BLIGH.

Extinction and transformation of resonance series spectra into band spectra. O. HEIL (Z. Physik, 1932, 74, 18—30).—Mols. (Se₂ and Te₂) that are rapidly extinguished by the presence of inert gases do not readily transform to give band spectra in place of the resonance series doublets; S₂ is not rapidly extinguished and readily gives a band spectrum.

A. B. D. CASSIE.

Polarisation of resonance radiation and hyperfine structure: the cadmium resonance lines. A. ELLETT and L. LARRICK (Physical Rev., 1932, [ii], 39, 294—298).—The Cd resonance lines λ 2288 and 3261 Å. excited by unpolarised radiation in a magnetic field parallel to the exciting light are 76.3 and 86—87% polarised, respectively. Mitchell's results (cf. A., 1931, 1104) are not supported.

N. M. BLIGH.

Absorption spectrum of I₂. I. I. AGARBICANU (Compt. rend., 1932, 194, 702—703; cf. A., 1923, ii, 669).—The heads of about 20 new bands between λ 6450 and 5230 have been measured, and previous measurements of Mecke confirmed.

C. A. SILBERRAD.

Absorption, fluorescence, and emission bands of caesium. R. ROMPE (Z. Physik, 1932, 74, 175—186). A. B. D. CASSIE.

Band spectrum of barium hydride. A. SCHAATSMA (Z. Physik, 1932, 74, 254—266; cf. this vol., 104). A. B. D. CASSIE.

Hyperfine structure of the mercury line 4916 Å. S. TOLANSKY (Nature, 1932, 129, 204).—A discussion. L. S. THEOBALD.

Polarisation of mercury resonance radiation. L. LARRICK and N. P. HEYDENBURG (Physical Rev., 1932, [ii], 39, 289—293).—The polarisation of the line λ 2537 Å. in resonance radiation, and the relative transition probabilities within a hyperfine multiplet, are calc. N. M. BLIGH.

Hyperfine structure of mercury. III. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 17, 299—306; cf. this vol., 2).—The hyperfine structure of the lines λ 5769.6, 5790.66, and 5789.69 is interpreted. The lines λ 4347.5, 4339.23, 3983.96, 6123.37, and 5461 were examined for isotope separation.

N. M. BLIGH.

ulv Emission in xenon and thallium III. W. M. HICKS (Phil. Mag., 1932, [vii], 13, 329—354).

H. J. EMELÉUS.

Theory of complex spectra. I. Energy levels. M. H. JOHNSON, jun. (Physical Rev., 1932, [ii], 39, 197—209; cf. this vol., 2).—Mathematical.

N. M. BLIGH.

Gas discharges at very high frequencies. L. RÖHDE (Ann. Physik, 1932, [v], 12, 569—599).—The behaviour of different gases in electric and magnetic fields of very high frequencies was investigated. The dependence of the min. ignition potential on pressure was determined. For gases other than inert there is a sharp min. in the pressure curve, of which the abs. val. is lower the lower is the wavelength. In the case of the inert gases, pressure was without effect. The ignition potential decreases with increasing frequency. The electrodeless ring discharge is also investigated. It can be produced up to 2.30 m. The use of high-frequency discharges for spectroscopic and other electro-optical purposes is mentioned.

A. J. MEE.

"Ultimate" rays. T. NEGRESKO (Bull. Math. Phys. Bucarest, 1931, 11, 191—194).—The lines last to disappear when the concn. of the element producing them is progressively diminished have been investi-

gated. The most lasting spark spectra lines are not the same as those in the arc. A. J. MEE.

Material transport in the luminous arc. L. S. ORNSTEIN and T. KOOPMANS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1099—1100).—The spectral lines of an electric arc, of which the anode and cathode consist of different metals, show a transition in intensity on passing from one electrode to the other. J. W. SMITH.

Optical investigation of collisions of gas molecules with a solid wall. W. R. VAN WIJK (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1201—1205).—An optical method of measuring the accommodation coeff. of gas mols. on a solid surface is described. The mols. reflected from a surface show no Boltzmann distribution of the rotation states, the higher rotation levels occurring in too great a proportion. This effect is qualitatively independent of the ratio N_1/N_2 of the mol. densities of the gas incident on the wall and emerging from it. J. W. SMITH.

Exchange of energy between gas atoms and solid surfaces. II. Temperature variation of the accommodation coefficient of helium. J. K. ROBERTS (Proc. Roy. Soc., 1932, A, 135, 192—205).—The accommodation coeff. of He with a W surface from which films of adsorbed gas have been removed is much lower than those ordinarily measured (A., 1930, 1340). Data are now given for the variation of the accommodation coeffs. between 22° and -194°. At -194° the very low val. of 0.025 is obtained. The results suggest that as 0° abs. is approached the accommodation coeff. would approach zero. L. L. BIRGUMSHAW.

Atom factors. W. EHRENBERG and K. SCHAFER (Physikal. Z., 1932, 33, 97—122).—A *resumé* of work on atom factors with a table of vals. A. B. D. CASSIE.

Scattering of X-rays by simple gases (N_2 , O_2 , CO_2 , CS_2 , NH_3 , H_2O). H. GAJEWSKI (Physikal. Z., 1932, 33, 122—131).—Experimentally determined angular distributions of scattered radiation fit theoretical curves obtained by assuming a finite distribution of electronic charge and by adjusting nuclear separations. A. B. D. CASSIE.

Absorption of X-rays in gases and vapours. II. J. A. CROWTHER and L. H. H. ORTON (Phil. Mag., 1932, [vii], 13, 505—523; cf. A., 1930, 1229).—The mass absorption coeffs. and relative ionisations of a number of gases and vapours were measured with Cu K- and Fe K-radiation. At. absorption coeffs. were deduced for C, N, O, Ne, Al, S, Cl, A, Zn, Br, I, and used to test the relation between at. absorption and at. no. and between at. absorption and wavelength. De Broglie's formula agrees with observations for elements in group I of the periodic table, but breaks down for elements of higher at. no. H. J. EMELÉUS.

Excitation potentials of light metals. I. Lithium. H. W. B. SKINNER (Proc. Roy. Soc., 1932, A, 135, 84—108).—The radiation emitted by metallic Li has been studied by the photo-electric method. The min. excitation potential for the K-radiation of Li is 9 volts below the K-ionisation potential of the Li atom, so that it is possible to excite

a K-resonance radiation in the metal. The observed crit. potentials of Li metal are correlated with the calc. energy levels of the free Li atom. An attempt is made towards a theory of the approx. linear relationship found between the intensity of radiation emitted from a metal and the voltage of the exciting electron beam. L. L. BIRGUMSHAW.

New lines in the K series of X-rays. W. DUANE (Proc. Nat. Acad. Sci., 1932, 18, 63—68).—In an examination of the K series lines of X-rays from Mo, reflected from the 100 plane of a calcite crystal, a new band has been discovered at a slightly shorter wave-length than the γ line of Mo. W. R. ANGUS.

Fine structure of X-ray absorption edges. D. COSTER and J. VELDKAMP (Z. Physik, 1932, 74, 191—208; cf. A., 1931, 993).—Further experimental evidence is offered in favour of Kronig's theory. Fine structure was measured in the K edge of Cu, Fe, and Zn, the last at temp. up to 405°, and in the L_{111} edge of Au and Pt. A. B. D. CASSIE.

Quadrupole lines in X-ray spectra. E. SEGRÈ (Atti R. Accad. Lincei, 1931, [vi], 14, 501—505).—All the forbidden lines of X-ray spectra can be attributed to quadrupole radiation. O. J. WALKER.

Ionising efficiency of electronic impacts in air. J. THOMSON (Proc. Roy. Soc. Edin., 1930—1931, 51, 127—141).—The energy spent in producing one pair of ions by total absorption of electrons (velocity corresponding with 50—270 volts) in air, measured by an ionisation chamber method, varies with the initial velocity of the electron and is asymptotic to the val. 37 ± 2 electron-volts when the energy of the electron is very great. H. E. BLAYDEN.

Attempt to detect high photo-electric absorption in caesium vapour at double the series limit. E. T. S. APPLEYARD (Phil. Mag., 1932, [vii], 13, 300—305).—No absorption in Cs vapour in the region λ 1500—1600, as would be expected as a thermodynamic inverse to the experiments of Davis and Barnes on He (cf. A., 1930, 393), could be detected. N. M. BLIGH.

Thermionic emission and space charge. N. H. FRANK (Physical Rev., 1932, [ii], 39, 226—236).—Mathematical. N. M. BLIGH.

Effect of surface changes on the photo-electric emission of silver and gold. T. E. CLARKE (Phil. Mag., 1932, [vii], 13, 624—632).—The influence of annealing, polishing, and of adsorbed gas on the photo-electric emission of Ag and Au was investigated. H. J. EMELÉUS.

Collision of electrons with rotating dipoles. H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1932, 28, 99—105). N. M. BLIGH.

New characteristic of the Dirac electron. A. PROCA (Compt. rend., 1932, 194, 691—693).—Mathematical. The Dirac electron has, besides the magnetic moment of Uhlenbeck and Goudsmit, a natural electric moment, distinct from that resulting from its magnetic moment; it behaves as if, besides its electric charge, e , it had a free magnetic charge $u = e$. C. A. SILBERRAD.

Influence of a cloud of electrons on structure of de Broglie waves. S. SZCZENIOWSKI and L. INFELD (Bull. Acad. Polonaise, 1931, A, 483—488).—Mathematical.

Angular distribution in the scattering of slow electrons by gas molecules. II. C. RAMSAUER and R. KOLLATH (Ann. Physik, 1932, [v], 12, 529—561; cf. A., 1931, 782, 1107, 1200).—The zone apparatus previously described is improved and a method devised which gives the scattering as a function of scattering angle for small angles. The angular distribution was found in He, Ne, A, H₂, CO, and CO₂ for electron velocities between 1 volt and the excitation potential of the gas. The angular range investigated was 15—167°.

A. J. MEE.

Collision of electrons with molecules. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1932, A, 135, 258—275).—The collision theories of Born and Oppenheimer (A., 1928, 1170) are applied to various phenomena occurring on electron impact with mols. Elastic scattering is considered and general formulæ are obtained for the case of diat. mols., including the relation between X-ray and electron scattering. The intensity of elastic scattering in mol. H₂ is calc. for all angles and velocities for which the Born theory is valid.

L. L. BROMSHAW.

Effect of electron attachment on the ion mobility curves in the Zeleny air-blast method of ion mobility measurement. L. B. LOEB and N. E. BRADBURY (J. Franklin Inst., 1932, 213, 119—154).—Zeleny's results (cf. A., 1931, 1207) are interpreted by the application of the simplified theory of electron attachment.

N. M. BLIGH.

Polarisation of electrons. E. RUPP (Physikal. Z., 1932, 33, 158—164).—Experiments are described which show the polarisation of electrons, (a) at grazing reflexion, (b) by scattering at 90°, followed by transmission of the rays through a thin metal foil. The polarisation is connected with the magnetic moment of the electron. Application of a longitudinal magnetic field causes a rotation of the polarisation. The effect of a transverse field in various positions with respect to the direction of the rays is also given.

A. J. MEE.

Artificial production of fast protons. J. D. COCKROFT and E. T. S. WALTON (Nature, 1932, 129, 242).—Protons with a velocity of 10⁹ cm. per sec. have a range in air of 8.2 mm., and in H₂, of 3.2 cm. at N.T.P. This supports Blackett's conclusions on the relative ranges of protons and α -particles.

L. S. THEOBALD.

At. wt. of fluorine. H. S. PATTERSON, W. CAWOOD, and R. WHYTLAW-GRAY (Nature, 1932, 129, 245).—A discussion of certain points in previous work on the at. wt. of F. Chemical evidence at present indicates a val. of 19.01 in preference to 19.00 (cf. this vol., 106).

L. S. THEOBALD.

Revision of at. wt. of lanthanum. I. Analysis of lanthanum bromide. II. Specific gravities of lanthanum chloride and bromide. III. Increased efficiency of calcium bromide as a drying agent at low temperatures. G. P. BAXTER and E. E. BEHRMANS (J. Amer. Chem. Soc., 1932, 54,

591—602; cf. A., 1922, ii, 298, 770).—By analysis of LaBr₃ the val. 138.923 has been obtained for the at. wt. of La. LaCl₃ has d^{25} 3.842 and LaBr₃ d^{25} 5.057. The efficiency of CaBr₂ as a drying agent improves on cooling at -21° or -72°.

L. P. HALL (c).

Element 87. F. ALLISON, E. R. BISHOP, A. L. SOMMER, and J. H. CHRISTENSEN (J. Amer. Chem. Soc., 1932, 54, 613—615).—By the magneto-optic method (A., 1930, 1541) characteristic minima are obtained for a cation with an equiv. wt. greater than Tl⁺, which are due, not to SnCl₂⁺ or ReCl⁺, but to element 87, which appears to have six isotopes and for which the name "virginium" and symbol Va are suggested. Small amounts of Va have been detected in pollucite, lepidolite, Searle's Lake brine, kainite, monazite sand, and samarskite.

L. P. HALL (c).

Isotope of uranium. G. EISEN (Rec. trav. chim., 1932, 51, 284—288).—On the assumption that active U is the isotope U²³⁹ and the at. wt. of U is 238.189, the amount of Ac-U present is approx. 16%. Taking van Grosse's new val. of 238.084, however (A., 1931, 15), there is 10% Ac-U in U. On the basis of the first val. the radioactive const. is 6.86×10^{-11} year⁻¹ and the period 1.01×10^{10} years. For 10% Ac-U the corresponding vals. are 1.17×10^{-11} year⁻¹ and 5.95×10^{10} years.

M. S. BURR.

High-tension supply for Geiger counters operated from a.c. mains. H. C. WEBSTER (Proc. Camb. Phil. Soc., 1932, 28, 121—123).—An arrangement to give const. voltage and freedom from a.c. ripple and other disturbances is described.

N. M. BLIGH.

Influence of radioactive substances on the Volta effect. L. BOUCHET (Compt. rend., 1932, 194, 605—607).—The radioactivity of U₃O₈ has very little influence on the Volta effect between gilt brass and Cd, Cu, Mg, Sn, or Zn (cf. A., 1882, 921).

C. A. SILBERRAD.

Attempt to detect the spontaneous transformation of helium into penetrating radiation. G. T. P. TARRANT and L. H. GRAY (Proc. Camb. Phil. Soc., 1932, 28, 124—127).—No evidence of production of any hard radiation by He in bulk in the neighbourhood of an ionisation chamber was obtained. Results indicate that atm. He cannot account for more than 2% of the effect of penetrating radiation, and interstellar He only if present in excess of 1%.

N. M. BLIGH.

Range and ionising power of H- and α -rays. E. RUCHARDT (Ann. Physik, 1932, [v], 12, 600—606).—The results of Gerthsen (A., 1930, 1083) are in good agreement with those obtained by entirely different methods.

A. J. MEE.

Loss of energy of α -particles and H-particles. P. M. S. BLACKETT (Proc. Roy. Soc., 1932, A, 134, 132—142).—Theoretical. The observed loss of energy of α -particles in H₂, He, and air is compared with the formula given by Bethe's theory of the loss of energy of fast particles (A., 1930, 972). The effect of capture and loss of electrons on the rate of loss of energy is discussed.

L. L. BROMSHAW.

Passage of α - and β -particles through matter and Born's theory of collisions. E. J. WILLIAMS

(Proc. Roy. Soc., 1932, A, 135, 108—130).—The non-relativity theory of the passage of electric particles through matter developed by Bethe on the basis of Born's theory of collisions (A., 1930, 972) is compared with experimental results for the stopping power, primary ionisation, total ionisation, straggling, and production of branches by α - and β -particles. Some of these phenomena (e.g., the stopping power of H_2 for slow β -particles) are accounted for by the new theory, but the total ionisation of the monat. gases and the straggling of α -particles in light elements still present difficulties. The experimental results for fast β -particles indicate a small relativity correction to Bethe's formulæ. L. L. BIRCUMSHAW.

Artificial disintegration by α -particles. II. Fluorine and aluminium. J. CHADWICK and J. E. R. CONSTABLE (Proc. Roy. Soc., 1932, A, 135, 48—68).—The proton emission from Al bombarded by α -particles from Po can be resolved into 8 groups, due to penetration of the α -particles through 4 resonance levels, each level giving rise to a pair of groups. The disintegration of F, which gives 6 groups of protons when bombarded by α -particles, is explained in a similar way. L. L. BIRCUMSHAW.

Scattering of β -rays. J. A. GRAY (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 57—64).—Experiments described indicate that the scattering of β -rays is accompanied by loss of energy, which is the greater the smaller is the at. no. of the scattering atom, and the greater is the angle of scattering. For single scattering, a radiator must be so thin that both the intensity and the average energy of the scattered rays are proportional to the thickness of the radiator. A. J. MEE.

Upper limit of energy in the β -ray spectrum of thorium-C''. F. R. TERROUX and N. S. ALEXANDER (Proc. Camb. Phil. Soc., 1932, 28, 115—120).—The upper part of the spectrum investigated by the expansion chamber method showed no "tail," and no tracks of H_p greater than 10,800; the end-point is placed at 9400 H_p . N. M. BLIGH.

Number of secondary β -rays emitted by radium. E. STAHEL (Compt. rend., 1932, 194, 608—610).—Using Ra free from emanation and active deposit spread on a diamond surface and the arrangement previously described (cf. A., 1931, 543), the no. of secondary β -rays per 100 atoms of Ra decomposed is 5 ± 1 . Preliminary experiments show that the no. of γ -rays emitted is approx. the same. The Ra atom must therefore decompose, either with emission of only a single α -particle, or with simultaneous emission of an α -particle and also of a γ -ray or the corresponding secondary β -ray. C. A. SILBERRAD.

Nomenclature for lines in the β -ray spectra of radioactive bodies. C. D. ELLIS (Nature, 1932, 129, 276).—A nomenclature is suggested.

L. S. THEOBALD.

Effect of absorption of γ -rays of very high frequency by projection from light nuclei. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1932, 194, 708—711).—The H particles ejected from paraffin by γ -rays of Po+Be (cf. this vol., 210), examined in a Wilson expansion chamber, show tracks of all

lengths to >12 cm., and also β -rays, some of energy $>10^6$ volts, due probably to a Compton effect. Comparison of μ/ρ of these γ -rays and of γ -rays from Th-C'' in Cu, C, and paraffin show that much energy is absorbed by the H nuclei, and a considerable amount by C; also the ionisation current produced by the Po+Be γ -rays in He is 4.6 times that produced in air at the same pressure. The phenomenon thus appears to be general. From considerations of the absorption by diffusion it is concluded that the absorption attributable to emission of H particles is a new method of interaction between radiation and matter. Deduction of wave-length from coeff. of absorption in cases of high quantum energies is erroneous. C. A. SILBERRAD.

Interval between the departure of the disintegration particle and the emission of the gamma radiation. P. WRIGHT (Proc. Camb. Phil. Soc., 1932, 28, 128—135).—No evidence of γ -ray emission from the space above a source of Ra-C liberating recoil atoms of Ra-C' was obtained, indicating that the interval between the departure of the disintegration particle and emission of the γ -ray quantum is $<10^{-5}$ sec. N. M. BLIGH.

Absorption of hard monochromatic γ -radiation. II. G. T. P. TARRANT (Proc. Roy. Soc., 1932, A, 135, 223—236; cf. A., 1930, 1085).—The absorption coeffs. of the γ -rays from Th-C'' have been measured, using an ionisation chamber containing gas at 120 atm. pressure. The vals. for the light elements are $3.1\% >$ those calc. from the Klein-Nishina formula (A., 1929, 373), indicating the possibility of nuclear absorption occurring for the light elements as well as for the heavy. The vals. per electron vary between the light and heavy elements as the square of the at. no. L. L. BIRCUMSHAW.

Abnormal absorption of heavy elements for hard γ -rays. C. Y. CHAO (Proc. Roy. Soc., 1932, A, 135, 206—213).—Approx. homogeneous γ -ray beams of varying wave-length are obtained from a strongly filtered Th-C'' primary radiation, by utilising the change of wave-length accompanying scattering. A rapid decrease of the extra-absorption of the scattered rays in lead is found between $\lambda=5.9$ and 6.6 X. This suggests the existence of an excitation or a disintegration potential. L. L. BIRCUMSHAW.

Active nitrogen. IX. Electric conductivity of active nitrogen. E. J. B. WILLEY and W. A. STRINGFELLOW. **X. Supposedly oxidisable variety of nitrogen.** E. J. B. WILLEY and S. G. FOORD (J.C.S., 1932, 142—152, 153—161).—IX. Charged particles probably play no part in the chemical reactions of active N. The conductivity of active N is a surface effect, due to the ejection of electrons from the testing electrodes by impact and deactivation of 8-volt metastable N_2 . The conductivity was shown not to be due to photo-electric emission from the testing electrodes.

X. No evidence was obtained for the existence of an oxidisable active species of N, or of an oxide of N, which reacts with O_3 but not with O_2 . Lowry's results (J.C.S., 1912, 101, 1152) may be explained by the very rapid reaction of NO and O_3 compared with that of NO and O_2 . H. J. EMELÉUS.

Determination of the Stefan-Boltzmann radiation constant, using a Callendar radio-balance. F. E. HOARE (Phil. Mag., 1932, [vii], 13, 380—392).—With a source of radiation at approx. 100° the mean val. obtained was 5.737×10^{-5} erg./sec./cm.²/deg.⁴.

H. J. EMELEUS.

Quantum mechanical theory of energy exchanges between inert gas atoms and a solid surface. J. M. JACKSON (Proc. Camb. Phil. Soc., 1932, 28, 136—164).—Mathematical.

N. M. BLIGH.

Continuous atomic matrix. W. R. MORGANS (Phil. Mag., 1932, [vii], 13, 664—673).—Mathematical.

H. J. EMELEUS.

Chemistry and the quantum theory of atomic constitution. N. BORN (J.C.S., 1932, 349—384).—Faraday Lecture.

Beryllium molecule. W. H. FURRY and J. H. BARTLETT, jun. (Physical Rev., 1932, [ii], 39, 210—225).—Mathematical. The stability of Be mol. states is investigated.

N. M. BLIGH.

Search for the band spectra of boron fluoride. N. R. TAWDE and R. C. JOHNSON (Phil. Mag., 1932, [vii], 13, 501—504).—New bands between λ 6400 and 4438 Å., which may be due to BF, were measured.

H. J. EMELEUS.

Absorption spectrum of iodine bromide in the visible. H. CORDES (Z. Physik, 1932, 74, 34—44).—The heat of dissociation of IBr is 1.80 volts, and of ICl 2.043.

A. B. D. CASSIE.

Absorption spectra of various series of rare-earth double nitrates. II. D. WYLLIE and J. A. HARRIS (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 107—113).—Various double and simple nitrates of Ce-free, Ce group rare earths have been repeatedly recryst. to test the val. of these salts in the separation of rare earths. A study of absorption spectra indicates that crystallisation of simple nitrates from conc. HNO₃ and formation of double nitrates with Pb and Cd do not provide satisfactory methods for the separation of the rare earths of the Ce group. Fractional recrystallisation of the double nitrates with NH₄ is the most efficient method for a preliminary separation of Pr from La and Nd. Mg, Co, and Zn double nitrates crystallise well, but give no marked separation. For the rapid separation of Sm the use of the double nitrate of the Ce group earths with Ni is recommended.

A. J. MEE.

Absorption spectra of rare-earth glazes. F. H. NORTON and D. T. H. SHAW (J. Physical Chem., 1931, 35, 3480—3485).—The spectro-photometric reflecting curves of glazes containing oxalates of Ce, Pr, Nd, Sm, and "didymium" have been obtained. The reflexion minima correspond closely with the absorption bands of aq. solutions of the salts, thus indicating that the absorption characteristics of the rare-earth atoms are not appreciably altered in the change from an aq. solution to a silicate glass. The characteristic absorption bands by which the elements may be easily identified are: Ce, 585 mμ; Pr, 592 mμ; Nd, 525 and 585 mμ; Sm, 470 and 560 mμ.

C. C. KIESS (c).

Number of excited atoms and the absorption spectra of various metallic vapours. A. T. WIL-

LIAMS (Physikal. Z., 1932, 33, 152—158).—By investigating the vapours of Cu, Ag, and Au, it was shown that the relationship $N_1/N = e^{-E/RT}$, where N_1/N is the ratio of the no. of excited to total atoms, and E is the absorbed exciting energy, is valid, apart from a few anomalies.

A. J. MEE.

Intensity measurements in ultra-violet spectra by means of photo-electric cells sensitised by sodium salicylate. A. CHEVALLIER and P. DUBOULOZ (Compt. rend., 1932, 194, 452—454; cf. this vol., 213).—The method is applied to the determination of the intensity of the fluorescent light as a function of the wave-length of the exciting light, giving a curve closely resembling that relating energy to wave-length in H₂ (cf. A., 1929, 616); also to the determination of the ultra-violet absorption spectrum of COMe, (cf. A., 1926, 774).

C. A. SILBERRAD.

Change in colour on heating of pyridine solutions of cobalt chloride. I. ROHDE and E. VOGT (Z. physikal. Chem., 1932, B, 15, 353—364).—Absorption curves of CoCl₂ dissolved in pyridine have been determined between -45° and 105°. The variation in the absorption with change in temp., visible as a colour change from red to blue between about 10° and 50°, actually goes on over the whole temp. range from the f. p. to the b. p. of the solution. The absorption spectrum consists of two superimposed curves, corresponding with two distinct mol. species. Change in temp. does not affect the separate spectra, but only the relative amounts of the two mol. species. At 503 mμ both forms have the same extinction coeff., for the absorption curves at all temp. intersect at this wave-length. The variation in temp. of the absorption coeff. for a selected wave-length (610 mμ) agrees with the assumption that the change red → blue is a unimol. reaction in respect of Co, the heat of reaction being 11,700 g.-cal. At 50°, when the solution appears to have a pure blue colour, the ratio of the blue form to the red form is 1:10, and reaches 1:1 only at 97°. The results tend to confirm the theory that the colour changes are due to such a reaction as $\text{CoCl}_2 \cdot 4\text{C}_5\text{H}_5\text{N} (\text{red}) \rightleftharpoons \text{CoCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N} (\text{blue}) + 2\text{C}_5\text{H}_5\text{N}$ (cf. A., 1927, 205).

R. CUTHILL.

Absorption spectra of sulphur compounds of various valencies. H. LEY and B. ARENDS (Z. physikal. Chem., 1932, B, 15, 311—324).—Solutions of H₂S in H₂O and hexane have practically the same absorption curve, with a max. at 189 mμ, which is attributed to the undissociated mol. In aq. Na₂S the max. has shifted to 227 mμ, and corresponds with the HS' ion. EtSH has a band at 193.5 mμ, and indications of another at about 225 mμ. No definite max. appear on the curves for EtSNa and Et₂S. Et₂S₂ has a band at 249 mμ and another below 185 mμ. The absorption bands of the alkali and alkyl sulphates, and probably also of the sulphonium salts, lie far in the ultra-violet, and could not be located with the apparatus used, the lower limit of which was about 185 mμ.

R. CUTHILL.

Ultra-violet absorption of some aromatic hydrocarbons. W. PESTEMER and J. CECILSKY (Monatsh., 1932, 59, 113—127).—Ultra-violet absorption data are recorded for diphenyl, dinaphthyl, anthracene, phenanthrene, and perylene dissolved in

hexane. From the results it is difficult to regard perylene as having a definite naphthalene or anthracene character. Perylene cannot be considered as a simple union of two $C_{10}H_8$ chromophores, as in the case of dinaphthyl, but as an individual chromophore or an individual system of chromophores. M. S. BURR.

Absorption in the ultra-violet of solutions of optically active organic compounds. R. LUCAS and M. SCHWOB (J. Phys. Radium, 1932, [vii], 3, 43—56).—Data for camphor in CCl_4 , cyclohexane, EtOH, AcOH, C_6H_6 , HCO_2H , and H_3PO_4 , fenchone in C_6H_{12} , *d*-cyanocamphor in cyclohexane and C_6H_6 , and tartaric acid in various solvents show that rotatory power varies with the solvent and concn., and absorption varies with the solvent and, contrary to Beer's law, with the concn. Possible explanations are discussed. N. M. BLIGH.

Ultra-violet absorption spectra of solutions of substituted phenyluracils. J. EVANS (J. Amer. Chem. Soc., 1932, 54, 641—646).—Ultra-violet absorption spectra curves of 6-phenyluracil, its 1-*N*- and 3-*N*-Me and 1:3-*NN*-Me₂ derivatives, Et 6-phenyluracil-3-*N*-acetate, Me 6-phenyl-1-*N*-methyluracil-3-*N*-acetate, 6-phenyl-1-*N*- and 3-*N*-methylhydouracils, and Et 6-phenyl-1-*N*-methylhydouracil-3-*N*-acetate are given. The absorption spectra of 1-*N*-substituted uracils differ from those of the 3-*N*- or non-substituted derivatives; the difference can be used to distinguish the 1-*N*- from the 3-*N*-substituted 6-phenyluracils. C. J. WEST (b).

Infra-red radiation of refractory substances. B. WREDE (Mitt. Kaiser-Wilh.-Inst. Eisenforsch., 1931, 13, 131—142; Chem. Zentr., 1931, ii, 1972).—The spectral distribution of the emission of silica (95% SiO_2), chamotte (55% SiO_2), sillimanite (33% SiO_2), corundum (70% Al_2O_3), and magnesite (80% MgO) refractories in the region 1—9 μ was determined. A. A. ELDRIDGE.

Normal vibrations of acetylene. A. R. OLSON and H. A. KRAMERS (J. Amer. Chem. Soc., 1932, 54, 136—138).—The ratios of the frequencies corresponding with the five normal modes of vibration of the C_2H_2 mol. have been recalcd. on the basis of classical mechanics. The vals. of ν_1 , ν_2 , and ν_3 are not inconsistent with Mecke's interpretation of the spectrum, but if the new vals. of δ_1 and δ_2 are correct, Mecke's correlation with experiments must be revised. C. J. HUMPHREYS (c).

Raman effect from the viewpoint of unimolecular reactions. A. GANGULI (Phil. Mag., 1932, [vii], 13, 306—310; cf. A., 1931, 1130).—Mathematical. N. M. BLIGH.

Raman spectrum of sulphuric acid and the action of an electric field on it. V. RICCA (Atti R. Accad. Lincei, 1931, [vi], 14, 288—290).—With 50 wt.-% H_2SO_4 there is a displacement of the Raman lines towards the violet when the electric current applied is such that the H^+ ions move away from the spectrograph and towards the red in the opposite case, and in both cases the intensity of the lines is diminished. O. J. WALKER.

Raman effect and molecular structure of some simple inorganic substances. A. DADIEU and K. W. F. KOHLRAUSCH (Physikal. Z., 1932, 33, 165—

172).—The Raman spectra of NH_3 , SO_2 , H_2S , and COS were investigated, and on the basis of these results and those of infra-red determinations, the mol. consts. were obtained. Experiments with butane, NOCl, and N_2O_4 led to no results, owing, in the last two cases, to their deep colour. A. J. MEE.

Relative efficiency of some of the mercury arc lines in exciting the Raman spectrum of benzene. (Miss) WERTH (Physical Rev., 1932, [ii], 39, 299—310).—The observed Raman frequencies are $\Delta\nu$ 606, 845, 992, 1175, 1585, 1603, 2947, 3060, 3183, and the corresponding exciting lines are 3650, 3654, 3663, 4047, 4078, 4108, 4339, 4347, and 4358 Å. Total intensities are tabulated. Relative intensities of Raman patterns for lines of single origin were measured. Rayleigh's fourth-power law was verified. N. M. BLIGH.

Raman spectra in liquid and gaseous methane. S. C. BISWAS (Phil. Mag., 1932, [vii], 13, 455—459).—The possibility of two physically distinct forms of CH_4 is discussed on the basis of differences in the Raman spectra of the liquid and gas. H. J. EMELEUS.

Raman effect in non-ideal binary solutions and in a series of mono-, di-, and poly-hydric alcohols. R. E. WHITING and W. H. MARTIN (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 87—98).—A solution of pyridine and AcOH, and of $COMe_2$ and CS_2 , both non-ideal, gave Raman spectra which were superpositions of those of the components. Careful purification and removal of dust caused disappearance of continuous portions from the spectra of MeOH, ethylene glycol, and sucrose solutions. Glycerol, under the same conditions, gave a strong continuous spectrum with a double structure. Raman frequencies for all these substances have been measured. Dust-free glucose solution gave a strong continuous spectrum which may be ascribed to photochemical decomp. A. J. MEE.

Raman effect in the terpenes. Hydrocarbons. G. B. BONINO and P. CELLA (Mem. R. Accad. d'Italia, 1931, 2, [Chim., 4], 51 pp.).—The Raman spectra of *d*- and *l*-pinene, limonene, sabinene, menthene, pinane, sabinane, and menthane have been studied. The complex spectra obtained are discussed in relation to the mol. structure, and those of *d*-pinene and limonene are compared with the infra-red absorption spectra. H. F. GILLBE.

Raman spectrum of sugar solutions. V. POLARA (Atti R. Accad. Lincei, 1931, [vi], 14, 293—298).—In the Raman spectrum of sucrose solutions five of the seven lines characteristic of glycerol and four lines of the alcohols are found as well as other lines usually attributed to various types of linkings in the aliphatic series. O. J. WALKER.

Raman spectra of carotenoids. H. VON EULER and H. HELLSTROM (Z. physikal. Chem., 1932, B, 15, 342—346).—The spectra in Et_2O solution of α - and β -carotene, leaf-xanthophyll, lycopene, and β -ionone have been determined, the first three compounds giving the same frequencies, one of which also occurs with ionone. R. CUTHILL.

Molecular symmetry and diffusion spectra. J. CABANNES and A. ROUSSET (Compt. rend., 1932,

194, 706—708; cf. this vol., 212).—From further results of a similar nature are deduced the angles between the linkings in NO_2 (in PhNO_2), NH_2 (in NH_2Me), and SO_2 , and the vals. of ρ in PCl_3 , POCl_3 , and CHCl_3 . The dopolarisation of the H_2O band at 3240 cm^{-1} and non-dopolarisation of that at 3418 are opposed to Kastler's theory (cf. A., 1931, 668). The case of allene (this vol., 109) is shown not to be exceptional. C. A. SILBERRAD.

Photography of fluorescence spectra and Raman spectra. F. ALMÄSY (Physikal. Z., 1932, 33, 221—222).—An apparatus is described by means of which weak spectra such as the above may be photographed. A. J. MEE.

A peculiar form of activity of matter. G. REBOUL (Compt. rend., 1932, 194, 602—603; cf. A., 1931, 666).—Experiments show that the action on a photographic plate of certain substances, e.g., paper, exposed to the action of a resistance cell is consistent with its being due to emission by the paper, in a manner analogous to phosphorescence, of very easily absorbable radiation belonging to an invisible portion of the spectrum, and produced by radiation from the cell. C. A. SILBERRAD.

Cathodic phosphorescence of rare earths in calcium oxide. S. FAGERBERG (Nova Acta Reg. Soc. Sci. Upsalensis, 1931, [iv], 7, No. 6, 59 pp.; Chem. Zentr., 1931, ii, 2424).—Modified apparatus and methods are described, and results are tabulated. New lines have been observed. A. A. ELDRIDGE.

Minute structure of phosphors and its relationships to atomic-chemical problems. E. TIEDE and E. WEISS (Ber., 1932, 65, [B], 364—372).—The formation of phosphors is studied by exposing SiO_2 tubes containing a layer of activator (CuS or Sb_2S_3) between two layers of fundamental sulphide (ZnS or MgS) (layer method) or a homogeneous mixture of activator and fundamental sulphide (mixture method) to gradually rising temp. Activation and consequent development of characteristic phosphors commences at about 330° in all systems examined. The anion of the metallic salt has no marked influence, CuS being replaceable by CuO or CuSO_4 . The activating influence of CdS or a pre-formed ZnS-Cu phosphor is observed at 650° . Very prolonged heating of ZnS-CuS at $280-320^\circ$ does not produce a phosphor. It appears, therefore, that the active metal atoms penetrate the lattice of the fundamental sulphide without causing an actual displacement of the components of the latter. The relationship of at. distance to production of phosphors is discussed (cf. A., 1931, 1253). H. WREN.

Emission of praseodymium in alkaline-earth phosphors. II. H. EVERT (Ann. Physik, 1932, [v], 12, 137—153).—The effect of temp. and type of excitation on the previously described phosphors (cf. this vol., 110) is studied. In the spectra of the sulphide and oxide Pr phosphors there are two bands, the lines differing in their properties as regards temp., excitation, distribution, and sharpness. A. J. MEE.

Dissociation of nitrogen and carbon monoxide by electron impact. J. T. TATE and W. W. LOZIER (Physical Rev., 1932, [ii], 39, 254—269).—Energies

of dissociation products, variation with electron energy of probability of ion production, and min. electron energy for the production of ions of specified energy were determined. Probable processes and heats of dissociation in volts were: $\text{N}_2 \rightarrow \text{N} + \text{N}$ (3.4 ± 0.5); $\text{N}_2^+ \rightarrow \text{N}^+ + \text{N} + e$ (7.1 ± 0.5); $\text{N}_2 \rightarrow \text{N}^+ + \text{N}^+ + 2e$; $\text{CO} \rightarrow \text{C} + \text{O}$ (0.3 ± 0.5); $\text{CO}^+ \rightarrow \text{C}^+ + \text{O}$ (6.4 ± 0.5); $\text{CO} + e \rightarrow \text{C} + \text{O}^-$; $\text{CO} \rightarrow \text{C}^+ + \text{O}^-$. N. M. BLIGH.

Efficiencies of ionisation and ionisation potentials of various gases under electron impact. J. T. TATE and P. T. SMITH (Physical Rev., 1932, [ii], 39, 270—277; cf. A., 1931, 665).—The gases investigated and ionisation potentials found were: N_2 , 15.7; H_2 , 15.6; CO , 14.1; O_2 , 12.5 and 16.1; NO , 9.5; C_2H_2 , 11.6 volts. Negative ions were formed by electron impact in the four last named. N. M. BLIGH.

Photo-electric association of sodium in rock-salt. E. REXER (Physikal. Z., 1932, 33, 202—204).—Irradiation with blue light of a rock-salt crystal coloured by at. Na causes an association of the Na to larger complexes, depending on the inner photo-effect. A. J. MEE.

Photochemistry of crystal structure faults. A. SIMEKAL (Physikal. Z., 1932, 33, 204—206).—A discussion of work on coloured specimens of rock-salt. A. J. MEE.

Photo-electric effect in semi-conductors. L. BERGMANN (Physikal. Z., 1932, 33, 209—213).—The use of the method described, which involves intermittent exposure of a special photo-cell to radiation, enables the photo-electric properties of exceedingly small quantities of substances to be investigated. A. J. MEE.

Transport phenomena in a degenerate gas. I. D. S. KOTHARI (Phil. Mag., 1932, [vii], 13, 361—379).—Mathematical. H. J. EMELEUS.

Effect of the character of the electrode surfaces on conduction in liquid dielectrics. H. EDLER and C. A. KNORR (Z. physikal. Chem., 1932, 158, 433—440).—The form of the current-voltage curve obtained with Pt electrodes in C_6H_6 is greatly influenced by the H content of the electrodes. For a given voltage, electrodes free from H give vals. for the current which are lower and more nearly reproducible than those obtained with electrodes charged with H. Addition of thiophen considerably reduces the current passing. R. CUTHILL.

Electrical conductivity of the alkali carbides and the nature of the combination. A. VON ANTROPOFF and J. F. MÜLLER (Z. anorg. Chem., 1932, 204, 305—314).— Na_2C_2 at temp. between 180° and 270° behaves as a typical ionic conductor. With direct current, polarisation and dendrite formation occur. The current is conveyed exclusively by Na^+ , and Faraday's law is applicable. The behaviour of Li_2C_2 containing about 20% of Li acetylide is similar. H. F. GILLBE.

Non-volatile and non-conducting crystals. F. HUND (Z. Physik, 1932, 74, 1—17).—Properties of crystals are discussed from the point of view of occupying available crystal proper functions with available electrons (cf. this vol., 10, 215). The crite-

mon for non-conductivity is that the ground term should not be bordered by a continuous succession of higher terms. Available proper functions divide into two equal classes, those giving binding and those giving loosening, and when the corresponding sets of energy vals. are separated by a finite interval, the crystal is non-conducting. Non-volatile, non-conducting at. crystals, such as diamond, have their binding proper functions filled, and fulfil the criterion for non-conductivity; non-volatile at. crystals have both classes filled, and must always be non-conductors.

A. B. D. CASSIE.

Dielectric polarisation of hydrogen chloride in solution. I. Benzene, cyclohexane, and carbon tetrachloride. F. FAIRBROTNER (J.C.S., 1932, 43—55).—The dielectric const. of the dry HCl solutions was measured by a resonance method, n with a modified Pulfrich refractometer, and d with a dilatometer. The molar refractivity of HCl in C_6H_6 solution was somewhat less than that of HCl gas. The dielectric polarisation of HCl in each solvent was greater than that of the gas. The electric moment of HCl in C_6H_6 is 1.28×10^{-18} e.s.u.

H. J. EMELEUS.

Dielectric constant and dipole moment of iron pentacarbonyl. W. GRAFFUNDER and E. HEYMANN (Z. physikal. Chem., 1932, B, 15, 377—382).—From measurements at 20° of n and the dielectric const. of $Fe(CO)_5$ and C_6H_6 solutions, the dipole moment is found to be 0.81×10^{-18} e.s.u., which supports the view that the CO groups are not symmetrically arranged about the Fe atom. R. CUTHILL.

Electric moments of certain cyclohexane derivatives. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1932, B, 15, 373—376).—Reasons are given for believing that β -hexachlorobenzene has zero dipole moment (cf. A., 1931, 900). The dipole moments of chloro-, bromo-, and iodo-cyclohexane are 2.1×10^{-18} , 2.1×10^{-18} , and 2.0×10^{-18} e.s.u., respectively.

R. CUTHILL.

Dipole moments of certain acetophenone derivatives. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1932, B, 15, 417—420).—The dipole moments of *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-amino-acetophenone are 2.29, 2.29, 2.23, and 4.3×10^{-18} e.s.u., respectively. These vals. correspond with an angle between the moment of PhAc and the group moment of the halogen of 53° in the Cl and Br compounds, and 49° in the I compound. This result indicates that in the CO group the C has excess positive charge and the O excess negative charge. R. CUTHILL.

Structure and electric moments of certain dihalogenocyclohexanes. E. HALMOY and O. HASSEL (Z. physikal. Chem., 1932, B, 15, 472—473).—A preliminary report of dipole moment measurements with cyclohexane derivatives of the type $C_6H_{10}X_2$ ($X=Cl, Br, I$). R. CUTHILL.

Dielectric constant of liquids. VI. Aqueous solutions of sulphamide. G. DEVOTO (Atti R. Accad. Lincei, 1931, [vi], 14, 432—434).—From the positive val. of the dielectric const.-concn. coeff., de/dc , it is probable that sulphamide has the polar structure $NH_2SO \begin{smallmatrix} < NH_3^+ \\ < O^- \end{smallmatrix}$. O. J. WALKER.

Dependence of dielectric constants of diluted strong electrolytes on frequency. H. FALEEN, HAGEN and E. L. VERNON (Physikal. Z., 1932, 33, 218—221).—A discussion of the general problem, and its application to sp. cases. An interpolation table is given by means of which the dispersion phenomena can be calc. in any special case. A. J. MEE.

Valency. XV. Dielectric constants of phosphorus trichloride and pentachloride. T. M. LOWRY and J. HORTON (J.C.S., 1932, 207—211).—The dielectric const. of PCl_3 at 17° is 3.498 and at 59.8° 3.139. That of PCl_5 at 22.8° is 4.23 and at 160° 2.85. The abnormal increase for PCl_5 on solidification is attributed to a change in mol. structure, as in SCl_4 (cf. A., 1930, 666). Hot PCl_5 attacks Pt and Ag, but Ni, Mo, and W were unattacked at 180° .

H. J. EMELEUS.

Molecular and atomic volumes. XXXIV. Densities of elements of the fourth to sixth groups at low temperatures. W. BILTZ and A. SAPPER [with E. WUNNENBERG]. XXXV. Volumetric determination of densities with small quantities of substance. A. SAPPER. XXXVI. Density of cuprous oxide. F. W. WRIGGE and K. MEISEL. XXXVII. Volumes of crystallised hydrides of [elements of] the fourth to seventh groups at low temperatures. XXXVIII. Volumes of silicates. W. BILTZ and A. LEMKE. XXXIX. Calculation of volumes of technical glasses. W. BILTZ and F. WEIBKE (Z. anorg. Chem., 1932, 203, 277—306, 307—311, 312—320, 321—329, 330—344, 345—364; cf. A., 1931, 1214).—XXXIV. Densities of halogen compounds (excepting fluorides) of elements of groups IV, V, and VI, including derivatives of CH_4 , have been determined at temp. down to -195° . Zero vols. of the compounds and of the halogen atoms concerned are calc.

XXXV. Technique of determining vols. of about 1.5 c.c. of substances at room temp. or -183° , with an accuracy of 0.01—0.06%, is described.

XXXVI. X-Ray diagrams of Cu_2O prepared both with and without org. reducing agents have been examined. No evidence of the existence of more than one form was obtained. The consts. were $a\ 4.259 \pm 0.002\ \text{\AA}$, $d\ 6.11 \pm 0.01$. Production of hollow spaces in the crystals of material made with org. reducing agents may lead to low pyknometric vals., but such irregularities do not affect the vals. derived from X-ray data.

XXXVII. Work described in Part XXXIV has been extended to the solid hydrides of elements of groups IV—VII, excepting CH_4 , NH_3 , and H_2O . The results are discussed theoretically.

XXXVIII. Previous measurements of densities of many silicates have been amplified and the data are collated.

XXXIX. Application of the principle of vol. additivity to the densities of a variety of glasses, with the aid of data given in Part XXXVIII, indicates that the glasses contain definite silicates in a state of mol. or submicronic dispersion in amorphous SiO_2 . Densities of glasses containing Al_2O_3 or B_2O_3 can be accounted for only by assuming that the latter are present as complex aluminosilicates or boro-silicates. F. L. USHER.

Refraction and dispersion of neon and helium. C. CUTHBERTSON and M. CUTHBERTSON (Proc. Roy. Soc., 1932, A, 135, 40—47).—Accurate measurements show that, although the difference between the free frequencies of the electrons in He and Ne is less than that formerly found (A., 1910, ii, 561), the anomaly in the frequency of Ne is real.

L. L. BIRCUMSHAW.

Atomic refractivity of fluorine. K. VON AUWERS (Z. physikal. Chem., 1932, 158, 411—420).—The procedure adopted by Schieman in determining the at. refractivity of F (A., 1931, 1355) is criticised.

R. CUTHILL.

[Atomic refractivity of fluorine.] G. SCHIEMANN (Z. physikal. Chem., 1932, 158, 421).—A reply to von Auwers (cf. preceding abstract).

R. CUTHILL.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. IV. Magneto-optical dispersion of acetic anhydride, *n*-butyric acid, and ethyl *n*-butyrate. W. J. LEWIS and E. J. EVANS (Phil. Mag., 1932, [vii], 13, 265—283; cf. A., 1931, 24).—Full data are recorded and an expression is deduced for the magneto-optical dispersion in the region 0.46—0.30 μ , and for the natural dispersion in the region 0.6678—0.2800 μ ; the wave-lengths of the absorption band for the three liquids are 0.1031, 0.1064, and 0.1081 μ , respectively. The calc. vals. $\times 10^{-7}$ of e/m are 0.923, 0.992, and 1.008 c.m.u., respectively.

N. M. BLIGH.

Magnetic rotatory power of blende as a means of measuring the field strength of an electromagnet with pierced pole-pieces. A. COTTON, G. DUPOUX, and M. SCHERER (Compt. rend., 1932, 194, 405—409).

C. A. SILBERRAD.

Double refraction of amorphous silica and quartz by compression, and its dispersion in the ultra-violet. G. BRUHAT and J. THOUVENIN (J. Phys. Radium, 1932, [vii], 3, 1—20).—A detailed account of work already noted (this vol., 6).

Double refraction of quartz along the optic axis. H. A. FERREIRA (Proc. Roy. Soc., 1932, A, 135, 214—223).—The vals. of the refractive indices of quartz along the optic axis are given for 22 wave-lengths between Li 6708 and Hg 2345. The mean of the two indices is the val. of n for the ordinary ray. The experimental vals. of the angular separation and of the difference of the two indices are in good agreement with those calc. from the Fresnel theory of rotatory polarisation.

L. L. BIRCUMSHAW.

Variations in the refractive index of benzene during intensive drying. J. J. MANLEY (Phil. Mag., 1932, [vii], 13, 249—264).—Using highly-purified C_6H_6 dried by Baker's method, μ for the liquid showed a gradual rise with time of drying; a similar rise was shown when the vapour was dried by P_2O_5 not in contact with the liquid. The irregular curve obtained on slowly melting dried and cryst. C_6H_6 indicates the formation in the liquid of complex and dense assemblages increasing in no. with drying to a max. val. and explaining the observed rise of b. p. During drying by various reagents the b. p. showed an irregular variation. $CaCl_2$ was inferior to KOH as a

drying agent, and H_2SO_4 and P_2O_5 showed superior and nearly equal efficiency.

N. M. BLIGH.

Optical rotatory power of vapours. I. Rotatory dispersion of camphor and camphorquinone, especially in the region of absorption. T. M. LOWRY and H. K. GOME (Proc. Roy. Soc., 1932, A, 135, 13—22).—Camphor vapour has $[M]_{589}^{25} + 83^\circ$ and the rotatory dispersion curve shows a sharp max. at $[\alpha]_{589}^{25} + 2000^\circ$ (approx.), followed by a reversal of sign at 3000 Å. and a negative max. $[\alpha]_{589}^{25} - 1860^\circ$ (approx.). Camphor in solution in cyclohexane shows a positive max. $[\alpha]_{589}^{25} + 2600^\circ$ (approx.), followed by a step-out, a reversal of sign, and a negative max. $[\alpha]_{589}^{25} - 2100^\circ$ (approx.). Camphorquinone vapour has $[M]_{589}^{25} - 146^\circ$, and the rotatory dispersion curve passes through a negative max. $[\alpha]_{589}^{25} - 500^\circ$ (approx.). In cyclohexane the negative max. is $[\alpha]_{589}^{25} - 450^\circ$ (approx.), followed by a reversal of sign at 4740 Å., and a positive max. $[\alpha]_{440}^{25} + 300^\circ$ (approx.).

L. L. BIRCUMSHAW.

Optical rotatory powers of *d*- β -octyl hydrogen phthalate and its salts in various concentrations and the influence of added electrolytes. H. G. RULE and J. M. HILL (J.C.S., 1931, 2644—2652).—Salt formation lowers the rotatory power of *d*- β -octyl H phthalate, the effect being in the order $Rb > K > Na > NH_4 > Li$; the rotation also decreases with concn. both with the acid and with the salts. Addition of alkali chlorides depresses the rotatory power of Na H phthalate, the effects being in the same order as above. Equiv. concns. of alkaline-earth cations produce still greater depressions, but $HgCl_2$, which is relatively non-ionised, has little effect. The changes are analogous to those observed with malic and tartaric acids, so it is concluded that the sensitivity of these acids to neutral electrolyte is related to the presence of the CO_2H group and not to the OH group as previously assumed.

J. W. SMITH.

Solvent action. II. Rotatory powers of *d*- β -octyl hydrogen phthalate and its methyl ester. H. G. RULE and J. M. HILL (J.C.S., 1931, 2652—2658).—In solvents of the aromatic series the rotatory power of *d*- β -octyl H phthalate is the lower the higher is the dipole moment of the solvent, but the effect with aliphatic solvents is irregular. The dipole may be screened by an alkyl group, since PhAc has much less depressing action than PhCHO. In *m*- and *p*-disubstituted benzenes the dipoles appear to act independently. The results are compared with the effect of addition of electrolyte (cf. preceding abstract). Analogous effects are observed with tartaric acid, but here both electrolytes and dipolar solvents increase the rotation.

J. W. SMITH.

Influence of thorium salts on the rotatory power of tartaric acid and tartrates. E. DARMOIS and YEU-KI-HENG (Compt. rend., 1932, 194, 703—706).—In view of the great influence of temp. on the rotatory power of mixtures of a Th salt and a tartrate pointing to complex formation, $[\alpha]$ was plotted against the amount of $ThCl_4$ added to aq. Na tartrate (followed by addition of NaOH) with results pointing to the formation of $ThO_2 \cdot C_4H_4O_6Na_2$, stable in excess of

alkali, and of $\text{ThO}_2 \cdot 2\text{C}_4\text{H}_4\text{O}_6\text{Na}_2$, less stable. $\text{Th}(\text{NO}_3)_4$ behaves similarly (cf. A., 1903, ii, 601).

C. A. SILBERRAD.

Rotatory power of some amino-acids as a function of p_{H} . E. VELLINGER (Compt. rend., 1932, 194, 718—720; cf. A., 1926, 778; 1927, 205).—Rotatory power- p_{H} curves for glutamic acid, leucine, and aspartic acid, calc. as before, are given. Darmon's scheme (cf. A., 1926, 1201) applies to the dispersion of glutamic acid, but not to that of leucine, aspartic acid, or alanine.

C. A. SILBERRAD.

General theory for the quantitative determination of the dependence of refractive indices of non-absorbing substances on changes of density. N. GUNTHER (Physikal. Z., 1932, 33, 175—177).—Mathematical. The theory has been verified experimentally with quartz.

A. J. MEE.

Intermediate products in thermal decomposition of ammonia. A. B. F. DUNCAN and D. A. WILSON (J. Amer. Chem. Soc., 1932, 54, 401—402).—The NH band, assumed to be at 3360—3370 Å., could not be detected in the absorption spectrum of decomposing NH_3 , a result which cannot be due either to insufficient decomp. of NH_3 or to the life of the NH mol. being too short. Either the mechanism of the surface decomp. is not $\text{NH}_3 = \text{NH} + \text{H}_2$, or the absorption coeff. is so low that the effective absorbing layer was too short.

C. J. WEST (c).

Co-ordination of hydrogen in associated liquids. J. C. SPEAKMAN (Nature, 1932, 129, 244).—The parachor for HF increases from 34.2 at -80° to 35.8 at 19.5° . The difference from the "theoretical" val. of 42.8 is nearly equal to that required for a liquid associated to double mols. and decreases steadily with a rise in temp.

L. S. THEOBALD.

Non-adiabatic chemical processes. F. LONDON (Z. Physik, 1932, 74, 143—174).—Theoretical. Perturbation coeffs. are developed as functions of the time and of mol. separations to express the dynamical interaction of two atoms or mols. Simple examples that require a dynamic as opposed to an adiabatic transition are sensitised ionisation and activation, and the formation of ionic mols. ($\text{Na} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{Cl}$); these processes are superficially similar to inelastic electronic collisions, but the chemical transition occurs much more suddenly. Expressions are deduced for reaction velocities.

A. B. D. CASSIE.

Dependence of pre-dissociation on temperature. G. JOOS and A. HERRMANN (Physikal. Z., 1932, 33, 213—214).—The explanation of pre-dissociation given by Henri is somewhat different from that based on quantum mechanics (Herzberg). The question has been settled by investigating the sharpness of the single bands of the NO_2 spectrum over a temp. range of -15° to 500° ; no sharp variation is found. This is in favour of the quantum-mechanics explanation.

A. J. MEE.

Distribution of electrons in the aromatic nucleus and the early stages of aromatic substitutions. A. LAPWORTH and R. ROBINSON (Nature, 1932, 129, 278).—Hückel's conclusions (A., 1931, 1356) concerning the distribution of

electrons in C_6H_6 derivatives and the mechanism of substitution are not accepted. L. S. THEOBALD.

Paramagnetic organic compound. J. KENYON and S. SUGDEN (J.C.S., 1932, 170—171).—The compound $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_2$ from COMe_2 and $\text{NHPh}\cdot\text{OH}$ (cf. A., 1926, 828) is diamagnetic, whilst its oxidation product $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}_2$, which is believed to contain N^{IV} or O^{I} , is strongly paramagnetic. The mol. has a moment close to 1.73 Bohr magnetons, corresponding with 1 unbalanced electron.

H. J. EMELÉUS.

Thermoelectric properties of ferromagnetic substances. L. F. BATES (Phil. Mag., 1932, [vii], 13, 393—412).—The thermoelectric power of Mn_3As_2 changes when it passes from the ferromagnetic to the paramagnetic state; some specimens have a positive and others a negative Thomson coeff. A rod of pure Mn_3As_2 has a negative Thomson coeff. at the ferromagnetic crit. point and hence should show a decrease in sp. heat at this point, which agrees with direct calorimetric measurements.

H. J. EMELÉUS.

Magnetism and valency. I. Copper and silver compounds. S. SUGDEN (J.C.S., 1932, 161—170).—The magnetic susceptibility of 10 Cu compounds and 9 Ag compounds was measured by the Gouy method. Compounds of Cu^{I} and Ag^{I} had zero moment, and in the bivalent state moments of 1.72—2.16 Bohr units, in agreement with predicted vals. for one unbalanced electron.

H. J. EMELÉUS.

Rendering visible circuits of different ferromagnetic states of solid bodies. W. GERLACH (Z. Physik, 1932, 74, 128—129).—Polemical, against von Harnos and Thiessen (*ibid.*, 1931, 71, 442).

A. B. D. CASSIE.

Interpretation of some ferromagnetic phenomena. F. BITTER (Physical Rev., 1932, [ii], 39, 337—344).—A review of contemporary theory.

N. M. BLIGH.

New experimental methods in ferromagnetism. S. L. QUIMBY (Physical Rev., 1932, [ii], 39, 345—353).—Methods of observing the magneto-elastic, mechanical, and thermal properties of single and polycryst. specimens of Ni are described.

N. M. BLIGH.

Effect of impurities on ferromagnetism. T. D. YENSEN (Physical Rev., 1932, [ii], 39, 358—363).—The effect of "interstitial" impurities, C, O, N, and S on the B - H and hysteresis curves of Fe and of Fe-Ni alloys is considered.

N. M. BLIGH.

Hydrogenised iron. P. P. CIOFFI (Physical Rev., 1932, [ii], 39, 363—367).—The improved magnetic characteristics of Fe with high-temp. heat treatment in H_2 are discussed.

N. M. BLIGH.

Magnetisation and thermal e.m.f. S. R. WILLIAMS (Physical Rev., 1932, [ii], 39, 368; cf. Sears, A., 1931, 1361).—The thermal e.m.f. between transversely and longitudinally magnetised wires is related to the Ettingshausen-Nernst effect.

N. M. BLIGH.

Faraday effect in ferromagnetics. H. R. HULME (Proc. Roy. Soc., 1932, A, 135, 237—257).—Theoretical. The rotation of polarised light transmitted through thin films of ferromagnetics is discussed, using the ordinary simple model for a ferro-

magnetic. For magnetisations in the region of saturation the rotation is found to be proportional to the magnetisation and to increase with the wave-length of the light. These results accord with experiment.

L. L. BIRCUMSHAW.

Gyromagnetic ratio for paramagnetic substances. III. Salts of the rare-earth group. W. SUCKSMITH (Proc. Roy. Soc., 1932, A, 135, 276—281; cf. A., 1930, 1100).—The Van Vleck development of the Hund theory (A., 1928, 572) is most successful in explaining the experimental results. For the ions Gd^{+++} , Nd^{+++} , Eu^{+++} , and Dy^{+++} the theoretical vals. of g , the Lande splitting factor, are 2.0, 0.75, 0.4, and 1.33, respectively, the corresponding experimental vals. being 2.12, 0.78, >4.5, and 1.36.

L. L. BIRCUMSHAW.

Quenching of mercury resonance radiation. II. Further hydrocarbons and nitric oxide. J. R. BATES (J. Amer. Chem. Soc., 1932, 54, 569—576; cf. A., 1930, 1489).—Vals. of the effective cross-section of the collision process $\times 10^{16}$ are: NO, 24.7; n -heptane, 24.0; $\beta\gamma$ -trimethylbutane, 19.7; Δ^7 -heptene, 55.9; Δ^8 -heptene, 45.8; C_6H_6 , 41.0. A general arrangement of mols. which correlates their effective cross-sections and structure is discussed.

J. B. AUSTIN (c).

Law of discontinuous distribution of Curie points. R. FORRER (Compt. rend., 1932, 194, 697—699).

C. A. SILBERRAD.

Physical properties and chemical constitution. I. Atomic refractions and observations on the parachor. J. D. A. JOHNSON (Ber., 1932, 65, [B], 294—302).—Determination of the mol. refraction of the chloride, Et and Bu^c esters of phenylmethylphosphinic acid shows that the mean val. of the at. refraction of P^{III} is 2.03 units lower in aliphatic than in aromatic compounds and the refraction of the aliphatic $\equiv P \rightarrow O$ group is 1.59 units smaller than that of the aromatic $\equiv P \rightarrow O$ group. If O in $\equiv P \rightarrow O$ has the same val. as in others, the mean val. of the semipolar double linking is -3.92 and -4.36 units in aliphatic and aromatic compounds, respectively. Optical data indicate the structure $PH(OEt)_2 \rightarrow O$ for Et phosphite. In aliphatic As compounds the semipolar double linking has the val. -3.5. The causes of variation in the refraction of the semipolar double linking and of the parachor are discussed at length. Bu^c phenylmethylphosphinate has b. p. 166°/11 mm., d_4^{20} 1.0608.

H. WREN.

Effects of thermal strain on intensity of reflexion of X-rays by certain crystals. Y. SAKISAKA and I. SUMOTO (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 135—142).

Influence of lattice binding forces on X-ray emission spectra. R. GLOCKER and M. RENNIGER (Naturwiss., 1932, 20, 122—123).—The theoretical significance of the influence of chemical binding on the long wave-length lines of the K series in simple elements may be best understood from consideration of allotropic modifications. Results for diamond and graphite are discussed. W. R. ANGUS.

Microstructure of pearlite. M. MIKAMI (Sci. Rep. Tohoku, 1931, 20, 710—714).—Photographs of

pearlite taken with various methods of illumination show that it is impossible to say which constituent of the eutectoid appears white and which appears dark. The top portion of lamellar cementite in relief appears white, whilst the side faces are dark, and the bottom of the lamellar ferrite between two neighbouring cementite lamellae also appears white, whilst both edges are dark.

A. R. POWELL.

Vitreous state. I. Glass as a fourth state of matter. E. BERGER (Z. tech. Physik, 1931, 12, 344—363; Chem. Zentr., 1931, ii, 1960).—A discussion.

A. A. ELDRIDGE.

Variation in the effective lattice constant of crystals with wave-lengths. J. M. CORK (Physical Rev., 1932, [ii], 39, 193—196; cf. Bearden, A., 1931, 887).—X-Ray wave-lengths determined by a calcite crystal compared with reflexion angles for particular emission wave-lengths over 1—5.5 Å. using a quartz crystal are consistent to 0.03%.

N. M. BLOCH.

Structure of very thin crystal sheets. F. KIRCHNER (Naturwiss., 1932, 20, 123—124).

W. R. ANGUS.

Variation in dimensions caused by annealing cold-worked copper. A. SCHWEITZER (Compt. rend., 1932, 194, 449—450).—The rate of variation increases with rise of temp. Up to 550° the variation is independent of the cold working, above that temp. it increases therewith.

C. A. SILBERRAD.

Crystal structure of copper electro-deposited in presence of gelatin. H. KERSTEN (J. Physical Chem., 1931, 35, 3644).—Comparison by X-ray examination of Cu deposited from a 10% gelatin solution on Au-plated brass with the deposit from a similar plating bath containing no gelatin indicates that the difference in the unit cell of the lattice is less than 0.01 Å.

CHEMICAL ABSTRACTS (c).

Crystal structures of krypton, xenon, hydrogen iodide, and hydrogen bromide in relation to the temperature. B. RUEHMANN and F. SIMON (Z. physikal. Chem., 1932, B, 15, 389—413).—Kr and Xe have the face-centred cubic lattice, and at 88—89° abs. have a 5.69 and 6.24 Å., and d 2.99 and 3.56, respectively. The existence of the transition point of Kr reported by Peters and Weil (A., 1930, 986) could not be confirmed. At 21°, 82°, and 125° abs., temp. between which lie the transition intervals revealed by sp. heat measurements, HI has a tetragonal face-centred lattice with c/a 1.08, which indicates that the transitions must be of the NH_4Cl type. At 125° abs. the lattice has a 6.19 Å. and d 3.17. X-Ray diagrams of HBr at 82—120° abs. suggest that the lattice is face-centred rhombic and that no fundamental crystallographic changes occur on passing through the transition intervals.

R. CUTHILL.

Crystal structure of the tetrahalides of the lighter elements. II. O. HASSEL and H. KRINGSSTAD (Z. physikal. Chem., 1932, B, 15, 274—280; cf. A., 1931, 897).— $TiBr_4$ and TiI_4 have the same kind of cubic lattice structure as SnI_4 , the lattice const. (a) being 11.25 and 12.00 Å., respectively.

R. CUTHILL.

Crystal structure of β -zirconium. W. G. BURGERS (Nature, 1932, 129, 281).— β -Zr is cubic

body-centred, with 2 atoms per unit cube, and α 3.61 Å. near the transition temp. (862°).

L. S. THEOBALD.

Crystal structure of lithium hydride. J. M. BIJVOET and A. KARSEN (Z. physikal. Chem., 1932, B, 15, 414—415).—Polemical against Zintl and Harder (A., 1931, 1358).

R. CUTHILL.

Crystal structure of lithium hydride. E. ZINTL and A. HARDER (Z. physikal. Chem., 1932, B, 15, 416).—A reply to Bijvoet and Karssen (cf. preceding abstract).

R. CUTHILL.

Complexity of arsenic trioxide. I. A. SMITS and E. BELJAARS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1141—1155).—The v. p. of As_2O_3 has been determined over the temp. range 240—380°. Below 200° the octahedral β -modification is stable and above 200° the monoclinic α -form. On prolonged keeping the β -form passes into a hitherto undescribed γ -form. The triple points are as follows: $S_{\alpha}-L-G$ 312.3° and 66.1 mm.; $S_{\beta}-L-G$ 272.1° and 26.1 mm.; $S_{\gamma}-L-G$ 289.6° and 40.7 mm. The α -modification on distillation yields a distillate with a higher v. p. and a residue with a lower v. p. than before distillation. It is concluded that the α -form is a mixed crystal phase in internal equilibrium.

J. W. SMITH.

X-Ray investigations of a sub-sulphide of cobalt used as a catalyst for the hydrogenation of phenol. V. CAGLIOTI and G. ROBERTI (Gazzetta, 1932, 62, 19—29).— CoS has a hexagonal structure: a 3.38, c 5.20, c/a 1.54, and Co_3S_2 a face-centred cubic structure, a 9.91. Both these sulphides catalyse the hydrogenation of aromatic rings containing substituent groups. The structure of Co_3S_2 is analogous to that of bornite, which appears to be Cu_3FeS_3 .

O. J. WALKER.

Dimensions of the atoms and univalent ions in crystal lattices. G. NATTA (Mem. R. Accad. d'Italia, 1931, 2, [Chim., 3], 31 pp.).—Solid HCl , HBr , and HI have been examined by the powder method. The face-centred cubic form of HCl has a 5.435 \pm 0.01 Å. at the transition temp., -175° ; 4 mols. in unit cell; d 1.49. HBr also is dimorphous; at -170° the face-centred cubic lattice has a 5.76 \pm 0.02 Å.; 4 mols. in unit cell; d 2.80. At temp. below -173° a form of lower symmetry, probably pseudo-tetragonal, is formed; a 5.60 \pm 0.02 Å., c/a 1.08; 4 mols. in unit cell. At -170° HI crystallises in the tetragonal system, with c/a 1.075, 4 mols. in unit cell; d 3.46. The radii of the Cl , Br , and I ions are 1.92, 2.04, and 2.21 Å., respectively, and derived vals. are given for the radii of F^- and CN^- and of the positive ions in various halides.

H. F. GILLBE.

X-Ray examination of the oxides of lead. J. A. DARBYSHIRE (J.C.S., 1932, 211—219).—Lattice consts. determined were: PbO (red), tetragonal (a 3.968, c 5.011 Å.); PbO (yellow), orthorhombic (a 5.459, b 4.723, c 5.859 Å.); PbO_2 , tetragonal (a 4.931, c 3.367 Å.). No definite suboxide of Pb was obtained. Pb_2O_3 prepared by two methods was amorphous. Pb_3O_4 had a characteristic structure, not examined in detail. X-Ray methods may be used for examining commercial samples of Pb oxides.

H. J. EMELEUS.

Polymorphism of lead monoxide. M. P. APPLINBEY and H. M. POWELL (J.C.S., 1931, 2821—2829).—Crystallographic measurements of the red form of PbO are given. The densities, solubilities in $NaOH$ solutions of concn. up to 20*N* at 84° and at 20°, and microscopical examination of various preps. of PbO show no definite evidence for a black modification. The black, green, and purple forms of PbO which have been described are due to the presence of Pb ; the red and yellow forms turn black on exposure to light or heat only in the presence of a trace of alkali.

J. W. SMITH.

Crystal structure of lithium hydroxide. T. ERNST (Naturwiss., 1932, 20, 124).— $LiOH$ crystals are tetragonal: a 3.55, c 4.34 Å.; 2 mols. in unit cell; parameter, $u=0.20$.

W. R. ANGUS.

Lattice constants of certain compounds of the spinel type. H. HAUPTMANN and J. NOVAK (Z. physikal. Chem., 1932, B, 15, 365—372).— Ga_2MgO_4 , Al_2MgO_4 , and Al_2ZnO_4 have face-centred cubic lattices and the spinel structure, and the vals. of a_o are 8.279 \pm 0.006, 8.059 \pm 0.004, and 8.093 \pm 0.004 Å., respectively.

R. CUTHILL.

Orientation of crystals deposited on cleavage plates of mica or chlorite. L. ROYER (Compt. rend., 1932, 194, 620—621).

C. A. SILBERRAD.

Alternation in long-chain compounds. New X-ray data for long-chain ethyl and methyl esters and iodides and a preliminary thermal examination of the esters. T. MALKIN (J.C.S., 1931, 2796—2805; cf. A., 1931, 290).—X-Ray crystallographic measurements have been made on the *Me* and *Et* esters of the higher fatty acids. Two crystal forms of *Et* esters exist, one being stable only over a small temp. range immediately below the m. p. Only *Me* esters of odd fatty acids exist in two forms. *Me* esters crystallise in layers of double mols. and *Et* esters in layers of single mols. It is suggested that this accounts for the slightly higher m. p. of the former. The theory of alternation is discussed and it is suggested that the essential feature of an alternating series is that the zig-zag C chain is tilted with respect to the terminal planes.

J. W. SMITH.

Crystalline carbon tetraiodide. O. HASSEL and H. KRINGSTAD (Teknisk Ukeblad, 1931, 78, 230; Chem. Zentr., 1931, ii, 2117).—The length of the side of the smallest possible unit cube is 9.14 Å.

A. A. ELDRIDGE.

Crystal forms of orthoform. A. KOFLER and A. MAYRHOFER (Mikrochem., 1932, 10, 460—466).—Orthoform exists in anhyd. tetragonal and hydrated monoclinic forms. In the micro-m. p. apparatus the former melts sharply at 142°, whilst the latter either liquefies or becomes cloudy, owing to dehydration, at 52—60°.

H. F. GILLBE.

X-Ray examination of β -methylxyloside. E. G. COX (J.C.S., 1932, 138—142).— β -Methylxyloside is monoclinic sphenoidal (a 7.82, b 6.89, c 7.74 Å.; 2 mols. in unit cell; space-group C_2^2). The probable mol. structure suggested resembles that of α -xylose.

H. J. EMELEUS.

Dimorphism of normal saturated fatty dicarboxylic acids as a function of temperature.

F. D. LA TOUR (Compt. rend., 1932, 194, 622—623).— β -Glutaric acid, monoclinic, is obtained on evaporating an EtOH solution; its unit cell has a 10.06, b 8.47, c 17.4 Å., β 132° 35', and contains 4 mols. The α (unstable) form is monoclinic, and has a 10.34, b 5.08, c 32.9 Å., β 129° 0', with 8 mols. in the unit cell; transition temp. 74—75°. a (in Å.) for the β and α forms, and the transition temp. of acids $C_nH_{2n-2}O_4$, for $n=11, 13, 15$, and 17 are respectively 11.3, 12.8, 91°, 13.35, 14.6, ?; 15.05, 16.8, ?; 17.1, 19.2, 103°. (Cf. A., 1929, 126; 1931, 1036.) C. A. SILBERRAD.

Molecular association, apparent symmetry of the benzene ring, structure of the nitro-group in crystalline *m*-dinitrobenzene, and valencies of nitrogen in some organic compounds. S. B. HENDRICKS and G. E. HILBERT (J. Amer. Chem. Soc., 1931, 53, 4280—4290).—The unit cell of *m*-dinitrobenzene contains 4 mols. and has a 13.27, b 14.06, c 3.820 Å.; the space-group is $Pbnm$ (V_4^m). The min. mol. symmetry is a plane of symmetry which contains the N, C, and H atoms of a mol. The compound is associated along the c axis. The crystallographic equivalence of the O atoms of a NO_2 group indicates NV. N is probably quinquivalent in many compounds in which it is joined to at least two O atoms, and tervalent in the nitrones, nitrenes, azoxy- and nitroso-compounds, which are free radicals chemically similar to some aldehydes and ketones. Evidence is given in support of the inner NH_4 salt structure of NMe_3 oxide. A. L. HENNE (c).

X-Ray investigation of the crystals of *o*-azotoluene. M. PRASAD and K. V. DESAI (Phil. Mag., 1932, [vii], 13, 600—603).—The crystals belong to the monoclinic prismatic class, with 4 mols. per unit cell; a 13.93, b 6.604, c 14.55 Å., space-group C_2^2 . The structure is compared with that of azobenzene.

H. J. EMELÉUS.

Structure of dianthracene. J. HENGSTENBERG and J. PALACIOS (Anal. Fis. Quim., 1932, 30, 5—11).—The rhombic crystals of dianthracene have a 8.18, b 12.15, and c 18.75 Å., with 8 anthracene groups in the unit cell; space-group V_4^h . The mol. structure is discussed; it is probable that the two anthracene mols. are linked at the 9 and 9' positions.

H. F. GILLBE.

X-Ray examination of *d*-mannitol and *d*-mannose. G. W. MCCREA (Proc. Roy. Soc. Edin., 1932, 51, 190—197).—The orthorhombic bisphenoidal crystals of the β -form of *d*-mannitol have a 8.66, b 16.58, c 5.50 Å.; 4 mols. in unit cell; space-group Q_4 . The measurements confirm Irvine and Steele's conclusion of an asymmetric configuration. The α -form of *d*-mannose has a 5.53, b 17.66, c 7.59 Å.; 4 mols. in unit cell; space-group Q_4 . The configuration has not been established, but is probably of the pyran ring type.

H. F. GILLBE.

Crystal structures of vitamin-D and related compounds. J. D. BERNAL (Nature, 1932, 129, 277—278).—Ergosterol, α -dihydroergosterol (and EtOH), calciferol, pyrocalciferol-calciferol, lumisterol, and cholesterol have a 9.75, 30.8, 20.8, 20.2, 20.3, and 16.4, respectively; b 7.4, 7.4, 7.15, 7.35, 7.25, and —, respectively; c 39.1, 43.1, 38.5, 40.0, 20.4 Å., and —, respectively; β 65°, 53°, 68°, 03°, 60°, and —,

respectively. The respective space-groups are $C_2^2-P2_1$, C_2^2-C2 , $C_2^2-P2_1$, C_2^2-C2 , $C_2^2-P2_1$, and C_1^1-P1 , and the no. of mols. per unit cell, 4, 12, 8, 8, 4, and —. From the similarities of properties of the crystals and the simple relation between their unit cells it is concluded that the unit cell of the calciferol-pyrocalciferol contains 4 mols. of each kind showing that calciferol is probably a simple substance structurally. Formulæ are discussed. L. S. THEOBALD.

Dependence of permeability of iron wires on high-frequency fields. M. WIEN (Physikal. Z., 1932, 33, 173—175). A. J. MEE.

Measurement of magnetic saturation [of iron]. E. GEROLD (Arch. Eisenhüttenw., 1931—1932, 5, 267—268).

Magneto-resistance and magneto-caloric effects in iron and Heusler alloys. H. H. POTTER (Phil. Mag., 1932, [vii], 13, 233—248; cf. A., 1931, 1116).—Measurements made give further evidence of the direct proportionality of the magneto-resistance change to the change in magnetic energy, but the proportionality factor varies considerably for different substances. N. M. BLIGH.

Magneto-strain and magneto-resistance. L. W. MCKEEHAN (Physical Rev., 1932, [ii], 39, 368—371).—A survey. N. M. BLIGH.

Magnetisation of single crystals. F. BITTER (Physical Rev., 1932, [ii], 39, 371—375; cf. A., 1931, 1117).—Experimental data are shown to be in satisfactory agreement with theory. N. M. BLIGH.

Barkhausen effect: orientation of magnetisation in elementary domains. R. M. BOZORTH (Physical Rev., 1932, [ii], 39, 353—356).

N. M. BLIGH.

Propagation of large Barkhausen discontinuities. K. J. SIXTUS and L. TONKS (Physical Rev., 1932, [ii], 39, 357—358).—A formula for the time of penetration for a large travelling Barkhausen discontinuity is discussed. N. M. BLIGH.

Hall effect, particularly in weak fields. M. CANTONE and E. BOSSA (Mem. R. Accad. d'Italia, 1930, 2, [Fis., 1], 31 pp.).—Measurements of the effect as a function of the field strength have been made with Fe, steel, Ni, Bi, Te, Sb, Cu, and many other diamagnetic and ferromagnetic metals and alloys.

H. F. GILLBE.

Hull magneton. L. PINCHERLE (Atti R. Accad. Lincei, 1931, [vi], 14, 290—293). O. J. WALKER.

Lattice distortion and hardness of heat-treated tungsten magnet steels. W. A. WOOD (Phil. Mag., 1932, [vii], 13, 355—360).—The decrease in magnetic quality and hardness on heating W steels to 900° is due to the disappearance of lattice distortion (indicated by a broadening of the lines of the X-ray spectrum). The distortion reappears on heating to 1250°.

H. J. EMELÉUS.

Supposed allotropy of lead. W. EDA (Sci. Rep. Tohoku, 1931, 20, 715—725).—No discontinuities occur in the differential thermal curve, the electrical resistance curve, and the hardness curve of single-crystal Pb between 20° and 300°. The hardness of polycryst. Pb quenched from different temp. shows

an abrupt increase at 200°, but, as this change does not occur in single crystals, it is probably a secondary effect due to the state of aggregation of the smaller crystals and is not, therefore, a sign of an allotropic transformation. A. R. POWELL.

Polish on metals. J. T. RANDALL and H. P. ROOKSBY (*Nature*, 1932, 129, 280—281).—A discussion (cf. this vol., 219). L. S. THEOBALD.

Determination of mol. wt. of dissolved substances by means of dynamic measurement of the lowering of vapour pressure. E. BOVALINI (*Atti R. Ist. Veneto Sci.*, 1930—1931, 90, 7—21; *Chem. Zentr.*, 1931, ii, 2105—2106).—Vals. for $\text{CO}(\text{NH}_2)_2$, NaCl, H_3BO_3 , mannitol, and galactose in H_2O , anethole in C_6H_6 , and for $\text{CO}(\text{NH}_2)_2$ and succinic acid in EtOH have been determined. Practically normal vals. were obtained for $\text{CO}(\text{NH}_2)_2$, boric acid (as HBO_2), and NaCl (conc.) in H_2O , anethole in C_6H_6 , and $\text{CO}(\text{NH}_2)_2$ in EtOH. A. A. ELDRIDGE.

Difference in the effect of magnetic and electric fields on the conductivity of heat in gases. H. SENFTLEBEN (*Physikal. Z.*, 1932, 33, 177—178).—Both a magnetic field and an electric field affect the conductivity of heat in gases, but the magnetic field decreases, whilst the electric field increases, the conductivity. If streaming takes place, the electric effect disappears, whilst the magnetic is unaffected. The magnetic effect is thus a pure heat conductivity effect, whilst the electric field probably gives rise to association of the gas mols. It is the later dissociation of these that causes the apparent increase in conductivity. A. J. MEE.

Resistance of lead and tin to high-frequency currents at superconducting temperatures. J. C. McLENNAN (*Trans. Roy. Soc. Canada*, 1931, [iii], 25, III, 191—193).—Pb shows a change to superconductivity at a lower temp. with alternating currents than with direct. With currents of frequencies 1.1— 1.6×10^7 per sec. a similar result was found for Sn. A. J. MEE.

Electrical conductivity of ruthenium, ruthenium carbide, and tungsten carbide. J. C. McLENNAN, J. F. ALLEN, and J. O. WILHELM (*Trans. Roy. Soc. Canada*, 1931, [iii], 25, III, 13—25).—Specimens of impure Ru have been found to be superconducting, whereas pure Ru is not. The superconductivity is due to the presence of both W and C, in the form W_2C . A. J. MEE.

[Velocity of sound in carbon dioxide.] O. HEIL (*Z. Physik*, 1932, 74, 31—33).—The discrepancy between Kneser's estimate of collisions per sec. (A., 1931, 553) and that from extinction of resonance spectra is due to neglect of the efficiency of each collision. A. B. D. CASSIE.

M. p. of iridium. H. VON WARTENBERG, H. WERTH, and H. J. REUSCH (*Z. Elektrochem.*, 1932, 38, 50).—Two differently prepared samples of Ir gave m. p. $2435 \pm 15^\circ$ and $2440 \pm 15^\circ$, respectively. The accuracy of measurement at these temp. is about 25° . A few % of Os or Ru raise the m. p. several hundred degrees. M. S. BURR.

F. p. of the two forms of methylene iodide. H. W. STONE (*J. Amer. Chem. Soc.*, 1932, 54, 112—

114).—When liquid CH_2I_2 is immersed in an air-bath surrounded by ice water an unstable form with f. p. 5.54° separates. A stable form with f. p. 6.01° is obtained by immersing directly in the cooling bath. L. KELLEY (c).

Specific heats of the diatomic gases. P. S. H. HENRY (*Nature*, 1932, 129, 200—201).—A discussion. L. S. THEOBALD.

Specific heat of magnesium and aluminium oxides at high temperatures. G. B. WILKES (*J. Amer. Ceram. Soc.*, 1932, 15, 72—77).—Sp. heats of pure Al_2O_3 and MgO were determined up to 1700° and 1800° , respectively. The apparatus consisted of a vertical carbon tube furnace and a special calorimeter. Errors are discussed; an accuracy of at least 0.5% is claimed. J. A. SUGDEN.

Heat capacities at low temperatures of sulphides of copper and lead. C. T. ANDERSON (*J. Amer. Chem. Soc.*, 1932, 54, 107—111; cf. A., 1931, 552).—The heat capacities of Cu_2S , CuS , and PbS were measured at 55— 300° abs. From these and auxiliary data the following vals. were calc. for these substances, respectively, at 298.1° abs.: entropy, S° , 28.9, 15.9, 21.9; heat content change on formation from the elements, ΔH° , —19,000, —11,600, —20,600; free energy of formation, ΔF° , —20,640, —11,720, —20,200. F. D. ROSSINI (c).

Quantum dynamical correction for the equation of state of real gases. H. MARGENAU (*Proc. Nat. Acad. Sci.*, 1932, 18, 56—62).—Deviations from the perfect gas law arise from forces due to the interaction of rapid electronic motions within the mols. Calculations of the second virial coeff. agree well with experimental vals. except for H_2 and He. This lack of agreement may be due to the existence of zero point energy associated with the vibration of mols. in quantised collision states which might render ineffective the attractive van der Waals forces. A mathematical investigation of this phenomenon and its effect on the equation of state are given. W. R. ANGUS.

Theory of equations of state. T. S. WHEELER (*Phil. Mag.*, 1932, [vii], 13, 604—615).—A general expression for the work of dilution of a system of charged particles in thermal equilibrium is deduced from thermodynamic and dimensional considerations. H. J. EMELEUS.

Influence of air on properties of organic solvents. J. HORIUTI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1932, 17, 257—264).—The effect of dissolved air on d and the v. p. is discussed. R. CUTHILL.

Density and molecular state of vapours of tellurium dibromide, tellurium tetrabromide, and selenium dioxide. D. M. YOST and J. B. HATCHER (*J. Amer. Chem. Soc.*, 1932, 54, 151—155; cf. A., 1931, 294, 1117).—The v. d. of TeBr_2 and TeBr_4 were determined at 440— 1000° . Above 750° TeBr_2 is appreciably dissociated into Te and Br. At 432° TeBr_4 is more than 90% decomposed into TeBr_2 and Br_2 , and at 600° dissociation is complete, but the TeBr_2 formed does not dissociate appreciably into Te and Br₂ below 1000° . The v. d. of SeO_2 is normal at

360–500°, and the yellow colour of the vapour is unexplained.

L. KELLEY (c).

Carbonyl selenide. I. Preparation and physical properties. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1932, 652–660).—*Carbonyl selenide*, COSe, is prepared by passing CO over heated Se. It is a colourless evil-smelling gas condensing to a colourless mobile liquid, b. p. $-22.9 \pm 0.2^\circ$ at 725 mm. and crit. temp. $121.1 \pm 0.2^\circ$. It freezes to a snow-white cryst. solid, m. p. $-122.1 \pm 0.5^\circ$. V. d. agrees with the formula COSe, which is also confirmed by analysis, d_4^{25} is 1.812 for liquid under its own v. p. The coeff. of expansion is 0.001756 between 4.1° and 21.1° . γ at 4.1° is 19.32 ± 0.1 dynes per cm. with temp. coeff. 0.156 between 4.1° and 21.6° . The observed parachor is 126.6 (calc. 133.7).

M. S. BURR.

Physical properties of carbonyl sulphide. T. G. PEARSON, P. L. ROBINSON, and J. TROTTER (J.C.S., 1932, 660–661).—The carbonyl sulphide was prepared by passing CO over heated S, drying by distillation over P_2O_5 , and fractionating. V. d. is 0.002668, giving mol. wt. 59.74 (calc. for COS, 60); d of liquid at 0° is 1.073, coeff. of expansion ($0-32.2^\circ$) 0.002710, and γ at 2.3° 13.00 dynes per cm. with temp. coeff. 0.1626. The Eotvos-Ramsay-Shields const. is 2.02, indicating absence of association. Parachor 111.1 (calc. 119.4).

M. S. BURR.

Two different liquid states. M. WOLFFKE and J. MAZUR (Z. Physik, 1932, 74, 110–127).—Temp. variation of the dielectric const., density measurements, and curves of rate of heating all indicate two distinct liquid states for CS_2 , $PhNO_2$, and Et.O.

A. B. D. CASSIE.

Physical properties of nitrobenzene in the neighbourhood of the m. p. N. B. MASSY, F. L. WARREN, and J. H. WOLFENDEN (J.C.S., 1932, 91–95).—The viscosity, density, and heating rate of $PhNO_2$ were measured from 6° to 14° . No evidence was found of reported discontinuities in physical properties at 9.8° (cf. A., 1931, 148, 741, 893).

H. J. EMELEUS.

[Physical properties of methyl bromide, dichloroethylene, and methylamine.] R. PLANK [with A. W. HSIA, L. VAHL, W. BUCHE, H. STAKELBECK, and W. H. SCHREIBER (Z. ges. Kalte-Ind., 1931, 38, 97–101; Chem. Zentr., 1931, ii, 2130).— $MeBr$: log v. p. = $10.3344 - 1375.625/T - 1.11078 \log T + 8.559 \times 10^{-4}T$; b. p. 3.2° ; f. p. -93° ; crit. temp. 194° , d_4^{20} 1.731. $s-C_2H_5Cl_2$: b. p. 48.46° ; log v. p. = $11.23645 - 1702.5468/T - 1.25137 \log T + 0.00023807T$; $as-C_2H_5Cl_2$: b. p. 59.75° ; log v. p. = $11.4651 - 1711.9275/T - 1.4394 \log T + 0.000569T$. NH_2Me : sp. heat 15° , 0.765 kg.-cal. per kg. ($^\circ C$). Thermal properties of the system NH_2Me -metallic chlorides, viscosities of CO_2 , NH_3 , and SO_2 at -20° to 20° or 31° , and the thermal conductivities of H_2O , CO_2 , NH_3 , and SO_2 at 20° are recorded.

A. A. ELDRIDGE.

Determination of isotherms for hydrogen between 0° and 100° up to 1000 atmospheres. A. MICHELS, G. P. NIEHOFF, and A. J. J. GERVER (Ann. Physik, 1932, [v], 12, 562–568).—The temp. used were approx. 0° , 25° , 50° , 75° , and 100° . Inter-

polated vals. were obtained for other temp. and pressures, and the virial coeff. was calc. A. J. MEE.

Possibilities in relativistic thermodynamics for irreversible processes without exhaustion of free energy. R. C. TOLMAN (Physical Rev., 1932, [ii], 39, 320–336).—Theoretical. N. M. BLIGH.

Density and surface tension of liquid hydrogen fluoride. J. H. SIMONS and J. W. BOURKNIGHT (J. Amer. Chem. Soc., 1932, 54, 129–135).—For liquid HF between -75° and $+5^\circ$ $d = 1.0020 - 0.0022625t + 0.000003125t^2$. The surface tension from -80° to $+19^\circ$ may be represented by $\gamma = 40.7[1 - (T/503.2)^{1.78}]$. γ and its temp. coeff. suggest that the liquid is polymerised.

A. L. HENNE (c).

Effect of intensive drying on the rate of distillation and on the vapour pressure of ethyl bromide. J. W. SMITH (J.C.S., 1931, 2573–2583).—After intensive drying over P_2O_5 , the rate of non-ebullitional distillation of EtBr between bulbs at const. temp. in an evacuated and sealed apparatus is retarded considerably. The v. p., however, remains unaltered and no difference could be detected between head and tail fractions after distillation. Ebullition occurs with more difficulty in the dried liquid. It is suggested that the internal equilibrium in a liquid is not disturbed by the intensive drying, but that the effects observed are due to some form of superheating probably induced by the removal of nuclei during the P_2O_5 treatment.

J. W. SMITH.

High-frequency stroboscopy. J. A. STRONG (Nature, 1932, 129, 203–204).—Density changes in a quartz crystal can be observed stroboscopically using the principle previously described (this vol., 115).

L. S. THEOBALD.

Physical constants. W. HERZ (Z. anorg. Chem., 1932, 203, 271–276).—Numerical relations between surface tension, viscosity, and temp. are discussed. Vols. of alkali halide mols. are calc. from refractive indices of their solutions, and vals. so obtained are compared with those derived by other methods.

F. L. USHER.

Viscosity of organic fluorine compounds. F. SWARTS (J. Chim. phys., 1931, 28, 622–650).—Determinations of viscosity over the range $20-60^\circ$ are recorded for $n-C_6H_{11}F$, $n-C_7H_{15}F$, $CHF_2 \cdot CHCl_2$, $CHCl_2 \cdot CHFCl$, $CF_2Cl \cdot CFCl_2$, $CH_2Br \cdot CHF_2$, $CH_2F \cdot CH_2OH$, $CHF_2 \cdot CH_2OH$, $CF_3 \cdot CHMe \cdot OH$, $CF_3 \cdot CMe \cdot OH$, $CH_2F \cdot CH_2OAc$, $CHF_2 \cdot CH_2OAc$, $CF_3 \cdot CHMe \cdot OAc$, $CH_2F \cdot CO_2Et$, $CHF_2 \cdot CO_2Et$, $CF_3 \cdot CO_2Et$, $CF_3 \cdot CO_2H$, $CHF_2 \cdot CO_2H$, CF_3Ac , PhF , 1:3- and 1:4- $C_6H_4F_2$, o -, m -, and p - C_6H_4MeF , $CPhF_3$, o -, m -, and p - $C_6H_4FNO_2$, o -, m -, and p - $C_6H_4F \cdot NH_2$, 1:2:5- $C_6H_3F_2 \cdot NH_2$, o -, m -, and p - $C_6H_4F \cdot OEt$, and trifluoromethylcyclohexane. The data are discussed in relation to those for related compounds not containing F and are compared with vals. obtained for b. p., n , and heat of combustion. No simple, additive rule is found. $CF_2Cl \cdot CFCl_2$, obtained by acting on C_2Cl_2 with SbF_3 in presence of $SbCl_3$, has b. p. 47.4° , f. p. -36.4° , d_4^{20} 1.6200.

E. S. HEDGES.

Necessity of using absolute viscosity coefficients or coefficients of absolute kinematic vis-

cosity as practical measure of viscosity. P. WOOD (Ann. Office Nat. combust. liq., 1930, 5, 805—829; Chem. Zentr., 1932, ii, 1114).—A comparison of theoretical and practical data. L. S. THEOBALD.

Allotropy of white tin and the equilibrium diagram of the system tin-cadmium. Y. MATUYAMA (Sci. Rep. Tohoku, 1931, 20, 649—680).—Measurements of the electrical resistance, thermal expansion, and thermoelectric power of Sn and thermal and X-ray analysis of Sn between 20° and the m. p. failed to show the existence of a transformation point. The eutectic point at the Sn end of the Cd-Sn system occurs at 5% Cd and 181.7° and the eutectoid point at 4.3% Cd and 130°. A. R. POWELL.

Equilibrium diagram of the iron-zirconium system. R. VOGEL and W. TONN (Arch. Eisenhüttenw., 1931—1932, 5, 387—389).—Fe and Zr combine readily with considerable evolution of heat when the metals are heated together in an atm. of A, forming the compound Fe_3Zr_2 , m. p. 1640°. This compound forms a eutectic with Zr at 88% Zr and 1350° and a eutectic with γ -Fe at 16% Zr and 1330°. The solubility of Zr in δ -Fe is 7% and this solid solution decomposes at 1335° into saturated γ -Fe with 0.7% Zr and liquid; hence alloys with up to 7% Zr have a "second m. p." The presence of Zr in δ -Fe lowers the $\delta \rightarrow \gamma$ transformation of Fe linearly with increasing Zr content from 1400° to 1335°. The solubility of Zr in α -Fe is 0.3% and the $\gamma \rightarrow \alpha$ transformation is thereby lowered from 900° to 835°; Zr has no effect on the magnetic transformation point of Fe. The transformation point of Zr is raised by addition of Fe from 862° to 1000° with 5% Fe, after which it remains const. The solubility of Fe in α -Zr is about 10% and in β -Zr about 5%. A. R. POWELL.

X-Ray experiments on the solubility of silver in copper. P. WIEST (Z. Physik, 1932, 74, 225—253).—Precision measurements were made of lattice consts. Solubility is greater in the single crystal, and the diffusion process proceeds more slowly. Deposition of Ag from supersaturated solutions was also studied. A. B. D. CASSIE.

Hall effect and other physical properties of the copper-cadmium series of alloys. W. RICHARDS and E. J. EVANS (Phil. Mag., 1932, [vii], 13, 201—225).—The electrical resistivities, temp. coeffs. of resistance, thermoelectric powers, Hall coeffs., and the sp. heats and densities of carefully annealed Cu-Cd alloys have been determined. Discontinuities in the electrical property-composition curves indicate the compounds CuCd_3 , Cu_2Cd_3 , Cu_4Cd_3 , and possibly Cu_2Cd . The Hall coeff.-composition curves follow generally the phase changes. N. M. BLIGH.

Segregation of cementite from austenite. R. F. MEHL, C. S. BARRETT, and D. W. SMITH (Nature, 1932, 129, 313—314).—Results differing from those of Hanemann and Schroder (this vol., 220) have been obtained. L. S. THEOBALD.

Density of mixtures of ethyl alcohol with petroleum distillation products. B. KARPIŃSKI (Przemysł Chem., 1932, 16, 1—4).—The densities of mixtures of EtOH with gasoline, benzene, or paraffin

oil are less than those calc. from the mixture rule, the greatest deviations being for mixtures containing 40—60% of EtOH. The deviation increases with diminishing d of the hydrocarbon.

R. TRUSZKOWSKI.

Vapour pressures of binary mixtures. A. W. PORTER (Trans. Faraday Soc., 1932, 28, 95—97; cf. A., 1928, 710).—Polemical. A formula used by Bancroft (this vol., 117) is a special case of Margules' general equation and is not applicable to dil. solutions. J. G. A. GRIFFITHS.

Binary azeotropic mixtures. W. SWIENTOSLAWSKI [with J. JUST, L. WAJGENBLITT, I. WUTTKE, and P. WOJTCZAK] (Rocz. Chem., 1932, 12, 48—57).— C_6H_6 and AcOEt do not form azeotropic mixtures. The b. p. for CS_2 - COMe_2 (33 mol.-% COMe_2) is 39.27°/760 mm., for C_6H_6 -EtOH 67.93°, and for PhMe -EtOH 76.83°. R. TRUSZKOWSKI.

Partial pressure isotherms. II. S. C. LEE (J. Physical Chem., 1931, 35, 3558—3582; cf. this vol., 117).—The isotherms for binary mixtures of C_6H_6 with MeOH and with Pr°OH were determined at 40°. The abnormality of the curves obtained is attributed to the tendency of the mixtures to separate into two layers. G. M. MURPHY (c).

The fluidity mixture law. E. C. BINGHAM and D. F. BROWN (J. Rheology, 1932, 3, 95—112).—Batschinski's formula is used to derive a "volume-corrected fluidity" which should be a linear function of vol. concn. for an ideal solution. New density and fluidity data are given for mixtures of C_6H_6 with Et_2O and COMe_2 . C. W. DAVIES.

Fluidities of non-aqueous mixtures. E. C. BINGHAM and H. E. ROGERS (J. Rheology, 1932, 3, 113—120).—The equation of Bingham and Brown (cf. preceding abstract) is compared with available data. Where fluidity curves show minima due to compound formation, the max. deviation from the linear graph (and not the position of the min.) occurs at the correct mol. ratio and is independent of temp. C. W. DAVIES.

Surface tensions of mixtures of n -propyl alcohol and benzene. R. C. BROWN (Phil. Mag., 1932, [vii], 13, 578—584).—The surface tension-composition curve shows a reversal of curvature at approx. 7% PrOH . A min. in the viscosity-composition curve occurs in the same region (cf. J.C.S., 1905, 87, 11). The formation of complex mols. $3\text{C}_6\text{H}_5\cdot 2\text{PrOH}$ is suggested. H. J. EMELEUS.

System iron-mercury and the solubility of nickel in mercury. E. PALMAER (Z. Elektrochem., 1932, 38, 70—76).—A val. of about 0.00007% has been found for the solubility of Fe in Hg by stirring the latter with an amalgamated Fe wire, shaking the Hg with an acid solution of Hg_2SO_4 in presence of excess of the salt, pptg. Hg with HCl, and determining Fe colorimetrically by NH_4CNS . The solubility does not change appreciably between 20° and 211°. When Fe is deposited electrolytically in presence of Hg, crystals of "Fe amalgam" are deposited. These, however, have been shown to be crystals of pure Fe in suspension. The solubility of Ni in Hg, determined by stirring Hg with an amalgamated Ni wire, is

approx. 0.00014% at 20°. The method of separating Ni is the same as for Fe, Ni being subsequently determined colorimetrically by dimethylglyoxime and aq. Br. M. S. BURR.

Velocity of crystallisation of sucrose. G. J. F. BREEDVELD and H. J. WATERMAN (Rec. trav. chim., 1923, 51, 239—247).—A method of measuring the velocity of crystallisation of sucrose from a supersaturated solution, giving reproducible results, has been devised. $P_2^3 - P_1^3 = \frac{1}{2} \alpha k t$, where P_1 is the wt. of the crystal at the beginning, P_2 at the end of the time t , α the velocity of crystallisation in mg. per sq. m. per min., and k a coeff. depending on the kind of crystal. For sucrose $k=4.12$. The supersaturation coeff. has been plotted against α and the results have been compared with those of Kucharenko (Planter Sugar Mfr., 1928). M. S. BURR.

Behaviour of formic, acetic, propionic, butyric, and isobutyric acids on extraction from aqueous solution with light petroleum. J. GROSSFELD and A. MIERMEISTER (Z. anal. Chem., 1932, 87, 241—262).—The constancy of the relation $c_1/\sqrt{c_2}$ (c_1 and c_2 are concn. in H_2O and light petroleum, respectively), previously observed for acids of higher at. wt. (A., 1931, 1270), is not maintained in the series examined, except for higher concn. of *n*- and *iso*-butyric acids. In general it diminishes as concn. diminishes. The ratio c_1/c_2 increases to a max. with diminishing concn., except for HCO_2H , where it diminishes. The % of acid extracted by equal vols. of light petroleum from solutions of different concn. is tabulated. The solubility of HCO_2H and $AcOH$ in light petroleum is extremely small. M. S. BURR.

Adsorption of gases by solids. H. S. TAYLOR (Trans. Faraday Soc., 1932, 28, 131—138).—A general statement of the present position and a reply to criticisms of the author's theory of activated adsorption (A., 1931, 421). J. G. A. GRIFFITHS.

Adsorption of gases by solids. Experimental methods. E. K. RIDEAL (Trans. Faraday Soc., 1932, 28, 139—147).—Methods of investigating the formation and nature of surface phases are summarised. J. G. A. GRIFFITHS.

Pressure measurements for investigating mutual behaviour of adsorbed hydrogen atoms. M. C. JOHNSON (Trans. Faraday Soc., 1932, 28, 162—165).—See A., 1931, 1006; 1930, 1385, 1084, 525.

Adsorption of saturated vapours by porous substances. Experimental methods. F. G. TRYBORN and W. F. WYATT (Trans. Faraday Soc., 1932, 28, 158—161).—Mainly a summary of methods previously described (cf. A., 1928, 118, etc.). J. G. A. GRIFFITHS.

Criticism of experimental evidence for activated adsorption. L. J. BURRAGE (Trans. Faraday Soc., 1932, 28, 192—194).—Unless surfaces are perfectly clean, fictitious vals. of the energy of activation of the adsorption process are obtained from velocity measurements. Traces of foreign gases cannot be entirely removed by evacuation alone, but are best removed by flushing out with gas at high temp.

"Cleaning up" effects may well account for some of the phenomena attributed to activated adsorption.

J. G. A. GRIFFITHS.

Sorption of gases by glass. F. P. BURT (Trans. Faraday Soc., 1932, 28, 179—184).—The sorption of NH_3 at const. pressures between 100 and 800 mm. has been investigated over long periods. The plot of log. sorption velocity against log. time affords two straight lines united by a short curve, and a general relation between sorption, time, pressure, and temp. is found. During desorption, the sorption halts at a higher val. than the corresponding point on the sorption curve, possibly owing to a balance between slow desorption and slow continued sorption. It is recommended that in density determinations the glass vessel be exposed for a long time to the gas at the max. pressure to be used. J. G. A. GRIFFITHS.

Adsorption of gases and vapours on plane surfaces. C. E. H. BAWN (J. Amer. Chem. Soc., 1932, 54, 72—86).—The adsorption of CO , O_2 , and A on mica at 90° and 193° abs. and at pressures from 1×10^{-4} to 2×10^{-2} cm. has been measured. At 90° the adsorption of CO and O_2 follows Langmuir's formula, but no simple equation will represent the adsorption of A . The isotherms at 193° are rectilinear up to 8×10^{-3} cm., but at higher pressures follow Langmuir's equation, which is also valid for the adsorption of $COMe_2$ at room temp. In no case does the adsorbed layer exceed one mol. in thickness.

CHEMICAL ABSTRACTS (c).

Thermionics in the study of adsorption of vapours and gases. J. A. BECKER (Trans. Faraday Soc., 1932, 28, 148—158).—Examples of previous work (e.g., A., 1929, 756; 1930, 127) demonstrate the utility of thermionic emission phenomena in the study of evaporation, migration, and diffusion at surfaces.

J. G. A. GRIFFITHS.

Vapour-pressure isotherms and submicroscopical structure of active carbon. II. P. KUBELKA and M. MÜLLER (Kolloid-Z., 1932, 58, 189—197).—Experiments previously reported (A., 1931, 794) have been extended to other vapours, some new forms of activated C, and also SiO_2 gel. In all cases the equilibrium conditions indicate capillary condensation. The structure relations previously described for C do not hold for SiO_2 gel, but whether the difference is qual. or quant. is not clear.

E. S. HEDGES.

Microtome method for determination of absolute amount of adsorption. J. W. MCBAIN and C. W. HUMPHREYS (J. Physical Chem., 1932, 36, 300—311).—A method of determining the amount of adsorption at an air- H_2O interface is described. The surface of the solution, which is contained in a shallow Ag trough and is in equilibrium with the gas phase above it, is caused to assume a convex form by paraffining the ends of the trough. By means of a rapidly-moving microtome blade a layer of uniform thickness (0.05—0.1 mm.) is cut off from a known area of the surface of the solution and collected in a cylinder on which the blade is mounted, and its concn. is compared with that of the bulk of the solution by means of an interferometer. The results obtained with solutions of *p*-toluidine, $PhOH$, and hydro-

cinnamic acid indicate, when compared with results obtained by the bubble method (A., 1927, 1022; 1930, 152), that the ideal conditions of the experiment are almost realised in the new method, and that Gibbs' equation is a limiting law. S. LENHER (c).

Desorption methods for measurements to 2° absolute. K. MENDELSSOHN (Z. Physik, 1931, 73, 482—501).—An apparatus is described by means of which a temp. of 1.6° abs. may be attained by desorption from charcoal. A. B. D. CASSIE.

Behaviour of adsorbed atoms. J. CHARITON, N. SEMENOV, and A. SCHALNIKOV (Trans. Faraday Soc., 1932, 28, 169—176).—When the temp. of the surface in contact with Cd vapour of fixed density is raised above the supposed "crit." val., a deposit of Cd appears if sufficient time is allowed. This time increases with rise of temp. Such deposits, unlike those obtained below the "crit. temp.," are irregular. The discrepancy between the theory of Semenov (A., 1930, 851) and the absence of a "crit. temp." is attributed to the inhomogeneity of the surface, condensation occurring at the most active points from which the deposits grow. Approx. calculations show that the elementary displacement of an adsorbed atom is many times greater than the interat. distances of the adsorbent and it is suggested that impurities make the surface energetically smooth. Mols. from the gas phase impinging on adsorbed mols. have little effect on the establishment of the surface equilibrium provided the surface density is not large. J. G. A. GRIFFITHS.

Mixture isotherms at active points. H. DOHSE and H. MARK (Trans. Faraday Soc., 1932, 28, 165—169).—Mixture isotherms for Pr^{OH} and H_2O on active points of bauxite are computed from the velocities of the unretarded and retarded dehydrations of Pr^{OH} on bauxite (A., 1929, 1231).

J. G. A. GRIFFITHS.

Inner adsorption in crystalline salts. IV. D. BALAREV [with S. SOTIROV and B. SREBROV] (Kolloid-Beih., 1932, 34, 441—461).—The observed inclusion of impurities in cryst. MgNH_4PO_4 , aq., ZnCO_3 , CdCO_3 , and CaCO_3 is in accordance with the principles of inner adsorption formerly described for BaSO_4 etc. (A., 1930, 684). The hygroscopicity of Al_2O_3 , CuO , MoO_3 , and WO_3 is traced to their fine capillary structure and is considered from the same point of view. Further evidence is adduced to support the view that crystals have a mosaic structure (cf. A., 1929, 263), which can provide adsorbent surfaces. E. S. HEDGES.

Heats of adsorption of oxygen on nickel and copper catalysts. W. W. RUSSELL and O. C. BACON (J. Amer. Chem. Soc., 1932, 54, 54—71).—The extent and heat of adsorption on promoted, unpromoted, supported, and unsupported catalysts have been measured. The approx. mol. heats of adsorption on Ni and Cu, each promoted with ThO_2 , are 98,000 and 82,000 g.-cal., respectively. The adsorption by both metals is irreversible, but a catalytically active surface can be produced by the adsorption of O_2 at 0° followed by heating at some suitable temp., which presumably converts the adsorbate into stable oxide. The variation in the

catalytic hydrogenating activity of a Cu catalyst with the extent and heat of O_2 adsorption suggests a relation between these properties.

CHEMICAL ABSTRACTS (c).

Selective adsorption by activated charcoal from solutions containing two organic acids. C. OCKRENT (J.C.S., 1932, 613—630; cf. A., 1930, 1514).—Using activated ash-free sugar charcoal as adsorbent, adsorption isotherms (25°) of BzOH , $\alpha\text{-OH-C}_6\text{H}_4\text{-CO}_2\text{H}$, $\alpha\text{-C}_6\text{H}_4\text{Me-CO}_2\text{H}$, $\text{CH}_2\text{Cl-CO}_2\text{H}$, AcOH , HCO_2H , and $\text{CCl}_3\text{-CO}_2\text{H}$ in aq. solution have been determined. Adsorption at equiv. concns. decreases in the order given. Adsorption from solutions containing pairs of the above acids is not proportional to their individual adsorptions, but the more adsorbable acid is selectively (in one case exclusively) adsorbed. Langmuir's theory applied to adsorption of two solutes is not valid without modification. Hydrolytic adsorption from salts of weak org. acids has been confirmed.

F. L. USHER.

Adsorption of dyes from aqueous solution by Japanese acid clay. Y. TANAKA, T. KUWATA, and S. FURUTA (J. Fac. Eng. Tokyo, 1932, 20, 53—64).—The adsorption of basic and acid dyes from aq. solution by Japanese acid clay in its natural state, after activation by elimination of acid-sol. Al and Fe, and after neutralisation, has been studied. Adsorption of basic substances is a result of the residual affinity of SiO_2 mols. oriented on the surface of the clay, which attract the OH groups of the H_2O and thus cause the formation of a new and active surface; salt formation then occurs at the outer surface. Acid dyes are adsorbed by replacement of the H^+ of the electrical double layer by the cation of the dye; if the free acid is insol. it is pptd. on the clay, but if it is sol. no adsorption occurs. Activation of the clay is due to the greater SiO_2 surface exposed on removal of Al_2O_3 and Fe_2O_3 . Basic dyes are adsorbed to a greater extent by the neutralised clay than by the acid clay, as the alkali liberated from the clay is free to combine with the anion of the dye; the adsorption of acid dyes is correspondingly reduced by neutralisation of the clay.

H. F. GILLBE.

Influence of the solubility of the adsorbate on the adsorption of electrolytes. (MILLE.) L. DE BROUCKERE (Bull. Soc. chim. Belg., 1931, 40, 737—740; cf. A., 1929, 757).—Previous work is extended to TiCl_4 . The adsorption of chlorides on BaSO_4 increases with diminishing solubility of the chloride.

C. W. DAVIES.

Adsorption of organic materials by the silver halides. S. E. SHEPPARD, R. H. LAMBERT, and R. L. KEENAN (J. Physical Chem., 1932, 36, 174—184).—In the adsorption of pinacyanol by AgBr at p_{H} 6.8, 1.69 Br^- are necessary for 1 dye mol. Pinacyanol is adsorbed in an alkaline medium with an excess of Br^- . Acid dyes, such as dichlorofluorescein, are adsorbed by AgBr in an acid medium with an excess of Ag^+ . Gelatin is also adsorbed, and even after boiling with H_2O for many hrs. a unimol. layer still remains. A 10% solution of H_2SO_4 alters the grains, but does not remove all the adsorbate.

S. LENHER (c).

Thickness of adsorbed films on mercury. H. CASSEL (Trans. Faraday Soc., 1932, 28, 177—179; cf. A., 1931, 1119, 1120).—The adsorption of CCl_4 on Hg at 11° has been investigated by an improved method. The surface density corresponds with a unimol. film when the first layer is saturated. The density increases to 3.6 times this val. at the v. p. of CCl_4 in bulk. The adsorption follows Henry's law over a considerable range.

J. G. A. GRIFFITHS.

Unimolecular films. Solid-liquid interface and sedimentation and flocculation of powders in liquids. W. D. HARKINS and D. M. GANS (J. Physical Chem., 1932, 36, 86—97).—A unimol. film of oleic acid on the surface of a fine powder suspended in a very dry, non-polar liquid deflocculates the powder, which settles to one quarter the vol. it would occupy in absence of the acid. The addition of very small amounts of H_2O to the C_6H_6 solution of the acid inhibits deflocculation. The extent of flocculation and of settling is not a simple function of the wettability of the powder by the liquid; the composition of the org. dispersing medium has a marked influence on the rate of settling. An adsorption method for the determination of the area of a fine powder is described.

F. URBAN (c).

Comparison of methods for determination of area of adsorbed molecules in interfacial films. F. E. BARTELL and G. L. MACK (J. Physical Chem., 1932, 36, 65—85).—The interfacial tension between H_2O and binary mixtures of PhNO_2 with C_6H_6 , PhMe , PhEt , and PhBu , and of NPhMe_2 with C_6H_6 has been determined. The average mol. areas calc. from these data by Langmuir's max. adsorption method, the mixture rule method of Mathews and Stamm, and by a modified mixture rule method are: PhNO_2 , 30.6, 32.1, and 21.8; NPhMe_2 , 35.5, 41.5, and 26.6×10^{-16} sq. cm., respectively. The most satisfactory agreement with the mixture rule is obtained by using vol. compositions.

F. URBAN (c).

Unimolecular films. Liquid-liquid interface and stability of emulsions. E. K. FISCHER and W. D. HARKINS (J. Physical Chem., 1932, 36, 98—110).—Evidence is adduced showing that in general the stability of an emulsion increases as the emulsifying film changes from an expanded to a condensed unimol. film. Distribution curves for the variation of interfacial area with diameter in aq. emulsions of paraffin oil and C_6H_6 produced by Na oleate, and a size distribution curve for oil are reproduced. Soap films are unimol.

F. URBAN (c).

Thin lamellae and their physical properties. H. DEVAUX (Kolloid-Z., 1932, 58, 129—143).—A summary of published work.

E. S. HEDGES.

Coloured stratifications. A. MARCELIN (J. Chim. phys., 1931, 28, 605—621).—A summary and discussion of published work on the interference colours produced by very thin plates of certain org. crystals (cf. A., 1930, 1111, 1366).

E. S. HEDGES.

Influence of particle size on the heat of wetting of powdered adsorbents. F. KRCZYL (Kolloid-Z., 1932, 58, 183—189).—A calorimeter for determining

heat of wetting is described. Different adsorbents (including C and SiO_2) were separated into fractions of different particle size by sedimentation and the heats of wetting of the fractions by EtOH and C_6H_6 were determined. The vals. obtained were independent of the particle size.

E. S. HEDGES.

Inversion of order of heats of wetting by pre-treatment of the powder to be wetted. B. ILJIN and S. VASSILIEV (Z. physikal. Chem., 1932, 158, 365—368; cf. A., 1915, i, 933).—The heat of wetting of a sample of Florida earth by aq. MeOH was found to decrease with the MeOH concn., but changed in the opposite direction when the earth was first dried at 120° or 350° .

R. CUTBILL.

Drainage of a vertical wetted plate, the shape of the profile, and thickness of the film. J. SATTERLY and L. H. COLLINGWOOD (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 215—225).—The mathematical solution of this problem by Jeffreys has been studied experimentally, and the calc. relations between the time, distance from the top of the wetted portion, and the thickness of the film have been confirmed by observations with glycerol and olive oil. The film has a parabolic outline near the top of the wetted portion, but the outline changes with time.

A. J. MEE.

Theory of flotation. W. OSTWALD (Kolloid Z., 1932, 58, 179—183).—Flotation depends on the formation of a three-phase system (solid-liquid-gas). The components of such a system cannot meet in a plane, but only at an edge. The flotation of a solid is determined by the formation of rings of the bounding edges. An ideal flotation agent will be "triphilic," possessing a metal-affine group, a hydrophilic group, and a capillary active group. The xanthates have such a structure.

E. S. HEDGES.

Surface tensions and interfacial tensions with an application to the problem of the plate ridge. J. SATTERLY and L. H. COLLINGWOOD (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 205—214).—The surface tensions and interfacial tensions of H_2O with a number of org. liquids have been found. There is a linear relation between the work of adhesion and the interfacial tension with H_2O . Interfacial tensions increase with rise of temp., the increase probably being connected with increased mol. orientation at the surface. No definite connexion has been found between the wt. of the "plate ridge" and the interfacial tensions and viscosities of liquids.

A. J. MEE.

Surface tension of soap solutions. P. L. DE NOUY (Nature, 1932, 129, 278—279).—A criticism (cf. this vol., 224).

L. S. THEOBALD.

Capillary activity in aqueous solution. H. MILLS (J.C.S., 1932, 419—430; cf. A., 1931, 1007).—The relation between surface tension and concn. has been determined with greater accuracy than heretofore for aq. solutions of $\text{C}_2\text{H}_{11}\text{OH}$, BuCO_2H , $\text{C}_5\text{H}_{11}\text{CO}_2\text{H}$, and $\text{C}_8\text{H}_{17}\text{CO}_2\text{H}$. Inflexions on the σ -c curves are observed in each case. The "coeff. of adsorption," denoted by the ratio (surface concn./bulk concn.) at the point of inflexion, is approx. const. over a wide range of concn. The

inflexions are considered to be due to attainment of saturation in the surface layer and subsequent accumulation there of a conjugate solution. The limitations of Gibbs' equation are explained in accordance with the theory. The rate of adsorption of $C_8H_{17}CO_2H$ is proportional to the square of the concn.

F. L. USHER.

Theory of hydrotropic solutions. II. Production of molecular compounds. A. VON KUTHY (Biochem. Z., 1932, 244, 308—318; cf. A., 1931, 1122).—As regards the solvent power and surface tension of solutions of their Na salts, cholic, dehydrocholic, deoxycholic, glyeochoic, and taurocholic acids differ only quantitatively, not qualitatively. No cryst. mol. compounds can be obtained from many such acids; it seems that those which yield cryst. compounds are structurally related to 3:7-dihydroxycholic acid. It is possible that there is a connexion between power to form mol. compounds (not necessarily crystallisable) and hydrotropy.

W. MCCARTNEY.

Electrocapillarity. IV. Effect of salts on electrocapillary curves of solutions containing surface-active substances. J. A. V. BUTLER and A. WIGHTMAN (J. Physical Chem., 1931, 35, 3293—3302; cf. A., 1931, 162).—The effect of inorg. salts on the electrocapillary curves of solutions containing EtOH, PhOH, and Na salicylate has been investigated. The adsorption curves for EtOH and PhOH become more symmetrical as the salt concn. is lowered. Br^- and I^- greatly reduce the adsorption of these solutes in the regions in which the ions themselves are adsorbed. In solutions containing Cl^- , NO_3^- , and SO_4^{2-} the surface tension lowering caused by the org. substances is increased by increasing the salt concn. in the region in which the salt is negatively adsorbed, and decreased in the region in which the salt is positively adsorbed. As the inorg. salt concn. falls the max. of the adsorption curve for Na salicylate moves towards positive potentials and its magnitude increases.

H. M. STARK (c).

Types of binary osmotic systems. F. A. H. SCHREINEMAKERS (Rec. trav. chim., 1932, 51, 218—232).—The different types of binary osmotic systems are classified and the influence of the composition and previous history of the membrane is discussed.

M. S. BURR.

Experimental study of negative osmosis. A. GROLLMANN and K. SOLLNER (Trans. Amer. Electrochem. Soc., 1932, 61, 81—88).—With membranes of MgO or Mg silicate, deposited in the walls of a porous pot, interposed between an aq. solution and H_2O or a solution of different concn., a flow of liquid sometimes occurs in a direction opposite to that of normal osmosis. When such a cell is filled with H_2O and immersed in 0.1N- $LiNO_3$, the entry of solution produces pressures as high as 300 mm. of H_2O . Such pressures rise to a max. in an hr. or two and then decrease again. The passage of solute through the membrane was shown by analysis, and in several cases the rate of passage of solution through the membrane was measured directly.

H. J. T. ELLINGHAM.

Experimental verification of a new theory concerning the mechanism of anomalous osmosis.

A. GROLLMANN and K. SOLLNER (Trans. Amer. Electrochem. Soc., 1932, 61, 89—99; cf. preceding abstract).—Anomalous (including negative) osmosis is attributed to electroendosmotic flow of solution through the larger pores in the membrane brought about by the p. d. developed at the smaller pores. Negative osmosis may occur if the less mobile ion of the solute forms the outer portion of the double layer on the membrane surface. This theory is supported by measurements of the pressures developed in cells devised to act as large-scale models of the conditions in a membrane with pores of differing sizes.

H. J. T. ELLINGHAM.

Membrane equilibrium and ion distribution. III. Dynamics of membrane permeability in relation to ion distribution. S. K. LIU (Kolloid-Z., 1932, 58, 144—155).—A general thermodynamical theory of membrane equilibrium and ion distribution for both diffusible and non-diffusible ions is worked out. The Donnan equilibrium is regarded as a special case, and the present theory reduces to the same form when it is assumed that the non-diffusible ion concn. can be neglected.

E. S. HEDGES.

Ionic equilibrium of sodium cellulose xanthate across a semipermeable membrane. T. SUGITA (J. Cellulose Inst. Tokyo, 1932, 8, 3—11).—Measurements have been made of the conductivity of viscose solutions separated from a NaOH solution by a parchment-paper membrane, and of the p.d. between the two solutions; the results indicate that a membrane equilibrium is set up. The decomp. of Na cellulose xanthate is a process of direct hydrolysis.

H. F. GILLBE.

Dependence of base exchange in permutits on the nature of the anions. II. E. UNGERER (Z. Pflanz. Dung., 1932, 23A, 353—362; cf. A., 1931, 163).—In aq. suspension the adsorption of hydrated cations by permutits is increased by anions in the order of the lyotropic series, $\frac{1}{2}Fe(CN)_6^{4-} > OAc^- > \frac{1}{2}CrO_4^{2-} > SO_4^{2-} > Cl^- = NO_3^- > ClO_3^- > I^- > CNS^-$. In EtOH suspensions this effect is not observed. Anions have little or no effect on feebly-hydrated cations, e.g., Ba^{2+} , Ag^+ , and their action in other cases is ascribed to a dehydrating effect.

A. G. POLLARD.

Mosaic membranes. K. SOLLNER (Biochem. Z., 1932, 244, 370—381; A., 1930, 688).—When solutions of an electrolyte of different concns. are separated by a membrane which is permeable to one of the ions only, the resistance of the solutions can be calc. because closed currents must flow in the system. The strength of the current and the amount of electrolyte which passes through the membrane in unit time can also be calc. Membranes which in certain regions are permeable to anions and in others to cations permit the passage of electrolytes in a precisely predictable manner. If a mosaic membrane of this kind is selective to one ion and also slightly permeable to the other, equalisation of the concns. of the solutions takes place.

W. MCCARTNEY.

Explanation of some anomalies in the f. p. of fatty acids in benzene and nitrobenzene solution. A. BOUTARIC and M. ROY (J. Pharm. Chim., 1932, [vi], 15, 161—166).—The fatty acids are associated in C_6H_6 and $PhNO_2$ solutions.

A. J. MEE.

Ebullioscopic study of molecular equilibria of pyrocatechol in solutions of chlorides of calcium and barium. (MLLE.) O. HUN (Compt. rend., 1932, 194, 716—718; cf. A., 1930, 689).—Results with solutions of CaCl_2 and BaCl_2 are of the same order as those with KCl and NaCl , association in aq. BaCl_2 being slightly greater than in aq. CaCl_2 .

C. A. SILBERRAD.

Apparent volume of salts in solution. II. Interpretation. A. F. SCOTT (J. Physical Chem., 1931, 35, 3379—3396; cf. A., 1931, 1122).—Assuming that as the concn. of the solution increases there is a continuous transition from the dissolved to the cryst. state on the part of the solute, the vol. of the solution in the limiting state may be taken as equal to V , the mol. vol. of the solid salt in the crit. disruptive state, i.e., that state in which the ions are so far apart that the net cohesive force is a max. The val. of ϕ/V , where ϕ is the apparent mol. vol. of the solute in the crit. disruptive state, obtained by extrapolation of apparent mol. vol.—concn. data, is about 0.64 for the alkali halides. J. BALOZIAN (c).

Physico-chemical properties of specific polysaccharides. M. HEIDELBERGER and F. E. KENDALL (J. Biol. Chem., 1932, 95, 127—142).—The polysaccharide of type III pneumococcus (A., 1927, 77, 1114) yields a highly-ionised Na salt characterised by a mobile negative ion of very high valency. Aq. solutions do not behave normally with respect to viscosity, the ratio sp. viscosity/concn. increasing to a max. with increasing dilution. This deviation and also that from the square root conductivity relation at high dilutions are explained by increasing dissociation and an orientation of the highly-charged polycarboxylate ion at high dilutions. Such phenomena occur to a smaller degree with the type I polysaccharide. The viscosity effects of both type II polysaccharide and sp. gum arabic (A., 1929, 1201; 1930, 66) decrease with the relative no. of CO_2H groups in the mol.

F. O. HOWITT.

Theory of the electrification of aerosols. H. S. PATTERSON (Phil. Mag., 1932, [vii], 13, 736; cf. this vol., 120).—A correction. H. J. EMELEUS.

Ultrasonic measurements of the compressibility of solutions and of solid particles in suspension. C. R. RANDALL (Bur. Stand. J. Res., 1932, 8, 79—99).—An ultrasonic interferometer is described. The apparatus has been used to determine ultrasonic velocities in H_2O and aq. sugar solutions at different concns. and temp. and from these data the compressibilities have been calc. Similar measurements were made with aq. suspensions of pyrex glass, containing particles $<2\ \mu$. The velocity decreases with increasing concn. of the suspension. E. S. HEDGES.

Preparation and properties of hydrated beryllium oxide sols. W. H. MADSON and F. C. KRAUSKOPF (J. Physical Chem., 1931, 35, 3237—3258).— BeO sols were prepared by igniting BeCl_2 , then adding H_2O and dialysing, the disperse phase being a hydrated oxide containing <0.5 mol. of H_2O per mol. of BeO . Flocculation vals., which followed the Schulze-Hardy rule, decreased as the time of dialysis increased up to 12—24 hr., subsequently remaining

fairly const. The concn. and $[\text{H}^+]$ of the sol varied similarly with the time of dialysis. The lyotropic series obtained from the flocculation vals. were: $\text{Fe}(\text{CN})_6''' < \text{Fe}(\text{CN})_6''' < \text{H}_3\text{PO}_4' < \text{AsO}_4''' < \text{SO}_4'' < \text{CrO}_4''' < \text{OAc}' < \text{CCl}_3\text{CO}_2' < \text{CHCl}_2\text{CO}_2' < \text{CH}_2\text{ClCO}_2' < \text{Cl}'$ and $\text{Na}' < \text{K}' < \text{NH}_4' < \text{Mg}''$. H. M. STARK (c).

Use of electro dialysed water for the preparation of gold sols by Zsigmondy's method. I. GUERRERO and R. WERNICKE (Anales Farm. Bioquim., 1931, 2, 35—39; Chem. Zentr., 1931, ii, 1112).—Good colloidal Au solutions can be obtained with H_2O electro dialysed between parchment paper or cellophane membranes. Collodion membranes are unsuitable. The content of electrolytes and org. matter increases during dialysis owing to contact with the membrane. Suitable H_2O can also be obtained by simple contact with cellophane or parchment paper at higher temp. L. S. THEOBALD.

Particle size and constitution of colloidal ferric oxide. I. J. B. NICHOLS, E. O. KRAEMER, and E. D. BAILEY (J. Physical Chem., 1932, 36, 326—339).—The particle-size distribution curve of an undialysed Fe_2O_3 sol prepared by hydrolysis of FeCl_3 was determined by the ultracentrifuge method. Dilution did not affect the curve. Digestion favoured dehydration and growth of cryst. hematite, the rate of growth increasing with the Fe_2O_3 concn. A negative sol produced with the aid of K citrate gave nearly the same curve as the above sol. The intermicellar liquid contained a semi-colloidal fraction of a dispersity approaching that of FeCl_3 , in addition to primary and secondary portions observed in the ultracentrifuge. F. URBAN (c).

Water relationships in colloids. II. "Bound" water in colloids. D. R. BRIGGS (J. Physical Chem., 1932, 36, 367—386; cf. A., 1931, 1231).—Bound H_2O is defined as that portion of the H_2O in a system containing colloid and crystalloid which is associated with the colloid and those ions which form part of the colloid complex. It varies with the activity of the H_2O in the system in a manner consonant with the v.-p. isotherm. In a system in which colloids and crystalloids are in equilibrium the amount of H_2O associated with or bound by a given wt. of any of the non-aq. components will always be the same for a given H_2O activity, provided that these components do not react with each other. Some of the methods which have been used for determining bound H_2O are interpreted on these lines. F. SAUNDERS (c).

Emulsions. III. Microscopical observations on the system xylene-phenol-sodium oleate-water. J. WEICHERTZ (Kolloid-Z., 1932, 58, 214—215; cf. A., 1929, 1379).—Photomicrographs are reproduced to demonstrate the existence of two regions of homogeneity as the H_2O content is increased. E. S. HEDGES.

Systematology of celluloses based on their viscosities in solution. H. FIKENTSCHER (Cellulosechem., 1932, 13, 58—64).—An empirical equation is given expressing the viscosity, k , of a colloid in terms of the relative viscosity, concn., and two consts. k is calc. for a no. of colloids dissolved

in various solvents and is found to be fairly const. in each solvent, although there are some discrepancies in the vals. of k for the same colloid in different solvents.

J. L. D'SILVA.

Alternating current effects on colloidal systems. M. SHIKATA and H. HUKUWATARI (J. Soc. Chem. Ind. Japan, 1932, 35, 25—27b).—The stability of certain (unquoted) colloidal systems and the adsorptive power of charcoal are not affected by a high-tension alternating field, which, however, modifies the Liesegang ring formation obtained with aq. NH_3 and MgCl_2 in gelatin, increases the viscosity and rate of evaporation of gelatin solutions, and retards the vol. contraction occurring when photographic gelatin is hydrated with H_2O or H_2O -EtOH solutions.

N. H. HARTSHORNE.

Emulsions and surface tension. K. C. CHANG (Trans. Sci. Soc. China, 1931, 7, 17—23).—Liquid-liquid emulsions are divided into 2 groups: (1) the interfacial film is part of either the oil or the water phase, (2) the emulsifying agent exists as a third phase between the two liquid phases. In the first group Antonov's rule holds. Measurements were made by the capillary rise method. CHEMICAL ABSTRACTS.

Solid-phase relations in the dissolution of cellulose acetate. W. OSTWALD and H. ORTLOFF (Kolloid-Z., 1932, 58, 215—225).—The solubility of cellulose acetate in EtOAc, Et acetoglycolate, MeOBz, Me phthalate, diacetone alcohol, cyclohexanone, and $\text{CH}_3\text{Ph}\cdot\text{OH}$ at 25° varies with the amount of solid phase used. The curves connecting solubility with the amount of solid phase do not show a pronounced max., as is observed in adsorption or dissolution peptisation, but are linear, convex, or concave, according to the solvent. The solid-phase rule also holds in certain binary mixtures of the above solvents, in which case the curves are concave to the axis representing the amount of solid phase. The solid-phase relation is ascribed to the mixed nature of cellulose acetate.

E. S. HEDGES.

Viscosimetric investigations on the reaction of cellulose with concentrated zinc chloride solutions. K. LETTERS (Kolloid-Z., 1932, 58, 229—239).—The dispersion of different forms of cellulose in conc. ZnCl_2 solutions has been followed by a viscosimetric method. All the curves obtained are complex in form and are believed to indicate swelling, disintegration, and hydrolysis. A reversible swelling region occurs between 55 and 63% ZnCl_2 , varying with the structure of the cellulose. In pure ZnCl_2 solutions swelling begins at 40° , whilst in the technical solutions containing 0.3M-CaCl₂ swelling begins at about 60° . The temp. variation of viscosity in two different solutions gives a means of characterising samples of cellulose.

E. S. HEDGES.

Coagulation. G. WIEGNER (Kolloid-Z., 1932, 58, 157—168).—A lecture on published work.

E. S. HEDGES.

Slow coagulation of sols. H. J. C. TENDELOO (Chem. Weekblad, 1932, 29, 151—153).—A survey of recent work. The simple theory of Smoluchowski is inadequate to account for the phenomenon of slow coagulation, possibly because of a gradual change of

the charge on the particles. The form of the particles and the forces of attraction, which are of little significance in rapid coagulation, may also be of importance.

H. F. GILLBE.

Dispersoid chemistry of kaolin earths. E. VON BOGUSLAVSKI (Kolloid-Beih., 1932, 34, 373—440).—Numerous experiments on the coagulation and sedimentation of kaolin suspensions, particularly under the influence of electrolytes, are described and discussed in relation to other work. All the observed phenomena are compatible with reversible surface reactions, which frequently involve the exchange-adsorption of ions. The formation of an insol. compound is not a necessary condition for exchange adsorption at the surface of kaolin particles. Addition of alkalis, particularly those having univalent cations, increases the stability of the suspensions, a considerable dispersing effect being observed when the concn. of alkali is 1—10 milliequiv. per litre. At higher concns. the alkali has a coagulating influence, increasing in the order $\text{NH}_4\text{OH} < \text{LiOH} < \text{KOH} < \text{Ba}(\text{OH})_2 = \text{Ca}(\text{OH})_2$. Since the same order holds for the dispersing influence, both effects are ascribed to the adsorbability and degree of dissociation of the alkali. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ also has a dispersing effect on kaolin suspensions.

E. S. HEDGES.

Flocculation of colloidal solutions. II. Flocculation of negatively- and positively-charged sols by electrolytes; normal and irregular series. A. LOTTERMOSER and K. MAY (Kolloid-Z., 1932, 58, 168—179).—The flocculation of a mastic sol by electrolytes is independent of the concn. of the sol. Irregular series are observed with FeCl_3 , AlCl_3 , $\text{Th}(\text{NO}_3)_4$, TiCl_3 , TiCl_4 , ZrCl_4 , and SnCl_4 , but μ measurements show that the phenomenon is not caused by the hydrolysis products of these salts. The electrolyte coagulation of $\text{Fe}(\text{OH})_3$ sols is independent of the sol concn. only in dil. sols. Irregular series are observed with $\text{K}_4\text{Fe}(\text{CN})_6$, K_2HPO_4 , Na_2WO_4 , $(\text{NH}_4)_2\text{MoO}_4$, NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 , Na_3AsO_4 , $\text{Na}_3\text{V}_3\text{O}_9$, $(\text{NH}_4)_3\text{V}_3\text{O}_9$, and $\text{Na}_4\text{P}_2\text{O}_7$. Irregular series are observed in the flocculation of positively- and negatively-charged sols of AgI by AgNO_3 or KI and by the salts mentioned above.

E. S. HEDGES.

Periodic precipitation. J. N. FRIEND and R. H. VALLANCE (Nature, 1932, 129, 205).—Morse's results (A., 1930, 1117) support the authors' view (J.C.S., 1922, 121, 472) that the main effect of the gel is to retard the release of supersaturation and thus to increase the relative effect of diffusion.

L. S. THEOBALD.

Choice of covering liquid in the exact measurement of cataphoretic migration velocity by the moving boundary method. J. N. MUKHERJEE (Kolloid-Z., 1932, 58, 155—157).—The covering liquid layer in electrophoretic measurements should have the same conductivity as the sol. This is not fulfilled when the ultrafiltrate is used as the covering liquid, except when the sol contains relatively large quantities of free electrolyte.

E. S. HEDGES.

Electrophoresis of agar-gold sols. E. B. R. PRIDEAUX and F. O. HOWITT (Trans. Faraday Soc., 1932, 28, 79—83).—Agar is a Ca sulphuric ester of a

hemicellulose, the cyclic structure of which is responsible for its capacity to gelate. The electrophoretic velocity of dialysed gelatin-free commercial agar (0.1%) with 0.02% of Au sol in 0.03*N*-acetate buffers is increased slightly by raising the p_H from 2.6 to 8.3 (cf. A., 1930, 568). The velocity is uniformly less than that of colloidal Au (cf. A., 1929, 27) and the results are such as would be expected for a colloid the negative charge of which is due to a form of partial ionisation in which the Ca ions remain bound near the surface as long as the cyclic structure due to co-ordination persists. The absence of amphoteric characteristics and the suitability of agar as a support in investigations of ionic diffusion in dil. acid or alkali are emphasised.

J. G. A. GRIFFITHS.

Streaming potential determinations on glass capillaries of various sizes. H. L. WHITE, F. URBAN, and E. T. KRIECK (J. Physical Chem., 1932, 36, 120—129).—The streaming potential in a pyrex capillary through which 0.0005*M*-KCl is flowing under 60 cm. pressure is the same for capillaries of diameter 60—110 μ , but with diameters between 4.5 and 40 μ lower potentials are observed. Time-potential curves for an 83 μ capillary are reproduced.

FRANK URBAN (c).

Coherent expanded aerogels. S. S. KISTLER (J. Physical Chem., 1932, 36, 52—64; cf. A., 1931, 683).—Aerogels can be obtained by the successive displacement of the liquid in a gel by other liquids, each of which is completely miscible with the preceding one and the last of which has a low crit. temp., so that it may be displaced by a gas. Aerogels of SiO₂, Al₂O₃, WO₃, Fe₂O₃, SnO₂, Ni tartrate, cellulose and its nitrate, gelatin, agar, and ovalbumin were made by removal of H₂O from the normal gels.

A. L. KIBLER (c).

Coacervation (separation) of mixtures of concentrated gum arabic and gelatin sols. H. G. B. DE JONG and J. LENS (Kolloid-Z., 1932, 58, 209—214).—The coacervation of mixtures of gum arabic and gelatin sols has no relation to the discharge of oppositely-charged sols, but is due to the desolvation of one of the colloids by the other. This view is supported by the fact that the effect of adding neutral salts is in accordance with the lyotropic series. The biological significance of this phenomenon is discussed.

E. S. HEDGES.

Effect of surface-active substances on gelatin. I. Swelling. II. Gel-sol transformation. III. Optical activity. A. VON KUTHY (Biochem. Z. 1932, 244, 319—330, 331—336, 337—341).—I. The extent to which surface-active substances are adsorbed by gelatin can be taken as a measure of their effect on its swelling. In so far as certain hydrotropic substances occupy a special position in this connexion it is due to the great extent to which they are adsorbed; even at relatively low concns. they cause considerable swelling.

II. With certain exceptions those substances which cause swelling of gelatin also stimulate the transformation of gelatin gel into sol, whilst those which hinder the swelling act in the opposite way.

III. Since, in general (exceptions are numerous), substances which cause swelling and sol formation in

gelatin likewise reduce its optical rotation and those which cause shrinkage and gel formation increase it, it is assumed that the factor common to the three processes is the transformation of the gelatin from the *A* into the *B* form.

W. MCCARTNEY.

Rhythmic splitting of silicic acid gels. E. C. H. DAVIES (J. Physical Chem., 1931, 35, 3618—3630).—Silicic acid gels cast in glass tubes split rhythmically whenever there is sufficient contraction, and the initial split occurs along some line other than the inside circumference of the tube or one of its diameters. The best conditions for rhythmic splitting are realised in tilted narrow tubes, open at the top, and not covered with an aq. solution. If L_0 is the wave-length of the rhythmic split and D the diameter of the tube, then $L_0 = 4.76D$, approx. Thus L_0 is about 1.5 times as great as for a true sine curve. Between 25° and 60°, L_0 decreases very slightly as the temp. rises, but the rate of splitting increases rapidly, especially in tubes of large D . The angle at which the tube is inclined does not affect the val. of L_0 . F. L. BROWNE (c).

Base exchange in permutit and surface adsorption by silica gel. I. R. HAAS (Chem.-Ztg., 1931, 55, 975—976).—The base-exchange properties of permutit are attributed to ionic diffusion and to the reduction of the negative properties of the SiO₂ groups by the Al present. The impossibility of removing Ca from apophyllite by treatment with solutions of Na or K salts is, on the other hand, due to the close proximity of numerous negative SiO₂ complexes. Removal of Ca and Mg from solutions of their salts by certain varieties of SiO₂ gel is purely a surface adsorption phenomenon due to the highly disperse nature of the gel.

A. R. POWELL.

Cryolysis of lyophilic colloids. X. Mechanism of enzyme action. O. M. VON RANKE-ABONYI and F. F. NORD (Kolloid-Z., 1932, 58, 198—208).—Freezing and subsequent thawing of solutions of albumin, gelatin, or gum arabic produces an increase in the surface tension, viscosity, electrical conductivity, and electrophoretic migration velocity, indicating an irreversible physical change, which is probably connected with an increase of sp. surface. The increased activity of zymase solutions after freezing and thawing is probably due to the same cause.

E. S. HEDGES.

Cryolysis of lyophilic colloids, and its bearing on the mechanism of enzyme action. F. F. NORD and O. M. VON RANKE-ABONYI (Science, 1932, 75, 54—55).—The surface tensions of solutions of ovalbumin, gelatin, gum arabic, and Na oleate are decreased by freezing at different temp. The viscosity is increased with ovalbumin, decreased with gelatin or gum arabic, and unaffected with Na oleate. The electrical conductivity of 0.01% solutions is increased, whilst that of solutions above 0.1% is decreased. The cataphoretic mobility of the colloidal particles of gelatin or ovalbumin is doubled by freezing. Lyophilic colloids may thus undergo aggregation as well as disaggregation after freezing. L. S. THEOBALD.

Swelling of collagen fibres. A. VON KUTHY (Biochem. Z., 1932, 244, 342—346).—Below certain threshold vals. (which correspond with high concns. of

the substance involved) collagen fibres do not swell under the influence of surface-active substances. Above these vals. considerable swelling occurs. In dil. AcOH swelling proceeds normally. It is inferred that the swelling in acids proceeds in an entirely anomalous manner or that the fibres are enveloped in a semi-permeable membrane through which acids but not the surface-active substances can pass. When the concn. of the latter attains a certain val. permeation occurs in accordance with theories previously discussed or because the membrane is destroyed. Other factors are also involved. W. MCCARTNEY.

Physical chemistry of the proteins. X. Solubility of hæmoglobin in solutions of chlorides and sulphates of varying concentration. A. A. GREEN (J. Biol. Chem., 1932, 95, 47—66).—The solubilities of horse carboxyhæmoglobin in aq. solutions of NaCl, KCl, Na_2SO_4 , K_2SO_4 , MgSO_4 , and $(\text{NH}_4)_2\text{SO}_4$ have been determined. The compound behaves as a globulin exhibiting a max. solubility in sulphates with increasing salt concns., the solvent power of sulphates being much less than that of the chlorides. In all cases the activity coeffs. found agree approx. with those calc. from a simplified Debye-Hückel equation, whilst the solubilities at 25° and at p_H 6.6 agree with the empirical equation $\log S = 1.30 + k_0 C$, where k_0 is a const. varying with the electrolyte.

F. O. HOWITT.

Physical chemistry of starch and bread-making. VIII. To what extent do substances related to native starch undergo gelatinisation and retrogradation? M. SAMEO and J. R. KATZ [with J. C. DERKSEN]. IX. The X-ray spectrum of α -diamoyle closely corresponds with that of certain starch preparations. J. R. KATZ and J. C. DERKSEN. X. Heating effects only limit gelatinisation. Significance of this fact in appraisal of methods of determining gelatinisation temperature. J. R. KATZ (Z. physikal. Chem., 1932, 158, 321—336, 337—345, 346—354; cf. B., 1931, 1069).—VIII. X-Ray examination shows that sol. starch, erythrogranulose, erythroamylose, and amylopectin undergo retrogradation from an α to a β form. These substances do not gelatinise when heated with H_2O , although gelatinised starch consists of the α form. In 10% solution glycogen does not undergo retrogradation. The behaviour of dextrin depends on the extent to which degradation has occurred.

IX. The resemblance of the X-ray diagrams of α -diamoyle I and II to the sharp V-spectrum of certain starch preps. is so pronounced as to afford strong support to the theory that starch is a polymerised α -diamoyle (A., 1921, i, 310).

X. When starch is heated with a little H_2O at 100° or with a large excess of H_2O at lower temp., gelatinisation proceeds up to a point and then ceases. In investigating gelatinisation it is therefore preferable to work at a const. temp. rather than at a slowly rising temp.

R. CUTRILL.

Photophoresis, electro- and magneto-photophoresis. M. REISS (Physikal. Z., 1932, 33, 185—202).—A summary of recent work on the movement of sub-microscopic particles in a beam of light, and

the effect of an electric and magnetic field on the movement.

A. J. MEE.

Thermal dissociation of arsenic di- and tri-sulphides. E. V. BRITZKE, A. F. KAPUSTINSKI, and L. F. TSCHENTZOVA (J. Chem. Ind. Russ., 1931, 8, No. 19, 1—7).—The densities of realgar vapour at 760—1080°, and of orpiment vapour at 820—1150°, show that the former contains As_2S_2 , As_4 , As_2 , and S_2 , whilst the latter contains As_2S_3 in addition. The heat of formation of As_2S_2 from As and rhombic S is 19.2 g.-cal.

R. TRUSZKOWSKI.

Variation of the affinity constants of substituted organic acids. A. EUCKEN (Angew. Chem., 1932, 45, 203—208).—A lecture. H. F. GILLBE.

Association of strong electrolytes. J. ZIRKLER (Z. Physik, 1932, 73, 707—708).—A verification of Nernst's method for determining the degree of association of strong electrolytes from conductivity data.

A. B. D. CASSE.

Iodine equilibrium in aqueous solutions. A. URMANCZY (Magyar Chem. Fol., 1931, 37, 161—173; Chem. Zentr., 1931, ii, 2410).—The solubility of I in 0.025N-KI, 0.5—3.0N- KNO_3 , 0.5—7.5N- NaNO_3 , 0.5—8.7N- LiNO_3 , 0.5—1.37N- K_2SO_4 , 0.25—3.5N- Na_2SO_4 , 0.5—5.0N- Li_2SO_4 , 0.5—4.0N-KCl, 0.5—5.0N-NaCl, and 0.5—13.5N-LiCl was determined. A new view of salting-out action is put forward; the dissociation consts. of I_2Cl , Br_3' , and $\text{I}_3\text{Br}'$ have been calc., the difficulties of calculation of the thermodynamic equilibrium consts. discussed, and the activity of I and the activity ratio I_3/I considered.

A. A. ELDRIDGE.

Bromine-bromide-tribromide equilibrium. R. O. GRIFFITH, A. McKEOWN, and A. G. WYNN (Trans. Faraday Soc., 1932, 28, 101—107).—The equilibrium const. $K = [\text{Br}_2][\text{Br}']/[\text{Br}_3']$ has been determined at 16.5° and 21.5° from partition experiments with free Br at concns. <0.01M and HBr, NaBr, KBr, and LiBr at concns. between 0.03 and 0.75N. Under these conditions, Br_3' formation is negligible. With NaBr, KBr, and LiBr, K increases with ionic strength, μ , and in some cases passes through a max. LiBr has the largest and KBr the smallest salt effect. HBr depresses K (cf. A., 1928, 841). When correction is made for the activity coeff. of Br, $K = 0.0568$ at 21.5°. Contrary to Lewis and Randall, the activity coeff. of Br_3' is approx. 16% greater than that of Br' when $\mu = 0.5$ and Na' is the cation.

J. G. A. GRIFFITHS.

Physico-chemical study of solution of magnesium citrate. M. OAKLEY and J. C. KRANTZ, jun. (J. Amer. Pharm. Assoc., 1932, 21, 132—135).—The p_H vals. of citric acid solutions have been determined. The threshold acid taste for the acid is at about 0.02%, p_H 3.16. The p_H changes occurring when pure MgO is added to citric acid solution indicate that when equiv. amounts are present, the solution contains $\text{MgHC}_6\text{H}_5\text{O}_7$ and $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2$.

E. H. SHARPLES.

Statistical mechanics of dilute and of perfect solutions. E. A. GUGGENHEIM (Proc. Roy. Soc., 1932, A, 135, 181—192).—Mathematical. Using the two characteristic functions ψ and ϕ of Planck and

the partition functions described by Fowler certain laws of dil. solutions are derived.

L. L. BIRCHUMSHAW.

Equilibrium diagrams. L. GRENET (*Aciers speciaux, Metaux, Alliages*, 1931, 6, 2—10; *Chem. Zentr.*, 1931, ii, 2266).—A discussion of 1- and 2-component systems.

L. S. THEOBALD.

Physico-chemical applications of thermodynamics to systems in motion. (MLLE.) Y. DUPONT (*Bull. Acad. roy. Belg.*, 1932, [v], 18, 83—94).—Theoretical. De Donder's theory of affinity is applied mathematically to the distribution of a solute in a centrifugal field (cf. A., 1931, 694), and to the distribution of suspended particles in a gravitational field.

C. W. GIBBY.

Reciprocal relations in irreversible processes. II. L. ONSAGER (*Physical Rev.*, 1931, [ii], 38, 2265—2279; cf. A., 1931, 546).—Theoretical.

N. M. BLIGH.

Thermodynamics applied to the iron-carbon system. F. H. JEFFERY (*Trans. Faraday Soc.*, 1932, 28, 98—100; cf. this vol., 15).—Polemical. The methods and conclusions of Chu-Phay (this vol., 15) are criticised.

J. G. A. GRIFFITHS.

Determination of free energy of ferrous hydroxide from measurements of electromotive force. M. RANDALL and M. FRANDSEN (*J. Amer. Chem. Soc.*, 1932, 54, 40—46).—The e.m.f. of the cell $\text{Fe}|\text{Fe}(\text{OH})_2(s)|\text{Ba}(\text{OH})_2 \cdot 0.05M, \text{HgO}(s)|\text{Hg}$, is 0.973 ± 0.005 volt at 25° . The calc. free energy of formation of $\text{Fe}(\text{OH})_2$ is $-115,400$ g.-cal. and that of the reaction $\text{Fe}(s) + 2\text{H}_2\text{O}(l) = \text{Fe}(\text{OH})_2(s) + \text{H}_2$ is -2280 g.-cal.

L. P. HALL (c).

[Determination of] activity coefficients of salts in acetic acid solutions from solubility measurements. R. P. SEWARD and C. H. HAMBLET (*J. Amer. Chem. Soc.*, 1932, 54, 554—563).—The solubility of KClO_4 in glacial AcOH in the presence of NH_4ClO_4 , NaNO_3 , and NaBr , and that of KNO_3 in the presence of NH_4Cl and NH_4NO_3 at 25° agrees, if a large enough ionic diameter is assumed, with the results calc. from the original Debye-Hückel theory, but better agreement is obtained with Gronwall, La Mer, and Sandved's theory. The properties of salt solutions cannot be explained solely in terms of the dielectric const. of the solvent.

G. M. MURPHY (c).

Formation of metal halides, especially silver bromide, from the viewpoint of Nernst's heat theorem. A. EUCKEN, K. CLUSIUS, and H. WITTNEK (*Z. anorg. Chem.*, 1931, 203, 39—56).—Measurements of the sp. heat of Ag and of AgBr at low temp. and electrometric determination of the reaction entropy have given results in accordance with Nernst's heat theorem. The reported apparent deviations from the theory are criticised.

E. S. HEDGES.

Water content of saturated air at temperatures up to 100° . J. H. AWBERRY (*Proc. Physical Soc.*, 1932, 44, 143—150).—The H_2O content has been determined by absorption and weighing between 29° and 94° with a probable accuracy of 2%.

C. W. GIBBY.

Vapour pressure of water over aqueous solutions of chlorides of the alkaline-earth metals. I. Experimental, with critical discussion of vapour-pressure data. II. Deviations from Raoult's law, as indicated by the molecular lowering of vapour pressure and van 't Hoff coefficients; with theoretical discussion. III. Correlation with other physical properties of the solutions. J. R. I. HEPBURN (*J.C.S.*, 1932, 550—566, 566—575, 575—582).—I. V. p. of solutions of the chlorides of Ca , Sr , and Ba over the concn. range $0.2N$ to saturation have been measured at 25° by the dew-point method previously described (A., 1928, 1190). Data from other sources are critically discussed. Attention is directed to an error in the data of certain workers due to the use of Regnault's tables for the v. p. of H_2O .

II. The author's results, in agreement with those of several other workers, show that the mol. lowering of v. p. or the van 't Hoff coeff. has a min. val. at a concn. between 0.1 and $0.5N$, for all three salts. For CaCl_2 and BaCl_2 there is also a max. at concns. approaching saturation. The existence of a min. is attributed to the opposing effects of dissociation of polymeric H_2O mols., and co-ordination of monomeric H_2O by the ions.

III. A review of the existing data for f. p. lowering, viscosity, and differential heat of dilution shows the existence of a close correlation between these properties and v. p. lowering, in respect of concn. No corresponding abnormalities are found in the sp. gr. of the solutions.

F. L. USHER.

Vapour pressures of saturated aqueous solutions of certain salts. H. W. FOOTE, B. SAXTON, and J. K. DIXON (*J. Amer. Chem. Soc.*, 1932, 54, 563—568).—The v. p. at 0 — 25° of saturated solutions of NaCl , KCl , CsCl , K_2SO_4 , and Na_2SO_4 have been determined by a new static method; the differences between the observed and calc. vals. of the temp. coeff. are within the limits of experimental error.

G. M. MURPHY (c).

Effect of solvent on activity of acids: vapour pressure of hydrogen chloride in glacial acetic acid solutions. W. H. RODEBUSII and R. H. EWART (*J. Amer. Chem. Soc.*, 1932, 54, 419—423).—The v. p. at 24.8° of HCl over solutions in which the mol. fraction of the solute is 0.00242 — 0.0208 has been determined. Comparison with v. p. over aq. solutions shows that the relative activity of HCl in an AcOH solution is 10^5 times as great as in an aq. solution in which its molar fraction is the same. The effect of the solvent on the activity of dissolved acids is discussed.

G. M. MURPHY (c).

Equilibria between water and chlorides of potassium and sodium from -23° to 190° . E. KORNEO and H. KROMBACH (*Compt. rend.*, 1932, 194, 714—716).—The composition of solutions saturated simultaneously with respect to the two salts has been determined between -22.9° and 189.6° . The presence of KCl lowers the transition point $\text{NaCl} \rightarrow \text{NaCl} \cdot 2\text{H}_2\text{O}$ to -2.3° , and the eutectic point to -22.9° . The solubility of NaCl is a min. at 105° . (Cf. B., 1930, 507.)

C. A. SILBERRAD.

Freezing of solutions as a method of investigation in pure chemistry. VII. Crystal-liquid equilibria in malic-tartaric mixtures. J. TMMERMANS and M. DUMONT (Bull. Soc. chim. Belg., 1931, 40, 689—709; cf. A., 1931, 676).—Mixtures of two optically active substances have been examined by cryoscopic and solubility measurements. *l*-Malic acid gives a eutectic with *l*-tartaric acid, but forms a compound with *d*-tartaric acid. Similar results are obtained with the acid NH_4 salts, so that in each case the *d*-compounds have similar configurations. Only eutectics are found, however, in mixtures of *d*-tartaric acid with *d*- or *l*-chlorosuccinic acid, and of NH_4 *l*-malate with NH_4 *d*- or *l*-chlorosuccinate.

C. W. DAVIES.

Phase study of the system ammonia-hydrogen sulphide. L. SCHLEFLAN and C. R. McCROSKY (J. Amer. Chem. Soc., 1932, 54, 193—202).—The v. p. and m. p. of mixtures of NH_3 and H_2S have been determined. The v. p.-composition diagram at 0° shows two regions of const. pressure, one of which represents the dissociation pressure of NH_4HS (80 mm. at 0°) and the other the pressure at which the solid compound is in equilibrium with solution and vapour at the same temp. The m.-p. data reveal the existence of NH_4HS , $(\text{NH}_4)_2\text{S}$, and a eutectic mixture of 95% NH_3 and 5% H_2S . Cryst. $(\text{NH}_4)_2\text{S}$ does not exist above -18°, at which temp. it decomposes into cryst. NH_4HS and melt. Probably only NH_4HS is stable above 0°.

E. S. HEDGES.

Thermal analysis of the systems phenylhydrazine-acetic acid. N. A. TRIFONOV and S. I. TSCHERBOV (Bull. Inst. rec. biol. Perm, 1929, 6, 313—318).—The m.-p. diagram shows an equimol. compound, m. p. 61.5°.

R. TRUSZKOWSKI.

Conductivity, surface tension, viscosity, and m. p. of certain binary systems. N. A. TRIFONOV [with K. I. SAMARINA, V. F. UST-KATSKINCEV, P. M. SALNIKOVA, A. I. MELNIKOVA, E. N. KOBELEVA, A. T. CHELESOVA, E. P. TELUSCHKIN, R. W. MERZLIN, M. S. PRONINA, A. I. MOGILNIKOV, A. N. POPOV, N. A. VASILIEVA, C. S. AVRUTOVA, and M. A. VORSINA] (Bull. Inst. rec. biol. Perm, 1931, 7, 343—406).—The conductivity curves for mixtures of allylthiocarbimide with piperidine, *o*-toluidine, or NH_2Ph exhibit 2 maxima, with a sharp min. at 50 mol.-%; for mixtures of H_2O with pyridine, piperidine, PhOH , or chloral, and of AcOH with NHPhEt or NPhEt_2 the curves have only one max. in the vicinity of the AcOH or H_2O axis. The surface tension isotherms for the system PhOH -piperidine have a max. at 75 mol.-% PhOH , for SnCl_4 - AcOEt at 33.3 mol.-% SnCl_4 , and for SnCl_4 - PhOH 2 maxima, at 5 and 70—80 mol.-% SnCl_4 ; for the systems $\text{C}_3\text{H}_5\text{NCS}$ -*o*- or *p*-toluidine, or NHPh_2 the max. is at 50 mol.-%, at which point $\text{C}_3\text{H}_5\text{NCS}$ - NHPhMe , NHPhEt , NHPh_2 , or piperidine, PhNCS - NHPhMe , and Ac_2O - H_2O exhibit minima, whilst for $\text{C}_3\text{H}_5\text{NCS}$ - NPhEt_2 or NPhMe_2 , PhNCS - NPhMe_2 , H_2O -chloral or pyridine, PhOH - NHPh_2 or *o*-toluidine, AcOH -pyridine, *o*-toluidine, quinoline, NHPhMe , or NPhMe_2 , and EtOH -piperidine no well-defined maxima or minima are observed. The viscosity isotherms for $\text{C}_3\text{H}_5\text{NCS}$ -*o*- or *p*-toluidine, and PhNCS - NPhHMe , NHPhEt , or NPhEt_2 .

have a max. at 50 mol.-%, at which point AcOH - $\text{NHPh}\cdot\text{NH}_2$ has a min.; for AcOH -*o*-toluidine max. viscosity occurs at 72 mol.-% AcOH , whilst the isotherm for EtOH -piperidine is concave over its entire length. The fusion diagrams for *p*-toluidine-cinnamic acid, NHPh_2 - AcOH , NPhMe_2 - BzOH , $\text{CO}(\text{NH}_2)_2$ - BzOH or cinnamic acid, benzoquinone- C_6H_6 , C_{10}H_8 , PhNO_2 , or BzOH , and bromocamphor- PhOH , resorcinol, or BzOH indicate the absence of compound formation. Equimol. compounds are formed by *p*-toluidine- AcOH , m. p. 42°, CHPh_2 - CO_2H , m. p. 54.5°, or salicylic acid, m. p. 83°; NH_2Ph -salicylic acid, m. p. 73°, $\text{CO}(\text{NH}_2)_2$ -quinol, m. p. 131.5°, or resorcinol, m. p. 101°, benzoquinone-*p*-nitrophenol, m. p. 62.8°, 2:4-dinitrophenol, transition point 70.8°, picric acid, m. p. 76—77°, or salicylic acid, transition point 93° at 38 mol.-% benzoquinone, and bromocamphor-resorcinol, m. p. 48°. The following compounds are also recorded: $\text{C}_6\text{H}_4\text{O}_2$ - 2PhOH , m. p. 69.4°, and $\text{C}_6\text{H}_4\text{O}_2$ - 2OH - $\text{C}_6\text{H}_4\text{OMe}$, m. p. 61°. The eutectic mixture of *o*- and *p*-toluidine (-33°) contains 12.5 mol.-% of the *p*-isomeride.

R. TRUSZKOWSKI.

Application of thermopiles to the measurement of the temperature in the dehydration and explosion of certain metal picrates. T. TUCHOLSKI (Rocz. Chem., 1932, 12, 58—66).—When cryst. Na, K, Pb, Ca, and Cu picrates are slowly heated, their temp. is lower than that of the surrounding atm., owing to evaporation of H_2O of crystallisation. When all the H_2O has been expelled, the two temp. are for a short interval equal, after which the temp. of the picrates rises above that of the environment, owing to thermal decomp., followed by explosion. The temp. of the environment and of the dry picrate at the moment of explosion are respectively 318° and 324.4° for Na, 333.1° and 338.8° for K, 260.6° and 267.8° for Pb, 318.3° and 325.8° for Ca, and 281.8° and 286.2° for Cu picrates.

R. TRUSZKOWSKI.

System sodium metasilicate-sodium fluoride. H. S. BOOTH and B. A. STARS (J. Physical Chem., 1931, 35, 3553—3557).—Thermal analysis shows the system to be of the one-eutectic type. The eutectic point is $913 \pm 2^\circ$, the liquid phase containing $28.5 \pm 1.0\%$ NaF . Tentative data for the system Na disilicate- NaF are given.

A. L. HENNE (c).

System Fe-C-O. E. JANECKE (Z. anorg. Chem., 1932, 204, 257—290).—A comprehensive survey of recent work, with an extensive bibliography. The author's diagram has been somewhat modified, and the equilibria at various pressures and temp. have been calc. The heat of formation of cementite is -6.5 kg.-cal., and that of pearlite -2.77 kg.-cal. Contrary to previous views, there is a max. pressure in the univariant system Fe-austenite-FeO-gas at 820°. The equilibria in the Fe-C-O system between 500° and 1000° and 0.2 and 5 atm. are represented by a three-dimensional model.

H. F. GELBE.

Recent investigations of the equilibrium of systems involved in the production of steel. F. SAUERWALD [with W. HUMMELTSON] (Arch. Eisenhüttenw., 1931—1932, 5, 355—366).—A crit. review of recent work on the systems Fe-O, Fe-FeO-CaO, Fe-O-C, Fe-Si-O, and Fe-MnO, and of equilibria

involving P and S in the steel bath is followed by a tabulated summary of the equilibrium consts. obtained by the various workers. A. R. POWELL.

Equilibria in the systems silica, lime, and alumina with carbon. R. BRUNNER (Z. Elektrochem., 1932, 38, 55—68).—Pressure-temp. relations have been investigated in the systems $\text{SiO}_2\text{--C}$, CaO--C , and $\text{Al}_2\text{O}_3\text{--C}$. In the first system a quintuple point has been found at 525 mm. and 1570° where the phases SiO_2 , $(\text{SiC})_2\text{O}$, SiC , C, and CO co-exist. A pressure-temp. curve for CO formation is obtained below the CaO--CaC_2 eutectic at approx. 1640°. In the system $\text{Al}_2\text{O}_3\text{--C}$ equilibria for both carbide and metal formation are obtained. The pressure-temp. curves for these intersect to give a quintuple point at 1.5 mm. and 2013°. In all three systems sublimates are formed by combination of metal and CO in the gaseous phase. M. S. BURR.

Phase boundaries in the systems silica and alumina with carbon. E. BAUR (Z. Elektrochem., 1932, 38, 69—70).—Phase diagrams have been constructed from the data in the preceding abstract. M. S. BURR.

System $\text{Na}_2\text{O--B}_2\text{O}_3\text{--H}_2\text{O}$. Isotherms at 35°, 20°, and 0° and polythermal diagram. U. SBOGGI (Gazzetta, 1932, 62, 3—14; cf. A., 1930, 1122).—The limits of existence between 90° and the cryohydric temp. of the ternary compounds, 1:5:10, 1:2:10, 1:2:5, 1:1:8, 1:1:4, 1:1:1, 2:1:1 (the figures representing the no. of mols. of Na_2O , B_2O_3 , and H_2O) and of H_3BO_3 and NaOH have been derived. O. J. WALKER.

[System sodium sulphate-aluminium sulphate-water.] J. T. DOBBINS and R. M. BYRD (J. Physical Chem., 1931, 35, 3673—3676).—Application of the residue method shows the existence at 25° of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. The efflorescent double salt may be obtained by evaporation at 25° of solutions between 5% Na_2SO_4 , 26% $\text{Al}_2(\text{SO}_4)_3$, and 19% Na_2SO_4 , 8% $\text{Al}_2(\text{SO}_4)_3$. G. M. MURPHY (c).

Ternary systems. XI. Magnesium iodate-sodium iodate-water. XII. Sodium iodate-potassium iodate-water. XIII. Potassium iodate-potassium chloride-water. XIV. Potassium iodate-potassium sulphate-water. A. E. HILL and J. E. RICCI (J. Amer. Chem. Soc., 1931, 53, 4305—4315; cf. A., 1931, 568).—The systems were investigated at 5°, 25°, and 50°, but no double salts were found. A method of algebraic extrapolation of tie-lines suitable for testing the composition of the solid phases and the precision of the solubility determinations is described. The existence of colloidal constituents in NaIO_3 and KIO_3 solutions may explain the length of time necessary to reach equilibrium in these systems. G. M. MURPHY (c).

Ternary systems. XV. Potassium iodate-potassium nitrate-water. XVI. Calcium iodate-sodium iodate-water. A. E. HILL and S. F. BROWN (J. Amer. Chem. Soc., 1931, 53, 4316—4320; cf. preceding abstract).—The system $\text{KIO}_3\text{--NaNO}_3\text{--H}_2\text{O}$ was investigated at 5°, 25°, and 50.4°, but no compound formation was observed. The solubility

of $\text{Ca}(\text{IO}_3)_2$ was determined at 5—90°, and a transition from $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ to $\text{Ca}(\text{IO}_3)_2$ found at 57.5°. The system $\text{Ca}(\text{IO}_3)_2\text{--NaIO}_3\text{--H}_2\text{O}$ was investigated at 25°.

G. M. MURPHY (c).

Ternary system potassium permanganate-potassium fluoborate-water. R. C. RAY and K. K. CHATTERJI (J.C.S., 1932, 384—386).—The composition of the liquid and solid phases at 25° has been determined. Within certain limits orthorhombic bipyramidal crystals of a double salt, $\text{KBF}_4 \cdot 6\text{KMnO}_4$, are formed. F. L. USHER.

System calcium oxide-sucrose-water. W. REINDERS and D. W. VAN GELDER (Rec. trav. chim., 1932, 51, 253—259).—Above concns. of 30, 35, and 40% sucrose, respectively, the stable solid phase at 12°, 25°, and 45° is no longer $\text{Ca}(\text{OH})_2$, but a saccharate of unknown composition. By dissolving finely-divided CaO in dil. sucrose solution a supersaturated solution is formed which deposits at first a metastable disaccharate at lower temp. or trisaccharate at higher temp. The proportion of Ca in this gradually increases, however, until only $\text{Ca}(\text{OH})_2$ is left as the stable phase. M. S. BURR.

Heat of dissociation of oxygen. A. K. DUTTA (Nature, 1932, 129, 317).— SO_3 vapour shows continuous absorption with a long wave-length limit at 3300 Å. corresponding with 86.7 kg.-cal. Assuming that the reaction due to light is $\text{SO}_3 + 86.7 = \text{SO}_2 + \text{O}$ (atomic) the calc. heat of dissociation of O_2 is 128 kg.-cal. L. S. THEOBALD.

Thermochemistry of thallium. W. A. ROTH and A. MEICHNER (Z. Elektrochem., 1932, 38, 87—93).—The heat of formation of Tl_2O , determined by dissolving Tl and Tl_2O in H_2SO_4 under the same conditions, is 43.2 kg.-cal. at 20° and const. pressure. The heat of dissolution of the metal is derived from e.m.f. as well as thermochemical data. Measurements of the heat of dissolution of Tl_2O and TlOH in H_2O give 3.3 kg.-cal. as the heat of hydration of Tl_2O . Other data obtained are: $[\text{Tl}] + \frac{1}{2}(\text{O}_2) + \frac{1}{2}(\text{H}_2) = [\text{TlOH}] + 57.4$ kg.-cal.; $[\text{Tl}] + \frac{1}{2}(\text{Cl}_2) = [\text{TlCl}] + 50.3$ kg.-cal.; $2[\text{TlOH}] + \text{H}_2\text{SO}_4$ (pure) $= [\text{Tl}_2\text{SO}_4] + 2\text{H}_2\text{O} + 50.8$ kg.-cal.; $[\text{Tl}_2\text{O}] + \text{SO}_3 = [\text{Tl}_2\text{SO}_4] + 75.4$ kg.-cal.; $2[\text{Tl}] + [\text{S}]_{\text{rhomb.}} + 2(\text{O}_2) = [\text{Tl}_2\text{SO}_4] + 223.2$ kg.-cal.; $[\text{TlOH}] + (\text{HCl}) = [\text{TlCl}] + \text{H}_2\text{O} + 38.2$ kg.-cal. The solubility of TlCl in H_2O and aq. HCl of different concn. has been measured at 20°. Heats of dissolution in mixed solvents, chiefly dil. H_2SO_4 , have been determined for different concns. of Tl_2O , TlOH , TlCl , Tl_2SO_4 , $\text{ZnSO}_4 \cdot 1.08\text{H}_2\text{O}$, Zn, and Tl. M. S. BURR.

Affinity and heat effect of hydrogenation of double linkings between carbon atoms. W. HILTNER (Z. physikal. Chem., 1932, 158, 398—410).—Oxidation-reduction potential measurements yield vals. for the affinity of the hydrogenation of liquid esters of cinnamic and crotonic acids which are inconsistent among themselves and with vals. deduced from heat effect data. This discrepancy is probably connected with the catalytic activity of the electrodes and the formation of absorbed films. R. CUTHILL.

Heats of combustion of methyl and ethyl alcohols. F. D. ROSSINI (Bur. Stand. J. Res., 1932,

8, 119—139).—The alcohol vapours were burned in a stream of purified air in a reaction vessel in the calorimeter. The heat of combustion, in international kilojoules per g.-mol., is 763.68 ± 0.20 for MeOH vapour at 25° and 1407.50 ± 0.40 for EtOH vapour at 32.50° . Combining these data with the heats of vaporisation the following vals. are obtained for the heat of combustion in the liquid state at 25° : MeOH 173.61 ± 0.05 , EtOH 326.61 ± 0.10 kg.-cal. (15°) per g.-mol. A rapid and accurate determination of the ratio C/H in a volatile org. liquid can be made by saturating a stream of inert gas with the vapour of the liquid and passing the mixture over hot CuO.

E. S. HEDGES.

Application of calorimetry to pyrroles. P. ROTHMUND and H. BEYER.—See this vol., 280.

Calorimetry. II. Influence of amorphous silicic acid on the heats of combustion of fatty oils. III. Heat of combustion of rubber. H. ENDOH (J. Soc. Chem. Ind. Japan, 1932, 35, 3—4B, 4—7B; cf. *ibid.*, 1928, 31, 186B).—II. Addition of pptd. silicic acid lowers the observed heats of combustion of BzOH and olive oil, and raises those of bean oil and whale oil.

III. The heats of combustion of Para rubber, smoked sheet, and pale crepe are 10,761.0, 10,680.4, and 10,681.6 g.-cal., respectively. Mechanical treatment thus appears to reduce the heat of combustion. The results of previous workers are criticised.

N. H. HARTSHORNE.

High-frequency conductivity of electrolytes by a calorimetric method. A. DEUBNER (Physikal. Z., 1932, 33, 223—227).—Two calorimetric methods are described for comparing the high-frequency conductivities of electrolytes which conduct equally at low frequencies. The accuracy of the methods is high.

A. J. MEE.

Dissociation constants of organic acids. V. Mobility of the hydrogen ion at 18° and at 25° . G. H. JEFFERY and A. I. VOGEL (J.C.S., 1932, 400—415; cf. A., 1931, 1012).—Conductivities of HIO_3 , HCl, and PhSO_3H have been measured in cells of SiO_2 at 25° and at concns. between 10^{-2} and $10^{-4}N$. Equations representing the relation between Λ and concn. are given. The mean val. for the mobility of the H ion at 25° is 349.0 or 348.0 ± 0.7 , the alternative depending on the choice of the cation transport no. for KCl. From measurements on HIO_3 at 18° the mobility is calc. to be 314.1 or 313.4 at 18° . The plot of Λ against $\sqrt{\text{concn.}}$ is parabolic in the case of all three acids, the curvature being very slight only for PhSO_3H .

F. L. USHER.

Conductivity of solutions of aniline hydrohalides in aniline. M. HEASKO and E. MICHALSKI (Rocz. Chem., 1932, 12, 35—47).—The mol. conductivity of HF, HCl, HBr, and HI dissolved in NH_2Ph has been measured at 25° . The conductivity and the degree of dissociation increase with the at. wt. of the halogen present. has a min. val. in all cases for $0.02N$ solutions; for $\text{NH}_2\text{Ph.HI}$ the λ_c -concn. curve shows a max. at $0.6N$. The val. of the concn. giving min. is given by Walden's formula: $C_{\min.} = (\epsilon/K)^3$. The above solutions con-

tain only undissociated mols. at concns. below $0.02N$; association occurs at higher concn.

R. TRUSZKOWSKI.

Transference number of lithium chloride as a function of the concentration. G. JONES and B. C. BRADSHAW (J. Amer. Chem. Soc., 1932, 54, 138—150).—Transference nos. for LiCl measured at 25° by the Hittorf method over the range 0.023 — $2.95N$ agree with the equation $t = [1.3337/(1 + 0.03605\sqrt{c})] - 1$. These results do not agree with previous vals. obtained by the e.m.f. method (A., 1920, ii, 466), but if the latter data are interpreted by the method of Jones and Dole (A., 1929, 767) the discrepancy is less.

M. DOLE (c).

Limiting law for transference numbers. M. DOLE (J. Physical Chem., 1931, 35, 3647—3648).—The expression for the change of transference no. with change of ionic concn. derived by means of the Debye-Huckel conductivity equation is similar to empirical equations previously published (A., 1925, ii, 398; 1929, 767).

M. DOLE (c).

Potential of lead electrode. W. R. CARMODY (J. Amer. Chem. Soc., 1932, 54, 210).—The electrolyte may be passed over a Pb amalgam electrode without affecting its potential, but the potential of a AgCl electrode may be changed by 6 mv. by passing a solution over it. If the results of Randall and Cann (A., 1930, 422) are corrected accordingly, the val. 0.1263 volt is obtained for the potential of the Pb electrode.

M. DOLE (c).

Standard electrode potential of iron, and activity coefficient of ferrous chloride. M. RANDALL and M. FRANDSEN (J. Amer. Chem. Soc., 1932, 54, 47—54; cf. A., 1926, 803).—From e.m.f. measurements with the cell $\text{Fe}|0.1M\text{-FeCl}_2, \text{HgCl}_2|\text{Hg}$, the single electrode potential of Fe at 25° has been found to be 0.4402 volt, and the free energy of formation of the Fe^{++} ion $-20,310$ g.-cal. Activity coeffs. of FeCl_2 have been calc. from existing data.

L. P. HALL (c).

Measurement of electromotive force in dilute aqueous solutions. II. Silver chloride electrode. W. R. CARMODY (J. Amer. Chem. Soc., 1932, 54, 188—192; cf. A., 1929, 1391).—The e.m.f. of the cell $\text{Pt}, \text{H}_2(g)|\text{HCl}, \text{AgCl}(s)|\text{Ag}(s)$ was measured at concns. below $0.01M$ at 25° . The standard electrode potential for AgCl obtained by extrapolation is -0.2223 volt, the val. calc. from f.-p. measurements being -0.2221 volt.

M. DOLE (c).

Measurement of glass electrode potentials by a valve electrometer. G. D. GREVILLE and N. F. MACLAGAN (J.C.S., 1932, 720—721; cf. A., 1931, 801).—A reply to a criticism by Morton (this vol., 24).

F. L. USHER.

Glass electrode studies: cupric hydroxy-acid complexes. C. MORTON (Trans. Faraday Soc., 1932, 28, 84—88).—Erroneous results are obtained with the H_2 electrode (A., 1930, 49). Electrometric titration, with the glass electrode, of CuSO_4 in excess of Na tartrate, citrate, malate, and salicylate affords two inflexions in the neutralisation curves; the first corresponds with the formation of the basic complexes $\text{Cu}_8(\text{OH})_{10}(\text{C}_4\text{H}_4\text{O}_6)_3$, $\text{Cu}(\text{OH})_2\text{C}_6\text{H}_5\text{O}_7$,

$\text{Cu}_2(\text{OH})_2\text{C}_4\text{H}_4\text{O}_6$, and $\text{Cu}(\text{OH})(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)$, respectively, and the second inflexion with complete alkaline decomp. into highly-basic hydrosols, of which only the salicylate is decomposed by boiling. $[\text{Cu}^{++}]$, determined by means of the Cu electrode, decreases at first slowly and then rapidly as the neutral point is approached and the point of inflexion coincides with the first inflexion in the corresponding p_{H} curve. Whereas in acid solutions all the Cu can be removed by dialysis, none can be removed from slightly alkaline solutions.

The neutralisation curves of CuSO_4 in excess of Na glycerate, lactate, glycolate, and mandelate have only one inflexion, and a blue basic ppt. appears during each titration. It is probable that no stable complexes are formed, and that the inflexion corresponds with the formation of basic sulphate. To the peptising properties of these OH-acid anions is attributed the absence of pptn. in alkaline solution in the presence of large excess of the Na salt.

J. G. A. GRIFFITHS.

Elimination of liquid contact potentials with potassium chloride and ammonium chloride. G. M. KLINE, M. R. MEACHAM, and S. F. ACREE (Bur. Stand. J. Res., 1932, 8, 101—110).—The results obtained with 4.1*N*-KCl as eliminator are within the accuracy of routine experimental errors and its general use is recommended for annulling contact potentials between (a) HCl and especially org. salts and buffers on the one hand and (b) KCl or Na H phthalate solutions used in standard electrodes. An approx. isoelectric eliminator, such as 3*N*-KCl+*N*-KNO₃ should be used for solutions with p_{H} vals. between 3 and 10.

E. S. HEDGES.

Potentiometric investigation of electrolytic dissociation. I. Cadmium halides. H. L. RILEY and V. GALLAFENT (J.C.S., 1932, 514—523).—The concn. of Cd^{++} ions in solutions of CdX_2 ($\text{X}=\text{Cl}$, Br, or I) has been determined by potentiometric titration using a suitable concn. cell, and the concn. of the several mol. and ionic species present has been calc. by means of a mass-action relationship. The significance of the results is discussed.

F. L. USHER.

Five new oxidation-reduction indicators. M. LERORT (Compt. rend., 1932, 194, 711—714).— E - p_{H} curves, where E is the normal oxidation-reduction potential for the p_{H} considered, are given for Nile-blue 2B (p_{H} 3.85—7.80), new-methylene-blue (3.85—8.50), Capri-blue (3.85—8.50), solid-cotton-blue (2.95—8.10), and muscarine DH (3.85—7.80), using 0.1*M* buffer solutions, TiCl_3 and $\text{Na}_2\text{S}_2\text{O}_4$ as reducers, and a H_2 electrode. The curves of the three indicators last named lie between those of the indophenols and cresyl-blue.

C. A. SILBERRAD.

Electrostatic potentials at the phase boundary electrolyte-unattackable electrode, and the physical chemistry of the flotation process. B. KAMIENSKI (Z. physikal. Chem., 1932, 158, 441—444).—The potential of a Pt, galena, or graphite electrode in contact with aq. KCl becomes more negative on addition to the liquid phase of an emulsion of K xanthate and terpeneol. This suggests that in the flotation process the adhesion of the sulphide

particles to the oil is due to static phase-boundary potentials.

R. CUTHILL.

Sour taste of acids. F. B. KENRICK (Trans. Roy. Soc. Canada, 1931, [iv], 25, III, 227—228).—The proportions of buffer solution required to bring the p_{H} of the various acids to 5 are approx. proportional to their sourness. The sourness can therefore be determined by titration with phosphate buffer to p_{H} 5. Threshold concns. for sour taste may be lowered by adding to the acids astringent or bitter substances.

A. J. MEE.

Electrolytic overvoltage and its dependence on the degree of curvature of the cathode. P. SEDERHOLM and C. BENEDICKS (Z. Elektrochem., 1932, 38, 77—86).—The overvoltage of H_2 at polished electrodes of sharply defined curvature has been determined. Globules of Hg, Pt, pure Ag, and an alloy of Ag were employed. The overvoltage is given by $\epsilon = k \log(a + b/r)$, where k is a const., a and b are consts. for a given metal, and r is the radius of curvature of the electrode, or $\epsilon = k \log a + k \log(1 + b/r)$, where $k \log a$ is the overvoltage at a plano surface and b/r is a const.

M. S. BURR.

Optical investigation of passivity of metals. I. Iron and steel. L. TRONSTAD (Z. physikal. Chem., 1932, 158, 369—397).—A detailed account of experiments of which the principal results have already been reported (A., 1931, 301).

R. CUTHILL.

Theory of passivity. XIV. Passivity of nickel. W. J. MULLER, H. K. CAMERON, and W. MACHU (Monatsh., 1932, 59, 73—92).—The natural oxide film on Ni is less easily attacked by H_2SO_4 than the corresponding film on Fe (A., 1931, 1238), so that the time of passivation is very short, and even in 15*N*- H_2SO_4 a freshly-polished or cut Ni electrode has a current-time curve of the $1/t^2$ character (*loc. cit.*). At voltages below 1.5 volts coating passivity is due to a salt of Ni^{++} . In *N*-acid the salt is not doubly-refracting and is obviously basic. When the concn. of acid is above 5*N* a strongly doubly-refracting layer appears, viz., $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. Above 2 volts chemical passivation sets in due to a porous superoxide coating. This layer is very stable and is unaffected by contact with Zn, but the passivation time can be increased by brushing in a concn. of H_2SO_4 above 7*N*. Cathodic charging activates Ni. In all circumstances Ni becomes momentarily passive in Na_2SO_4 . Cathodic charging with H_2 , however, results in a finite time of passivation. The resistance to corrosion of Ni as compared with Fe is due to the greater stability of the natural oxide layer.

M. S. BURR.

Velocity coefficient of interchange reactions. H. PELZER and E. WIGNER (Z. physikal. Chem., 1932, B, 15, 445—471).—Application of the methods of wave-mechanics shows that the essential condition which must be fulfilled for double decomp. such as $\text{H} + \text{Cl}_2 \rightleftharpoons \text{HCl} + \text{Cl}$ to take place adiabatically as postulated by London (A., 1930, 1097) is that the lowest energy surface shall, in point of energy, be far removed from the others. By means of the theory an equation giving the abs. velocity coeff. of the trans-

formation of para-H into normal H (cf. A., 1931, 688) has been derived. R. CUTHILL.

Role of surface adsorption in chain reactions. C. N. HINSHELWOOD (Trans. Faraday Soc., 1932, 28, 184—191).—The criteria for deciding whether reaction chains in a steady reaction originate and terminate in the gas phase or at the surface are examined. Various explanations (cf. recent papers) offered for the existence of "explosion limits" are discussed.

J. G. A. GRIFFITHS.

Oxidation of fuel vapours in air. E. W. J. MARDLES (Trans. Faraday Soc., 1932, 28, 69—79).—A discussion by others of the author's work (A., 1931, 1372).

J. G. A. GRIFFITHS.

Oxidation of pentane and other hydrocarbons. I, II. L. M. PIDGEON and A. C. EGERTON (J.C.S., 1932, 661—676, 676—686).—I. The temp. at which reaction proceeds rapidly in C_5H_{12} - O_2 mixtures rises as the pressure falls and is lowest for a 50% mixture. The temp. is also lower in SiO_2 than in glass and is raised with increase of surface, but lowered by addition of N_2 . Reaction velocity is affected more by change of C_5H_{12} concn. than of O_2 concn. The effect of temp. and pressure on reaction velocity has also been studied. The results indicate the existence of reaction chains. There is an induction period during which active centres accumulate. The chains are initiated in the gas and broken at the walls. The effect of temp., pressure, surface, and diluents on the period of induction is rather irregular.

II. In the slow combustion of C_6H_{14} the temp. at which oxidation becomes rapid and the influence of total pressure and concn. on the reaction have been investigated. The decrease in pressure observed in the case of C_6H_{14} is mainly due to formation of a condensable product, but in the case of anylene to the direct absorption of O_2 . The influence of these compounds on the oxidation of C_5H_{12} has been observed. C_6H_{14} , which has a lower reaction temp. than C_5H_{12} , initiates reaction at a lower temp. in the latter than occurs with C_5H_{12} - O_2 mixtures alone. This is probably due to the active centres formed by the C_6H_{14} and is additional evidence for the chain reaction theory. Valeraldehyde has a still more marked effect, but anylene and H_2O are inactive, which may be regarded as evidence against the theory of dehydrogenation of the reacting mol. and the theory of hydroxylation, respectively. $PbEt_4$ acts as an inhibitor, but the Pb has to be oxidised before it can become effective. M. S. BURR.

Rate of rise of pressure in the combustion of some gas-oxygen mixtures. C. CAMPBELL, W. B. LITTLE, and C. WHITWORTH (J.C.S., 1932, 339—348).—The rates of rise of pressure, as determined by a diaphragm pressure-recording apparatus, when mixtures of O_2 with H_2 , C_2H_4 , CH_4 , or CO are ignited in a steel explosion cylinder, are slower when there is an excess of either O_2 or combustible gas than when the proportions theoretically necessary for complete combustion are employed. In the latter case, except for $2CO + O_2$, the rate of rise is so rapid that measurement becomes impossible. The explosion wave in CH_4 - O_2 mixtures travels most rapidly in the 50% mixture, corresponding with the reaction $CH_4 + O_2 \rightarrow$

$CO + H_2 + H_2O$. In the 33% mixture the second O_2 is probably acting as a diluent. The rate of rise of pressure in moist CO - O_2 mixtures is increased by the addition of small amounts of other combustible gases. The effect for equal additions increases in the order H_2 , C_2H_2 , C_2H_4 , CH_4 , and C_5H_{12} . The limiting composition of gas mixtures for detonation, as determined by different observers, is in close agreement with the composition of the mixture reaching its max. pressure 0.04 sec. after the first sign of pressure rise, in the apparatus used. M. S. BURR.

Theory of gaseous explosions and oxidation of hydrogen sulphide. H. W. THOMPSON (J. Physical Chem., 1931, 35, 3639—3643).—The equation used by Taylor (A., 1931, 1240) is corrected to $\log P/T = A/T + B$, in accordance with Semenov's theory, and from this the heat of activation is calc. It is agreed that the oxidation of H_2S is a chain reaction.

J. E. AUSTIN (c).

Dissociation of ozone and mechanism of its thermal decomposition. O. R. WULF (J. Amer. Chem. Soc., 1932, 54, 156—160; cf. A., 1927, 631, 834, 943).—The mechanism of the thermal decomp. of O_3 is represented by $O_3 \rightarrow O_2 + O$, $O_3 + O \rightarrow 2O_2$. The entropy of gaseous O_3 calc. from other entropies is $S_{298} = 52.6$. Using this val., the equilibrium const. for the first step of the mechanism has very nearly the requisite val., i.e., the no. of collisions between O and O_3 corresponds approx. with the observed second-order rate. Since there are more than 10^4 more collisions than reactions between O_3 and O , the O_3 mol. probably requires activation before it will react with O atoms. For low rates and high total pressures, the reaction of O atoms with O_3 moles. is probably the principal cause of the thermal decomp. of O_3 .

L. KELLEY (c).

Kinetics of the bromine-oxalate reaction. R. O. GRIFFITH, A. MCKEOWN, and A. G. WINN (Trans. Faraday Soc., 1932, 28, 107—126; cf. A., 1928, 715).—The kinetics of the reaction at 21.5°, 16.5°, and 11.5° between $M/600$ — $M/300$ -Br and $H_2C_2O_4$, neutral and acid oxalates, and mixtures of the latter, in the presence of 0—0.5*N*-bromides and HBr (total ionic strength, μ , is between 0.0 and 0.8) are in accord with the reactions (I) $H_2C_2O_4 \rightarrow H^+ + HC_2O_4^-$, (II) $Br_2 + H_2O \rightarrow H^+ + Br^- + HOBr$, and (III) $HC_2O_4^- + HOBr \rightarrow H_2O + 2CO_2 + Br^-$ of which (III) determines the over-all rate. The second ionisation const. (k_2) of $H_2C_2O_4$ is computed to be 7×10^{-5} at $\mu = 0$ and 21.5°, k_2 increases with ionic strength, NaBr having a slightly greater effect than KBr. The hydrolytic const. of Br_2 increases markedly with μ and for reaction (III) the bimol. velocity coeff. is 2×10^4 approx. (units: litres, g.-mol., min.) and the crit. increment 15,400 g.-cal. The abnormally high temp. coeff., 6 approx., of the net reaction is attributed to the combined effects of temp. on equilibrium (II) and reaction (III).

J. G. A. GRIFFITHS.

Velocities and heats of saponification of amides. E. CALVET (Compt. rend., 1932, 194, 610—612).—The heats, Q , and velocities of saponification at 17°, k_{17} , and 0°, k_0 , and the temp. coeff., c , per 10° between 0° and 17°, of mono-, di-, and tri-chloroacetamide are

respectively 23.2, 7.5, 1.952, 9000; 335, 136, 1.698, 10,100; 1110, 464, 1.67, 10,700. k_{17} and c are connected with Q by the relations $\log k_{17} = 0.001005(Q - 7600)$, and $\log c = 0.0000476(15,200 - Q)$, which also hold for the normal fatty amides with 2-4 C atoms (cf. A., 1929, 1389; 1931, 916). There is no appreciable hydrolysis of a chloroacetamide in aq. solution, nor in aq. NaOH of the Cl as compared with that of NH_2 .

C. A. SILBERRAD.

Velocity of decomposition of diazo-compounds in water. VII. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 11-13B; cf. A., 1930, 1529).—The decomp. velocities of *m*- and *p*- $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ and 2-nitro-*p*-toluenediazonium chloride in H_2O have been measured at different temp. The decomp. is unimol.

N. H. HARTSHORNE.

Rates of formation of the active reductants of several sugars. M. H. ROEPKE and J. M. ORT (J. Physical Chem., 1931, 35, 3596-3611).—The rate of formation of the active reducing agents in slightly alkaline aq. solutions of glucose, mannose, galactose, fructose, maltose, and lactose has been determined by adding an excess of $\text{K}_3\text{Fe}(\text{CN})_6$ and measuring its rate of reduction. At const. temp. and const. p_{H} the rate of reduction is const. The influence of p_{H} is represented by $\log V = 1.116p_{\text{H}} + C$, where C is a const., except for galactose, in which case $\log V = 0.86p_{\text{H}} + C$. Comparison of these results with the dissociation consts. of the sugars suggests that the active reducing agent is derived from the sugar ion; the influence of other electrolytes supports this view. A secondary effect of p_{H} , influencing galactose in one direction and the remaining sugars in the other direction, suggests that increasing p_{H} causes a shift in the equilibrium from the 1:5- to the less stable 1:4-oxide ring structure in the glucose series and in the reverse direction in galactose. The rate of formation of the active reducing agent from glucose is increased 100-fold by a rise in temp. of 22.5°, and increases linearly with concn. over the range 1-60%. The concn. relation may be due to an increase in the dissociation const. of glucose with increasing concn. The rate of formation is not influenced by the presence of $\text{Fe}(\text{OH})_2$. The rates measured are believed to be the rates of formation of the 1:2-enediol forms for the aldoses studied and both the 1:2- and 2:3-enediols in the case of fructose.

E. S. HEDGES.

Steric hindrance in the hydrolysis of benzylidene chloride. G. LOCK and F. ASINGER (Monatsh., 1932, 59, 152-160).—By the substitution of a Cl atom in the *o*-position in CHPhCl_2 the velocity of hydrolysis of the side-chain is considerably reduced, and by substitution in both *o*-positions it is practically inhibited. The hydrolysing agents used were a mixture of equal proportions of COMe_2 and dil. aq. K_2CO_3 , concn. H_2SO_4 , and anhyd. $\text{H}_2\text{C}_2\text{O}_4$.

M. S. BURR.

Kinetics of reaction between potassium persulphate and sodium thiophenoxide. T. B. DOUGLAS (J. Physical Chem., 1931, 35, 3280-3285).—This stoichiometrically termol. reaction is kinetically bimol. The velocity coeff. of the simple velocity equation varies with the OH^- concn. and the concn. of

reactants, an anomaly which is ascribed to increased activation caused by complex ion formation.

R. H. CHERRY (c).

Theory of the rate of dissolution of gas into liquid. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1932, 7, 8-17).—The rate of dissolution of O_2 in H_2O , and oxidation velocities in solution, are better explained by the author's theory (A., 1931, 437) than by the theory of diffusion from a saturated surface layer.

C. W. DAVIES.

Kinetics of dissolution of readily soluble salts in water. K. JABECZYNSKI and J. GUTMAN (Rocz. Chem., 1932, 12, 9-22).—Spectrophotometric measurements of solutions in which crystals of coloured salts are being rotated indicate that the velocity of dissolution, K , is proportional to that of diffusion from the solid to the liquid phase. The temp. coeff. of the reaction is 1.44 for $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, 1.52 for $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$, and 1.35 for $\text{K}_2\text{Cr}_2\text{O}_7$. The absorption of red light by aq. CuSO_4 is increased by addition of EtOH. The val. of K of salts in aq. EtOH is smaller than that in H_2O alone, owing to reduction in velocity of diffusion, and varies directly with the solubility of a given salt.

R. TRUSZKOWSKI.

Kinetics of dissolution of substances in non-aqueous media. K. JABECZYNSKI and A. WALCZAK (Rocz. Chem., 1932, 12, 23-34).—Measurements of K of rotated cylinders of picric acid or azobenzene in EtOH, aq. EtOH, and EtOH- CCl_4 mixtures indicate that the process of dissolution proceeds according to the same laws as for solutes in H_2O (cf. preceding abstract). K varies directly with the CCl_4 content of the solvent (EtOH), and inversely with the H_2O content. The temp. coeff. of reaction is 1.08 for azobenzene, and 1.50 for picric acid in EtOH.

R. TRUSZKOWSKI.

Thermal decomposition of nitrous oxide and its catalysis by nitric oxide. F. F. MUSGRAVE and C. N. HINSHELWOOD (Proc. Roy. Soc., 1932, A, 135, 23-39).—The unimol. reaction, relatively important in the low-pressure decomp. of N_2O , is homogeneous. Its velocity coeff. falls at low pressures, the change belonging to the quasi-unimol. class. The abs. rate has the order of magnitude expected for activation in two square terms. It is suggested that the high- and low-pressure parts of the reaction necessitate the changes $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$ and $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$, respectively. The formation of NO during the decomp. of N_2O has been investigated; it may be produced by the action of at. O on N_2O . NO exerts a catalytic action on the decomp. of N_2O , the rate being proportional to $[\text{NO}][\text{N}_2\text{O}]$.

L. L. BIRCHINSHAW.

Sulphurous acid and its salts. X. Decomposition of sulphurous acid catalysed by iodide ions. F. FOERSTER and E. GRÜNER (Z. anorg. Chem., 1932, 203, 245-270; cf. A., 1923, ii, 853).—The rate of decomp. of aq. H_2SO_3 in presence of I^- has been studied at room temp., 100°, 125°, and 150°, with and without the addition of other substances. According to the relative amounts of positive and negative catalysts present, the velocity curves may be linear, concave to the time axis, or S-shaped. The net change, $3\text{H}_2\text{SO}_3 \rightarrow 2\text{H}_2\text{SO}_4 + \text{S} + \text{H}_2\text{O}$, is retarded by H^+ , and accelerated by $\text{S}_2\text{O}_3^{2-}$, S, or I^- . I^- forms

complex ions with SO_2 , notably $[\text{I}(\text{SO}_2)_4]'$, whereby the retarding influence of H^+ is mitigated. It also promotes the formation of $\text{S}_2\text{O}_6^{2-}$, which is considered to be the intermediate product responsible for the autocatalysis.

F. L. USHER.

Kinetics of a catalysed isomeric change in solution. R. C. TRAILL (Phil. Mag., 1932, [vii], 13, 225—233).—Data for the velocity of mutarotation of Be benzoylcampor in CCl_4 , and also in CHCl_3 , catalysed by pyridine, EtOH, and *p*-cresol are analysed by the law of mass action, and give velocity coeffs. in agreement with those of Lewis' equation for a bimol. gaseous reaction.

N. M. BLIGH.

Catalytic decomposition of hydrogen peroxide by cadmium iodide. R. U. GOODING and J. H. WALTON (J. Physical Chem., 1931, 35, 3612—3617).— Cd^{2+} has no appreciable catalytic effect, the active agents being I^+ , CdI^+ , and CdI_2 . I^+ decomposes H_2O_2 more than twice as fast as CdI_2 , the rate of decomp. being in each case proportional to the concn. of the active ion. The kinetic data thus confirm the ionic complexity of aq. CdI_2 (cf. A., 1905, ii, 371). Addition of I^- causes a considerable diminution in the velocity coeff. if the concn. of CdI_2 is low, but in conc. solutions has very little effect.

F. L. BROWNE (c).

Change of acidity produced by salts in sulphurous acid solutions at high temperature. E. HAGGLUND (Biochem. Z., 1932, 244, 278—283; cf. Kullgren, B., 1930, 984).—The rate of hydrolysis of starch by H_2SO_4 at 110° and 120° is greatly affected by the presence of salts, being lowered by NaHSO_3 or NaSO_3 and increased by NaCl or NaNO_3 . There is a direct relation between the rate and the $[\text{H}^+]$ of the solutions which depends on the nature and amount of salt present. The inversion of sucrose by H_2SO_4 is similarly affected by Na_2SO_4 and it is suggested that the influence of Na_2SO_4 in the sulphite pulp process is analogous.

W. MCCARTNEY.

Heavy metal catalysts. I. Fission of starch by artificial peroxidase. T. OMORI (J. Biochem. Japan, 1931, 14, 331—337).— H_2O_2 in presence of 0.01—0.002*M* Mn, Co, Ni, and especially V, Cu, and Fe salts exhibits an amylolytic activity which is accelerated by the presence of tyrosine, pyrocatechol, quinol, or *p*-cresol. The mechanism of such a fission, however, is not identical with that of diastatic action.

F. O. HOWITT.

Effect of change of medium on velocity of hydrolysis of ethyl orthoformate. H. S. HARNED and N. N. T. SAMARAS (J. Amer. Chem. Soc., 1932, 54, 1—8).—The hydrolysis at const. p_H has been investigated, and the catalytic coeff. of the hydronium ion determined. The velocity coeff., k , in aq. solutions of MeOH, EtOH, Pr^nOH , Pr^iOH , Bu^nOH , COMe_2 , and glycerol is given by $\log_e k_0 - \log_e k = 0.07(D_1 - D)$, where k_0 is the velocity coeff. when the org. solvent is absent, and $(D_1 - D)$ the lowering of the dielectric const. caused by the org. solvent. In an aq. solution of glycine both k and D increase with the glycine concn., but not in a linear manner.

S. LENHER (c).

Medium changes in homogeneous catalysis and an approach to their theoretical interpretation. H. S. HARNED and N. N. T. SAMARAS (J.

Amer. Chem. Soc., 1932, 54, 9—23).—In order to take account of the effect of the solvent medium in homogeneous catalysis the replacement of the kinetic factor, F , in the velocity equation $v = k_c c_B \dots F$ by $e^{-W/RT}$ is suggested, and approx. equations for W , which is related to the change in dielectric const. produced by a neutral substance, have been derived. For the hydrolysis of Et orthoformate (cf. preceding abstract) the theory leads to a relation between the change in dielectric const. and the change in velocity coeff. which agrees satisfactorily with the experimental data. The primary medium effect in the reaction of MeI with $\text{Na}_2\text{S}_2\text{O}_3$ and the transformations of substituted aminobenzenes also agrees with the theory.

S. LENHER (c).

Inversion of sucrose. E. TOPORESCU (Compt. rend., 1932, 194, 724—726).—Since the inversion of sucrose by 0.25*N*-HCl in aq. solution at 25° is almost inhibited by addition of $\text{CO}(\text{NH}_2)_2$ (75 to 10 g. sucrose in 100 c.c.) it is suggested that the inversion is effected not by H^+ ions but by depolymerised H_2O mols., the function of the acid being depolymerisation.

J. W. BAKER.

Mechanism of racemisation. A. N. CAMPBELL and A. J. R. CAMPBELL (Nature, 1932, 129, 281).—The sp. rotation of Na NH_4 tartrate decreases with an increase in concn. of added NaOH and eventually becomes strongly negative. The change in sign occurs with approx. 10*N*-NaOH. This is taken to show that racemisation by NaOH is accompanied, and probably conditioned, by complex formation. The usual view of racemisation is discussed in relation to these results, and the stereochemical conception of optical activity as a static phenomenon is considered to be not entirely satisfactory.

L. S. THEOBALD.

Induced oxidation of glucose in presence of insulin acting as an inductor. H. L. DUBE and N. R. DHAR (J. Physical Chem., 1932, 36, 444—448).—If air is passed at 25° through a solution of glucose containing insulin, the former is appreciably oxidised, and the oxidation is markedly accelerated by phosphates, $\text{Ce}(\text{OH})_3$, and $\text{Fe}(\text{OH})_2$. The insulin also is oxidised, but more slowly than when glucose is absent, so that the oxidation of the insulin must be assumed to induce the oxidation of the glucose, which is the probable explanation of the increased oxidation of glucose in the presence of insulin in the animal body. In presence of Na_2CO_3 , which apparently inactivates insulin, there is no induced oxidation.

F. SAUNDERS (c).

Catalytically active surfaces. I. H. J. PRINS (Chem. Weekblad, 1932, 29, 66—72).—A discussion of the conditions assumed to obtain at active surfaces.

S. I. LEVY.

Catalytically active surfaces. II. H. J. PRINS (Chem. Weekblad, 1932, 29, 89—92).—A review.

H. F. GILLBE.

Conversion of para-hydrogen into ortho-hydrogen over iron synthetic ammonia catalysts. P. H. EMMETT and R. W. HARKNESS (J. Amer. Chem. Soc., 1932, 54, 403—404).—On passing a stream of para- and ortho- H_2 in the ratio 49:51 over an NH_3 catalyst at -20° to 40° a considerable amount of the para form is converted into the ortho form, the

approach to the equilibrium being the closer the higher is the temp. C. J. WEST (c).

Mechanism of the reaction $H_2 + I_2 \rightarrow 2HI$, and of similar reactions at boundary surfaces. H. EKSTEIN and M. POLANYI (Z. physikal. Chem., 1932, B, 15, 334—341).—It is suggested that the atoms of the I_2 mol. first move apart, then attack the H_2 mol., one at each end, approaching it along its axis. Assuming that the energy required for the first step is equal to the heat of dissociation of I_2 , the heat of activation of the second step, calc. by the method previously described (A., 1931, 688), is sufficiently small for the heat of activation of the reaction as a whole to agree satisfactorily with the observed val. An explanation of the intermediate formation in the catalysed wall reaction of hydrides on the catalyst surface is advanced. R. CUTHILL.

Hydrogen-carbon dioxide reaction. E. H. BOOMER and H. E. MORRIS (J. Amer. Chem. Soc., 1932, 54, 407).—After passing over a Zn-Cu-Al catalyst at 325°, a mixture of 27% CO_2 , 71% H_2 , and 2% N_2 under 1700 lb. pressure contained 4% CO, suggesting that the first step in the synthesis of MeOH from CO_2 and H_2 involves the reduction of CO_2 and the nature of the catalyst determines the extent to which the resultant CO will be hydrogenated. As the activity of the catalyst decreases, the reaction giving MeOH is affected most; the same catalyst produced an appreciable amount of CO_2 from water-gas. C. J. WEST (c).

Thermal decomposition of ammonia on the surface of osmium. E. A. ARNOLD and R. E. BURK (J. Amer. Chem. Soc., 1932, 54, 23—32).—The reaction at 288—367° is of zero order, and is retarded by the products in such a way that the free surface may be represented by the term $(1 - \text{concn. of products})$ in the velocity equation. The calc. energy of activation is 47,600 and 42,200 g.-cal. per mol. over the temp. range. S. LENHER (c).

Catalytic effect of alkali and alkaline-earth sulphides on reaction between phosphorus trichloride and sulphur. W. H. WOODSTOCK and H. ADLER (J. Amer. Chem. Soc., 1932, 54, 464—467).—Small amounts of alkali sulphides, alkaline-earth sulphides, or similar substances catalyse the formation of $PSCl_3$ from PCl_3 and S at 150°.

CHEMICAL ABSTRACTS (c).

Catalytic decomposition of hydrogen peroxide by platinum-black. A. SIEVERTS and H. BRUNING (Z. anorg. Chem., 1932, 204, 291—304).—The decomp. of H_2O_2 in presence of Pt-black is an approx. unimol. reaction; an initial rise of the velocity coeff. is ascribed to the increased activity of the catalyst during the early stages of the decomp., and a later slow fall to increasing poisoning or reduction of active surface of the Pt. The influence of stirring and of temp. on the reaction indicates that diffusion is the factor which determines the apparent velocity; the temp. coeff. falls from 1.66 at 25—35° to about 1.4 at 45—55°. Traces of NaOH accelerate the decomp., and larger quantities cause retardation. The velocity in presence of 0.02N- H_2SO_4 is a linear function of the activity of the catalyst ("catalytic concn."), and

may therefore be employed as a measure of this quantity. O_2 adsorbed on the Pt-black is removed during the reaction; O-free Pt is at first inactive, but the reaction commences after a short time. Hydrated PtO is an active catalyst and is unchanged after the reaction. H. F. GILLBE.

Velocity of catalysed hydrogenation. II. A. KAILAN and J. KOHBERGER (Monatsh., 1932, 59, 16—43).—The velocity of hydrogenation of olive oil, oleic acid, and Et oleate has been investigated at $180^\circ \pm 5^\circ$ and H_2 pressures of 360, 760, and 1160 mm. Hg, using as catalysts Ni on Al_2O_3 and Ni and Co both separately and together on kieselguhr. The velocity coeff. calc. for a unimol. reaction increases approx. as the power 1.5 of the H_2 pressure between 760 and 1160 mm. and approx. as the power 1 between 360 and 760 mm., whether the substance to be hydrogenated contains one double linking in the mol., e.g., oleic acid and Et oleate, or three, e.g., triolein in olive oil. The results contradict Thomas' theory of the reaction mechanism (A., 1920, ii, 169). The Ni-kieselguhr catalyst is far more active than Ni- Al_2O_3 . Co and Ni on kieselguhr have about the same activity and are each more active than the mixed metals. The velocity of hydrogenation of Et oleate is greatest, but the difference is within the limits of experimental error. M. S. BURR.

Catalytic chlorination and bromination of gases rich in methane hydrocarbons. M. ZAPAN (Diss., Univ. Paris, 1930, 9—99).— CH_4 , C_2H_6 , coal gas, and petroleum gas were chlorinated with catalysts mounted on pumice treated with $FeCl_3$ or $CuCl_2$. $SbCl_5$, $TiCl_4$, and $SnCl_4$ were effective in that order. Bromination was effected in presence of $FeBr_3$. Yields of chlorination products up to 75% on the CH_4 in coal gas and 12—49% yields of brominated products are recorded.

CHEMICAL ABSTRACTS.

Slow combustion of acetylene. R. SPENCE (J.C.S., 1932, 686—696).—At 320° wall activation predominates in the slow oxidation of C_2H_2 , and increase in the relative amount of surface results in a shorter induction period and increased velocity of reaction. There is also an inhibiting effect in vessels <4 mm. diameter, but in vessels of diameter >6 mm. inhibition by the walls is small compared with inhibition by O_2 . Wall inhibition can be brought into prominence again, however, by coating with KCl. This is probably due to a smaller efficiency of the KCl in catalysing the production of active centres. The results point to a branched chain mechanism, and a similar mechanism may be shown to operate in the slow oxidation of C_2H_4 . M. S. BURR.

Effect of concentration of electrolyte on the formation of the anodic film on aluminium. S. SETOH and A. MIYATA (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 319—382).—The formation of the anodic film on Al in 0.5—8.0% $H_2C_2O_4$ solutions at 0—60° has been examined, using a.c., d.c., and a.c. superimposed on d.c. The thickness of the active film is proportional to the p.d. it sustains, as shown by measurements of electrostatic capacity and counter-e.m.f., but does not increase indefinitely as the applied e.m.f. is increased. There is no definite thickness for the active layer and no crit. e.m.f. In general, the

film is the thinner the higher is the temp., the greater the concn. of electrolyte, and the lower the c.d. The thinner film is more compact. At room temp. the current efficiency is greatest (about 80%) with 2–4% solutions of $\text{H}_2\text{C}_2\text{O}_4$, using 50–60 volts and 15 milliamp. per sq. cm. The apparent density of the film is nearly 3.0. E. S. HEDGES.

Mixed borides of thorium and cerium. L. ANDRIEUX (Compt. rend., 1932, 194, 720–722; cf. A., 1930, 305).—By electrolysis between C electrodes mixtures in varying proportions of ThO_2 and CeO_2 in a bath of B_2O_3 , MgO , and MgF_2 at 1150° , with a current of 25 amp. at 8 volts, a series of solid solutions of ThB_2 and CeB_2 is obtained. The relative amounts of Th and Ce in the product depend on those of ThO_2 and CeO_2 in the bath; that of B is approx. const. The amount of Ce is relatively greater than that of Th in accordance with the smaller heat of formation of CeO_2 , but Th is never absent.

C. A. SILBERRAD.

Relation between Kolbe's reaction and hydro-ion concentration. Mechanism of Kolbe's reaction. H. R. MATSUDA (Bull. Chem. Soc. Japan, 1932, 7, 13–27).— H_2O_2 is formed during electrolysis of KOAc and NH_4OAc ; by comparison of the ratio $\text{H}_2\text{O}_2:\text{C}_2\text{H}_6$ produced it is concluded that Ac_2O_2 is first formed at the anode. This may give H_2O_2 by way of the peracid, or may decompose to C_2H_6 and CO_2 ; the former is favoured by high n_{H} .

C. W. DAVIES.

Reactions of hydrocarbons in the glow discharge. E. G. LINDER and A. P. DAVIS (J. Physical Chem., 1931, 35, 3649–3672).—The decomp. of 57 hydrocarbons in the glow discharge has been investigated under identical conditions. The rate of gas evolution per unit current increases with mol. wt., which is attributed to the fact that with increase in the no. of degrees of freedom the mol. may absorb energy in other ways than by ionising. The amount of insol. residue increases with decrease of the ratio H:C in the original hydrocarbon. Analyses of the gaseous products are given. A theory of chemical action in the glow discharge is advanced.

G. M. MURPHY (c).

Triatomic halogen molecules in photochemical reactions. G. K. ROLLEFSON and H. EYRING (J. Amer. Chem. Soc., 1932, 54, 170–177).—By using the quantum mechanical equation for the potential energy of systems of three atoms, it has been shown that for all the halogens mols. of the type X_3 are stable at room temp. with respect to the decomp. into X_2 and X. The significance of this fact in relation to the mechanism of the reactions of Cl_2 with H_2 and with CO, and to Senftleben and Germer's optical dissociation experiments on halogens (A., 1929, 1209) is discussed. CHEMICAL ABSTRACTS (c).

Reaction between hydrogen and oxygen under the influence of photochemically produced hydrogen atoms, and connexion with the "knallgas" reaction at higher temperatures. W. FRANKENBURGER and H. KLINCKHARDT (Z. physikal. Chem., 1932, B, 15, 421–444).—See A., 1931, 1136.

Hydrazine. Photochemical oxidation of hydrazine by ferricyanide. E. C. GILBERT (J. Physical

Chem., 1931, 35, 3631–3634; cf. A., 1929, 1017).—The rate of oxidation at 25° in a $0.2M\text{-Na}_2\text{HPO}_4$ buffer solution is increased by about 10% by exposure to weak light, the effective radiation being that absorbed by the ferricyanide. G. M. MURPHY (c).

Photochemical reaction between hydrogen and chlorine in presence of oxygen. M. RITCHIE and R. W. G. NORRISH (Nature, 1932, 129, 243–244).—The presence of HCl markedly inhibits this reaction. The formula $\gamma_{\text{HCl}} = k_1/(\text{O}_2)([\text{HCl}] + k_2)$ represents the quantum efficiency for O_2 pressures from 10 to 350 mm., and for a ten-fold variation in intensity. The inhibiting action of HCl is sp. and there is no inert gas effect. The kinetics of the reaction are discussed.

L. S. THEOBALD.

Temperature coefficient of photochemical formation of hydrogen chloride. E. HERTEL (Z. physikal. Chem., 1932, B, 15, 325–333).—The temp. coeff. of the formation of HCl from a mixture of H_2 and Cl_2 free from O_2 in light of wave-lengths lying in the visible portion of the continuous absorption spectrum of Cl_2 is 1.37 ± 0.02 at $25\text{--}55^\circ$. If a considerable amount of O_2 is present, the val. is 1.12 ± 0.02 . If the amount of O_2 is sufficient to play a notable part in breaking the reaction chains but not sufficient to be solely responsible for this, the velocity coeff. will lie between these two limits, and this seems to have been the case in Lind and Livingston's experiments (A., 1930, 434). The temp. coeff. for a mixture free from O_2 exposed to light of wave-length greater than corresponds with the convergence point in the banded spectrum of Cl_2 is 1.48 ± 0.04 .

R. CUTHILL.

Action of light on mixtures of ozone and chlorine. II. Results with high ozone concentration. Discussion. A. J. ALLMAND and J. W. T. SHINKS (J.C.S., 1932, 599–612).—The mist observed in a previous investigation (A., 1931, 1018) when a $\text{Cl}_2\text{-O}_3$ mixture is insolated contains HClO_3 and HClO_4 due to the intermediate formation of ClO_3 or Cl_2O_5 from ClO_2 and O_3 . In experiments with a high concn. of O_3 and low Cl_2 the behaviour previously observed is accentuated. The quantum efficiency γ is far higher (max. 59) and shows a distinct temp. coeff. (approx. 1.5). There is a tendency to approx. to the $I^{1/2}$ law. The dark reaction is also greater. γ falls rapidly while much of the O_3 is still present. It is concluded that O_3 disappears by (a) a primary reaction, (b) an incipient chain reaction of one complete term in the gas phase, (c) a chain mechanism of which one constituent reaction, viz., $\text{ClO}_3 + \text{O}_3 \rightarrow \text{ClO}_2 + 2\text{O}_2$, takes place on the surface of the cell. (a) gives $\gamma=2$ without dependence on O_3 concn., λ , or T . (b) can add a max. of 4 to the val. of γ and causes the divergence from $\gamma=2$ in dil. mixtures and the effect of λ . (c) is favoured by high concn. of O_3 and low concn. of Cl_2 . It accounts for the $I^{1/2}$ relation and the dependence of γ on T , but independence of λ . This mechanism is in accord with most of the experimental observations such as the induction period, due to formation and decomp. of adsorbed ClO_3 , the final rise of velocity, due to catalysis by Cl atoms of an adsorbed Cl_2O_6 layer, and the rapid fall of γ in conc. O_3 , due to the fact that O_3 and Cl_2O_6 do not react as do O_3 and ClO_3 so as to continue the

chain. The corresponding thermal reaction is briefly discussed. The temp. coeff. with conc. O_3 gives an activation energy of 7.4 kg.-cal., but this result has a qual. val. only. M. S. BURR.

Photosensitised decomposition of nitrogen trichloride. II. Effects of surface and inert gases, and the mechanism of reaction. J. G. A. GRIFFITHS and R. G. W. NORRISH (Proc. Roy. Soc., 1932, A, 135, 69—83).—The photosensitised decomp. of NCl_3 by Cl_2 is a homogeneous change propagated by a chain mechanism. In a vessel washed with H_2O or heated to above 100° the quantum efficiency is abnormally high, but in a matured vessel the quantum efficiency is independent of the illuminated surface and of the total surface. The maturing of the surface is due to an invisible film of NH_4Cl . The quantum efficiency is depressed by inert gases to a limiting val. of about 2, according to the equation $\gamma=1/(\Sigma(k_t[X]))+2.5$, where $\Sigma(k_t[X])$ refers to the sum of the effects of the various gaseous species present. A theory based on a chain reaction initiated by Cl atoms is developed and found to agree with the experimental results. L. L. BIRCHUMSHAW.

Optical sensitisation in photography. W. D. BANCROFT, J. W. ACKERMAN, and C. A. GALLAGHER (J. Physical Chem., 1932, 36, 154—173).—An optical sensitiser in photography is a coloured substance which is adsorbed by $AgBr$ but does not form a colour screen by dissolving in gelatin, and is a strong enough reducing agent to form a latent image with $AgBr$ when activated or reduced by light. It is probable that the $AgBr$ is reduced by the activated dye and not by a reaction product. The optical sensitisation of aq. $FeCl_3$ and $AgNO_3$ with a no. of light-sensitive dyes was studied. Sensitisation was observed when Na eosinate was added to a mixed solution of ammoniacal CuO and $NHPh\cdot NH_2$ which was of such composition that it was bleached by light, but stable in the dark. S. LENHER (c).

Photochemical reaction of carbon monoxide with ammonia and with amines. H. J. EMELÉUS (Trans. Faraday Soc., 1932, 28, 89—94; cf. A., 1931, 1251).—The apparent rate of photochemical decomp. of 3—30 cm. of NH_3 at 100 — 150° in the full radiation of the quartz-Hg vapour lamp is approx. doubled by the addition of 14—26 cm. of CO . Less than 5% of the NH_3 reacting affords N_2 and H_2 , the principal primary product being $HCO\cdot NH_2$, which undergoes secondary changes. The mechanism of the reaction is discussed. Preliminary experiments indicate that NH_2Me and NH_2Et react with CO under similar conditions. J. G. A. GRIFFITHS.

Photo-reduction of carbonic acid, hydrogen carbonates, and carbonates to formaldehyde. N. R. DHAR and A. RAM (Nature, 1932, 129, 205).— H_2CO_3 , carbonates, and H carbonates are reduced to CH_2O by Mg and Zn, the yield being greater in light than in the dark. HCO_2H could not be detected (cf. J.C.S., 1907, 91, 687). The yield is increased by photosensitisers such as ZnO . 100 c.c. of a 10% solution of $KHCO_3$ and 1 g. of powdered Mg in the presence of ZnO give 0.0045 g. of CH_2O after 5.5 hrs. exposure to sunlight. No reducing sugar is detect-

able. $FeCO_3$ also brings about photo-reduction of these substances. L. S. THEOBALD.

Photochemical polymerisation of acetylene. S. C. LIND and R. LIVINGSTON (J. Amer. Chem. Soc., 1932, 54, 94—106).—When C_2H_2 is irradiated with light from a Hg arc in the absence of Hg vapour a yellow solid, apparently cuprene, but no H_2 , is formed. At lower pressures the rate of polymerisation is proportional to the pressure, but at 65 cm. it approaches a const. val., indicating that the rate is directly proportional to the intensity of absorbed light, but otherwise independent of the pressure. The temp. coeff. for a C_2H_2 pressure of 10 cm. is 1.25. Wave-lengths longer than 2537 Å. are either not absorbed or photochemically ineffective. The quantum efficiency for an average wave-length of 2150 Å. is 9.2 ± 1.5 , independent of the C_2H_2 pressure and of the radiation absorption. This val. is approx. equal to the average yield per ion. E. J. ROSENBAUM (c).

Photochemical polymerisation of cyanogen. T. R. HOGNESS and L. TS'AI (J. Amer. Chem. Soc., 1932, 54, 123—129).—The absorption spectrum of C_2N_2 has a set of diffuse bands from 2200 Å. to the transmission limit of quartz, from which it is concluded that C_2N_2 dissociates into CN radicals, one of which may be excited. No fluorescence was observed. C_2N_2 at 1 atm. absorbs 8.8% of radiation of effective wave-length 2150 Å. The quantum efficiency of the polymerisation of C_2N_2 to paracyanogen is 3. This val. can be accounted for by a second reaction, $C_2N_2 + CN \rightarrow (CN)_3$; the $(CN)_3$ could polymerise further to paracyanogen. E. J. ROSENBAUM (c).

Photochemical decomposition of chloroform. D. G. HILL (J. Amer. Chem. Soc., 1932, 54, 32—40).—The decomp. of $CHCl_3$ vapour by light in the far ultra-violet has been studied. 4 mols. of HCl but no Cl_2 are formed per quantum absorbed. The yield is proportional to the square of the pressure of added O_2 . CHEMICAL ABSTRACTS (c).

Photochemical studies. XIII. Photochemical reaction between chlorine and benzene in the gaseous phase. C. E. LANE, jun., and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1932, 54, 161—169; cf. A., 1931, 442).—The rate of the reaction in light of wave-length 4500—6000 Å. is proportional to $[Cl_2]$. The first step is the production of $PhCl$. This soon condenses out on the walls and the succeeding reactions are chiefly those of addition, C_6H_6 hexachloride, one of the products found, probably representing the final stage in the addition of Cl to C_6H_6 dissolved in the $PhCl$ on the walls.

W. E. VAUGHAN (c).

Reactions of chlorine with solid carbonates. I. Sodium carbonate. F. ISHIKAWA, T. MUROOKA, and H. HAGISAWA. II. Potassium carbonate. F. ISHIKAWA and H. HAGISAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 284—296, 297—303).—I. The main reaction is $2Na_2CO_3 + 2Cl_2 = 4NaCl + 2CO_2 + O_2$. Na_2CO_3 prepared by heating $NaHCO_3$ at 350° reacts more easily with Cl_2 than that prepared at 500° . $NaClO_4$ is also formed, particularly with Na_2CO_3 prepared at 350° .

II. The reaction is similar to that with Na_2CO_3 .

KClO₄ is also formed in small amount. The reaction of Cl₂ with Li₂CO₃ and MgCO₃ was also studied; no perchlorate was formed. E. S. HEDGES.

Potassium dibromiodide hydrate. G. H. CHEESMAN and J. H. MARTIN (J.C.S., 1932, 586—588).—The crystals obtained by slow evaporation of a saturated solution of KIBr₂ in H₂O over syrupy H₃PO₄ have the composition KIBr₂·H₂O. The dissociation pressure-temp. curves have been drawn for the monohydrate and the anhyd. salt, pressure for the former being much higher than for the latter. The hydrated salt melts at 59°, causing a slight break in the dissociation curve. M. S. BURR.

Reactivity of alloys and its dependence on fusion or transformations in the solid state. I. Interaction of copper-tin alloys and lime or quartz in oxygen. J. A. HEDVALL and F. ILANDER (Z. anorg. Chem., 1932, 203, 373—389; cf. A., 1926, 695).—Measurement of the quantity of O₂ absorbed by mixtures of CaO with CuSn or Cu₃Sn heated at temp. up to 750° are considered to support the author's view that chemical reactivity is enhanced during the breaking down of a crystal lattice. Similar experiments were performed with SiO₂. The effect observed does not depend on fusion. Cu-Sn alloys attack refractories containing CaO or SiO₂ at or above 400°. F. L. USHER.

Synthesis of calcium silicates. II. S. NAGAI and K. AKIYAMA (J. Soc. Chem. Ind. Japan, 1932, 35, 8—10b; cf. B., 1932, 262).—On heating a mixture of CaCO₃ and SiO₂ in the mol. ratio of 2 : 1 for 1 hr. at various temp. the amount of combination increases with rise of temp., and the products are 3CaO, 2SiO₂ + 2CaO, SiO₂ from 900° to 1100°, 2CaO, SiO₂ from 1200° to 1450°, and 2CaO, SiO₂ + 3CaO, SiO₂ from 1500° to 1550°. The compressive strength of 2CaO, SiO₂ cements is greater than that of CaO, SiO₂ cements, but both are poor compared with those of Ca aluminate cements. N. H. HARTSHORNE.

Ammoniates of zinc, copper, and manganese sulphates. O. R. FOZ and L. LE BOUCHER (Anal. Fis. Quím., 1932, 30, 21—30).—Study of the decomposition-pressure-temp. curves has confirmed the existence of ZnSO₄·5NH₃ and CuSO₄·5NH₃, but MnSO₄·5NH₃, described by Ephraïm, does not appear to exist. ZnSO₄ forms also compounds containing 4, 3, 2, 1, and 0.5 mols. of NH₃; the v.-p. curves and heats of formation have been determined. CuSO₄ forms a tetra- and a di-ammoniate. H. F. GILLBE.

Homogeneous and heterogeneous complex salts in solution. III. G. SPACU and P. SPACU (Bul. Soc. Stiinte Cluj, 1931, 5, 473—487; Chem. Zentr., 1931, ii, 1118; cf. A., 1931, 1380).—The following compounds have been prepared:

[CdI₂Br₂][Cu en₂], [CuCl₂Br₂][Cu en₂], [CdCl₄][Cu en₂], [BiCl₆][Co en₃], 2H₂O, [CdCl₄][X]₂(I₆), [CuCl₄][X]₂(I₆), [BiCl₆][X]₃(I₆), [HgBr₄][X]₂(I₆), [CdI₄][X]₂(I₆), [CdI₄][X]₂(I₆), [CdBr₄][X]₂(I₆), [SnCl₆][X]₂(I₆), [SnCl₃][X]₃(I₆), [HgI₄][Co en₂CO₃], and [AgI₂][Co en₂CO₃], where X is Co en₂Cl₂. The cation [Co en₂Cl₂] in the *cis*-form remains unchanged only in the compound [CdI₄][X]₂(I₆). In most other cases the *trans*-compound is preserved owing to the

greater solubility of the *cis*-salts; the former are green and the latter violet in colour. The complex [SnCl₄][X]₂ could not be prepared.

L. S. THEOBALD.

Boron hydrides. I. Preparation of diborane, bromodiborane, and pentaborane. H. I. SCHLESINGER and A. B. BURG (J. Amer. Chem. Soc., 1931, 53, 4321—4332).—If a mixture of BCl₃ and H₂ obtained by passing H₂ through liquid BCl₃ at -40° is subjected to the action of a high-tension electric discharge, about 25% of the BCl₃ undergoes reaction, the chief product, apparently *chlorodiborane*, B₂H₅Cl, being accompanied by much smaller amounts of B₂H₆. At 0°, however, B₂H₅Cl decomposes: 6B₂H₅Cl ⇌ 5B₂H₆ + 2BCl₃. When B₂H₆ is heated at 120—130° in presence of a little HCl a considerable proportion is converted into B₅H₉. A good yield of B₅H₉·Br is obtained by interaction of B₂H₆ and BBr₃.

H. STOERTZ (c).

Alkali aluminosilicates. IV. [with E. HIRSCH]. Action of alkali sulphide and polysulphide solutions on permutites. **V. Relationship between sulphide permutites and ultramarines.** E. GRUNER (Z. anorg. Chem., 1932, 204, 232—246, 247—256).—IV. Alkali and alkaline-earth permutites, when treated with alkali sulphide or polysulphide solution in presence of air, become blue; the blue substance is decolorised by H₂O, with liberation of H₂S and S. In absence of air only the polysulphides cause the appearance of the blue compound, whereas the sulphides react with formation of colourless compounds containing 2 atoms of S per 3 mols. of permutite; these sulphide permutites yield with H₂O H₂S but no S. The curve relating the quantity of S absorbed with the concn. of the sulphide solution resembles an ordinary adsorption isotherm. During the removal of S from the solution the *p_H* increases, presumably owing to the interchange of OH' from the permutite and SH' from the solution. This ionic exchange proceeds rapidly, but the subsequent oxidation is slow and has a velocity coeff. of 0.039 for Na₂(Al₂Si₂H₄O₁₀) and of 0.061 for Na₂(Al₂Si₂H₄O₁₀)·H₄SiO₄.

V. The sulphide permutites are of the type Na₆[Al₆Si₆H₁₀O₂₈(SH)₂]; on oxidation the SH groups are converted into S₂ or S₂H groups, and by hydrolysis they are replaced by OH groups, yielding the original permutite. The polysulphide permutites probably exist in dynamic equilibrium with S and the monosulphide compound, in accordance with the theory of Hofmann and Biltz. The analogous Na polyselenide permutite is red and readily decomposes with liberation of Se. Faint blue colorations are produced by the action of alkali sulphide solutions on basic or amphoteric hydroxides, such as those of Al, Cr, Th, and Zr, but not with acidic hydroxides (Si, Ti). If the blue polysulphide permutites are prepared at temp. above about 200° they are of much greater stability and yield the same X-ray diagram as ultramarine. H. F. GILLBE.

Removal of free carbonic acid from water. J. TILLMANS, P. HIRSCH, and H. LÜRMANN.—See B., 1932, 242.

Persilicates. F. KRAUSS (Z. anorg. Chem., 1932, 204, 318—320).—*Na persilicate*, Na₂SiO₃·2H₂O·H₂O,

has been prepared as a non-hygroscopic, stable, and very sol. powder by adding H_2O_2 to a solution of Na_2SiO_3 and evaporating to dryness in vac.

H. F. GILLBE.

Alkali salts of fluotitanic acid. IV. H. GINSBERG (Z. anorg. Chem., 1932, 204, 225—231).—Pure anhyd. Na_2TiF_6 has been prepared by pptn. with EtOH from its aq. solution. The solubilities and m. p. of all the alkali salts have been determined; the solubilities in EtOH are very small (0—0.01%). The thermal decomp. of these compounds is not normally a hydrolytic process, but it is accelerated by the presence of H_2O and of O_2 , and becomes mainly hydrolytic when the atm. is saturated with H_2O . The TiF_3 evolved when the salts are heated at 600—660° (Li 430°) yields on the walls of the containing vessel a deposit of TiO_2 .

H. F. GILLBE.

Action of hydrocyanic acid on halides of ter- and quadri-valent metals. T. KARANTASSIS (Compt. rend., 1932, 194, 461).— TiCl_4 and HCN , cooled in ice and salt, combine to form $\text{TiCl}_4 \cdot 2\text{HCN}$, which sublimes as yellow crystals at 70°. SnCl_4 and HCN form a very volatile white ppt. (cf. Annalen, 1850, 74, 85). AlCl_3 forms $\text{AlCl}_3 \cdot 2\text{HCN}$ (cf. this vol., 132). No compounds are formed with SnI_4 , SnI_2 , SnBr_4 , SbCl_3 , AsCl_3 , or CrCl_3 .

C. A. SILBERRAD.

Heteropoly-acids of germanium. II. A. BRUKL and B. HAHN (Monatsh., 1932, 59, 194—201).—12-Tungstogermanic acid (I), $\text{H}_8\text{Ge}(\text{W}_2\text{O}_7)_6$, is prepared +4, 15, and 22 H_2O (cf. A., 1930, 1538). Electro-metric titration of (I) with NaOH indicates only four readily replaceable H atoms, but a Hg_2^{2+} salt (+5 H_2O) can be prepared from (I) and HgNO_3 . A K H salt, $3\text{K}_2\text{O} \cdot 2\text{GeO}_2 \cdot 24\text{WO}_3 \cdot 30\text{H}_2\text{O}$ (loses 17 H_2O at 95—100°), is occasionally prepared. (I) (1 mol.) and K_2CO_3 (5.5 mols.) give the salt, $7\text{K}_2\text{O} \cdot 2\text{GeO}_2 \cdot 20\text{WO}_3 \cdot 24\text{H}_2\text{O}$ [corresponding Ag salt (+6 H_2O)], convertible into the guanidine salt, $(\text{CH}_2\text{N}_3)_7\text{GeO}_2 \cdot 10\text{WO}_3 \cdot 13\text{H}_2\text{O}$ (loses 8 H_2O at 130°); the free (10-tungstogermanic) acid could not be isolated. (I) and K_2CO_3 (7.5 mols.) give a product containing Ge hydroxide; addition of NH_4NO_3 to a dil. solution affords the salt, $8\text{NH}_3 \cdot 3\text{K}_2\text{O} \cdot 2\text{GeO}_2 \cdot 20\text{WO}_3 \cdot 17\text{H}_2\text{O}$. The existence of other tungstogermanic acids is not indicated.

H. BURTON.

Decomposition of nitrates and nitrites of metals with different valencies. II. Stannous nitrate. C. MONTEMARTINI and E. VERNAZZA (Ind. chim., 1931, 6, 632—638; Chem. Zentr., 1931, ii, 1117—1118; cf. A., 1931, 583).— $\text{Sn}(\text{NO}_3)_2$ has been prepared from SnCl_2 or SnSO_4 [from $\text{Sn}(\text{OH})_2$ and H_2SO_4] and $\text{Pb}(\text{NO}_3)_2$, or from $\text{Sn}(\text{OH})_2$ and HNO_3 . Sn^{2+} is determined using KMnO_4 in H_2SO_4 solution after addition of $\text{Fe}_2(\text{SO}_4)_3$ or Fe alum. Aq. $\text{Sn}(\text{NO}_3)_2$ solutions are completely stable at room temp. in an atm. of CO_2 . Heating in a stream of CO_2 leads to the formation of $\text{Sn}(\text{OH})_2$, basic nitrate, SnO_2 , and $\text{Sn}(\text{OH})_4$; whilst in contrast with $\text{Fe}(\text{NO}_3)_3$, NO , N_2O , and N_2 are evolved and NH_3 is formed in the solution. The decomp. is very rapid in its final stages, and is accelerated by the addition of HNO_3 ; the more conc. is the acid the greater is its effect.

L. S. TREOBALD.

Rhombic modification of lead chromate. F. QUITTNER, J. SARGIR, and N. RASSUDOVA (Z. anorg. Chem., 1932, 204, 315—317).—Rhombic PbCrO_4 is obtained when $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added to a neutral solution of a Pb salt at room temp., provided that the concn. of the Pb solution does not exceed 10% and that the product is dried at a temp. below 25°. The substance is of a brilliant yellow colour and is stable for about 1 month at room temp. When ground with linseed oil it darkens very rapidly. The Debye-Scherrer diagram closely resembles that of PbSO_4 (anglesite).

H. F. GILLBE.

Mechanism of precipitation processes. VIII. Precipitations with lead and iodide ions. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1932, 203, 390—400; cf. A., 1931, 1021).—When an aq. solution of $\text{Pb}(\text{NO}_3)_2$ is added to one of H_2SO_4 in presence of KI the resulting ppt. contains I which is gradually given up to the liquid. The ppt., initially white, becomes yellow. The process is expressed by: $2\text{PbI}^+ + \text{SO}_4^{2-} \rightarrow (\text{PbI})_2\text{SO}_4$, followed by $(\text{PbI})_2\text{SO}_4 \rightarrow \text{PbI}_2 + \text{PbSO}_4$. Similar results were obtained in presence of KCl and KBr, but not KCNS; or when $\text{Na}_2\text{C}_2\text{O}_4$ or $(\text{NH}_4)_2\text{CrO}_4$ is substituted for H_2SO_4 .

F. L. USHER.

Ammonium thiosulphate. W. KLEMP, F. BRODKORB, and H. ERLBACH.—See B., 1932, 179.

Anhydrous hydrazine. V. Hydrazinates of calcium trinitride. A. L. DRESSER and A. W. BROWNE (J. Amer. Chem. Soc., 1931, 53, 4235—4242).—Ca azide dihydrazinate, $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$, prepared by crystallisation of $\text{Ca}(\text{N}_3)_2$ from anhyd. N_2H_4 , is isomeric and possibly identical with the Ca derivative of either of the unknown compounds Δ^1 -pentazine, $\text{NH}_2\text{N} \cdot \text{NH} \cdot \text{NH} \cdot \text{NH}_2$, and Δ^2 -pentazine, $\text{NH}_2\text{N} \cdot \text{NH} \cdot \text{N} \cdot \text{NH}_2$. The monohydrazinate, $\text{Ca}(\text{N}_3)_2 \cdot \text{N}_2\text{H}_4$, was prepared by gradual dehydrazination of the solute.

H. STOERTZ (c).

Absorption and evolution of hydrogen sulphide from solutions containing both sodium carbonate and arsenious oxide. H. A. J. PIETERS and J. SMEETS (Chem. Weekblad, 1932, 29, 73—74).—The presence of As_2O_3 enables a solution of Na_2CO_3 to take up more H_2S , but on regeneration the amount evolved is diminished.

S. I. LEVY.

Structure of ultramarine. K. LESCHIEWSKI and H. MÖLLER (Ber., 1932, 65, [B], 250—253; cf. A., 1931, 1380).—White ultramarine obtained from the blue compound and HCO_2Na or HCO_2K and "U blue 2," obtained by heating the white substance, are distinguished from the original material by higher alkali content. The total S content is unchanged, but combined S is doubled. Oxidation of white ultramarine or "U blue 2" with molten NaClO_3 or NaNO_3 regenerates ultramarine. In consequence of hydrolysis, formate ultramarine becomes pale blue when treated with boiling H_2O . The conversion of blue into pale pink ultramarine by boiling ethylene chlorohydrin is accompanied by great diminution of the Na content and not by removal of S. Fusion with NaCl restores the colour. A white ultramarine is obtained by this process from an original material with 7.9% S; this becomes coloured by molten or dissolved Na_2S but not by NaCl.

H. WREN.

Salts of trithionic acid. C. G. KATRAKI (Praktika, 1929, 4, 120—123; Chem. Zentr., 1931, ii, 1116).—A solution of $\text{Na}_2\text{S}_2\text{O}_3$, containing an excess of NH_3 , gives on warming and cooling with a conc. solution of CuSO_4 blue crystals of $\text{Cu}_2\text{S}_3\text{O}_{11} \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{NH}_3$ which are insol. in EtOH and in CO_2 and sparingly sol. in H_2O . NH_3 is evolved with cold H_2O and some $\text{Cu}(\text{OH})_2$ formed. CuS is first formed on heating, and then NH_3 and SO_2 are evolved. BaCl_2 gives $\text{BaS}_3\text{O}_{11}$, and AgNO_3 forms Ag_2S on warming. The S is oxidised to H_2SO_4 with KMnO_4 or I, whilst reducing agents yield H_2S and SO_2 .

L. S. THEOBALD.

Impurity and radical chains in the mechanism of the reaction of organic and enzymic processes. F. HABER and R. WILLSTATTER (Ber., 1931, 64, [B], 2844—2856).—The primary action in the oxidation of H_2SO_3 by Cu^{++} is formulated: $\text{SO}_3^{--} + \text{Cu}^{++} + \text{H}_2\text{O} = \text{SO}_3\text{H} + \text{Cu}^+ + \text{OH}^+$; it is succeeded by the chain reactions, $\text{SO}_3\text{H} + \text{O}_2 + \text{H}_2\text{O} + \text{SO}_3^{--} = 2\text{SO}_4^{--} + \text{OH} + 2\text{H}^+$ and $\text{OH} + \text{SO}_3^{--} + \text{H}^+ = \text{OH}^+ + \text{SO}_3\text{H}$. The following cases involve the same principles as a consequence of which the contact substance (enzyme) suffers univalent reduction (Fe^{+++} to Fe^{++}) and the substrate univalent oxidation. The product of dehydrogenation is therefore a radical with a free valency which can occur at C or S. Schemes are proposed for the biological oxidation of EtOH and MeCHO . Since the radical produced by dehydrogenation of an aldehyde is identical with that formed by a so-called mutase, it depends on experimental conditions whether autoxidation or disproportionation occurs. The following cases are considered in detail: Cannizzaro's disproportionation of PhCHO ; conversion of methylglyoxal into lactic acid in presence of an aldehyde-mutase; dehydrogenation of succinic acid by succinodehydrase; peroxidase and catalase action; catalytic hydrogenation.

H. WREN.

Reaction of violet solutions of chromium salts. II. C. MONTEMARTINI and E. VERNAZZA (Ind. chim., 1931, 6, 492—497; Chem. Zentr., 1931, ii, 1167—1168; cf. A., 1931, 1140).—With ZnO , $\text{Zn}(\text{OH})_2$, $\text{Zn}(\text{HCO}_3)_2$, and ZnCO_3 , green Cr salt solutions give ppts. the composition of which varies with conditions but is different from that of the pinkish-violet ppt. obtained with violet Cr solutions. The pptn. of violet solutions of $\text{Cr}(\text{NO}_3)_3$ and CrCl_3 with $\text{Zn}(\text{NO}_3)_2$ or ZnCl_2 and KHCO_3 in the absence of SO_4 gives no definite compound, but the addition of 1 mol. of SO_4 to 1 of Cr_2O_3 yields ppts. of $\text{Cr}_2\text{O}_3 \cdot 4\text{ZnO} \cdot \text{SO}_3$ which contain neither Cl^+ nor NO . L. S. THEOBALD.

Characteristic reactions for violet solutions of chromium salts. V. C. MONTEMARTINI and E. VERNAZZA (Ind. chim., 1931, 6, 862—866; Chem. Zentr., 1931, ii, 2135).—In a sufficiently alkaline solution lilac ppts. of $\text{Cr}_2\text{O}_3 \cdot 4\text{ZnO} \cdot \text{N}_2\text{O}_5$ and $\text{Cr}_2\text{O}_3 \cdot 4\text{ZnO} \cdot \text{Cl}_2$ can be obtained. The group $\text{Cr}_2\text{O}_3 \cdot 4\text{ZnO}$ is very stable; when the salts are boiled with alkali salts the anions are exchanged.

A. A. ELDRIDGE.

Reactions of tungsten hexachloride. A. J. COOPER and W. WARDLAW (J.C.S., 1932, 635—637).— $\text{C}_6\text{H}_5\text{N}$ reacts with a solution of WCl_6 in CCl_4 to give a

green insol. compound, $(\text{C}_6\text{H}_5\text{N})_2[\text{WCl}_5 \cdot \text{H}_2\text{O}]$, instead of a co-ordination compound of the type $\text{WCl}_6 \cdot x\text{C}_6\text{H}_5\text{N}$. Attempts to produce the corresponding green quinoline compound resulted in a brown compound $(\text{C}_6\text{H}_5\text{N})_8[\text{W}_3\text{Cl}_{17}]$, which may be a compound of the series $\text{R}_3\text{W}_2\text{Cl}_7$ associated with the co-ordination compound $(\text{C}_6\text{H}_5\text{N})_5[\text{WCl}_6]$. A modification of Roscoe and Hill's method for the prep. of WCl_6 is described.

M. S. BURR.

Luminescent compounds. A. SCHLOEMER (J. pr. Chem., 1932, [ii], 133, 51—59).—Details are given for the prep. of some luminescent tungstates, molybdates, vanadates, uranates, and silicates, and of a ZnS (containing NaCl , MgF_2 , and Cu) as luminescent as the best commercial product. R. S. CAHN.

Reaction chains in oxidative processes. H. KAUFFMANN (Ber., 1932, 65, [B], 179—184; cf. Haber and Willstätter, this vol., 352).—Addition of H_2O_2 to a hypochlorite bleaching liquor causes immediate evolution of O_2 and enhanced bleaching activity during the change. The effect is judged by the time required for discharging the colour of orange II, suitability of period being obtained by regulated addition of NaOH . The dye is very resistant to alkaline H_2O_2 . The effect is not attributable to nascent O , since enhanced bleaching activity is also observed after addition of N_2H_4 , NH_2OH , semicarbazide, carbamide, oxamide, succinimide, and veronal. The activator differs from a catalyst, since it is decomposed during the change. The primary radical is considered to be ClO obtained by discharge of ClO^+ , the second radical OH . The processes may be summarised: $\text{ClO} + \text{ClO}^+ + \text{OH}^- = 2\text{Cl}^+ + \text{O}_2 + \text{OH}^-$ and $\text{OH} + \text{ClO}^+ = \text{ClO} + \text{OH}^+$.

Activators are substances which cause the occurrence of OH in the bleaching liquor, their action depending on the union of the liberated OH with the dye, cellulose, or other substrate thus: $\text{RH}_2 + \text{OH} = \text{RH} + \text{H}_2\text{O}$ and $\text{RH} + \text{ClO}^+ = \text{R} + \text{Cl}^+ + \text{OH}^+$. In absence of catalyst or activator, high activity of a bleaching liquor is attributed to hydrolytically formed HOCl in equilibrium with hypochlorite. The production of OH by this means is shown by the scheme $\text{HOCl} + \text{ClO}^+ = \text{ClO} + \text{Cl}^+ + \text{OH}^+$. The equation further explains the lack of high oxidising power in ClO^+ or HOCl singly and their powerful action when in conjunction and also the repression of the activity of bleaching liquors by addition of alkali hydroxide.

H. WREN.

Bromine hydrate. I. W. H. HARRIS (J.C.S., 1932, 582—585).—Investigation of the system $\text{KBr} \cdot \text{H}_2\text{O}$ at 0° , for concns. of KBr below approx. 16%, indicates that one Br hydrate only, $\text{Br}_2 \cdot 10\text{H}_2\text{O}$, exists at this temp.

M. S. BURR.

Preparation and crystal form of pure iodic acid. A. PÉREZ-VITORIA and J. GARRIDO (Anal. Eis. Quím., 1932, 30, 12—20).—Details are given of the prep. of HIO_3 by oxidation of I with fuming HNO_3 ; hydrates of HIO_3 do not separate from a HNO_3 solution, whatever the concn. Crystallographic data are given. H. F. GILLBE.

Rhenium pentoxide. W. A. ROTH and G. BECKER (Ber., 1932, 65, [B], 373; cf. Briscoe and others, this vol., 32).—Formation of Re_2O_5 is observed during the combustion of Re to Re_2O_7 in the calorimetric bomb in presence of paraffin oil and O_2 under pressure.

H. WREN.

Concentration, acids, and lithium salts of element 85. F. ALLISON, E. R. BISHOP, and A. L. SOMMER (J. Amer. Chem. Soc., 1932, 54, 616–620; cf. A., 1930, 1541).—The name "alabamine" and symbol Am are suggested for element 85. By the magneto-optic method its partial concn. from monazite sand was followed, its compounds were studied, and its at. wt. was found to be about 221. Minima for HAm, HAmO, HAmO₂, HAmO₃, and HAmO₄ and the Li salts were found. Am is oxidised in alkaline solution and more readily in acid. The peralabamates are the most stable of the compounds.

L. P. HALL (c).

New type of complex platinum compounds. Ter- and quinque-valent platinum. IV. P. C. RAY and S. C. S. GUPTA (Z. anorg. Chem., 1932, 203, 401–404; cf. A., 1931, 810).—A solution of $\text{PtClEt}_2\text{S}_2$ in CHCl_3 when boiled with Br gives the compound $\text{PtBrEt}_2\text{S}_2$ (I). If in the prep. of $\text{PtClEt}_2\text{S}_2$ the filtrate from the first crop of crystals is boiled with EtOH for several days, the compound $\text{Pt}_3\text{Cl}_2\cdot 3\text{Et}_2\text{S}_2$ is formed, and this, on treatment with Br, is converted into (I).

F. L. USHER.

Quantitative spectral determinations with gaseous mixtures. A. GATTERER (Physikal. Z., 1932, 33, 64–73).—A special form of gas burette for preparing mixtures is described. The spectral change with concn. of six binary systems was photographed and the intensity of blackening determined by a microphotometer. The intensity of blackening is proportional to log. concn. There are definite deviations from this for a few mixtures, but these can be explained. The application of the work to the quant. analysis of gaseous mixtures and org. elementary analysis is discussed.

A. J. MEE.

Standards for acidimetry. G. CALCAGNI and M. STURNAJOLO (Annali Chim. Appl., 1932, 22, 16–24).— Li_2CO_3 , K_2CO_3 , CaCO_3 , BaCO_3 , MgO , CaO , Na , K , and Mg may be used for standardising acid solutions. Some of these substances are simpler to use than Na_2CO_3 and the results are equally accurate.

O. F. LUBATTI.

Micro-acidimetry. II. J. MIKA (Mikrochem., 1932, 10, 384–396).—Error due to CO_2 may be compensated by using an indicator correction. The most satisfactory standard alkali solution (approx. 0.01N) is prepared by saturating a $M\text{-CaCl}_2$ solution with Ca(OH)_2 , filtering, and adding 3.5 vols. of $M\text{-CaCl}_2$ solution. Standardisation is effected by titrating with a solution of 20 mg. of $\text{KIO}_3\cdot\text{HIO}_3$ to p_H 4.8 (Me-red), using a citric acid- Na_2HPO_4 buffer solution for comparison. Details are given of vessels suitable for handling the solutions and for the titrations.

H. F. GILLBE.

Micro-alkalimetry and -acidimetry. S. K. TSCHIRKOV (Bull. Inst. rec. biol. Perm, 1931, 7, 427–441).—The wt. of acid used (A) in the titration of alkali is given by $A - V'f - 0.001MV'([H'] - [OH'])$,

where V' is the vol. of acid added, f is its titre, M its equiv. wt. in g., and V is the final vol. of the solution. Applying the above formula, and using solutions not more conc. than 0.01N, the experimental error is $\pm 5 \times 10^{-7}$ g.

R. TRUSZKOWSKI.

Possibilities and limitations of potentiometric analysis. F. L. HAHN (Angew. Chem., 1932, 45, 77–80).—A discussion, especially of conditions which must be observed when titrating weak acids or weak bases. Certain factors, such as the degree of accuracy of the potential measurement necessary to obtain a result with a given limit of error, are dealt with in detail.

H. F. GILLBE.

Determination of the end-point and the turning potential in potentiometric titration. F. L. HAHN (Z. anal. Chem., 1932, 87, 263–268).—In a potentiometric titration the region of most rapid potential change, and therefore the end-point of the titration, can be determined with considerable accuracy, but it is not possible to obtain a very exact val. for the true potential at the end-point. The turning potential determined by Knop (A., 1931, 1261) for the Fe-KMnO_4 titration cannot therefore be regarded as giving the true const. for this reaction, although the method gives a satisfactory val. for the point of equivalence.

M. S. BURR.

Titration of hydrogen peroxide in presence of alkali oxalates. W. FEHRE (Z. anal. Chem., 1932, 87, 180–185).—The solution is neutralised if acid, then excess of a 10% aq. solution of BaCl_2 is added in the cold. After 2 hr., in the course of which the BaC_2O_4 settles out, the clear liquor is titrated with KMnO_4 . This procedure is recommended for the analysis of bleaching baths.

R. CUTHILL.

Electrometric determination of chlorides. I. Use of portable p_H apparatus. A. ITANO. II. Determination of chloride in soils. A. ITANO and A. MATSUURA (Ber. Ohara Inst. Landw. Forsch., 1931, 5, 145–150, 171–176).—I. The authors' apparatus is applied to the determination of Cl' (cf. Best, A., 1930, 1124).

II. Results obtained agreed well with those of the direct (chromate) titration method, small discrepancies occurring only when the Cl' content was very low. The Cl' content of soils decreased as the source of irrigation was approached.

A. G. POLLARD.

Preparation of nephelometric test solutions. A. F. SCOTT and J. L. MOILLIET (J. Amer. Chem. Soc., 1932, 54, 205–209; cf. A., 1920, ii, 633).—The formation of Ag halide suspensions by various different methods was studied. Variations in the turbidity originate apparently in the speed with which the precipitant is added to the saturated solution rather than in the rate of mixing; the more rapidly the precipitant is added, the weaker is the turbidity.

L. KELLEY (c).

Winkler titration in methylene-blue media. G. MARSH (J. Biol. Chem., 1932, 95, 25–27).—In the iodometric titration of dissolved O_2 (A., 1889, 79) starch is replaceable by methylene-blue in a concn. of 0.00005M. Addition of MnCl_2 and $\text{NaOH} + \text{KI}$ to an aq. solution of methylene-blue results in the formation of the leuco-compound, which regains its

original colour in about 2 min. This re-oxidation is due to the Mn, the reduction of the dye being completely reversed and hence introducing no error in the determination of dissolved O_2 .

F. O. HOWITT.

Sensitivity of lead paper towards hydrogen sulphide. H. LEROUX (*J. Usines Gaz*, 1931, 55, 117—122; *Chem. Zentr.*, 1931, ii, 1166).—Filter-paper strips moistened with 1% $Pb(OAc)_2$ solution were exposed for 15 min. to gases with different H_2S contents and a velocity of 105 litres per hr. The limiting detectable amounts were in H_2 0.10, town gas 0.15, N_2 0.60, and CO_2 3.50 g. H_2S per 100 cu. m. The sensitivity increases with the Arnold diffusion coeff.

L. S. THEOBALD.

Determination of nitrogen peroxide. E. J. B. WILLEY and S. G. FOORD (*Proc. Roy. Soc.*, 1932, A, 135, 166—181).—The method depends on the measurement of the light transmitted by a column of NO_2 by a K photo-cell. The apparatus, including an arrangement for amplifying the photo-electric current, is fully described. The Beer-Lambert law is shown to be applicable over a wide range of NO_2 concn. The conditions for max. sensitivity and max. accuracy of the method are discussed, and several applications suggested.

L. L. BIRCHUMSHAW.

Ronchese's method. Application to the determination of ammonia in Kjeldahl determinations. V. COLOMBARO (*Anal. Farm. Biochim.*, 1931, 2, 3—25; *Chem. Zentr.*, 1931, ii, 1169).— $K_2C_2O_4$ or Hg is the catalyst and H_2SO_4 free from H_3PO_4 is used in the Kjeldahl method. The resulting liquid is made neutral to phenolphthalein with NaOH and aliquot parts are treated with excess of neutral 20% CH_2O solution. The acid liberated by the formation of $(CH_2)_6N_4$ from the NH_3 salts and CH_2O is titrated with 0.1N-NaOH. The no. of c.c. of 0.1N-NaOH used is multiplied by 0.001446. The Hg catalyst, if used, is removed by $Na_2S_2O_3$.

L. S. THEOBALD.

Micro-determination of phosphoric acid with strychnine molybdate. E. RAUTERBERG (*Mikrochem.*, 1932, 10, 467—482).—Available methods are reviewed and an account is given of the photometric measurement of the turbulence produced. The reagent is prepared by dissolving 7.5 g. of MoO_3 in 60 c.c. of H_2SO_4 (d 1.785), cooling, and pouring into 900 c.c. of a solution containing 2 g. of strychnine sulphate. After boiling for 15 min. and cooling, the solution is diluted to 1000 c.c., and after a few days it is filtered. The reagent may be used for determining $2.5—40 \times 10^{-6}$ g. of P_2O_5 in 15—20 c.c. of solution.

H. F. GILLBE.

Determination of boric acid. II. Determination of boric acid in natural and artificial silicates. E. SCHULEK and G. VASTAGH (*Z. anal. Chem.*, 1932, 87, 165—172).—In applying the distillation method for the determination of boric acid (*A.*, 1931, 812) to silicates, a much greater amount than usual of the mixture of MeOH and H_2SO_4 must be added to the mixture to be distilled, and the concn. of H_2O must be kept within certain limits. Under these conditions SiO_2 does not begin to separate until near the end of the distillation, and then appears largely

as a powder; errors due to adsorption of boric acid by gelatinous SiO_2 are thus avoided. With many silicates, particularly those containing Fe, the distillation must be repeated. Methods of procedure for both the macro- and the micro-determination are described.

R. CUTHILL.

Colorimetric determination of silica, especially in water. A. JOLLES (*Angew. Chem.*, 1932, 45, 150).—A claim for priority (cf. this vol., 34).

H. F. GILLBE.

Colorimetric determination of silica, especially in water. O. LIEBKNECHT (*Angew. Chem.*, 1932, 45, 150).—A reply to Jolles (cf. preceding abstract).

H. F. GILLBE.

Rapid determination of carbon monoxide. P. BORINSKI and H. MÜRSCHHAUSER (*Chem. Fabr.*, 1932, 41—42).—The apparatus described is fitted with an electrically-driven pump which forces the air to be analysed through an electrically heated tube containing I_2O_5 and then through a solution containing starch and a known quantity of $Na_2S_2O_3$. When the solution becomes blue the no. of strokes made by the pump is noted, and from this and the vol. of the pump cylinder is calc. the vol. of air which has passed through the apparatus. Results are accurate with air containing up to about 0.2% of CO, and with higher concns. the accuracy is sufficient for most purposes. The apparatus is portable, and determinations take but little time and may be carried out by persons without special training.

H. F. GILLBE.

Determination of traces of carbon dioxide. J. LINDNER and N. FIGALA (*Mikrochem.*, 1932, 10, 440—445).—Errors arise when using the method previously described (*A.*, 1930, 1543) owing to occlusion of OH' by the $BaCO_3$ ppt. In the modified method described the solution is heated for 10 min., after a preliminary end-point (phenolphthalein) has been obtained, and is then re-titrated. An apparatus for producing known quantities of CO_2 from Na_2CO_3 is described.

H. F. GILLBE.

Detection of traces of metals by physical development. G. KOEGL (*Mikrochem.*, 1932, 10, 452—455).—Paper coated with gelatin is treated with aq. NH_3 or dil. HCl, brought into contact with the metal, and immersed in 1% $AgNO_3$ solution for a few secs. The Ag which is thus liberated forms the nucleus for a further quantity liberated by development. The developer used is made by dissolving 4 g. of metal in 100 c.c. of 50% AcOH and diluting to 1500 c.c. Images may be produced also by reduction in a similar manner of $Cu_3[Fe(CN)_6]_2$, $FeFe(CN)_6$, $Pb_3[Fe(CN)_6]_2$, and $(UO_2)_3[Fe(CN)_6]_2$; suitable solutions are mentioned.

H. F. GILLBE.

Systematic detection of cations. G. VORTMANN (*Z. anal. Chem.*, 1932, 87, 190—196).—The material for analysis is fused with Na_2CO_3 and S, and the product treated with H_2O . The insol. material is boiled with NH_4Cl to dissolve Ca, Sr, and Mg, and then roasted to convert the sulphides into oxides. By fusion with $K_2S_2O_8$ followed by extraction with H_2O , Cu, Ag, Cd, Tl, Fe, Mn, Zn, Co, Ni, U, and Cr are brought into solution, whilst $BaSO_4$ and Pt re-

main in the residue. The aq. extract from the original melt may contain Al, Be, As, Sb, Sn, Mo, W, V, Se, Te, and Au; it is warmed with NH_4Cl and aq. NH_3 to ppt. Al and Be, and the sulphides pptd. on addition of acid are roasted and subjected to treatment with $\text{K}_2\text{S}_2\text{O}_8$ to separate As, Mo, and V (sol.) from W, Sb, and Sn. The detection of the individual metals after carrying out the above separation is largely by means of dry reactions. Iodide sublimes for the purpose of identifying metals of the H_2S group are obtained most readily by heating the substance for examination with KI in the microcosmic salt bead under a cool surface.

R. CUTHILL.

Quantitative analysis of alloys by means of X-ray spectroscopy. C. E. EDDY and T. H. LABY (J. Physical Chem., 1931, 35, 3635—3638; cf. A., 1931, 702).—Defects in technique, by the elimination of which trustworthy results can be obtained, are discussed. Data for alloys of elements of nearly equal at. no. are reproduced.

CHEMICAL ABSTRACTS (c).

Reactions of several metallic ions in the presence of organic acids. S. HAKOMORI (Sci. Rep. Tohoku, 1931, 20, 736—763).—The reactions of Mo, Ti, V, Fe^{2+} , Fe^{3+} , Cr, Al, Cu, Ni, Co, UO_2^{2+} , Be, Pb, Zr, and Mn with NaOH in the presence of oxalic, succinic, malic, and citric acids have been investigated by conductivity measurements and by spectrographic, ultramicroscopic, and colorimetric observations. The results in many cases confirmed the formation of complex compounds. The yellow colour produced in MoO_3 solutions by H_2O_2 is intensified by addition of citric, tartaric, or succinic acid.

A. R. POWELL.

Tests for element 87 (virginium) by the use of Allison's magneto-optic apparatus. J. L. McGEE and M. LAWRENZ (J. Amer. Chem. Soc., 1932, 54, 405—406; cf. A., 1931, 1348).—HCl solutions of samarskite, pollucite, and lepidolite and crude CsCl , all of which contain element 87, and solutions of SnCl_4 and ReCl_2 , were examined. There are no corresponding minima for Re and Sn in sulphate solutions of these minerals. None of the minima attributed to ViCl was found in the solutions of SnCl_4 or ReCl_2 .

C. J. WEST (c).

Peculiar adsorption and peptisation reaction of calcium oxalate. Colour detection of calcium in the presence of strontium. F. L. HAHN (Ber., 1932, 65, [B], 207—209).—In the presence of an alkaline solution of 1:2:5:8-tetrahydroxyanthraquinone, CaO or CaCO_3 becomes at most pale pink, but blue to bluish-black if $\text{C}_2\text{O}_4^{2-}$ is added. Preformed and even coarsely cryst. CaC_2O_4 becomes cornflower-blue and partly peptised, since the supernatant liquid is dark blue. CaCO_3 , CaSO_4 , $\text{Ca}_2\text{FeC}_2\text{N}_6$, SrC_2O_4 , and BaC_2O_4 do not give a similar reaction. Since the reaction involves the pptn. of CaC_2O_4 , it is not more sensitive than this reaction, but is more distinctive and particularly useful for the detection of Ca in presence of much Sr.

H. WREN.

Micro-analysis of glasses. IV. W. GEILMANN. —Sec B., 1932, 228.

Determination of radium in alkaline-earth sulphates. A. KARL (Compt. rend., 1932, 194,

613—614).—An equimol. mixture of NaCl, KCl, and LiCl, m. p. 485° , dissolves 36% of BaSO_4 , giving a product of m. p. 495° , quite limpid and emitting no vapours at 520 — 530° . The material containing Ra as RaSO_4 is fused ($\approx 36\%$ of the whole) in such a mixture in pyrex glass, and the emanation determined by passing a current of air through the molten solution.

C. A. SILBERRAD.

Error in ferrocyanide titration of zinc. B. PARK (J. Amer. Chem. Soc., 1932, 54, 180—181).—A standard solution of $\text{K}_4\text{Fe}(\text{CN})_6$ often contains a little ferrieyanide, which, if H_2S is present in the solution to be titrated, will be reduced, thus increasing the pptg. power of the solution towards Zn.

W. T. HALL (c).

Acidimetric determination of lead salts. F. VIEBOCK and C. BRECHER (Arch. Pharm., 1932, 270, 109—114).—Two volumetric methods of determining Pb are described.

R. S. CAHN.

Determination of mercuric oxide and "mercuric ammonium chloride." E. J. SCHORN and R. M. McCONE (Pharm. J., 1932, 128, 187—188).—Dissolution of HgO in aq. $\text{Na}_2\text{S}_2\text{O}_3$ instead of aq. KI gives a clearer end-point on titration with 0.1N-HCl. NH_2HgCl is more readily sol. in aq. KI than in aq. $\text{Na}_2\text{S}_2\text{O}_3$. Me-red is recommended as an indicator.

T. McLACHLAN.

Reduction of mercuric salts by hypophosphorous acid. JEAN (Bull. Soc. Pharm., Bordeaux, 1930, 68, 239—243; Chem. Zentr., 1931, ii, 1168).— Hg^{2+} salts are quantitatively reduced to Hg by H_3PO_2 . Reduction with NaH_2PO_4 is quant. only when sufficient HCl is present to liberate the requisite amount of H_3PO_2 .

L. S. THEOBALD.

Sensitisation of the mercury iodide reaction for the detection of mercuric ions. G. DENIGES (Bull. Soc. Pharm. Bordeaux, 1930, 68, 207—209; Chem. Zentr., 1931, ii, 1168).—Since the ppt. of HgI_2 is sol. in excess of KI, a solution of $\text{HgI}_2 \cdot 2\text{KI}$ is used to replace KI in testing for Hg^{2+} ions. This reagent is added to the Hg^{2+} salt solution until a permanent red ppt., insol. in excess, is obtained. The reaction is $\text{HgI}_2 \cdot 2\text{KI} + \text{HgCl}_2 = 2\text{HgI}_2 + 2\text{KCl}$.

L. S. THEOBALD.

Volumetric determination of the mercuric ion. J. BARCELÓ (Anal. Fis. Quím., 1932, 30, 71—75).—The Hg^{2+} is pptd. with a solution prepared by dissolving 4 g. of benzidine in 20 c.c. of warm 50% AcOH, pouring gradually into 1 litre of H_2O at 70° , and filtering after 24 hr. The pptd. complex is dissolved in dil. HCl, the benzidine is pptd. as sulphate by adding Na_2SO_4 solution, and the ppt. is titrated with 0.1N- Na_2CO_3 and phenolphthalein; 1 c.c. of 0.1N- Na_2CO_3 corresponds with 0.01002 g. of Hg. The error rarely exceeds 0.4%.

H. F. GILLBE.

Spectral analysis by sensitive lines within the range of the glass spectrograph. II. W. KRAEMER (Z. Elektrochem., 1932, 38, 51—53; cf. this vol., 35).—By the examination of W carbides containing rare earths and Mo, alloys of Ag, Au, and Ni, resistance wire of unknown composition, and brass, sensitive lines for the following elements and for one radical have been determined, using as control the A

lines obtained in an air Geissler tube: Hg, Mg, Pb, Si, Hf, Ce, Th, Sm, Y, La, Dy, Nd, Pr, Tb, Er, Gd, Au, Ag, Mo, Zn, Cd, Mn, Ni, Co, As, Ca, Al, Fe, Cu, Ti, Zr, S, P, I, CN, H₂.
M. S. BURR.

Determination of aluminium. Formation of lithium aluminate. J. T. DOBBINS and J. P. SANDERS (J. Amer. Chem. Soc., 1932, 54, 178—180).—To the solution containing about 0.1 g. Al in 100 c.c. are added a slight excess of 10% LiCl solution, and sufficient dil. aq. NH₃ to make slightly alkaline to phenolphthalein in the cold. After ignition, the ppt. has the formula Li₄Al₁₀O₁₇. W. T. HALL (c).

Volumetric determination of aluminium. F. VIEROCK and C. BRECHER (Arch. Pharm., 1932, 270, 114—124).—The Al solution is treated with Na NH₄ tartrate and BaCl₂ and forms a sol. complex Ba Al tartrate, which is neutral to phenolphthalein. Addition of KF liberates KOH equiv. to the Al present. This decomp. is not immediate, but requires several min.; excess of Ba⁺⁺ is inhibitive and should be removed by K₂SO₄. The liberated KOH is treated with excess of 0.1N-H₂SO₄ and the excess is titrated back with 0.1N-KOH. Special notes are given on the analysis of certain pharmaceutical preps. containing Al.

E. S. HEDGES.

Use of X-rays in quantitative analysis. V. CAGLIOTI and P. AGOSTINI (Atti R. Accad. Lincei, 1931, [vi], 14, 301—305).—The ratios of the intensities of the Cu K α and K β lines are measured before and after passing the X-ray beam through the sample to be analysed. The method has been tested for mixtures of Al₂O₃ containing up to 4% NiO. The ratio of the intensities of the two lines is proportional to the % NiO in the mixture. O. J. WALKER.

Determination of zirconium in rocks. H. F. HARWOOD (Tidsskr. Kjem. Berg., 1932, 12, 23).—The rock powder is decomposed by repeated evaporation with HClO₄ and HF. The unattacked residue (which contains practically the whole of the zircon) is collected and fused with Na₂CO₃. The melt is extracted with H₂O, the solution filtered, the residue fused with Na₂S₂O₇, and the melt taken up with dil. H₂SO₄. The Zr in this solution is then pptd. as usual with Na₂HPO₄ after addition of H₂O₂. The original HClO₄ solution is also tested for Zr with Na₂HPO₄ and H₂O₂, any ppt. formed being added to the previous one. H. F. HARWOOD.

Quantitative separation of germanium and arsenic. H. J. ABRAHAMS and J. H. MULLER (J. Amer. Chem. Soc., 1932, 54, 86—94).—From a solution less than 0.09N in respect of HCl or H₂SO₄, As^{III} can be pptd. completely as As₂S₃, but no GeS₂ separates until the acidity is increased. In mineral analysis, therefore, it is advisable to remove AsCl₃ and GeCl₄ by distillation, and then ppt. As₂S₃ from dil. acid solution containing NH₄ salt and ppt. GeS₂ in the filtrate after increasing the acidity. The mineral germanite probably has the composition 7CuS.FeS.GeS₂. W. T. HALL (c).

Volumetric determination of vanadium and molybdenum (reducing activity of metallic copper). G. SCAGLIARINI and P. PRATESI (Atti R. Accad. Lincei, 1931, [vi], 14, 298—300; cf. A.,

1929, 532).—In presence of H₂SO₄ at the b. p. of the solution vanadates and molybdates are rapidly reduced by Cu to V^{III} and Mo^V, respectively, and the solution is then titrated with KMnO₄ as for Fe and U.

O. J. WALKER.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXI. Quantitative separation of titanium from tantalum and niobium. W. R. SCHÖELLER and C. JAHN (Analyst, 1932, 57, 72—78; cf. A., 1928, 1047; 1929, 902, 1160).—The oxalate-salicylate method for the separation of Ti from the earth acids has been perfected, and the H sulphate-tannin method is employed for the recovery of the last traces of earth acids from the bulk of the Ti. An almost quant. separation is achieved, less than 1 mg. of TiO₂ being left in the earth acids; this may be allowed to counteract unavoidable loss. Results are accurate to within 0.5%. The basis of the separation is due to the fact that the earth acids do not, whilst Ti does, form sol. salicylic acid complexes, and that the earth acids do not, whilst Ti does, form sol. sulphates, nitrates, and chlorides. Earlier attempts were unsuccessful owing to the formation of hydrolysis ppts.; this is overcome by the addition of tannin. T. McLACHLAN.

Cathode-ray tube in X-ray spectroscopic analysis of niobium and tantalum. G. R. FONDA (J. Amer. Chem. Soc., 1932, 54, 115—122).—A procedure for the determination of Nb and Ta by the cathode-ray method is described. There is an abs. error of about 2%, independent of the quantity of material analysed. R. H. LAMBERT (c).

Determination and separation of rare metals from other metals. XX. Determination of iridium and separation from platinum and other metals. L. MOSER and H. HACKHOFER. XXI. Determination of rhodium and its separation from platinum and other metals. L. MOSER and H. GRABER (Monatsh., 1932, 59, 44—60, 61—72).—XX. Ir is obtained as sol. Na₂IrCl₆ by heating with an equal wt. of NaCl in a stream of Cl₂ at 400°. It may be separated from Pt in aq. HCl by neutralising with Na₂CO₃, treating the boiling solution with NaBrO₃ and NaBr, and reducing the pptd. IrO₂.xH₂O in a stream of H₂. The metallic Ir is then weighed. The Pt solution is treated with HNO₃ to remove Br, decomposed with NH₄OAc, and the Pt reduced with N₂H₄.2HCl and weighed. A similar method is used in the separation from Au. In the separation from Pd a large proportion of Pd is carried down by the IrO₂ ppt., owing to the induced pptn. observed with metals of the Pt group, and must be subsequently removed from metallic Ir by repeated treatment with aqua regia, which dissolves Pd but not Ir. Pd is determined by a method similar to that used for Pt. Cu is also pptd. with the Ir, but may be readily removed by treating the metallic mixture with aq. HNO₃. Cu is subsequently determined electrolytically. Ir is separated from Fe by treating the slightly acid solution of Na₂IrCl₆ and FeCl₃ with an excess of hot H₂C₂O₄ until sol. complexes are formed. H₂S is passed through and excess of aq. NH₃ added. FeS is pptd. and weighed after calcining in a stream of H₂ and H₂S. The Ir

solution is evaporated and the resulting Ir_2S_3 reduced in H_2 and weighed. The solubility of IrO_2 in H_2O is 0.1×10^{-4} mol. per litre and in $0.002N\text{-HCl}$, 0.2×10^{-5} mol. per litre.

XXI. The separation of Rh from Pt is difficult but necessary, since small quantities of Rh make Pt brittle when heated. Rh is separated from both Pt and Au by the $\text{NaBrO}_3\text{-NaBr}$ method. Separation from Cu is effected by treating the solution with H_2SO_4 until the acidity is $0.1N$, adding $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ until the concn. is $0.1M$, and then passing H_2S into the hot solution. The sulphides are collected, washed with aq. H_2S , calcined to form the oxides, and reduced in a current of H_2 . The Cu may then be removed with HNO_3 and determined electrolytically. The metallic Rh may be weighed after further washing and heating in H_2 . To separate from Fe use is made of the fact that Rh may be pptd. quantitatively as sulphide in solutions of acidity up to $N/7$ HCl . The Fe^{3+} in solution is oxidised and pptd. with aq. NH_3 . To separate Rh from Pb the solution is heated with H_2SO_4 until SO_3 vapour is evolved. After cooling, diluting, and keeping for several hrs., it is filtered through a Gooch crucible, Pb pptd. by $2N\text{-H}_2\text{SO}_4$, collected, and weighed. The Rh solution is evaporated almost to dryness, and the Rh pptd. as sulphide and weighed as metal.

M. S. BURR.

Sensitive flexible thermostat. J. R. ROEBUCK (Rev. Sci. Instr., 1932, [ii], 3, 93—100).—Full details are given for the construction and operation of a thermostat which remains const. to $<0.01^\circ$ between -190° and 300° .

C. W. GIBBY.

Automatic temperature regulators. J. FUCHS (Chem. Fabr., 1932, 49—52).—A description of recent types of apparatus.

E. S. HEDGES.

Air thermoregulator. J. B. M. COPPOCK, J. COLVIN, and J. HUME (Chem. and Ind., 1932, 140).—The pressure of air in a bulb placed in the furnace is balanced by a column of Hg in a vertical tube surrounded by more Hg in an annular column. The space above both the columns is evacuated and shut off from the atm. by a tap, and contact between the two is made by a Pt wire when the inner one rises. Changes in atm. temp. are compensated for by the annular column, and the action is independent of changes in the barometric pressure.

C. W. GIBBY.

Oscillator for the crystal of an X-ray spectrograph. G. W. FOX (Rev. Sci. Instr., 1932, [ii], 3, 71—72).—The platform of the crystal holder is rotated by a worm gear, and itself reverses the direction of rotation of the worm by operating a fast-and-loose pulley mechanism.

C. W. GIBBY.

Formula for the evaluation of colorimetric measurements. M. WINKLER (Chem.-Ztg., 1932, 56, 86—87).—Calculations made according to Beer's law give high results in dil., and low results in more conc., solutions. Correct results are obtained with the formula $(c_1 + k)d_1 = (c_2 + k)d_2$, where k is the apparent colour of the solvent and is determined by colorimetric measurement of two solutions of known but different concn.

A. R. POWELL.

Interference optical lever for pressure gauges, galvanometers, etc. W. E. ROSEVEARE (J. Amer. Chem. Soc., 1932, 54, 202—205).—A simple optical system is described by means of which it is possible to measure deflexions of a 3-metre optical lever with an average error of about 0.003 mm. The principle was used in the construction of an all-glass optical lever pressure gauge capable of measuring small pressure changes with errors of as little as 0.0002 mm.

H. F. JOHNSTONE (c).

Radiation thermopiles. J. STRONG (Rev. Sci. Instr., 1932, [ii], 3, 65—70).—A design of thermopile giving max. sensitivity with two junctions is described. They may be welded in position by a condenser discharge, eliminating delicate manipulation. Soldering of Bi-Sn and Bi-Sn alloy wires is facilitated if they are protected from tarnishing by storage in C_6H_6 . In welding receivers to thermocouple wires by a condenser discharge the receiver must not be so thick that the thermocouple wires are heated sufficiently to destroy their temper. By vac. distillation of Ag on to Cu, films which can easily be removed are formed.

C. W. GIBBY.

Vacuum thermocouples. J. JAFFRAY (Compt. rend., 1932, 194, 451—452; cf. this vol., 36).—The figures for K and n for the old and new models are respectively for 15° and 22° . If the temp. of the galvanometer is const. while that of the thermocouple rises, e.g., from 0 to 40° , Δ decreases linearly. When the two instruments are at different temp. only K varies, n being almost independent of temp.

C. A. SILBERRAD.

Tellurium-bismuth vacuum radiation thermocouple. C. H. CARTWRIGHT (Rev. Sci. Instr., 1932, [ii], 3, 73—79).—The technique required for the prep. of thermocouples with Te wires welded to Au leaf receivers is described. They are three times as sensitive as those made with Bi alloy wires.

C. W. GIBBY.

Simple automatic cryostat. F. FENÉ (Z. Elektrochem., 1932, 38, 53—54).—A more satisfactory arrangement for regulating pressure has been substituted in a cryostat previously described (A., 1927, 335; 1928, 1348). The method of application for the difficult temp. range $10\text{--}30^\circ$ is given.

M. S. BURR.

Micro-extraction apparatus. H. HETTERICH (Mikrochem., 1932, 10, 379—383).—The apparatus described is especially suitable for the extraction of, e.g., paint films. It consists essentially of a filter-plate, which carries the material to be extracted, supported on a perforated plate resting on a ridge formed in the extraction vessel. The lower end of the vessel is of smaller diam. than the upper part and fits into a stand which is placed on the water-bath. Extraction with CHCl_3 of samples of paints obtained from an Egyptian wall painting (3000 B.C.) showed the binder to be beeswax, and the pigments basic Cu carbonate, Ca Cu silicate, and Fe_2O_3 .

H. F. GILLBE.

Continuous extraction of precipitates. M. A. SIMMONDS (Chem. Eng. Min. Rev., 1932, 24, 132).—An apparatus for the repeated washing of ppts. with the same small quantity of washing liquid is described.

N. H. HARTSHORNE.

Apparatus for taking water samples from different levels. J. A. REYNIERS (*Science*, 1932, 75, 83—84).
L. S. THEOBALD.

Simple apparatus for mercury distillation. M. KLEIBER (*Science*, 1932, 75, 196).
L. S. THEOBALD.

Air dryer for analytical balances. E. LOWENSTEIN (*Chem.-Ztg.*, 1932, 56, 127).— SiO_2 gel, of 2–6 mm. particle size, is more satisfactory than CaCl_2 or H_2SO_4 . It will absorb up to 23% of its own wt. of H_2O , without change of form, and may be regenerated by heating at 130–150°.

H. F. GILLBE.

High-vacuum distillation with the help of liquid air. L. ANSCHUTZ (*J. pr. Chem.*, 1932, [ii], 133, 81–83; cf. A., 1926, 1118).—Lewin's apparatus (A., 1930, 884) is criticised.

H. BURTON.

Application of organic substances in high-vacuum practice, especially in the working of high-vacuum pumps. M. VON BRANDENSTEIN and H. KLUMB (*Physikal. Z.*, 1932, 33, 88–93).—Using org. substances, such as Bu^n_2 phthalate, in simple air-cooled diffusion pumps, it is possible, with liquid air, to attain vac. of the order 10^{-3} dyne per sq. cm.

A. J. MEE.

Vacuum technique for the chemist. K. HICKMAN (*J. Franklin Inst.*, 1932, 213, 119–154).—Degrees of vac., apparatus for vac. distillation, and low-pressure gauges are described and discussed.

N. M. BLIGH.

New types of micro-balance. L. FUCHS (*Mikrochem.*, 1932, 10, 456–459).—A criticism of various types; that of Welharticky and Pachmann is preferred to the Kuhlmann balance, as the latter tends to "stick" somewhat frequently and needs constant cleaning.

H. F. GILLBE.

Preparative microchemistry. J. WINCKELMANN (*Mikrochem.*, 1932, 10, 437–439).—Compounds prepared on a cover slip coated with hardened gelatin may be washed etc. without difficulty. Drop reactions also may be carried out on coated cover slips, and the specimen may be allowed to dry and be preserved by mounting in Canada balsam. Methods of preserving preps. under collodion, and of applying the formation of Liesegang rings to the prep. of permanent specimens, are described. H. F. GILLBE.

Apparatus for exact gas analysis using samples of about 5 c.c. E. OTT and A. SCHMIDT.—See B., 1932, 211.

Portable apparatus for gas analysis especially in mines. A. SCHMIDT.—See B., 1932, 211.

Safety device for pipettes. VON HUTTER (*Gas- u. Wasserschiff*, 1932, 75, 91–92).—A small glass cylinder is interposed between the operator's mouth and the pipette, being attached to the latter by a rubber connexion. Within the cylinder is a pear-shaped glass float which rests on projections on the cylinder walls. If the liquid enters the cylinder it rises and closes the upper orifice.

C. IRWIN.

Regulation of vacuum filtration. ANON. (*Food Tech.*, 1932, 1, 233).—A non-return valve, of the Bunsen type or of glass, prevents sucking back in vac. filtration; a release tap is also useful.

E. B. HUGHES.

Magnesia apparatus for qualitative chemical analysis. E. WEDEKIND (*Chem.-Ztg.*, 1932, 56, 107).— MgO rods made by the Steatit-Magnesia A.-G. are suitable for flame tests, borax bead tests, and the fusion tests for Cr and Mn, and may be used in place of Pt for these purposes.

A. R. POWELL.

Sensitive flames. G. B. BROWN (*Phil. Mag.*, 1932, [vii], 13, 161–195).—The conditions for producing flames sensitive to sound waves and the causes of the phenomenon have been investigated.

H. J. EMELÉUS.

Action of a transverse electrostatic field on a propane flame. J. K. MCNEELY, A. O. BROWN, and C. D. CROSO (*Iowa State Coll. J. Sci.*, 1931, 5, 269–283).—Flames are repelled from the positive plate. The colour changes as the voltage is increased from 4600 to 28,000 volts. Two types of ions are formed; one may be positive and the other positive or negative.

CHEMICAL ABSTRACTS.

Improving the visibility of lecture experiments. H. VON WARTENBERG (*Angew. Chem.*, 1932, 45, 209–210).—Burettes, nitrometers, etc. are illuminated from the rear by lamps placed behind a paper screen.

H. F. GILLBE.

Geochemistry.

Distribution of ozone in the earth's atmosphere. D. CHALONGE (*J. Phys. Radium*, 1932, [vii], 3, 21–42).—The inadequacy of available data and methods is discussed. A study of the radiation of the clear sky indicates that O_3 exists in diffuse layers in the atm., and a new theory is developed showing that it must exist from a height of 20–80 km. in quantities increasing with altitude.

N. M. BLIGH.

Variation of tension of fulminating matter as a function of temperature and mol. wt. E. MATHIAS (*Compt. rend.*, 1932, 194, 413–416).

C. A. SILBERRAD.

Mineralisation of the spring waters of the southern and eastern slopes of Mt. Alaghez. V. K. VOSKRESSENSKI (*Bull. Inst. rec. biol. Perm.*, 1931, 4, 407–425).—The carbonate hardness of spring water increased in the summer of 1928 with distance from the summit of the mountain. This increase was, however, not continuous, pointing to the possibility of intermittently acting demineralising factors.

R. TRUSZKOWSKI.

Lead and helium in oceanic alkali halides. O. HAHN (*Naturwiss.*, 1932, 20, 86–87).— NaCl and KCl of oceanic origin may contain some PbCl_2 , the

Pb probably arising as end-product in the disintegration of dissolved radioactive salts. The possibility of finding He is also discussed.

W. R. ANGUS.

Determination of dissolved oxygen content of the mud at the bottom of a pond. A. E. COLE (Ecology, 1932, 13, 51—53).—Sampling apparatus is described in which the H_2O sample filters through an alundum cap into a glass tube in which contact with air is excluded by means of a paraffin layer.

A. G. POLLARD.

Radioactivity and its significance in problems of geochemistry. O. HAHN (Sitzungsber. preuss. Akad. Wiss., Phys.-Math. Kl., 1932, II, 15 pp.).—A discussion of published work, mainly on the inclusion of Pb in the mixed-crystal form in rock-salt and sylvine, and the production of He in these salts and in carnallite. U and Th do not enter the space lattices of the minerals with which they are associated.

E. S. HEDGES.

Siderolite from Bencubbin, Western Australia. E. S. SIMPSON and D. G. MURRAY (Min. Mag., 1932, 23, 33—37).—The mass (54 kg.) found in 1930 consists of a skeleton of Ni-Fe (68.8%) with enclosed crystals up to 1 cm. across of greyish-white enstatite (13.5%) and dark olivine (12.5%). Detailed analyses are given of the metallic portion (Fe:Ni=15:1:1) and of the stony portion (MgO:FeO=8.5:1). The meteorite is classed as a mesosiderite with an unusually high percentage of Ni-Fe.

L. J. SPENCER.

Pallasite from Alice Springs, Central Australia. L. J. SPENCER [with M. H. HEY] (Min. Mag., 1932, 23, 38—42).—A fragment (1084 g.) found in 1924 in the desert near Alice Springs on the north side of the MacDonnell Ranges is a typical pallasite consisting of 40% olivine (with FeO:MgO=4.6:1) and 60% nickel-iron (with Fe:Ni=12.7:1). Small angular fragments of olivine are embedded in the kamacite, suggesting that the olivine had been broken up before kamacite crystallised out. The granular texture of the metal also suggests that the kamacite had been broken up with the development of Neumann lines before the separation of the taenite and plessite, and that the fragments had been partly redissolved in the residual melt, giving the reaction-rim of taenite. Finally, the plessite eutectic separated out in the interspaces.

L. J. SPENCER.

Hoba (South-West Africa), the largest known meteorite. L. J. SPENCER [with M. H. HEY] (Min. Mag., 1932, 23, 1—18).—A mass of metal measuring 10×9 ft. on the surface and estimated to weigh 60 metric tons was found in 1920 embedded in surface limestone on Hoba West farm near Grootfontein. It is surrounded by a zone 1 ft. thick of laminated "iron-shale" formed by the oxidation of the metal. Analysis gave Fe 83.44, Ni 16.24, Co 0.76, Cu 0.03, S, P traces, C 0.02=100.49%; d 7.96. This meteorite is a Ni-rich ataxite showing under a high magnification a very minute duplex structure similar to that of plessite. The magnetic "iron-shale" contains Fe_2O_3 58.14, FeO 13.25, NiO 16.13, CoO 0.39, H_2O 11.83=99.74%, corresponding with 51.84% of trevorite ($NiFe_2O_4$). A list is given of ten other known large meteoric irons ranging in weight from 33.1 to 3.4

metric tons. The largest known meteoric stone of 820 lb. was seen to fall on Feb. 17, 1930, at Paragould, Arkansas.

L. J. SPENCER.

Meteorite stone from Suwahib, Arabia. W. C. SMITH [with M. H. HEY] (Min. Mag., 1932, 23, 43—50).—A fragment (241 g.) found in 1931 in the Rub' al Khali desert, S.E. Arabia, has a glazed surface of limonite; d 3.52. Micro-sections show chondrules of enstatite and olivine with some glass and feldspar and specks of nickel-iron and troilite. The meteorite is classed as a black spherical chondrite of the Cronstadt type. Insufficient material being available for a magnetic separation, a new method of analysis is described by M. H. HEY, in which the powder is heated at 250—300° in a current of dry Cl_2 ; the metallic portion is thereby attacked, but not the silicates. The analysis gave Fe 17.54, Ni 0.96, Co 0.12, S 1.98, SiO_2 38.48, TiO_2 0.20, Al_2O_3 4.42, FeO 10.16, MnO 0.28, CaO 1.90, MgO 21.25, Na_2O 1.33, K_2O 0.25=98.97%.

L. S. SPENCER.

Diatomaceous earth. II. Nature and amount of extraneous matter in diatomites. W. HUGILL (Trans. Ceram. Soc., 1932, 31, 75—78; cf. B., 1931, 657).—The origin, amount, and determination of the various kinds of impurities are discussed.

J. A. SUGDEN.

Structure of precious opal. E. BAIER (Z. Krist., 1932, 81, 183—218).—Precious opal consists of separate grains embedded somewhat as quartz in sandstone, and having a lamellar structure with microscopic twinning. The distances between lamellae are of the order 200—500 m μ . It seems probable that the structure is due to the presence of calcite in the original SiO_2 gel, which has since disappeared.

C. A. SILBERRAD.

Structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopical and X-ray diffraction examinations. S. B. HENDRICKS, W. L. HILL, K. D. JACOB, and M. E. JEFFERSON (Ind. Eng. Chem., 1931, 23, 1413—1418).—X-Ray diffraction photographs of fluorapatite ($9CaO, 3P_2O_5, CaF_2$), chlorapatite, hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_6$], oxyapatite, and $Ca_3(PO_4)_2$ were made, using pure crystals or synthetically prepared compounds. Similar photographs of natural phosphates showed that animal bone is a carbonate apatite [$Ca_{10}CO_3(PO_4)_6, H_2O$] (taking chemical analysis into consideration). On fossilisation the CO_3 and H_2O are replaced by F. American phosphate rocks are chiefly fluorapatite often containing some excess F. Gypsum, quartz, etc. are present as impurities. Na in small amount apparently replaces Ca. Al_2O_3 is perhaps due to the presence of clay minerals. Nauru, Christmas and Ocean Island phosphates have the composition $Ca_{10}(OH,F)_2(PO_4)_6$, about half the OH being replaced by F. Curaçao phosphate was much lower in F content, and, unlike other samples, on ignition at 900° yielded $Ca_3(PO_4)_2$.

C. IRWIN.

Granites of Finland. E. L. BRUCE (Trans. Roy. Soc. Canada, 1931, [iii], 25, IV, 269—284).—A general geological study.

N. H. HARTSHORNE.

Granite contact action in Eastern Ontario. H. C. HORWOOD (Trans. Roy. Soc. Canada, 1931,

[iii], 25, IV, 227—242).—A description and discussion of the variations in composition occurring at granite-gneiss and granite-limestone contacts. The variations are similar at both contacts, except for a $\text{CaO-K}_2\text{O}$ exchange at the latter, and the granite loses most of its basic oxides. N. H. HARTSHORNE.

Upper cretaceous volcanic ash beds in Alberta. J. O. G. SANDERSON (Trans. Roy. Soc. Canada, 1931, [iii], 25, IV, 61—70).—Mainly geological. Analyses of Edmonton tuffs are recorded. N. H. HARTSHORNE.

Oolites [of Lorraine]. J. P. AREND (Compt. rend., 1932, 194, 736—738).—By the putrefaction of a mass of animal matter mixed with ferruginous sediments and buried in schists and calcareous deposits, a colloidal solid suspension is formed consisting of carbonates and H carbonates of Fe^{II} and Ca, colloidal Al_2O_3 and SiO_2 , and phosphates, and holding in suspension quartz grains, clay, and numerous remains of zoölites. This magma is stable until reached by O, when $\text{Fe}(\text{OH})_3$ is formed: $2\text{FeH}_2(\text{CO}_3)_2 + \text{CaH}_2(\text{CO}_3)_2 + \text{O} = 2\text{Fe}(\text{OH})_3 + \text{CaCO}_3 + 5\text{CO}_2$. The phosphate acts as coagulant, as is shown by shaking in air a solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ with varying amounts of $\text{Ca}_3(\text{PO}_4)_2$ and/or NaHCO_3 . Flocculation of $\text{Fe}(\text{OH})_3$ will begin where phosphate is most conc., but once begun the $\text{Fe}(\text{OH})_3$ will deposit on any particle, usually microscopic. Each such particle forms the nucleus of an oolite grain, which then grows by accretion of $\text{Fe}(\text{OH})_3$ gel carrying with it the Fe and Ca compounds of the intermicellar liquid. This alternates with deposition of Fe phosphates and adsorption of colloidal Al_2O_3 and SiO_2 ; the SiO_2 then reacts with the phosphates, liberating the acid which re-forms $\text{Ca}_3(\text{PO}_4)_2$.

C. A. SILBERRAD.

Formation of coal. P. KRASSA (Angew. Chem., 1932, 45, 21—22).—A sample of "Palo podrido" (a product of the fungal decomp. of wood) from the virgin forests of S. Chile was found to contain 20.8% of anhyd. matter in which were present cellulose (84%), pentosans (3.3%), ash (0.26%), and 2% of reducing substances sol. in H_2O (this value was not altered by hydrolysis of the aq. extract with HCl). Photomicrographs indicate that this material possesses the structure of the cellulose of the original wood, and is formed by destruction of the lignin in preference to the cellulose. It is suggested that it might be an intermediate in the formation of the coal found in the same district. H. A. PIGGOTT.

Bacteria of coal. R. LIESKE (Ges. Abhandl. Kennt. Kohle, 1930, 9, 27—29; Chem. Zentr., 1931, ii, 1657).—Non-pathogenic bacteria which produce H_2 were found, but not those, described by Galle, which produce CH_4 . A. A. ELDRIDGE.

Occurrence of bacteria in bituminous coal. R. LIESKE (Ges. Abhandl. Kennt. Kohle, 1930, 9, 30—34; Chem. Zentr., 1931, ii, 1657).

Bacterial content of the earth at great depths. R. LIESKE and E. HOFMANN (Ges. Abhandl. Kennt. Kohle, 1930, 9, 21—27; Chem. Zentr., 1931, ii, 1657).—Experiments were made down to 1089 m. Gram-positive spore-forming bacteria, rods of the *B. subtilis* group, and cocci were found.

A. A. ELDRIDGE.

Classification of peat soils. A. P. DACHNOWSKI-STOKES (J. Wash. Acad. Sci., 1932, 22, 50—59).—A discussion. C. W. GIBBY.

Organic Chemistry.

Configurative relationship of hydrocarbons. IV. Optical rotations of hydrocarbons of the isoamyl series. Configurative relationship of substituted carboxylic acids containing an isobutyl and an isoamyl group to those of the corresponding normal carboxylic acids. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1932, 95, 1—24).—d- γ -Methylhexoic acid, b. p. 115°/16 mm., $[\alpha]_D^{20} +3.09$ ($+13.59^\circ$), prepared from α -chloro- γ -methylpentane, gives the Et ester (I), b. p. 80°/20 mm., $d_4^{20} 0.888$, $[\alpha]_D^{20} +2.38^\circ$, which may be reduced by Na in PhMe to d- δ -methylhexanol, b. p. 77°/20 mm., $d_4^{20} 0.818$, $[\alpha]_D^{20} +2.19^\circ$ ($+11.9^\circ$) (the figures in parentheses are the corresponding calc. max. for [M] assuming no racemisation to have occurred). The carbinol and PBr_3 yield α -bromo- δ -methylhexane, b. p. 78°/44 mm., $[\alpha]_D^{20} +2.61^\circ$ ($+21.9^\circ$), which is converted through the Grignard compound into d- γ -methylhexane, b. p. 92°/760 mm., $d_4^{20} 0.681$, $[\alpha]_D^{20} +1.64^\circ$ ($+9.67^\circ$). The action of MgMeI on (I) affords the carbinol which, when dehydrated with $\text{H}_2\text{C}_2\text{O}_4$ (cf. A., 1931, 709), gives the unsaturated hydrocarbon, reduced by H_2 in presence of Pt to β -methyl- ϵ -ethylhexane, $[\alpha]_D^{20} +2.75^\circ$, also obtained by the action of Pd and NaOH on the Br-compound prepared from the carbinol.

The following are similarly prepared: d- γ -methylheptoic acid, b. p. 132°/22 mm., $d_4^{20} 0.882$, $[\alpha]_D^{20} +2.11^\circ$ (Et ester, b. p. 104°/32 mm., $d_4^{20} 0.859$, $[\alpha]_D^{20} +1.41^\circ$); d- β -methyl- ϵ -n-propylhexane, b. p. 156°/760 mm., $d_4^{20} 0.725$, $[\alpha]_D^{20} +1.09^\circ$; l- γ -methyl-octoic acid, b. p. 149°/22 mm., $d_4^{20} 0.871$, $[\alpha]_D^{20} -1.34^\circ$ (Et ester, b. p. 112°/23 mm., $d_4^{20} 0.861$, $[\alpha]_D^{20} -0.64^\circ$); l- β -methyl- ϵ -n-butylhexane, b. p. 109°/100 mm., $d_4^{20} 0.738$, $[\alpha]_D^{20} -0.49^\circ$; l- γ -methylnonoic acid, b. p. 156°/22 mm., $d_4^{20} 0.871$, $[\alpha]_D^{20} -0.60^\circ$ (Et ester, b. p. 120°/22 mm., $d_4^{20} 0.862$, $[\alpha]_D^{20} -0.12^\circ$); l- β -methyl-n-amylohexane, b. p. 122°/100 mm., $d_4^{20} 0.739$, $[\alpha]_D^{20} -0.05^\circ$; l- β -methylheptoic, $[\alpha]_D^{20} -4.21^\circ$, and l- β -methyl-octoic acid, $[\alpha]_D^{20} -5.14^\circ$ (resolved through the quinine salts in COMe_2 at -15°); l- δ -methylnonane, b. p. 76°/30 mm., $d_4^{20} 0.726$, $[\alpha]_D^{20} -1.56^\circ$ (-2.47°); d- $\beta\delta$ -dimethylhexoic acid, b. p. 124°/20 mm., $d_4^{20} 0.899$, $[\alpha]_D^{20} +1.65^\circ$ (Et ester, b. p. 85°/20 mm., $d_4^{20} 0.856$, $[\alpha]_D^{20} +1.13^\circ$); d- $\gamma\epsilon$ -dimethylhexanol, b. p. 105°/45 mm., $d_4^{20} 0.815$, $[\alpha]_D^{20} +1.46^\circ$; l- α -bromo- $\gamma\epsilon$ -dimethylhexane, b. p. 91°/45 mm., $d_4^{20} 1.099$, $[\alpha]_D^{20} -0.50^\circ$; d- $\gamma\epsilon$ -dimethylhexane, b. p. 111—112°/760 mm., $d_4^{20} 0.696$, $[\alpha]_D^{20} +2.99^\circ$; d- $\beta\epsilon$ -dimethylheptoic acid, b. p. 140°/25 mm., $d_4^{20} 0.901$, $[\alpha]_D^{20} +2.44^\circ$ (Et ester, b. p. 112°/30 mm., $d_4^{20} 0.862$, $[\alpha]_D^{20} +1.39^\circ$); d- $\beta\epsilon$ -dimethylheptanol, b. p. 102°/18 mm., $d_4^{20} 0.823$, $[\alpha]_D^{20} +2.21^\circ$; l- α -bromo- $\gamma\epsilon$ -

dimethylheptane, b. p. 108°/25 mm., d_4^{25} 1.090, $[\alpha]_D^{25}$ -2.20°; *d-βε-dimethylheptane*, b. p. 134°/760 mm., $[\alpha]_D^{25}$ +4.19°; *d-80-dimethyloctanol*, b. p. 115°/15 mm., d_4^{25} 0.824, $[\alpha]_D^{25}$ +0.81°; *d-βε-dimethyloctane*, b. p. 156°/760 mm., $[\alpha]_D^{25}$ +1.02°.

The conclusions reached from considerations of the rotations are that the Pr^{β} group introduces a special rotatory contribution only when located directly on the asymmetric C atom or at a distance of only 1 C atom from it. The Bu^{β} has a higher negative val. than Bu^{α} , whereas *isoamyl* has only a slightly higher val. than the corresponding normal group. *d-βδ-Dimethylhexoic acid* is configuratively related to *l-β-methylhexoic acid* and will lead to a hydrocarbon of opposite sign to that obtained from *d-β-methylheptoic acid*.
F. R. SHAW.

Highly-polymerised compounds. LX. Relationships between the length of chains of thread molecules and the specific viscosity of their solutions. H. STAUDINGER (Ber., 1932, 65, [B], 267—279).—Comparison of the viscosities of compounds belonging to different polymeric homologous series shows that hydrocarbons with thread mols. of the same mol. wt. have the same sp. viscosity in chain-equiv. solution in the same solvent (C_6H_6 or tetrahydronaphthalene), independently of the presence of the C atoms in the main or side-chain, provided that the solutions are dil. Equally viscous solutions of hydrocarbons of the same concn. contain thread mols. of approx. equal chain length. Different hydrocarbons which show the same sp. viscosity in equally concn. solution have mol. wts. proportional to the chain-equiv. wts. The consts. for solutions of polyoxymethylenes and polyethylene oxides are approx. the same as those of the hydrocarbons. It appears that in these chains the no. of mols. and their length are the decisive factors and that the nature of the members of the chain is not vitally important. Higher consts. are observed for the polytriacylcelloglucan diacetates in *m*-cresol and for cellulose in Schweitzer's reagent. The bearing of the length and diameter of the mols. on the viscosity and the nature of colloidal solution is discussed.
H. WREN.

Polymerides and polymerisation. IV. Polymerisation of isoprene and $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene. G. S. WHITBY and R. N. CROZIER (Canad. J. Res., 1932, 6, 203—225; cf. A., 1931, 1031).—Polymerisation of isoprene, b. p. 33.4—33.9°/744 mm., or $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene (prep. described) between 10° and 145° does not afford any open-chain diene, polymerisable to caoutchouc, such as the β -myrcene of Ostromisslenski. The products isolated are oily cyclic dimerides which are not intermediate steps in the conversion of the dienes into caoutchoucs. Dipentene is shown (from its tetrabromide) to be present in considerable amount in these oils, together with one or more other oily cyclic dimerides. During polymerisation the mol. wt. of the rubber increases as the percentage of polymerisation increases, and the higher is the temp., the lower is the mol. wt. of the rubber; as polymerisation progresses, the viscosity of sols of the product rises. Measurements of η and mol. wt. are made on samples

of rubber dried in vac., after pptn. from C_6H_6 -EtOH and subsequent treatment by a standardised method. Polymerisation of $\beta\gamma$ -dimethylbutadiene at 85° is followed by observing the changing refractive index of the liquid. Fractional pptn. by EtOH of a solution of dimethylbutadiene caoutchouc in C_6H_6 gives fractions yielding sols of different η , showing that the rubber consists of a mixture of polymerides of different degrees of polymerisation. Caoutchouc sols show a marked decrease in η on keeping, probably due to oxidation of the synthetic rubber. NPhMe_2 prevents this decrease. Certain inorg. salts (SbCl_5 , SnCl_4 , etc.) polymerise these dimerides rapidly in the cold, yielding polymerides which may be isomerides of rubber.
J. L. D'SILVA.

Addition of sulphite to $\beta\gamma$ -dimethylbutadiene. H. J. BACKER and J. A. BOTTEMA (Rec. trav. chim., 1932, 51, 294—298).— $\beta\gamma$ -Dimethylbutadiene (I) and saturated aq. NH_4HSO_3 (2 mols.) at 120° give 3:4-dimethyl-2:5-dihydrothiophen 1:1-dioxide (II), m. p. 135° (crystallographic data given), also formed from (I) and SO_2 in Et_2O at 100° or H_2SO_3 at room temp. (II) and Br in C_6H_6 afford the dibromide, m. p. about 215° (decomp.), hydrolysed by boiling H_2O to 3:4-dihydroxy-3:4-dimethyltetrahydrothiophen 1:1-dioxide, m. p. 175° (*Ac.* derivative, m. p. 138°).

H. BURTON.

Nuclear synthesis in the olefine series. III. Hexenes. C. G. SCHMITT and C. E. BOORD (J. Amer. Chem. Soc., 1932, 54, 751—761).—The following are prepared by the methods previously described (A., 1930, 1269; 1931, 709): *Et* α -chloroisobutyl ether, b. p. 43°/24 mm.; *Et* $\alpha\beta$ -dibromoisobutyl ether, b. p. 88—89°/22 mm.; α -bromo- β -ethoxy- γ -methylpentane, b. p. 74—75°/13 mm.; β -bromo- γ -ethoxyhexane, b. p. 73°/12 mm.; β -bromo- γ -ethoxy- γ -methylpentane, b. p. 79.5°/25 mm.; δ -bromo- γ -methoxyhexane, b. p. 65—66°/12 mm.; α -bromo- β -ethoxy- γ -methylpentane, b. p. 81—82°/19 mm.; α -bromo- β -ethoxy- $\beta\gamma$ -dimethylbutane, b. p. 78—79°/15 mm.; α -bromo- β -ethoxy- β -ethylbutane, b. p. 79—81°/17 mm.; impure β -bromo- γ -ethoxy- β -methylpentane, b. p. 65—67°/20 mm. The action of Zn in PrOH on the above β -Br-ethers gives the corresponding hexenes; the following are prepared: Δ^{α} -hexene, b. p. 63.4—63.7° (all b. p. are at 760 mm. unless stated otherwise) (dibromide, b. p. 89—90°/18 mm.); γ -methyl- Δ^{α} -pentene, b. p. 53.6—54.0° (dibromide, b. p. 99°/30 mm.); δ -methyl- Δ^{α} -pentene, b. p. 53.6—53.9° (dibromide, b. p. 87°/21 mm.); Δ^{β} -hexene, b. p. 67.9—68.1° (dibromide, b. p. 90°/16 mm.); δ -methyl- Δ^{β} -pentene, b. p. 57.7—58.5° (dibromide, b. p. 78°/22 mm.) and 54.2—55.2° (dibromide, b. p. 72—73°/18 mm.); Δ^{γ} -hexene, b. p. 66.6—67.0° (dibromide, b. p. 80—81°/13 mm.); β -methyl- Δ^{α} -pentene, b. p. 61.5—62.0° (dibromide, b. p. 87—88°/20 mm.); $\beta\gamma$ -dimethyl- Δ^{α} -butene, b. p. 56.0—56.5° (dibromide, b. p. 80°/17 mm.); α -ethyl- Δ^{α} -butene, b. p. 66.2—66.7° (dibromide, b. p. 87°/21 mm.); β -methyl- Δ^{β} -pentene, b. p. 67.2—67.5° (dibromide, b. p. 71—72°/18 mm.). Other data (lit.) for the hexenes and their dibromides are recorded. The b. p. of the olefins are raised by accumulation of Me groups on the unsaturated C atoms and by movement of the double linking towards the centre of the chain. Branching

of an alkyl group attached to an unsaturated C atom causes a lowering of the b. p. C. J. WEST (b).

Spectrochemistry of acetylenic derivatives. F. STRAUS and R. KUHNEL (Ber., 1932, 65, [B], 154—158; cf. this vol., 374).—The vals. of the increment for the acetylenic linking are calc. from the optical data for Δ^8 -heptinene, prepared by purifying the technical material through the Na derivative. The Cu compound is less suitable, since it is not decomposed by oxy-acids and the concn. of the halogen acid employed cannot be so reduced that danger of subsequent halogenation is excluded. H. WREN.

Preparation of γ -chloroallyl bromide and iodide. L. BERT and E. ANDOR (Compt. rend., 1932, 194, 722—724).—The bromide, b. p. 130°, and iodide, b. p. 58°/19 mm., are prepared (70% yield) by fission of Ph γ -chloroallyl ether (A., 1931, 952) with the theoretical quantity of HBr or HI in AcOH without cooling. J. W. BAKER.

Iodination in liquid ammonia. T. H. VAUGHN and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1932, 54, 787—791).—When C_2H_2 is passed into I+liquid NH_3 , C_2I_2 , decomp. $125 \pm 4^\circ$ (detonated by a sharp blow), is obtained in 54—63% yield. C_2I_2 is also obtained from C_2HNa and I in liquid NH_3 ; the reaction is instantaneous. $COMe_2$ similarly gives 8—12% of CHI_3 , also formed in smaller yield from $COMeEt$. NH_2Bu , $NHBu_2$, $CH_3(CO_2Et)_2$, and $CH_3Ac \cdot CO_2Et$ also react with I in liquid NH_3 , but definite products could not be isolated; C_6H_6 , C_2H_4 , $COMe_2 \cdot CHMe$, C_3H_6 , $CHPh_3$, and pentane do not react. C. J. WEST (b).

Detection of chloropicrin. E. V. ALEXEEVSKI (J. Chem. Ind. Russ., 1931, 8, No. 20, 50—51).—Air containing chloropicrin (I) is passed through H_2O , and the solution is treated with Ca; HNO_3 formed by reduction of (I) is detected by Griess' reagent (β - $C_{10}H_7 \cdot NH_2$ and sulphanic acid). This method serves for the detection of 0.002 mg. in 1 c.c. of H_2O . It cannot be applied to the colorimetric determination of (I), owing to partial further reduction of HNO_3 to NH_3 . R. TRUSZKOWSKI.

Action of phenylhydrazine and of thiocarbamide on aliphatic nitro-compounds. A. K. MACBETH and W. B. ORR (J.C.S., 1932, 534—543).—Action of alkaline solutions of $NHPh \cdot NH_2$ on $C(NO_2)_4$ (and other aliphatic polynitro-compounds) indicates the successive removal of NO_2 -groups forming $MeNO_2$. Determination of evolved H_2 directly and of $-NO_2$ in the reduced solution is described. Thiocarbamide (neutral or slightly acid) is reduced similarly; the gases evolved by its action on the HNO_2 produced in reduced solution are determined. A new method of prep. of K nitroform is described. D. E. KAHN.

New general reagent for enols. Mercurous nitrate. E. V. ZAPPI (Bull. Soc. chim., 1932, [iv], 51, 54—59).—Esters, aldehydes, ketones, and phenols which possess an enolic structure, $\cdot C(OH) \cdot CH$, and substances possessing the ψ -imino-alcohol, $\cdot C(OH) \cdot NH$, thioimino-, $\cdot C(SH) \cdot NH$, carbylamine, carbimido-, thiocarbimido-, or oximino-structures in EtOH have a reducing action on $Hg_2(NO_3)_2$, giving a deposit of finely-divided Hg the

intensity of which is proportional to the concn. of the enol present. The reaction is more general than the $FeCl_3$ reaction, and can be used to detect the presence of the enols in MeCHO (1 part in 15,000 parts), Et malonate (1 in 10,000), or Et acetoacetate (at least 1 in 15,000). The fact that camphor does not give the reaction confirms Bredt-Savelsberg's observation that enolisation of camphor occurs only in presence of NaOEt or Grignard reagent. Theobromine gives a positive result, confirming the enolic structure. Certain substances with active unsaturated groupings such as $CH_2R \cdot CH \cdot CH_2$, $CH_2R \cdot CH \cdot CHR$, and $CHR \cdot CHR$, have a similar reducing action.

R. BRIGHTMAN.

Reduction of *l*-n-butylvinylcarbinol to ethyl-n-butylcarbinol. R. I. JOHNSON and J. KENYON (J.C.S., 1932, 722; cf. A., 1925, i, 771).—The ethyl-n-butylcarbinol produced is dextrorotatory.

D. E. KAHN.

Preparation of true acetylenic primary alcohols. R. LESPIEAU (Compt. rend., 1932, 194, 287—288).— n - Δ^8 -Pentinenyl alcohol (from δ -bromo- n - Δ^8 -pentenyl alcohol), b. p. 154—155°/766 mm. (Ag salt, m. p. 115°, explodes at 200° on Maquenne block; phenylurethane, m. p. 42.5—43.5°), gives $\delta\epsilon$ -tri-iodo- n - Δ^8 -pentenyl alcohol, m. p. 112.5—113.5°. Me γ -iodo- n -propyl ether and Na acetylide in liquid NH_3 give the Me ether (II) of (I), b. p. 109—109.5° (Ag salt), which with Br gives, amongst other products, Me $\delta\epsilon$ -dibromo- n - Δ^8 -pentenyl ether, b. p. 76—76.5°/6 mm., whence by HBr $\alpha\beta\epsilon$ -tribromo- n - Δ^8 -pentene, b. p. 120—121°/14 mm., was obtained. $\delta\epsilon$ -Dibromo- n - Δ^8 -pentenyl alcohol has b. p. 127—128°/16 mm. (I) was also obtained in poor yield from γ -iodo- n -propyl alcohol and Na acetylide, and from (II).

R. S. CAHN.

Action of hydriodic acid on glycerol. L. SATTLER (J. Amer. Chem. Soc., 1932, 54, 830—831).—*cyclo*Propanol is postulated as an intermediate in the formation of allyl iodide from glycerol and HI.

C. J. WEST (b).

Complex ferric compounds of polyhydric alcohols. W. TRAUBE and F. KUHBIER (Ber., 1932, 65, [B], 187—190).—Addition of $FeCl_3$ in H_2O to a hot aq. solution of NaOH, $BaCl_2$, and mannitol yields the compound $C_6H_9O_6BaFe \cdot 2H_2O$ (also heptahydrate), converted by $NaHSO_4$ into the substance $C_6H_{10}O_6NaFe \cdot 3H_2O$. The compound $C_6H_9O_6CaFe \cdot 2H_2O$ dissolves more freely in cold than in hot H_2O . Sorbitol affords the substances $C_6H_9O_6BaFe \cdot 6H_2O$ and $C_6H_{10}O_6NaFe \cdot 4H_2O$, whereas the compound $[(C_3H_5O_3)_2FeOH]Ba_2 \cdot 2H_2O$ is derived from glycerol. H. WREN.

Autoxidation of the ferric compounds of polyhydric alcohols. W. TRAUBE and F. KUHBIER (Ber., 1932, 65, [B], 190—195; cf. preceding abstract).—Mannitol in 6% KOH is indifferent to O_2 , whereas after addition of $FeCl_3$ marked autoxidation occurs. The products are CO_2 , HCO_2H , and probably a hydroxymonocarboxylic acid, whereas H_2O_2 or $H_2C_2O_4$ could not be detected. Diminution in the concn. of KOH does not greatly affect the rate of reaction; change occurs more slowly in presence of K_2CO_3 . It is not necessary that the polyhydroxy-

compound should be present entirely as the Fe^{III} complex. Sorbitol and erythritol resemble mannitol in their behaviour, whereas glycerol is not autoxidised.

H. WREN.

Syntheses of glycol ethers. M. GODCHOT and M. IMBERT (Compt. rend., 1932, 194, 378—380; cf. A., 1927, 444).—The action of 5 mols. of MgMeI on Et methyl diglycolate affords $\beta\beta$ -dihydroxy- $\alpha\beta\beta$ -trimethyldipropyl ether (I), b. p. 112°/10 mm., d_{20}^{25} 0.960, whilst with 4 mols. the product is α -acetyldiethyl β -hydroxy- β -methylpropyl ether, b. p. 108—109°/10 mm., d_{20}^{25} 0.983, converted by excess of MgMeI into (I). Similarly, MgPhBr affords $\beta\beta$ -dihydroxy- $\beta\beta\beta'$ -tetraphenyl- α -methyldiethyl ether, m. p. 94°, converted on warming in AcOH into β -methyl- $\alpha\alpha\alpha'$ -tetraphenyl-diethylene dioxide, m. p. 126—127°. The action of MgMeI on Et dilactylate affords a mixture of optical isomerides of di(di- β -hydroxy- $\alpha\beta$ -dimethyl)propyl ether. The (*r*-) form, which predominates, has m. p. 76°; meso-form, m. p. 56°. Similarly, MgPhBr affords two inactive forms, m. p. 122° and 149°. MgMeI with Et phenyldiglycolate yields β -hydroxy- α -phenyl- β -methylpropyl β -hydroxy- β -phenylpropyl ether, m. p. 84—85°.

J. L. D'SILVA.

Affinity capacity and migratory power. XIX. Affinity capacity of the amyl and isoamyl radicals compared with that of hydrogen. (Mlle.) J. LEVY and R. PERNOT (Bull. Soc. chim., 1931, [iv], 49, 1838—1840).— Δ^2 -Heptene oxide, b. p. 143—145°, and isoeptene oxide, b. p. 140—145°, obtained by perbenzoic acid oxidation of the hydrocarbons in Et_2O , do not isomerise on distillation. In presence of ZnCl_2 they resinify, but when passed over kieselguhr at 275—280° the former yields heptaldehyde and the latter isoeptaldehyde (semicarbazone, m. p. 114°), the oxide ring being ruptured on the side of the amyl and isoamyl radicals. Similarly, the dehalogenation with AgNO_3 of the iodohydrin from isoeptene affords Me isoamyl ketone and the amyl and isoamyl radicals have thus affinity capacities superior to that of H.

R. BRIGHTMAN.

Compounds of bivalent carbon. V. Rearrangement products of carbon monoxide diethylacetal formed by the action of alkoxides on ethyl diethoxyacetate. H. SCHEIBLER, W. BEISER, and W. KRABBE (J. pr. Chem., 1932, [ii], 133, 131—153; cf. this vol., 143).—Interaction of dry NaOEt and $\text{CH}(\text{OEt})_2 \cdot \text{CO}_2\text{Et}$ (I) at 100° in vac. gives CO , a distillate containing EtOH and a little $\text{C}(\text{OEt})_2$, and a dark-coloured residue which is decomposed by H_2O or by dry H_2SO_4 or HCO_2H in Et_2O into EtOH , a little $\text{C}(\text{OEt})_2$, unchanged (I), tetraethoxyethylene, and fractions of high b. p. The $[\text{C}(\text{OEt})_2]_2$ accompanies (I) in a fraction b. p. 70—90°/18 mm., and is identified by its reducing action on alkaline KMnO_4 and the formation of Et diethoxyorthoacetate (II), b. p. 75°/12 mm., 170°/1 atm., by the action of cold aq. NaOH , owing to hydrolysis of (I) and addition of the EtOH formed to $[\text{C}(\text{OEt})_2]_2$; (II) and $\text{CH}(\text{OEt})_2 \cdot \text{CO} \cdot \text{NH}_2$ are also formed from this fraction by the action of NaNH_2 in Et_2O or of NH_3 in EtOH . The reducing power of this fraction is not diminished by distillation at atm. pressure, and it is therefore concluded that $\text{C}(\text{OEt})_2$ is not formed by decomp. of

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its dimeride, as previously suggested. The mechanism $\text{CH}(\text{OEt})_2 \cdot \text{CO}_2\text{Et} + \text{NaOEt} \rightarrow \text{C}(\text{OEt})_2 \cdot \text{C}(\text{OEt}) \cdot \text{ONa} + \text{EtOH}$; $\text{C}(\text{OEt})_2 \cdot \text{C}(\text{OEt}) \cdot \text{ONa} \rightarrow \text{C}(\text{OEt})_2 + \text{C}(\text{OEt}) \cdot \text{ONa}$ is suggested. The higher-boiling fractions contain a substance, $\text{CO}_2\text{C}(\text{OEt})_2$, b. p. 140—142°/18 mm., possibly $\text{CO} < \begin{smallmatrix} \text{C}(\text{OEt})_2 \\ \text{C}(\text{OEt})_2 \end{smallmatrix}$. KOEt gives the same results as NaOEt .

$\text{Mg}(\text{OEt})_2$ and $\text{Al}(\text{OEt})_3$ react similarly to NaOEt at 170—200°, but very little CO or other gas is evolved, and the saline residue gives resins on decomp. with acids. $\text{Mg}(\text{OEt})\text{Cl}$ and $\text{Mg}(\text{OEt})\text{Br}$ behave similarly, giving EtCl or EtBr and the $\text{EtOH} \cdot \text{C}(\text{OEt})_2$ fraction at 145—150°. Separation of EtOH from the fraction b. p. 78°/1 atm. did not give $\text{C}(\text{OEt})_2$ in a state of purity, and there was evidence of the presence of compounds of the type $\text{C}(\text{OEt})_2 \cdot \text{C}_2\text{H}_4$ or $\text{C}(\text{OEt})_2 \cdot 2\text{C}_2\text{H}_4$, and also of a little Bu_2O or BuOEt .

H. A. PIGGOTT.

Organic peroxides. I. Propyl and isopropyl hydrogen peroxide. S. S. MEDVEDEV and E. N. ALEXEEVA (Ber., 1932, 65, [B], 133—137).— Pr^nH peroxide, b. p. 107—109°, prepared in about 50% yield by the action of 30% H_2O_2 and KOH on Pr^nSO_4 , is relatively stable in quartz vessels or in acidic or neutral aq. solutions. In alkaline solution, it decomposes rapidly, giving COMe_2 . Acid KMnO_4 acts only in presence of Mn^{II} salts. Quinol is unaffected by it in anhyd. Et_2O , but transformed into quinhedrone in H_2O or moist Et_2O . It liberates I quantitatively from HI . When treated with $\text{Ba}(\text{OH})_2$, Pr^nH peroxide affords the salt $\text{Pr}^n\text{O} \cdot \text{O} \cdot \text{Ba} \cdot \text{OCO}_2\text{H} \cdot 3\text{H}_2\text{O}$, converted by terephthalyl chloride into Pr^n , perterephthalate, $\text{C}_6\text{H}_4(\text{CO} \cdot \text{O} \cdot \text{OPr}^n)_2$, m. p. 59°, which slowly decolorises indigotin, does not liberate I from KI solutions, and slowly passes into COMe_2 and terephthalic acid in faintly acidic solution. Pr^nH peroxide could not be obtained pure and is isolated as the salt $\text{Pr}^n\text{O} \cdot \text{Ba} \cdot \text{CO}_2\text{H} \cdot 3\text{H}_2\text{O}$. It decomposes in aq. solution, yielding EtCHO . Pr^n , perterephthalate decomposes so rapidly into EtCHO that it could not be analysed.

H. WREN.

Pentaerythrityl thioethers. H. J. BACKER and N. D. DIJKSTRA (Rec. trav. chim., 1932, 51, 289—293).—Pentaerythrityl thioethers, $\text{C}(\text{CH}_2\text{SR})_4$, are obtained in good yield from $\text{C}(\text{CH}_2\text{Br})_4$ (1 mol.) and NaSR (5 mols.) in EtOH ; the alkyl mercaptans used are prepared by hydrolysis of alkylisothiocarbamides with KOH . The following are described: tetra-methyl, b. p. 209—211°/15 mm.; -ethyl, b. p. 218—220°/15 mm.; -propyl, b. p. 222—225°/3 mm.; -isopropyl, b. p. 192—193°/2 mm.; -allyl, b. p. 214—217° (slight decomp.)/2 mm.; -butyl, b. p. 226—230°/2 mm.; -isobutyl, b. p. 206—208°/2 mm.; -tert.-butyl, m. p. 123.5°; -benzyl, m. p. 73°, and -phenyl, m. p. 86°, pentaerythrityl thioethers.

H. BURTON.

isoPropyl sulphate and benzyl p-toluenesulphonate. S. S. MEDVEDEV and E. N. ALEXEEVA (Ber., 1932, 65, [B], 131—133).— Pr^nSO_4 , b. p. 94°/7 mm., is obtained in 25% yield by the action of a deficiency of SO_2Cl_2 in Et_2O on NaOPr^n in Et_2O at -15° to -10°. The reported instability of the compound is not observed in the absence of traces of mineral acid. Pr^nSO_4 is obtained similarly in 50%

yield. CH_2Ph *p*-toluenesulphonate, m. p. 58° , can be preserved for more than a week in a desiccator over CaCl_2 , but decomposes within 15–20 min. over H_2SO_4 .

H. WREN.

Esters of pyrophosphorous, hypophosphoric, and pyrophosphoric acids. III. Diethylphosphoroyl chloride and the preparation of tetraethyl pyrophosphite therefrom. A. E. ARBUSOV and B. A. ARBUSOV (Ber., 1932, 65, [B], 195–199; cf. A., 1931, 1268).—Diethylphosphoroyl chloride, $(\text{OEt})_2\text{P}(\text{Cl})$, b. p. 63 – $65^\circ/30$ mm., 153 – $155^\circ/760$ mm., d_4^{20} 1.0747, is prepared in 4–4.5% yield by the action of Cl_2 on NaEt_2PO_3 in presence of ligroin, the main product being Et_4 pyrophosphite, $\text{O}[\text{P}(\text{OEt})_2]_2$, b. p. 146 – $147^\circ/3.5$ mm., d_4^{20} 1.2045. The chloride reacts almost explosively with H_2O , is very readily oxidised, and dissolves Cu_2Cl_2 without yielding cryst. products. With NaOEt it affords Et_3PO_3 ; it yields Et_4 pyrophosphite with NaEt_2PO_3 in Et_2O . It can also be obtained by the interaction of 2 mols. of NaOEt on PCl_3 , but its subsequent separation from Et_3PO_3 is difficult.

H. WREN.

Enzymic hydrolysis of phosphoric esters and spontaneous hydrolysis of phosphosalicylic acid. C. MANAKA (J. Biochem. Japan, 1931, 14, 191–213).—Resorcinol-diphosphoric acid and the following mono-*o*-phosphoric esters were prepared: chloroethyl; α -dichloropropyl; $\alpha\alpha'$ -dichloroisopropyl; pyrocatechol; resorcinol; quinol; *o*-, *m*-, and *p*-carboxyphenyl. The enzymic hydrolysis of these esters was investigated and their relation to the structure of the substrates discussed. Phosphosalicylic acid has a min. stability at p_H 5.5. The dissociation curve, determined by electrometric titration, indicates that at p_H 5.5 the dissociation of one OH and of the CO_2H group is complete, whilst the remaining OH remains undissociated.

F. O. HOWITT.

Glycidol. III. Reactions with acid chlorides. T. H. RIDER (J. Amer. Chem. Soc., 1932, 54, 773–776; cf. A., 1930, 737).—Glycidol (I) heated with AcCl , gives 69% of monochlorohydrin diacetate, b. p. 96.5 – $97^\circ/0.4$ – 0.6 mm., converted by MeOH-HCl into AcOMe and monochlorohydrin (II), which contains both α - and β -isomerides. (I) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ (1 : 1) give a mixture, b. p. 205 – $207^\circ/0.8$ mm., of the mononitrobenzoates of monochlorohydrin, whilst (II) affords a product, b. p. $207^\circ/1.5$ mm. (I) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ (1 : 2) give 85% of a mixture, m. p. 97 – 98° , of the di-*p*-nitrobenzoates of α - and β -monochlorohydrins; (II) similarly affords a di-*p*-nitrobenzoate, m. p. 108 – 109° . β -Monochlorohydrin di-*p*-nitrobenzoate has m. p. 121 – 122° .

C. J. WEST (b).

Synthetic glycerides. III. Mixed triglycerides of the distearin series. H. E. ROBINSON, J. N. ROCHE, and C. G. KING (J. Amer. Chem. Soc., 1932, 54, 705–710).—The following are new: α -, m. p. 42.7° , and β -, m. p. 47.2° , -hexodistearins; α -, m. p. 47.6° , and β -, m. p. 51.8° , -octodistearins; α -, m. p. 48.2° , and β -, m. p. 56.2° , -decodistearins. The solubilities and n_D of these and α -, m. p. 50.6° , and β -, m. p. 59.8° , -laurodistearins, α -, m. p. 58.5° , and β -, m. p. 63.5° , -myristodistearins, and α -, m. p. 62.6° , and β -, m. p. 68° , -palmitodistearins are recorded.

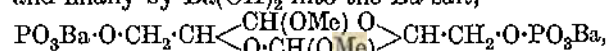
The m. p. of the glycerides increase with rise in the C content, and the *syn*-compounds have higher m. p., higher *n*, and lower solubilities than their *as*-isomerides. SOCl_2 is preferred for the prep. of acyl chlorides. Glycerol α -hexoate (isopropylidene derivative, b. p. $124^\circ/3$ mm.) has b. p. $162^\circ/4$ mm.

C. J. WEST (b).

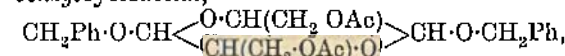
Preparation of esters of glycerol and amino-acids and of mixed esters of amino-acids and fatty acids. I. WEIZMANN and L. HASKELBERG (Bull. Soc. chim., 1932, [iv], 51, 59–72).—The following glycerides have been obtained by the action of the corresponding Na salt of the amino-acid on α -chloro- or -bromo-hydrin at 100° : dl-alanylglyceride [β' - γ' -dihydroxypropyl α -aminopropionate], m. p. 219° ; α -glycylglyceride, decomp. 200 – 250° . The following mixed glycerides were obtained from α -iodohydrin, by conversion into the α -iododiglyceride with acyl chloride in presence of pyridine or quinoline and heating the α -iododiglyceride with the Na salt of the NH_2 -acid at 150 – 160° : α -glycylidipalmitin, m. p. 215° ; α -glycylidistearin, m. p. 170° after softening at 122° ; α -dl-alanyldipalmitin, m. p. 216° ; α -dl-alanyldistearin, m. p. 223° ; α -dl-leucylidipalmitin, m. p. 218° ; and α -dl-leucylidistearin, m. p. 150° ; dipalmitin α -iodohydrin has m. p. 43.6° . The NH_2 -group exerts a dominant influence on the properties of the mixed glycerides. With triketohydrindene the aminoglycerides yield the blue coloration characteristic of aminocarboxylic acids, the mixed aminoglycerides reacting less readily than the aminoglycerides.

R. BRIGHTMAN.

Glyceraldehyde- γ -phosphoric acid. H. O. L. FISCHER and E. BAER (Ber., 1932, 65, [B], 337–345).—Glyceraldehyde methylcycloacetal is converted by POCl_3 in quinoline followed by H_2SO_4 and Ag_2CO_3 and finally by $\text{Ba}(\text{OH})_2$ into the Ba salt,



which could not be hydrolysed without extensive liberation of H_3PO_4 . Acetobromoglyceraldehyde, $\text{CH}_2\text{Ph}\cdot\text{OH}$, and Ag_2CO_3 afford acetylglcyceraldehyde benzylcycloacetal,



m. p. 140 – 141.5° , transformed by H_2 -Pd in AcOH into acetylglcyceraldehyde, m. p. 118.5° , and by $\text{Ba}(\text{OH})_2$ in aq. EtOH into glyceraldehyde benzylcycloacetal, m. p. 109 – 110° . The last-named is converted by POCl_3 in quinoline into glyceraldehyde benzylcycloacetalphosphoric acid ($+2\text{H}_2\text{O}$ or $+0.5\text{H}_2\text{O}$, decomp. 185 – 188°), which yields a dibasic and Ba salt, but titrates electrometrically as a monobasic acid. Its reductive fission leads to glyceraldehyde- γ -phosphoric acid, $\text{CHO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{PO}_3\text{H}_2$ (2 : 4-dinitrophenylhydrazones).

H. WREN.

Complexes of zinc and cadmium iodides with alkylsulphonium iodides. (Sir) P. C. RAY, N. ADHIKARI, and S. K. BANERJEE (J. Indian Chem. Soc., 1931, 8, 739–751).— CdI_2 (1 mol.), Et_3S (or Et_3S_2) (2 mols.), and EtI (2 mols.) in cold COMe_2 give the compound (I), $(\text{Et}_3\text{S})_2\text{CdI}_4$, m. p. 156 – 157° (lit. 145°), the conductivity of which (in H_2O) is of the same order as that of K_2CdI_4 . The following complexes are prepared similarly, using R_3S , RI , and CdI_2 :

(Et₂MeS)CdI₂, m. p. 75°; (Et₂PrS)₂CdI₂, m. p. 150°; (Et₂BuS)CdI₂, m. p. 116°; (Me₂S)₂CdI₂, m. p. 204°; (Me₂EtS)₂CdI₂, m. p. 185°; (Me₂PrS)₂CdI₂, m. p. 120°; (Me₂BuS)CdI₂, m. p. 130°; (Pr₂S)₂CdI₂, m. p. 151—152°; (Pr₂EtS)CdI₂, m. p. 77—78°; (Bu₂S)₂CdI₂, m. p. 110°. The compound, (Et₂S)₂CdBr₂I₂ (conductivity data given) is prepared from Et₂S, EtBr, and CdI₂ or from Et₂S, EtI, and CdBr₂. (I) and NH₃ in COMe₂ give Et₂SI and CdI₂·2NH₃.

ZnI₂, Me₂S (or Me₂S₂), and MeI (in the mol. ratio 1 : 2 : 2) in COMe₂ give the complex, Me₂S₂·ZnI₂, m. p. 208°; with EtI, the compound, (Me₂EtS)₂ZnI₂, m. p. 184—185°, results. The complexes, (Et₂S)₂ZnI₂ (II) (conductivity data given), m. p. 149°; (Et₂MeS)₂ZnI₂, m. p. 173—174°, and (Et₂PrS)₂ZnI₂, m. p. 145°, are also described. (II) and NH₃ in COMe₂ afford Et₂SI and ZnI₂·4NH₃. H. BURTON.

Aliphatic sulphonyl fluorides. W. DAVIES and J. H. DICK (J.C.S., 1932, 483—486).—Aliphatic sulphonyl fluorides can be prepared from the corresponding chlorides (cf. A., 1931, 1405) and are more stable than these. The following are described: methane- (1), ethane-, α -chloroethane-, cyclohexane-, ω -toluene-sulphonyl fluorides (b. p. 124.2°/754 mm.), 134—135°, 138—139°, 218°, m. p. 90—91°. (1) forms a piperidide, m. p. 48°, b. p. 167—168°/4 mm.

D. E. KAHN.

Esterification with mixed anhydrides and mixtures of anhydrides. II. A. ROLLETT and F. SCHOLZ (Monatsh., 1932, 59, 1—6; cf. A., 1931, 934).—When BzCl, NaOAc, and EtOH are heated together in the mol. proportions 1 : 1 : 2 the max. yield of BzOEt is reached at 100°. This decreases rapidly with fall of temp., so that at 70° the same total yield of ester contains only about half as much BzOEt. At 50° the total yield is diminished, but the proportions of the two esters remain practically the same as at 70°. Decomp. of the anhydride is practically complete in 2 hr. at 50°, but even at this temp. there is considerable esterification by EtOH of the acid set free.

M. S. BURR.

Relation between Kolbe's reaction and hydrogen-ion concentration. Mechanism of Kolbe's reaction. H. R. MATSUDA.—See this vol., 348.

Parallelism between colour and reactivity of a chromophoric group. (MME.) RAMART-LUCAS (Compt. rend., 1932, 194, 726—728).—Theoretical. The chromophores CO₂H in Me[CH₂]_n·CO₂H and NH₂ in Me[CH₂]_n·NH₂, respectively, give rise to the same absorption spectra in all cases where $n > 2$, and such compounds also exhibit the same velocity of chemical reaction (e.g., esterification and reaction with allyl bromide, respectively).

J. W. BAKER.

[Ring-chain tautomerism of partly acetylated polyhydric alcohols.] H. HIBBERT (Ber., 1932, 65, [B], 199—200).—Cases similar to that examined by Meerwein and Sonke (A., 1931, 1395) have been investigated by the author, who has also considered the possibility of equilibrium mixtures.

H. WREN.

Properties of conjugated compounds. XV. Catalytic hydrogenation of butadiene- α -carboxylic acids. E. H. FARMER and R. A. E. GALLEY (J.C.S., 1932, 430—439; cf. A., 1928, 613, 1111).—

Separative and degradative (oxidation with KMnO₄) analyses are used to determine the proportions of $\alpha\beta$ -, $\alpha\delta$ -, $\gamma\delta$ -, and $\alpha\beta\gamma\delta$ -additive products obtained from β -vinylacrylic, sorbic, α -methyl- and β -dimethyl-sorbic acids by action of Pd-H₂ (1 mol.). The proportions are found to be different for each acid.

D. E. KAHN.

Walden inversion. XVII. Optical rotations in homologous series of carboxylic acids. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1932, 95, 153—164).—The optical rotations are given of a series of acids, CHRR'·[CH₂]_n·CO₂H, where R is const., R' is a normal alkyl radical progressively increased, and n varies from 0 to 3; the significance of these figures is discussed. (The figures in parentheses are the calc. max. for [M].) 1-*Methyl*octoic, b. p. 127°/5 mm., d_4^{25} 0.901, $[\alpha]_D^{25}$ -0.37° (-3.67°), 1-*Methyl*nonoic, b. p. 130°/3 mm., d_4^{25} 0.897, $[\alpha]_D^{25}$ -0.50° (-1.6°), 1-*Methyl*decoic, b. p. 135°/3 mm., d_4^{25} 0.893, $[\alpha]_D^{25}$ -0.18° (-0.6°), and d-*Methyl*octoic acid, b. p. 139°/20 mm., d_4^{25} 0.899, $[\alpha]_D^{25}$ +2.49° (+12.22°), have been prepared from Et malonate and the corresponding bromomethylparaffin, whilst CO₂ and the Grignard compound of the paraffin have given d-*Methyl*hexoic, b. p. 115°/16 mm., d_4^{25} 0.923, $[\alpha]_D^{25}$ +3.09° (+13.6°), d-*Methyl*heptoic, b. p. 132°/22 mm., d_4^{25} 0.882, $[\alpha]_D^{25}$ +2.11° (+6.9°), l-*Methyl*octoic, b. p. 149°/22 mm., d_4^{25} 0.871, $[\alpha]_D^{25}$ -1.33° (-4.1°), l-*Methyl*nonoic, b. p. 156°/22 mm., d_4^{25} 0.871, $[\alpha]_D^{25}$ -0.59° (-1.9°), and d-*Methyl*heptoic acid, b. p. 128°/20 mm., d_4^{25} 0.893, $[\alpha]_D^{25}$ +2.47° (+11.07°). 1- β -*Methyl*hexylamine, b. p. 62°/22 mm., d_4^{25} 0.773, $[\alpha]_D^{25}$ -11.75°, has been prepared from β -methylheptoic acid. F. R. SHAW.

Conjugated double linkings. XXII. Extended Thiele's rule. R. KUHN and M. HOFFER (Ber., 1932, 65, [B], 170—175; cf. A., 1928, 291).—Reduction of a number of unsaturated fatty acids by Na-Hg causes addition of 2 H atoms preferably at the ends of the conjugated system. $\Delta^{8,9}$ -Octatrienoic acid is transformed in 65% yield into $\Delta^{8,9}$ -octadienoic acid, b. p. 134—135°/11 mm., m. p. about 2°, $d_4^{17.5}$ 0.9703 [amide, m. p. 124° (corr.)]. Cautious oxidation by KMnO₄ (O=8) converts it into EtCO₂H in 70% yield. Prolonged boiling with 15% NaOH causes partial isomerisation of the $\Delta^{8,9}$ -acid to $\Delta^{7,8}$ -octadienoic acid, m. p. 74° (corr.), oxidised to PrCO₂H. $\Delta^{7,8,9}$ -Decatrienoic acid gives $\Delta^{8,9}$ -decatrienoic acid, m. p. 96° (corr.) after softening at 94°, oxidised to EtCO₂H. The dihydro-acids are isolated in 50—65% yield, the remainder being polymerised, mainly dimerised. From sorbic acid "dihydrodisorbic acid" (2C₆H₈O₂+2H) is obtained as a non-homogeneous, viscous oil of aliphatic structure, since catalytic hydrogenation establishes the presence of two double linkings in the acid and its ester. Its formation is probably due to a pinacol condensation of 2 mols. of acid each of which has absorbed 1 H atom.

H. WREN.

History of the development of the chemistry of fats. E. ANDRÉ (Bull. Soc. chim., 1932, [iv], 51, 1—29, 145—170).—A lecture.

Action of potassium hydroxide on halogen derivatives of palmitic acid. M. ROBINET (Bull.

Soc. chim. Belg., 1931, 40, 710—725).— α -Iodopalmitic acid and KOH in hot EtOH give a difficultly separable mixture of α -hydroxypalmitic (α -ethoxypalmitic acid, m. p. 45°) and Δ^6 -hexadecenoic acid (I), m. p. 49°; (I) with HI in AcOH gives β -iodopalmitic acid, m. p. 48—49°, converted by KOH-EtOH into (I) (the structure of which is proved by ozonolysis in CHCl_3) and β -hydroxypalmitic acid, m. p. 83—83.5° (Ac derivative, m. p. 58°). HBr leads similarly to β -bromopalmitic acid, m. p. 44°. R. S. CAHN.

d-Ricinoleates of l- α -phenylethylamine and l-ephedrine. E. ANDRÉ and C. VERNIER (Compt. rend., 1932, 194, 469—471).—The d-ricinoleates of l- α -phenylethylamine, m. p. 39.5—40°, and l-ephedrine, m. p. 54.2°, are prepared from acids of slightly different $[\alpha]_D$. Both give on regeneration d-ricinoleic acid, $[\alpha]_D^{25} + 7.9^\circ$. From the mother-liquors of the ephedrine salt a salt of indefinite m. p. was obtained, and gave on regeneration an acid of lower $[\alpha]_D$. It is concluded that natural ricinoleic acid is a mixture of isomerides. H. A. PIGGOTT.

Structure of couepic acid. E. ROSSMANN (Rec. trav. chim., 1932, 51, 248—252).—The density and optical exaltation of couepic acid indicate that it is not a geometrical isomeride of α - and β -elaeostearic acids as suggested by van Loon and Steger (A., 1931, 1034). Couepic acid may contain a cyclobutane ring. H. BURTON.

Oxidation of metabolites. I. Mechanism of the oxidation of α -hydroxy-fatty acids with potassium permanganate. II. Shift in the point of rupture in a given α -hydroxy-fatty acid in the presence or absence of free alkali. E. J. WITZELMANN (J. Biol. Chem., 1932, 95, 219—245, 246—262).—I. Oxidation of a series of α -hydroxy-*n*-fatty acids with known amounts of KMnO_4 in neutral or slightly alkaline solution takes place thus: $\text{CH}_2\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, (A) $+ 2\text{O} \rightarrow \text{CH}_2\text{R}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} + \text{CO}_2$, and (B) $+ 5\text{O} \rightarrow \text{RCO}_2\text{H} + 2\text{H}_2\text{O} + 2\text{CO}_2$. The percentage of (B) formed is: lactic 16, α -hydroxy-butyric 52, -valeric 84, -hexoic 88, and -heptoic, -octoic, -decoic, -lauric, -palmitic, and -stearic acid 100.

II. Oxidation of lactic, α -hydroxy-butyric, -valeric, and -hexoic acids with KMnO_4 in presence of varying amounts of alkali shows a shift of the point of rupture of the chain from loss of 1 to 2 C atoms as soon as there is 1 mol. of alkali in excess, more alkali tending to complete oxidation. When 2 C atoms are lost, $\text{H}_2\text{C}_2\text{O}_4$ may be isolated, showing that these are severed together. Loss of 1 C atom is due to oxidation of the α -keto-acid, whilst loss of 2 C atoms follows the oxidation of its enolic isomeride. F. R. SHAW.

Polymerisation and ring formation. X. Reversible polymerisation of six-membered cyclic esters. W. H. CAROTHERS, G. L. DOROUGH, and F. J. VAN NATTA (J. Amer. Chem. Soc., 1932, 54, 761—772).—Examples (lit. and new) of the reversible polymerisation of six-membered cyclic esters are discussed. The following conclusions are reached: reversible polymerisation is generally characteristic of six-membered cyclic esters; ester-rings containing five or more than six atoms are not polymerised by heat. The tendency of the six-membered cyclic

esters to polymerise is closely related to their susceptibility towards hydrolysis; both tendencies are diminished by the presence of substituent groups. The polymerides formed are linear poly-esters and, in certain cases, the chains are open and terminated by OH and CO_2H groups. Both polymerisation and depolymerisation consist essentially of a process of ester interchange. The peculiar position occupied by the six-membered cyclic esters is readily explained by stereochemical considerations based on the Sachs-Mohr theory. *Et propylphenoxypropylmalonate*, b. p. 195—200°/4 mm., *8-bromo- α -propylvaleric acid*, b. p. 148—150°/5 mm., and *α -propyl- δ -valerolactone*, b. p. 118—120°/10 mm., are described. Details are given for the prep. of lactide, and polymerides of δ -valerolactone and of the lactone of hydroxyethylglycolic acid are described. C. J. WEST (b).

Ethyl acetoacetate-choleic acid. H. SOBOTKA and J. KAHN (Ber., 1932, 65, [B], 227—232).—Deoxycholic acid and Et acetoacetate give an additive product (3 : 1), m. p. 154° (corr.); analogous compounds of choleic acid with acetyl- and benzoyl-acetone have been prepared. In the solid compound the Et acetoacetate is present exclusively or nearly exclusively in the enolic form. In EtOH or amyl alcohol this preponderance of enol is not maintained, but the acetoacetate equilibrium is displaced appreciably towards the enolic side in comparison with the normal equilibrium. A similar effect is recorded with cholic or dehydrocholic acid. The action of the bile acids is not due to an unsp. H-ion effect, but these compounds, with cholesterol and digitonin, appear to belong to a group which modifies the enolising action of the solvent. In EtOH at 0°, the maximal enol vals. are not observed until a very short time after dissolution is complete. With tri-choleic acid-benzoyl- or -acetyl-acetone, the max. val. of 99% enol is attained after 1 min. The behaviour of choleic acid-Et acetoacetate in the solid, molten, and dissolved state towards Br suggests that it must undergo a change in mol. or co-ordinative structure before it can add Br at the double linking. Probably mol. dissociation of the co-ordination compound takes place at a rate which exceeds the velocity of tautomerisation. H. WREN.

Behaviour of oxalate and tartrate solutions of niobium and tantalum oxides. E. H. EDMISTER and G. G. ALBRITTON (J. Amer. Chem. Soc., 1932, 54, 438—442).—Freshly-pptd. hydrated oxides of Nb and Ta dissolve slowly in hot aq. tartaric acid to form niobo- and tantalato-tartaric acids, $\text{OH}\cdot\text{M} \left(\begin{smallmatrix} \text{O}\cdot\text{CH}\cdot\text{CO}_2\text{H} \\ \text{O}\cdot\text{CH}\cdot\text{CO}_2\text{H} \end{smallmatrix} \right)_2$, where M = Nb or Ta. The ion containing Nb or Ta migrates towards the anode. A similar migration of the metal-containing ion of the complex formed similarly, using $\text{H}_2\text{C}_2\text{O}_4$, indicates the structure $\text{H}_5\text{M}(\text{C}_2\text{O}_4)_5$. The complex salts are not affected by acids. F. D. SNELL (b).

Thermal stability of some alkylated malonic acids. F. C. B. MARSHALL (Rec. trav. chim., 1932, 51, 233—238).—The dialkylmalonic acids are more stable towards heat than the unsubstituted acid, and the latter than the monoalkyl derivatives. The order is that of the m. p. No simple relation between

the results and polar and steric influences can be deduced.

M. S. BURR.

Mechanism of racemisation. A. N. CAMPBELL and A. J. R. CAMPBELL.—See this vol., 346.

Pectin. II. Typical reaction of *d*-galacturonic acid and pectin. F. EHRLICH (Ber., 1932, 65, [B], 353—358; cf. A., 1929, 1273).—Aq. solutions of α - or β -*d*-galacturonic acid give a white, flocculent ppt. with basic Pb acetate, sol. in excess of the reagent. The clear solution when heated in boiling H₂O becomes pink and turbid and rapidly deposits a dark blood- to bile-red ppt. Complete redissolution of the ppt. is unnecessary provided that the solution is distinctly alkaline to litmus. 1 mg. of the acid can be thus detected. Reaction is independent of light and atn. O₂ and occurs slowly at room temp. Glycuronic acid behaves somewhat similarly to galacturonic acid, but the coloration is yellow to rust-brown. Gluconic, galactonic, and arabonic acid remain clear and colourless when heated with basic Pb acetate, saccharic and mucic acids afford dense white ppts. unchanged when heated, pyruvic and hydroxypyruvic acids yield white ppts. becoming pale yellow, or grey when heated, whilst saccharic and dihydroxymaleic acids do not give red colours. Pb pectate and tetragalacturonate become yellowish to orange-yellow when heated. The application of the reaction to the detection of pectin and galacturonic acid in plant material is described. The presence of galacturonic acid or pectin residues in wood is established. It appears that the OH' of the basic Pb acetate attacks the CHO group of galacturonic acid with formation of the corresponding ketogalactonic acid, which is further degraded to a C₄ or C₅ compound. Under certain conditions the basic Pb salt of a carbonylcarboxylic acid is produced the peculiar colour of which is attributed to certain by-products of the change.

H. WREN.

Synthesis of hexuronic acids. I. Synthesis of *dl*-galacturonic acid from mucic acid. C. NIEMANN and K. P. LINK (J. Biol. Chem., 1932, 95, 203—211).—Mucic acid monolactone is reduced by Na-Hg in acid solution to cryst. *dl*-galacturonic acid, isolated as the Ba salt (cf. Fischer, A., 1891, 1193; 1892, 824).

F. R. SHAW.

Preparation of *d*-mannuronolactone. E. SCHOEFFEL and K. P. LINK (J. Biol. Chem., 1932, 95, 213—218).—Alginic acid obtained from *Macrocystis pyrifera* is hydrolysed by 2.5% H₂SO₄ to mannuronic acid (Ba salt), which when crystallised from AcOH gives *d*-mannuronolactone.

F. R. SHAW.

Mechanism of production of thiol acids (RSH) and sulphonc acids (RSO₃H) from dithio-acids (RS₂R). II. Action of mercuric salts. P. W. PREISLER and D. B. PREISLER (J. Biol. Chem., 1932, 95, 181—188).—The reaction between dithiodi- β -propionic acid and HgBr₂ proceeds to at least 75% formation of β -sulphopropionic acid (Ba salt, +5H₂O) and CO₂H·CH₂·CH₂·S·HgBr, the latter also being obtained from HgBr₂ and β -thiolpropionic acid. The reaction $3\text{RS}\cdot\text{SR} + 3\text{H}_2\text{O} = 5\text{RSH} + \text{RSO}_3\text{H}$ is accelerated by the removal of RSH as the slightly ionised derivative of BrHg⁺.

F. R. SHAW.

Polymerisation reactions under high pressure. II. Mechanism of the reaction. J. B. CONANT and W. R. PETERSON (J. Amer. Chem. Soc., 1932, 54, 628—635; cf. A., 1930, 735).—Peroxides are essential for the polymerisation of aliphatic aldehydes and isoprene under high pressures. A chain mechanism is suggested which seems to account for all the observed facts. Attempts to stabilise the polymeric aldehydes were not successful. *cyclo*Hexene oxide is polymerised with great difficulty. The rate of decomp. of the polymeride from PrCHO in dioxan is studied; the polymeride shows no positive test for an OH group, since treatment with various reagents either has no effect or causes decomp.

C. J. WEST (b).

Photo-reduction of carbonic acid to form-aldehyde. N. R. DHAR and A. RAM.—See this vol., 349.

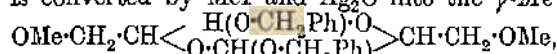
Action of diazomethane on formaldehyde and formic acid. L. IRRERA (Gazzetta, 1932, 62, 30—33; cf. A., 1907, i, 185, 478; 1909, i, 553).—No definite products can be isolated from the reaction between CH₂O and diazomethane. HCO₂H with diazomethane gives MeOAc.

E. E. J. MARLER.

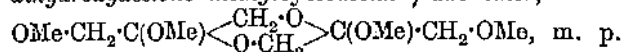
Derivatives of tribromoethyl alcohol [Avertin]. S. CHECHIK (J. Amer. Pharm. Assoc., 1932, 21, 20—24).—Choral and bromal with tribromoethyl alcohol give the compounds CCl₃·CH(OH)·O·CH₂·CBr₃, m. p. 69—70°, and CBr₃·CH(OH)·O·CH₂·CBr₃, m. p. 60—62°. With aq. H₂SO₄ or HNO₃ the alcohol affords *di*(tribromoethyl) ether, m. p. 63°, and with H₂SO₄·EtOH it gives *Et* $\beta\beta\beta$ -tribromoethyl ether, m. p. 60—62°. $\beta\beta\beta$ -Tribromoethyl *N*-phenylcarbamate, m. p. 66—67°, and $\beta\beta\beta$ -tribromo- β' -hydroxydiethyl ether, m. p. 70—71°, are described.

E. H. SHARPLES.

Derivatives of trioses and their transformations. H. O. L. FISCHER and E. BAER (Ber., 1932, 65, [B], 345—352).—Glyceraldehyde benzylcycloacetal is converted by MeI and Ag₂O into the γ -Me ether,



m. p. 110—111°, transformed by H₂-Pd into dimeric glyceraldehyde γ -Me ether, m. p. 120—121° (2:4-dinitrophenylhydrazones, m. p. 123—124°), which passes when treated with anhyd. pyridine at 125—130° into α -hydroxy- γ -methoxyacetone (2:4-dinitrophenylhydrazones, m. p. 175°). α -Hydroxy- γ -acetoxyacetone is transformed by CH(OEt)₃ and NH₄Cl in EtOH into the diethylacetal, b. p. 89—91°/0.3 mm., hydrolysed by aq. Ba(OH)₂ in H₂O to dihydroxyacetone diethylacetal, m. p. 90°. Glyceraldehyde is converted by MeCHO in presence of 84% H₃PO₄ into dimeric ethyleneglyceraldehyde, m. p. 309—310° (corr. in sealed capillary), obtained also by use of saturated MeOH-HCl. Dihydroxyethyleneglyceraldehyde, m. p. 161—162°, is obtained from CO(CH₂·OH)₂, MeCHO, and H₃PO₄. Glyceraldehyde, PhCHO, and P₂O₅ afford benzylideneglyceraldehyde. Glyceraldehyde methylcycloacetal γ -Me ether, m. p. 99—100°, and dihydroxyacetone methylcycloacetal γ -Me ether,



m. p. 59.5—61.5°, are described. γ -Acetyl glyceraldehyde and BzCl in pyridine give the compound

$\text{AcO}\cdot\text{CH}_2\cdot\text{CH}\langle\begin{smallmatrix} \text{H}(\text{OBz})\cdot\text{O} \\ \text{O}\cdot\text{CH}(\text{OBz}) \end{smallmatrix}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{OAc}$, m. p. 203.5—204°. The prep. of $\beta\gamma$ -diacetylglyceraldehyde, b. p. 90—96°/0.8 mm., is described. H. WREN.

Conversion of ketones into liquid hydrocarbons. A. MAHLE and R. NAUDIE (Compt. rend., 1932, 194, 462—464).—Passage of COMe_2 , COEt_2 , and COPr_2 over SiO_2 gel at 700—750° yields mainly gases, comprising CO , CH_4 , olefines (mainly C_2H_4 with COEt_2 and C_3H_6 with COPr_2), and a little H_2 , and a small amount of liquid product consisting mainly of C_6H_6 and in addition PhMe , m -xylene, C_{10}H_8 , anthracene, and higher hydrocarbons. H. A. PIGGOTT.

Formation of semicarbazones with bromo- and chloro-acetone. A. P. J. HOOGEVEEN and M. P. J. M. JANSSEN (Rec. trav. chim., 1932, 51, 260—264).—Chloroacetonesemicarbazone, m. p. about 150° (decomp.) (lit. 163—165°), and bromoacetonesemicarbazone, m. p. 135° (decomp.), heated with H_2O or EtOH give hydrazinedicarbonylamine and the semicarbazone of $\text{COMe}\cdot\text{CH}_2\cdot\text{OH}$. Diacetonyl sulphide, m. p. 85°, is obtained in poor yield from $\text{COMe}\cdot\text{CH}_2\text{Br}$ and aq. Na_2S . H. BURTON.

Ethyl ethers of α -glycols. III. Dialkyl ketones derived from ethyl ethers. D. BARDAN (Bull. Soc. chim., 1931, [iv], 49, 1875—1880).—The following ketones have been obtained by dehydration of the Et ethers of α -glycols with $\text{H}_2\text{C}_2\text{O}_4$ or 20% H_2SO_4 : COMePr^s (yield 58%), b. p. 92—95° (semicarbazone, m. p. 112°); γ -ethylpentan- β -one, b. p. 38—42°/19 mm., 138—140°/760 mm. (semicarbazone, m. p. 99°); ξ -methyl- γ -isoamylheptan- β -one, b. p. 119—124°/29 mm.; γ -propylhexan- β -one (50%), b. p. 80—88°/29—30 mm., 174—176°/760 mm. (semicarbazone, m. p. 67—68°); Me benzhydryl ketone (yield 90%), m. p. 61—62° (semicarbazone, m. p. 168°); δ -ethylhexan- γ -one, b. p. 54—57°/14 mm. (semicarbazone, m. p. 50—51°); δ -propylheptan- γ -one, b. p. 73—75°/15.5 mm.; δ -butyloctan- γ -one (yield 96%), b. p. 113—116°/11 mm.; $\alpha\alpha$ -diphenylbutan- β -one (yield 48%), b. p. 177—180°/13 mm.; Ph α -ethylpropyl ketone, b. p. 119—122°/15.5 mm.; Ph α -propylbutyl ketone (yield 50%), b. p. 127—133°/16—17 mm.; Ph α -butylamyl ketone, b. p. 148—151°/13 mm.; Ph benzhydryl ketone, m. p. 134.5°.

R. BRIGHTMAN.

Preparation of pinacolone. D. E. BADERTSCHER and F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 825—826).—Addition of a dil. solution of Mg *tert.*-BuCl in Et_2O to an excess of AcCl in Et_2O gives 40% of Me *tert.*-Bu ketone. Somewhat lower yields are obtained with other combinations of *tert.*-Grignard reagents and acyl halides. C. J. WEST (b).

d-Threose. W. FREUDENBERG (Ber., 1932, 65, [B], 168—170).—d-Diacetylxytal (cf. A., 1929, 1277) in AcOH is transformed by O_3 and subsequent treatment with Zn dust and Et_2O into d-threose 2 : 3-diacetate (I), m. p. 140—142°, $[\alpha]_D^{25} +83.52^\circ$ to $+34.31^\circ$ in CHCl_3 in 5 hr. Hydrolysis with aq. $\text{Ba}(\text{OH})_2$ affords d-threose, $[\alpha]_D^{25} +29.09^\circ$ to $+19.59^\circ$ in H_2O in 1.5 hr., the osazone of which is identical with d-erythrose. H. WREN.

Colorimetric micro-determination of pentoses. K. SUMINOKURA (J. Biochem. Japan, 1931, 14, 343—359).—The substance (1—20 mg.) is distilled in a current of steam and CO_2 at 150° with 12.5N- H_2SO_4 in presence of K_2SO_4 and ZnSO_4 . Furfuraldehyde is then colorimetrically determined in the distillate by xylydine and AcOH . F. O. HOWITT.

Volumetric determinations of pentoses and pentosans. G. M. KLINE and S. F. ACREE (Bur. Stand. J. Res., 1932, 8, 25—35).—The yield of furfuraldehyde from pentoses or pentosans is not improved by steam-distillation (B., 1923, 1238A). The loss arises from incomplete conversion of the xylose into furfuraldehyde, since recovery of the latter by either distillation method is quant. Nitrates, which reduce the yield, are best removed by nitron before addition of HCl , and loss of the aldehyde occurs by exposure of the distillate to air, whilst not all the aldehyde is collected in the 360 c.c. of distillate given in the official method. Comparison of (1) gravimetric thiobarbituric acid method (A., 1917, ii, 53), (2) electrometric KBr - KBrO_3 titration method (*loc. cit.*, 1923), and (3) Powell and Whittaker's excess Br titration method (J.S.C.I., 1924, 43, 35T) for determination of furfuraldehyde shows that (3) is much more rapid and accurate than (1) or (2) especially for amounts <0.01 g. for which the pptn. method gives very low results. J. W. BAKER.

Pentose reactions. II. Derivatives of xylose. C. D. HURD and L. L. ISENHOUR (J. Amer. Chem. Soc., 1932, 54, 693—698; cf. this vol., 279).—Xylosan (I), $[\alpha]_D +68.3^\circ$ in H_2O , formed when xylose is heated at the b. p. of xylene/2 mm., is readily oxidisable, shows a normal mol. wt. in cold AcOH , but is termol. in H_2O . When a solution in AcOH is heated to 100°, polymerisation occurs and the colourless solution turns brown. The unimol. form of (I) changes at 95—97° and atm. pressure to a dark brown solid, which is converted at 205—210° (without melting) into another form, and when heated under 0.3 mm. darkens slightly and shrinks at 119—120°, and is apparently converted into a new product at 163—165°. Acetylation of (I) in the cold gives a Ac_2 derivative $[\alpha]_D +38^\circ$ in CHCl_3 , which darkens at 88—89°, and becomes much darker at 95—100° (with apparent polymerisation), and is termol. in C_6H_6 . Diacetylxylosan or a mixture with diacetylxylosan is formed from BzO_2H and diacetylxytal. Glucosan has properties closely resembling those of (I).

C. J. WEST (b).

Precipitation of sugars and polyhydric alcohols by heavy metal hydroxides in alkaline medium. P. FLEURY and J. COURTOIS (Compt. rend., 1932, 194, 728—731).—The amount of glucose or mannitol absorbed by the metal hydroxide when alkali [NaOH , or better, $\text{Ba}(\text{OH})_2$ or aq. NH_3] is added at 0° to a solution of the sugar and a heavy metal nitrate increases in the order Zn , Hg , Bi , Co , Ni , Pb , Cr , Cu , Cd , Al , Fe . Since comparable results are obtained with various sugars and polyhydric alcohols, the absorption is of general character. Greater absorption occurs with acetates than with mineral acid anions.

J. W. BAKER.

Rates of formation of the active reductants of several sugars. M. H. ROEPKE and J. M. ORT.—See this vol., 345.

The methylglucoses of Pacsu. II. R. SCHINLE (Ber., 1932, 65, 315—320; cf. A., 1931, 1399; Pacsu, this vol., 254).—Re-examination of Pacsu's "4:5:6-trimethylglucose dibenzylmercaptal," m. p. 98°, $[\alpha]_D^{25}$ -63.9° in pyridine, shows the compound to contain only 1 OMe and hence to be 4-methylglucose dibenzylmercaptal. This view is confirmed by the prep. of the Ac_4 derivative, m. p. 69—70°. Removal of the mercaptal residues followed by treatment with $NHPh \cdot NH_2$ affords, therefore, 4-methylglucosazone, m. p. 159°, $[\alpha]_D^{25}$ -13° in EtOH (final val.). Since methylation of isopropylidene-glucose dibenzylmercaptal, m. p. 04°, followed by hydrolysis with 0.1N-HCl affords 2-methylglucose dibenzylmercaptal, m. p. 191°, it follows that the OMe_2 group is attached in the 5:6 position. The diisopropylidene compound which yields a 4-methylglucose has the groups in the positions 2:3 and 5:6. H. WREN.

Catalytic fission of triphenylmethyl ethers by hydrogen and oxygen. F. MICHEEL (Ber., 1932, 65, [B], 262—265).—Mannitol in pyridine is converted by the successive action of CPh_3Cl and Ac_2O into 1:6-ditriphenylmethylmannitol 2:3:4:5-tetra-acetate, m. p. 180—181°, $[\alpha]_D^{25}$ +46.4° in $CHCl_3$, transformed by $HCl-CHCl_3$ into mannitol 2:3:4:5-tetra-acetate, m. p. 123—125°, $[\alpha]_D^{25}$ +3° in $CHCl_3$. In AcOH in presence of spongy Pt it is converted by H_2 into the tetra-acetate and $CHPh_3$, whereas with a mixture of H_2 and O_2 it affords the tetra-acetate, ditriphenylmethyl peroxide, and $CHPh_3$. 6-Triphenylmethyl- α -methylglucose 2:3:4-triacetate with H_2 yields a mixture of methylglucoside 2:3:4- and 2:3:6-triacetate (acetylated to α -methylglucoside 2:3:4:6-tetra-acetate, m. p. 101°) and $CHPh_3$. These products are also obtained when a mixture of H_2 and O_2 is used; the peroxide does not appear to be formed. H. WREN.

Reactions of trimethylamine compounds of sugars. F. MICHEEL and H. MICHEEL (Ber., 1932, 65, [B], 258—261).—Glucosidotrimethylammonium bromide and CPh_3Cl in $CHCl_3$ afford 6-triphenylmethylglucosidotrimethylammonium bromide (I), m. p. 183—185°, $[\alpha]_D^{25}$ +14.8° in EtOH, and 6-triphenylmethylglucosidopyridinium chloride, m. p. 177°, $[\alpha]_D^{25}$ +42.4° in EtOH. Glucosidopyridinium chloride has m. p. 176°. 6-Triphenylmethyl- β -methylglucoside, m. p. 103—105°, $[\alpha]_D^{25}$ -45.5° in $CHCl_3$, is obtained from (I) and $NaOH-MeOH$. Triacetyl- β -xylosido- and triacetyl- β -isorhamnosido-trimethylammonium bromide are very slowly decomposed by alkali. There appears little tendency towards the formation of a 1:3 ring. H. WREN.

Products of oxidation of d -galactose by atmospheric oxygen and ammoniacal copper oxide at room temperature. (Mlle.) Y. GARREAU and J. PARROT (Compt. rend., 1932, 194, 657—659).—By passing air through an aq. solution of d -galactose containing $Cu(OH)_2$ and NH_3 (A., 1931, 852) are obtained $H_2C_2O_4$, glyoxaline, 4-d-lyxotetrahydroxy-

butylglyoxaline, m. p. 132° (picrate, m. p. 164°), and its 2-OH- CH_2 derivative, m. p. 201°.

J. W. BAKER.

1:6-Acetodibromogalactopyranose. H. SCHLUBACH and E. WAGENITZ (Ber., 1932, 65, [B], 304—308).—The action of HBr on β -penta-acetyl-galactose for 6 hr. at room temp yields 1:6-acetodibromogalactopyranose (I), m. p. 100°, $[\alpha]_D^{25}$ +203° ($\pm 0.5^\circ$) in $CHCl_3$, converted by Ag_2CO_3 and $MeOH$ into triacetyl- β -methylgalactoside 6-bromohydrin, m. p. 92°, $[\alpha]_D^{25}$ -4.9° ($\pm 0.9^\circ$) in $CHCl_3$. The bromohydrin in $MeOH$ is converted by H_2-Pd into triacetyl- β -methyl- d -fucoside, m. p. 98.5°, $[\alpha]_D^{25}$ -5.9° ($\pm 0.5^\circ$) in $CHCl_3$, hydrolysed by $NaOMe$ in $MeOH$ to β -methyl- d -fucoside, m. p. 120°, $[\alpha]_D^{25}$ -24.4° ($\pm 0.5^\circ$) in $CHCl_3$, and thence by $N \cdot H_2SO_4$ to d -fucose. H. WREN.

Preparation of crystalline methyl- d -gulosides by means of co-ordination compounds with calcium chloride. H. S. ISBELL (Bur. Stand. J. Res., 1932, 8, 1—8).—By refluxing α - d -gulose, $CaCl_2 \cdot 2H_2O$, and anhyd. HCl in $MeOH$, neutralisation with $CaCO_3$, and evaporation are obtained the compounds α - $S_2CaCl_2 \cdot 2H_2O$, m. p. 185—190°, $[\alpha]_D^{25}$ +66.8° in H_2O , converted by crystallisation from EtOH into $(\alpha-S)_2CaCl_2 \cdot 3H_2O$, $[\alpha]_D^{25}$ +82.8° in H_2O , m. p., after becoming anhyd., 215° (decomp.); β - $S_2CaCl_2 \cdot 2H_2O$, m. p. 155°, $[\alpha]_D^{25}$ -45.7° in H_2O , converted by crystallisation from EtOH into $(\beta-S)_2CaCl_2$, m. p. 238° (decomp.), $[\alpha]_D^{25}$ -64.9° in H_2O (S =methyl- d -guloside). From these, either by treatment with $Ag_2C_2O_4$ (α) or by crystallisation from hot H_2O (β), are obtained α -, + H_2O , m. p. 77°, $[\alpha]_D^{25}$ +109.4° in H_2O (converted by Ac_2O and pyridine into its Ac_4 derivative, m. p. 98°, $[\alpha]_D^{25}$ +97.3° in $CHCl_3$), and β -, m. p. 176°, $[\alpha]_D^{25}$ -83.3° in H_2O (Ac_4 derivative, m. p. 66—67°, $[\alpha]_D^{25}$ -32.1° in $CHCl_3$), -methyl- d -guloside. J. W. BAKER.

Modification of the Selivanov and Ihl-Pechmann reactions for fructose. C. I. KRUISHEER (Rec. trav. chim., 1932, 51, 273—278).—The interference of glucose, galactose, mannose, and other monosaccharides (aldoses) with the Selivanov and Ihl-Pechmann reactions for fructose is abolished by oxidation of the aldose with $I+NaOH$ and removal of excess I (as Cu_2I_2 by treatment with $CuSO_4$ and Na_2SO_3), prior to carrying out the reactions. The interference of di- and poly-saccharides is only partly abolished by this treatment, owing to the production of aldose during the heating with HCl and $m-C_6H_4(OH)_2$ or $NHPh_2$. The new technique can be applied to the determination of 0.05% of fructose in urine. H. BURTON.

Mechanism of carbohydrate oxidation. XV. Behaviour of 3-glucosidoarabinose hepta-acetate towards aqueous solutions of potassium hydroxide. W. L. EVANS and C. C. CLARK (J. Amer. Chem. Soc., 1932, 54, 698—705; cf. this vol., 148).—The amounts of lactic acid and pyruvaldehyde obtained by the alkaline degradation of 3-glucosidoarabinose hepta-acetate are approx. the same as those from cellobiose and maltose under the same con-

ditions, in accordance with the view that 3-glucosido-arabinose is an intermediate in the alkaline degradation of the disaccharides. The yields of HCO_2H from maltose and approx. 3.2*N*-KOH, and cellobiose and 2*N*-KOH, tend towards lower vals. than those for the hepta-acetate; since small amounts of HCO_2H in much AcOH are determined only with difficulty, the vals. reported only indicate the tendency of the reaction.

C. J. WEST (b).

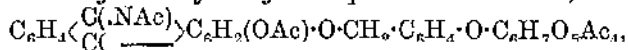
Anthraglucosides, especially aloin and peristaltin. F. HAUSER (Pharm. Acta Helv., 1931, 6, 79—85; Chem. Zentr., 1931, ii, 1709).—Aloin was boiled for 30 min. with aq. $\text{Na}_2\text{B}_4\text{O}_7$ and the dark, fluorescent (green) solution treated with HCl ; the ppt. when recryst. (C_6H_6 , AcOH) had m. p. 194—195°. Its yellow solution in dil. NaOH in absence of air exhibited a green fluorescence, and in air became red from the surface downwards, finally not fluorescing. Aeration of the alkaline solution followed by acidification affords aloe-emodin, m. p. 224°. Aloin is aloe-emodinanthranol-*d*-arabinoside (the 9- or 10- $\text{CHO}[\text{CH}(\text{OH})_3\text{CH}_2\text{O}$ derivative of 1:8-dihydroxy-3-hydroxymethylanthracene, preferably the 9-compound, the 10-derivative representing barbaloin). Peristaltin from *Cortex Rhamni purshianae* behaves similarly; the glucosides are therefore rhamnosides of the anthranols of crysophanic acid, of frangulaemodin Me ether, and of cascariol.

A. A. ELDRIDGE.

Composition of salinigrin. H. A. D. JOWETT (J.C.S., 1932, 721—722).—Salinigrin is identical with piceoside; its aglucone is *p*-hydroxyacetophenone.

D. E. KAHN.

Coupling of hydroxyanthraquinones with salicin. A. MULLER (Ber., 1932, 65, [B], 329—337; cf. A., 1931, 826, 940).—Alizarin is converted by acetobromosalicin and Ag_2O in quinoline into 2-acetosalicosylalizarin [1:2-dihydroxyanthraquinonyl 2-*o*- β -acetoglucoxybenzyl ether], m. p. 188°, $[\alpha]_D^{25}$ —26.19° in CHCl_3 , transformed by Ac_2O in pyridine into 2-acetosalicosyl-1-acetylalizarin, m. p. 198°, and by NaOH - EtOH into 2-salicosylalizarin (+0.5 H_2O), m. p. 267—269° (*Na* salt). Treatment of acetosalicosylalizarin with NH_3 - MeOH at 100° yields non-cryst. 1-acetoxy-2-acetoglucoxyanthraquinone-9-acetimine,



m. p. 205° (decomp.) after darkening at 185°, transformed by boiling HCO_2H into 2-acetosalicosyl-1-acetylalizarin, m. p. 198°. With MeI and Ag_2O , acetosalicosylalizarin gives the *Me* ether,

$\text{C}_{36}\text{H}_{34}\text{O}_{14}\cdot\text{H}_2\text{O}$, m. p. (indef.) 126—128° after softening at 85°, $[\alpha]_D^{25}$ —42.05° in CHCl_3 . Chrysazin, acetobromosalicin, and Ag_2O in quinoline afford 1:8-dihydroxyanthraquinonyl 8-*o*- β -acetoglucoxybenzyl ether (8-acetosalicosylchrysazin), m. p. 159°, $[\alpha]_D^{25}$ —60.83° in CHCl_3 , whence by Ac_2O in pyridine, 1-acetyl-8-acetosalicosylchrysazin, m. p. 206—207°. With NH_3 - MeOH at 60—80°, acetosalicosylchrysazin gives the imine dihydrate, $\text{C}_{29}\text{H}_{25}\text{O}_9\text{N}\cdot 2\text{H}_2\text{O}$, m. p. 215°, whereas at 100° the imine, m. p. 245°, is produced. Treatment of the imine with Ac_2O in pyridine yields 9-imino-1:8-dihydroxyanthraquinonyl 8-*o*- β -acetoglucoxybenzyl ether, m. p. 140—142°, with some

acetylacetosalicosylchrysazin. It is hydrolysed by dil. HCl (which does not attack acetylacetosalicosylchrysazin) to acetosalicosylchrysazin. With NaOAc and Ac_2O the imine yields an (?) anthrapyridine derivative.

H. WREN.

[Hydrolysis of polysaccharides.] F. KLAGES (Ber., 1932, 65, [B], 302—304).—In reply to Freudenberg and others (A., 1930, 1025), it is shown mathematically that the differentiation between main valency chain mols. and small mols. cannot be effected by measurements of the rates of hydrolysis of polysaccharides.

H. WREN.

Heavy metal catalysts. I. Fission of starch by artificial peroxidase. T. OMORI.—See this vol., 346.

Starch. A. ECKERT and A. MARZIN (J. pr. Chem., 1932, [ii], 133, 110—113).—Amylopectin is readily obtained from starch by treatment with boiling 0.1*N*- MeOH - HCl , whereby the amylose is dissolved. The yields of amylopectin from potato, arrowroot, maize, wheat, and rice starches are 83, 80, 75, 63, and 80%, respectively.

H. BURTON.

Cellulose. J. DUCLAUX (Bull. Soc. chim. Belg., 1932, 41, 1—29).—A lecture.

Molecular structure of cellulose and of amylose. W. N. HAWORTH (Nature, 1932, 129, 365).—Evidence has been obtained that cellulose is a limited straight chain containing not more than 100 cellobiose or 200 glucose units, representing a mol. wt. of approx. 30,000. Similarly, the amylose portion of starch has 10 maltose or 20 α -glucose units in a limited chain with a mol. wt. \approx 4000.

L. S. THEOBALD.

Synthesis of ethylcellulose. S. N. USCHAKOV and I. M. SCHNEER (Plast. Massi, 1931, 1, 17—26).—Bleached cotton linters containing 92% of α -cellulose was mercerised with 20 mols. of 50% NaOH during 48 hr., the excess of alkali removed by pressing the material until it contained 110—125% of moisture, and the alkali-cellulose heated with 4—35 mols. of EtCl ; C_6H_6 was added to keep the vol. const. when less than 12 mols. of EtCl were employed. The best results were obtained by using 6 mols. of EtCl . Increased length of heating (from 8 to 18 hr.) increases both the yield and the OEt content (up to 99% and 39%, respectively) and raising the temp. to 130° has a similar effect, but above 130° the yield diminishes and the product is coloured; the optimum temp. is 120—130°. Mercerisation with 40% alkali leads to diminished yields and impaired quality; increased duration of mercerisation causes a slight improvement. Removal of the residual H_2O by means of C_6H_6 or PhMe (moisture content 90—40%) raises the OEt content of the product at the expense of its tensile qualities and viscosity. The viscosity also decreases from 20 to 5 when the amount of EtCl is raised from 6 to 35 mols.; treatment of the finished material with H_2O or EtOH - NH_3 under pressure does not cause an appreciable diminution of its viscosity. Ethylcellulose, especially with an OEt content $>45\%$, is very resistant to dilute H_2SO_4 , NH_3 , and H_2O .

G. A. R. KON.

X-Ray examination of cellulose xanthate. I. SAKURADA and K. HUTINO (Sci. Papers Inst. Phys.

Chem. Res. Tokyo, 1932, 17, 294—296).—Cellulose xanthate giving a characteristic X-ray diagram different from that of alkali-cellulose and having a fibre period of 10.3 ± 0.2 Å. has been prepared. The composition corresponds with the formula $C_{12}H_{19}O_9 \cdot CS_2Na$.

R. CUTHILL.

Chemical reactivity of certain classes of amines. M. GRUNFELD (Compt. rend, 1932, 194, 892—895).—In agreement with views previously expressed (this vol., 365) the velocity of formation of substituted malonamides by interaction of bases of the type $R \cdot [CH_2]_n \cdot NH_2$ with $CH_2(CO_2Et)_2$ in EtOH at 100° is the same for *n*-amyl-, *n*-octyl-, and *n*-dodecyl-amines (24% in 30 hr.), a similar agreement (9.5% in 30 hr.) being observed with 8-amino-*n*-heptane, cyclohexyl- and 2-methylcyclohexyl-amine [all of type $NH_2 \cdot CH \cdot [CH_2]_n \cdot R'$]. The following are described: *s*-di-*n*-dodecyl-, m. p. 120—121°; di(cyclohexyl)-, m. p. 273° (block); di-(2-methylcyclohexyl)-, m. p. 265° (block), -oxamide: *s*-phenyl-*n*-dodecylcarbamide, m. p. 84—85°; *s*-di-*n*-octyl-, m. p. 126°; di-*n*-dodecyl-, m. p. 127°; di-(*n*-propyl-*n*-butyl)-, m. p. 147°; di(cyclohexyl)-, m. p. 167.5° (block); and di-(2-methylcyclohexyl)-, m. p. 210.5° (block), -malonamide.

J. W. BAKER.

Some complex peroxides of hexamethylenetetramine. A. PERRET and A. M. KRAWCZYNSKI (Compt. rend., 1932, 194, 376—378).—Interaction of hexamethylenetetramine and Bz_2O_2 in EtOH or $CHCl_3$ affords the products $C_6H_{12}N_4 \cdot Bz_2O_2$, m. p. 135—136°, and $2C_6H_{12}N_4 \cdot Bz_2O_2$, decomp. 193° after partial melting at 136°. Reaction of the base with $Bz_2O_2 \cdot Ac$ gives the compounds $C_6H_{12}N_4 \cdot Bz_2O_2 \cdot Ac$, m. p. 134—135°, and $3C_6H_{12}N_4 \cdot Bz_2O_2 \cdot Ac$, decomp. 205°. Other additive products cannot be obtained by varying the proportions of the reactants. J. L. D'SILVA.

Configurations of α - and β -forms in the sugar series. II. Configuration of glucosamine. F. MICHEEL and H. MICHEEL (Ber., 1932, 65, [B], 253—258; cf. A., 1930, 455).— α -Acetobromo-*d*-xylose in C_6H_6 is transformed by NMe_3 in EtOH- H_2O into 2:3:4-triacetyl- β -xylosidotrimethylammonium bromide, m. p. 181° (decomp.), $[\alpha]_D^{20} -20.8^\circ$ in H_2O . Similarly, acetobromoisorhamnose affords 2:3:4-triacetyliso-rhamnosidotrimethylammonium bromide, m. p. 162—163°, $[\alpha]_D^{20} +8.3^\circ$ in H_2O . Acetobromoglucosamine hydrobromide and NMe_3 in EtOH yield non-cryst. triacetylglucosaminotrimethylammonium bromide hydrobromide, transformed by boiling HCl-MeOH into 6-glucosaminotrimethylammoniumchloridehydrochloride, m. p. 140—143°, $[\alpha]_D^{20} +16.0^\circ$ in H_2O . Probably glucosamine has the glucose configuration.

H. WREN.

Hydrolysis of chitin by hydrochloric acid. II. L. ZECHMEISTER and G. TÓTH (Ber., 1932, 65, [B], 161—162; cf. A., 1931, 1279).—The isolation of chitotrioso as the undeca-acetate, $C_{13}H_{24}O_{13} \cdot N_3Ac_{11}$, m. p. 315° (corr., decomp.), $[\alpha]_D^{20} +33^\circ$ in AcOH, from the products of the hydrolysis of chitin by HCl is described. Fresh solutions of chitin in HCl (*d* 1.21) are levorotatory, but become inactive at room temp. in about 8 hr. If the strongly levorotatory solution is so diluted with ice that a ppt. is not produced, the val. of $[\alpha]_D$ decreases immediately. Determination of

mol. wt. in boiling AcOH is advocated for peracetylated sugars. H. WREN.

Preparation of diacetoneamine. T. SUZUKI and C. HORIE (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 383—388).—Addition of the following substances to $COMe_2$ saturated with NH_3 causes formation of the stated percentage of diacetoneamine in 24 hr. at room temp.: SO_2 , 25; NH_4NO_3 , 41; NH_4NO_2 , 45; KCN , 27; NH_4CNS , 31; NH_4OAc , 17%.

R. S. CAHN.

Imide and amide chlorides of non-aromatic acids. I. Preparation of substituted glyoxalines. A. HEYMONS (Ber., 1932, 65, [B], 320—329; cf. A., 1930, 613).—Heptoethylamide, b. p. 154°/15 mm., from heptoyl chloride and NH_2Et , is converted by gradual addition of PCl_5 to its solution in C_6H_6 at 0° into α -chloro- Δ^8 -heptenylhepto- NN' -diethylamidine, $C_5H_{11} \cdot CH_2 \cdot C(NEt) \cdot NEt \cdot COCl \cdot CH \cdot C_5H_{11}$ (chloroplatinate, m. p. 119°), which passes slowly at room temp., very rapidly when heated, into 1-ethyl-4(5)-amyl-2-hexylglyoxaline ethochloride, m. p. 99° (chloroplatinate, m. p. 130°; corresponding ethiodide, m. p. 81°). When heated above its m. p. the ethochloride yields $EtCl$ and 1-ethyl-4(5)-amyl-2-hexylglyoxaline, b. p. 193—199°/15 mm. (non-cryst. picrate, hydrochloride, and oxalate). $NHEt \cdot OAc$ and PCl_5 yield the chlorovinyl base, $C_8H_{15}N_2Cl$ (chloroplatinate, decomp. 188°), which is so sensitive towards alkali that when liberated from its hydrochloride it is mainly hydrolysed either to acetylacet- NN' -diethylamidine, b. p. 102—103°/12 mm. [chloroplatinate, m. p. 161° (decomp.); non-cryst. picrate and hydrochloride; picrolonate, m. p. 189°], or to $NHEt \cdot OAc$. The chlorovinyl base is readily isomerised to the corresponding, very hygroscopic ethochloride, which loses $EtCl$ when heated and forms 2-methyl-1-ethylglyoxaline (picrate, m. p. 171°). The instability of the chloroalkenyl bases diminishes with increasing size of the acid residue and increase in the number of C atoms of the group attached to N. Hexoethylamide, b. p. 152—154°/14 mm., yields α -chloro- Δ^8 -hexenylhexo- NN' -diethylamidine (chloroplatinate, m. p. 127°), from which are derived 1-ethyl-4-butyl-2-amylglyoxaline ethochloride (chloroplatinate, m. p. 135°), and 1-ethyl-4(5)-butyl-2-amylglyoxaline, b. p. 168—174°/14 mm. (non-cryst. hydrochloride and oxalate; picrates, m. p. 96° and 71°, respectively). $CH_2Ph \cdot CO \cdot NHEt$ yields the very unstable β -chlorostyrylphenylacet- NN' -diethylamidine [chloroplatinate, m. p. 171° (decomp.)] and 4(5)-phenyl-2-benzyl-1-ethylglyoxaline, b. p. 225—235°/14 mm. (non-cryst. ethochloride; picrates, m. p. 155—157° and 133—135°, respectively). $Et \cdot CO \cdot NHEt$ yields the unstable α -chloropropenylpropion- NN' -diethylamidine (chloroplatinate, m. p. 195°) and 4(5)-methyl-1:2-diethylglyoxaline, b. p. 103—112°/14 mm. (ethochloride, m. p. 103°; hydrochloride; picrate). Propionylpropion- NN' -diethylamidine, b. p. 113—116°/13 mm. (non-cryst. hydrochloride; picrate, m. p. 76°), is described. 2-Methyl-1-benzylglyoxaline benzyl chloride, m. p. 208°, has been prepared. H. WREN.

Chemistry of three-carbon system. XXVIII. Nitriles of butenoic and hexenoic acids. Analysis of unsaturated nitriles by halogen addition. R. A. LETCH and R. P. LINSTED (J.C.S., 1932,

443—456; cf. A., 1929, 1294).—Nitriles of butenoic, *n*- and *iso*-hexenoic acids are prepared; bromometric and iodometric methods for analysing the mixtures of $\alpha\beta$ - and $\beta\gamma$ -unsaturated nitriles are discussed. Corresponding nitriles are obtained from unsaturated amides. Δ^{α} -*n*-Hexenoamide, m. p. 122°, yields Δ^{α} -hexenonitrile, b. p. 50°/10 mm.; Δ^{β} -*n*-hexenoamide, m. p. 86°, yields Δ^{β} -hexenonitrile, b. p. 58/15 mm. Dehydration of *n*-valeraldehyde cyanohydrin yields α -hydroxy-*n*-hexenitrile, b. p. 116°/14 mm.; α -cyano- Δ^{α} -hexenoic acid, m. p. 102°, and *isovaleraldehyde* cyanohydrin yield mixtures of nitriles. Tautomeric changes undergone by nitriles with alkalis are followed quantitatively; heat has little effect. Δ^{β} -*n*-Hexenonitrile and NaOEt gave β -ethoxy-*n*-hexenonitrile, b. p. 82°/11 mm. D. E. KAHN.

Syntheses with diazomethane. VII. Reaction of aldehydes and ketones. F. ARNDT, J. AMENDE, and W. ENDER.—See this vol. 383.

Supposed optical activity of ethyl diazsuccinate. II. A. WEISSBERGER and H. BACH (Ber., 1932, 65, [B], 265—267; cf. this vol., 151).—Homogeneous Et diazsuccinate, m. p. about -24°, $[\alpha]_{D}^{20} \pm 0^{\circ}$, is prepared by diazotising Et *l*-aspartate in presence of H_2SO_4 , washing the product in Et_2O with NH_3 and then with H_2O , distilling in a high vac., and crystallisation from a mixture of Et_2O and light petroleum. The "optically active ester" is treated with H_2 in presence of colloidal Pd and the product distilled in a high vac., thus giving Et *d*-malate, $\alpha_D +7.92^{\circ}$ or $+8.06^{\circ}$ ($l=1$). H. WREN.

Aliphatic diazo-compounds. III. Action of aliphatic diazo-compounds on thion esters and a new type of ethane derivatives. A. SCHONBERG, S. NICKEL, and D. CERNIK (Ber., 1932, 65, [B], 289—293; cf. A., 1931, 218).—Addition of Ph_2CS_2 to diazomethane in Et_2O yields 4:4:5:5-tetraphenylthioltrimethylene I:3-disulphide, $CH_2 \begin{smallmatrix} S-C(SPh)_2 \\ S-C(SPh)_2 \end{smallmatrix}$, decomp. about 140° when rapidly heated, whereas with diazoethane the product is 1:1-diphenylthiol-2-methylethylene sulphide, $(PhS)_2C \begin{smallmatrix} CHMe \\ S \end{smallmatrix}$, m. p. 64—67° to a turbid liquid. 4:5-Dimethylthiol-4:5-di- α -naphthyltrimethylene 1:3-disulphide, m. p. (indef.) 140° (decomp.), is obtained from $C_{10}H_7CS_2Me$. Reversible changes in colour are observed when the following solutions are heated: $C_{10}H_7CS_2Me$ in $BzOEt$; Ph diphenyldithioacetate in $C_6H_4Me_2$; Ph_2CS_2 in $BzOEt$; Ph_2 diselenide in PhMe. H. WREN.

Thermal reactions of cycloparaffins and cycloolefines. G. EGLOFF, H. T. BOLLMAN, and B. L. LEVINSON (J. Physical Chem., 1931, 35, 3489—3552).—The literature on the reactions of hydrogenated cyclic compounds (naphthenes) and unsaturated compounds of the type of tetrahydronaphthalene and cyclohexene at various temp. and pressures and in the presence of different catalysts is reviewed. The reactions which occur are: C—C scission, hydrogenation or dehydrogenation, polymerisation or depolymerisation, and isomeric change. Any or all of these may take place when a hydrocarbon is treated with some activating agent, such as heat or a reagent. L. KELLEY (c).

Slow combustion of 1:3-dimethylcyclopentane in heterogeneous system. G. CHAVANNE and O. MILLER (Bull. Soc. chim. Belg., 1931, 40, 611—625; cf. A., 1927, 452).—Slow oxidation of the liquid at 80° yields a number of products, which have been investigated. AcOH, α -keto- β -methyl-*n*-hexoic acid, and Me isoamyl ketone preponderate.

C. W. DAVIES.

Preparation of 1:1-dimethylcyclohexane and 1:1-dimethylcyclopentane. Stability of these hydrocarbons to oxygen. G. CHAVANNE, M. O. MILLER, and (Mlle.) CORNET (Bull. Soc. chim. Belg., 1931, 40, 673—688).—Reduction of 1:1-dimethyl-5-chloro- Δ^4 -cyclohexen-3-one by H_2 in presence of Ni at 215° (or less well by Adams' method) gives mainly 1:1-dimethylcyclohexan-3-one (I), b. p. 178—178.5°/748 mm., 72—73°/25 mm. [semicarbazone, m. p. 219° (lit. 203°)], and 1:1-dimethylcyclohexan-3-ol (II) (*p*-nitrobenzoyl derivative, m. p. 83°), with a little 1:1-dimethylcyclohexane (III) and unsaturated hydrocarbons. (I) affords (II) on reduction in presence of Pt. Dehydration of (II) by *p*-toluenesulphonic acid gives a mixture of 1:1-dimethyl- Δ^2 - or - Δ^3 -cyclohexane, readily reduced to (III). 1-Chloro-1-methylcyclopentane and $MgMeI$ give 1-methyl- Δ^1 -cyclopentene and some (10%) 1:1-dimethylcyclopentane (IV). Catalytic reduction of 1:1-dimethylcyclopentan-2-one affords the alcohol (allophosphate, m. p. 158—159°), which with *p*-toluenesulphonic acid at 145° gives 1:2-dimethyl- and some 1:1-dimethyl-cyclopentene, both reduced catalytically to the saturated compounds. Cyclisation of $\beta\beta$ -dimethyladipic acid [prepared by oxidation of the mixture of (I) and (II) with HNO_3] by Al_2O_3 gives 1:1-dimethylcyclohexan-3-one, reduced in presence of Ni at 165° to the corresponding alcohol, b. p. 157—161°, which with Al_2O_3 at 350° yields 1:1-dimethyl- Δ^2 -cyclopentene, readily reduced in AcOH in presence of Pt-black to (IV), m. p. -77°. (III) and (IV) are stable to O_2 at 110° and 80°, respectively. It is considered that O_2 attacks hydrocarbons at the CH₃ group. R. S. CAHN.

Reaction of unsaturated hydrocarbons with nitrous anhydride and nitrogen peroxide. Products of the action of nitrous anhydride on cyclopentene. N. I. DEMJANOV and V. V. WILLIAMS (Bull. Acad. Sci. U.S.S.R., 1931, 1123—1140; cf. A., 1899, i, 845).—Previous work on this subject is discussed. The action of N_2O_3 on cyclopentene in Et_2O yields:

(1) the ψ -nitrosite, $CH_2 \begin{smallmatrix} CH(NO) \\ CH_2 \end{smallmatrix} > CH-NO$, m. p. 104—105° (decomp.), which forms an uncrystallisable nitrolamine when treated with NH_2Ph in $EtOH$, and is converted by the action of KOMe into a mixture of nitrocyclopentene, b. p. 105—108°/30 mm., d_4^{20} 1.305, with methoxynitrocyclopentane (not obtained pure); with NaOMe, the latter gives the Na derivative, $OMe-CH_2-C_3H_6-CN-NO_2$. (2) A liquid product which gives cyclopentanone, 1:2-diaminocyclopentane (picrate, m. p. 221°), and 1-hydroxy-2-aminocyclopentane, m. p. 63—64° (picrate, m. p. 155°), on reduction with Sn and HCl. T. H. POPE.

Slow combustion of 1:3-dimethylcyclohexane in heterogeneous system. G. CHAVANNE, (MME.) PAHLAVOUNI, and (Mlle.) KATZENSTEIN (Bull. Soc.

chim. Belg., 1931, 40, 626—641; cf. A., 1930, 768).—Absorption of O_2 at room temp. is extremely slow in diffused light, more rapid in sunlight. On prolonged treatment with O_2 at 100° the liquid gives mainly 1:3-dimethylcyclohexanol, with AcOH, a methyl- ϵ -ketoheptonic acid, and other products.

C. W. DAVIES.

Synthesis and nitration of phenylcyclohexane. O. NEUNHOEFFER (J. pr. Chem., 1932, [ii], 133, 95—109).—cyclohexyl chloride, C_6H_5 , and $AlCl_3$ give a mixture of (mainly) phenylcyclohexane (I), some *p*-dicyclohexylbenzene (II), m. p. 102° [oxidised by HNO_3 (d 1.04) to p - $C_6H_4(CO_2H)_2$], and a little 1-phenyl-2-methylcyclopentane [oxidised by O_3 (above 15% concn.) to 2-methylcyclopentane-1-carboxylic acid]. The yield of (I) increases and that of (II) diminishes when a large excess of C_6H_5 is used. Nitration of (I) with Ac nitrate in AcOH gives *p*- (III), b. p. $142^\circ/0.5$ mm., and *o*-, b. p. $113^\circ/0.5$ mm., m. p. 45° , -nitrophenylcyclohexanes in the ratio 78:22 (cf. Mayes and Turner, A., 1929, 550); (III) exists in trimorphous forms (m. p. 54° , 56° , and 57°). Electrolytic reduction of (III) gives *p*-cyclohexylaniline, converted by the usual methods into (I), m. p. 6° , *p*-iodophenylcyclohexane, b. p. $117^\circ/0.5$ mm., m. p. 4° , and *p*-cyclohexylbenzonitrile, b. p. $123^\circ/0.5$ mm., m. p. 41° . *o*-cyclohexylaniline, b. p. $106^\circ/0.5$ mm., m. p. 13° (Ac, m. p. 101° , and Bz, m. p. 154° , derivatives), is also prepared by electrolytic reduction of the NO_2 -derivative.

H. BURTON.

Benzylidenecyclohexane. D. N. KURSANOV (J. Gen. Chem. Russ., 1931, 1, 926—932).—Mg cyclohexyl bromide reacts with PhCHO giving 34% of phenylcyclohexylcarbinol and 18% of $CH_2Ph\cdot OH$; the carbinol was converted into the K xanthate, which gave 70% of the corresponding Me ester, m. p. 54 — 55° , by the action of MeI in C_6H_6 . The ester when heated under reduced pressure gave benzylidenecyclohexane, b. p. 117 — $118^\circ/10$ mm., d_4^{20} 0.9579, oxidised by $KMnO_4$ to cyclohexanone and BzOH. The hydrocarbon differs from that previously obtained from cyclohexene and $CH_2Ph\cdot OH$ (A., 1931, 349), which is considered to be identical with Auwers and Treppmann's benzylcyclohexene (A., 1915, i, 789).

G. A. R. KON.

Synthesis of homologues of benzene by the Friedel-Crafts method. B. V. TRONOV, (MLLE.) L. V. LADIGINA, and I. M. KARPENKO (J. Gen. Chem. Russ., 1931, 1, 910—916).—Study of the formation of CH_2Ph_2 from C_6H_6 and CH_2PhCl in the presence of $AlCl_3$, $SiCl_4$, $SnCl_4$, PCl_3 , $SbCl_3$, and $SbCl_5$ suggests that the activity of the halogen in the catalyst and the capacity of the central atom to assume a higher valency are of no importance (cf. A., 1931, 610). All the compounds capable of catalysing the reaction have a tendency to form mol. complexes and this is held to support the view that the formation of such a complex is the first stage in the reaction. This takes place owing to the attraction between the positive nucleus of the central atom of the catalyst and one of the (alternate) C atoms of the C_6H_6 ring which, according to Lowry's theory, have a complete octet of electrons. As the result, the H atom attached to the C in question is

more readily removed (cf. Dougherty, A., 1929, 421). Compounds such as PCl_3 and $SbCl_3$ are also capable of complex formation, but the central atom is attracted only to the positively-charged C atoms of the C_6H_6 ring, and this will tend to increase the control of the latter over the attached H atoms; these compounds cannot therefore catalyse the reaction between C_6H_6 and CH_2PhCl . Complex formation between the catalyst and the C_6H_6 ring of CH_2PhCl , with a consequent increase in the reactivity of the halogen, may explain the much greater reactivity of CH_2PhCl as compared with EtBr; the activities of the halogen in the two compounds are approx. equal, but EtBr is incapable of complex formation.

G. A. R. KON.

Solubility of water in benzene, toluene, and cyclohexane. D. N. TARASSENKOV and E. V. POLOSHINZEVA (Ber., 1932, 65, [B], 184—186).—Known wts. of H_2O and hydrocarbon are heated until complete dissolution is attained and the temp. of appearance and disappearance of turbidity are determined. The solubilities of H_2O in C_6H_6 , PhMe, and cyclohexane are recorded for the temp. intervals, $+5^\circ$ to 73° , -9° to $+93^\circ$, and $+14^\circ$ to $+53^\circ$, respectively.

H. WREN.

Steric hindrance in the hydrolysis of benzylidene chloride. G. LOCK and F. ASINGER.—See this vol., 345.

Nitrobenzenesulphonhydrazides. A. A. M. WITTE (Rec. trav. chim., 1932, 51, 299—319).—Curtius and Lorenzen's interpretation (A., 1899, i, 148) of the reaction between benzenesulphonhydrazide and I is incorrect, since *s*-dibenzenesulphonhydrazide is unaffected by conc. HI in boiling EtOH. *m*- $NO_2\cdot C_6H_4\cdot SO_2Cl$ (in C_6H_6) added to cold $N_2H_4\cdot H_2O$ gives *m*-nitrobenzenesulphonhydrazide (I), m. p. 126 — 127° (decomp.) [Ac, m. p. 155° (decomp.); Bz, m. p. 177° ; benzylidene, m. p. 153° ; isopropylidene, m. p. 153° (decomp.); anisylidene, m. p. 134° ; cinnamylidene, m. p. 188° (decomp.); salicylidene, m. p. 168° ; piperonylidene, m. p. 171° ; benzenesulphonyl, m. p. 180 — 185° , and *m*-nitrobenzenesulphonyl, decomp. 200 — 210° without melting, derivatives], converted by I in boiling EtOH into 3:3'-dinitrodiphenyl disulphoxide (II). *p*- $C_6H_4Cl\cdot NO_2$ and Na_2S_2 give (*p*- $NO_2\cdot C_6H_4\cdot S$) $_2$, and (*p*- $NO_2\cdot C_6H_4$) $_2S$, which are oxidised by fuming HNO_3 to *p*- $NO_2\cdot C_6H_4\cdot SO_3H$ [NH $_4$; Na (+3H $_2O$); Ca (+8H $_2O$), and Ba (+3H $_2O$), salts] and 4:4'-dinitrodiphenyl sulphoxide, m. p. 173° [corresponding sulphone, m. p. 254° (lit. 282°)], respectively. *p*-Nitrobenzenesulphonhydrazide (III), m. p. 146 — 147° (decomp.) [Ac, m. p. 218° ; Bz, m. p. 227° ; benzylidene, m. p. 142° ; isopropylidene, m. p. 172° ; anisylidene, m. p. 160° ; salicylidene, m. p. 178 — 179° ; piperonylidene, m. p. 185° , and *p*-nitrobenzenesulphonyl, decomp. 235 — 236° (darkens slowly above 180°), derivatives], is similarly converted by I into 4:4'-dinitrodiphenyl disulphoxide (IV), m. p. 159° . (I) and (III) heated to about 145° or at about 110° in presence of a little I, give (II) and (IV), respectively. 2:2'-Dinitrodiphenyl disulphoxide, chars about 200° , is obtained in small amount from I and *o*-nitrobenzenesulphonhydrazide, m. p. 97° (lit. 101°) (Ac, m. p. 194° ; benzylidene, m. p. 91° ; isopropylidene, m. p. 144° , and

piperonylidene, m. p. 177°, derivatives). *p*-Nitrobenzenesulphon-phenylhydrazide, m. p. 150°, and *p*-nitrophenylhydrazide, m. p. 172—173° (lit. 160° and 171—172°), and 4-chloro-2-nitrobenzenesulphon-phenylhydrazide, m. p. 151°, are described. Oxidation of the reaction product from 1:4-dichloro-2-nitrobenzene and Na_2S_2 with fuming HNO_3 gives 4-chloro-2-nitrobenzenesulphonic acid (the hydrazide could not be prepared) and a little 4:4'-dichloro-2:2'-dinitrodiphenyl sulphoxide. H. BURTON.

Spectrochemistry of acetylenic derivatives. K. VON AUWERS (Ber., 1932, 65, [B], 146—153).—Re-examination of the data of Krestinski and Persianzeva (A., 1931, 1412), in such a manner as to eliminate the influence of variation in mol. wt. shows that their conclusion that each new conjugation CPh:C increases the exaltations in refractive and dispersive power is invalid and that the supposition that the high exaltations are due in part to the alcoholic nature of the compounds is without foundation. Comparison of the recorded spectroscopic data of a series of ethylenic and acetylenic substances indicates no marked difference in the exaltation of the refractive indices for compounds with a sample conjugation except in the instances of ethylenic and acetylenic ketones and propiolonitrile. Similar results are obtained with compounds with three unsaturated groups, exceptions being $\Delta^{\alpha,\gamma}$ - α -phenylpentadiene and phenylpropiolonitrile. Diphenyldiacetylene exhibits an unusually high exaltation, but comparison with diphenylbutadiene is complicated by the occurrence of the latter in three forms. The dispersive power of acetylenic compounds is usually less enhanced than that of ethylenic derivatives. The consts. of *cis-cis*- and *cis-trans*-diphenylbutadiene, Ph propargyl ether, and Et propiolate are recorded. H. WREN.

***p*-Bromophenylacetylene.** C. DUFRASSE and A. DEQUESNES (Bull. Soc. chim., 1931, [iv], 49, 1880—1882).—*p*-Bromoacetophenone and PCl_5 afford about 52% of α -dichloro- α -*p*-bromophenylethane, b. p. 126—127°/18 mm., converted by 25% EtOH-KOH into *p*-bromophenylacetylene, m. p. 64—65°, b. p. 88—90°/16 mm., and α -chloro-*p*-bromostyrene, b. p. 118—122°/18 mm., yielding with Br a dibromide, m. p. 55—56°, and with KOAc in EtOH a white substance, m. p. 92°. R. BRIGHTMAN.

Orientation effects in diphenyl series. XI. Quantitative mono- and di-nitration of 4:4'-difluorodiphenyl. (Miss) F. R. SHAW and E. E. TURNER (J.C.S., 1932, 509—513).—Mononitration of 4:4'-difluorodiphenyl (I) gives not less than 97% of 2- NO_2 -compound (II). Nitration of (II) yields 35—36% of 4:4'-difluoro-2:2'-dinitrodiphenyl (III), m. p. 165°, and 64—65% of 2:3'-(NO_2)₂-compound; the action of KOH on the nitration product produces 4-fluoro-2:3'-dinitro-4'-ethoxydiphenyl. The synthesis of (III) is described. Dinitration of (I) is more complicated than for Br and Cl analogues. D. E. KAHN.

2-Nitro-4':4''-dimethyltriphenylmethane. I. TANASESCU and A. SILBERG (Bull. Soc. chim., 1932, [iv], 51, 97—99).—Condensation of *o*-nitrobenzylidene chloride with PhMe in presence of AlCl_3 affords 2-nitro-4':4''-dimethyltriphenylmethane, oxidised by

$\text{CrO}_3\text{-H}_2\text{SO}_4$ to 2-nitrobenzophenone-4'-carboxylic acid, m. p. 234—235°. HNO_3 or KMnO_4 did not oxidise the nitrotriphenylmethane.

R. BRIGHTMAN.

Polycyclic aromatic hydrocarbons. IX. Synthesis of methyl and isopropyl homologues of 1:2-benzanthracene. J. W. COOK (J.C.S., 1932, 456—472; cf. A., 1930, 903; this vol., 153).—6- and 7-isoPropyl-1:2-benzanthracenes, m. p. 130° and 125°, respectively (*picrates*, m. p. 118°, 152°; *quinones*, m. p. 94°, 114°), are synthesised from 1-cuminoyl-2-naphthoic (I), m. p. 215°, and 2-cuminoyl-1-naphthoic (II) acid, m. p. 160°, respectively. (I) and (II) (*acetoxylactones*, m. p. 215° and 126°, respectively) are derived from cumene and naphthalene-1:2-dicarboxylic anhydride. 3-(III) and 10-isoPropyl-1:2-benzanthracenes (IV), m. p. 92° and 94°, respectively, are synthesised, the latter from 1:2-benz-10-anthrone by the Grignard method. 1-isoPropylnaphthalene (V), b. p. 132°/12 mm. (*picrate*, m. p. 83.5—86°), is formed from the dimeride of 1-isopropenylnaphthalene, m. p. 194°. (V) condensed with phthalic anhydride forms 4'-isopropyl-1'-naphthoyl-2-benzoic acid, m. p. 206—208°, from which the *quinone* of (III), m. p. 154°, is derived. Pyrolysis of Me derivatives of 1:2-benzanthracene is described and the accompanying intramol. migrations are discussed. The following are described: 1:2-benzanthracene, m. p. 158—159°; 6-, 7-, 2'-, and 3'-methyl-1:2-benzanthracene, m. p. 151°, 182°, 149°, 160° [*picrates*, m. p. 152°, —, 180°, 144°; *quinones*, m. p. 174° (not new), 167°, 189°, 168°]; 6:7-, 2':6-, 2':7-, 3':6-, and 3':7'-dimethyl-1:2-benzanthracenes, m. p. 174°, 164°, 236°, 186°, 189° (*picrates*, m. p. 170°, 199°, —, —; *quinones*, m. p. 193°, 160°, 177°, 205°, 157°); 1-(3':4'-dimethylbenzoyl)-2-methylnaphthalene, m. p. 109°; 1-benzoyl-2:6- and -2:7-, 1-m-toluyol-2:6- and -2:7-, 1-p-toluyol-2:6- and -2:7'-dimethylnaphthalenes, m. p. 84°, 91°, 82°, 115°, 109°, 98°. D. E. KAHN.

Hydrogenation of rubrene. Two stereoisomeric dihydrorubrenes, $\text{C}_{42}\text{H}_{30}$. C. DUFRASSE, B. MASUMOTO, and R. BURET (Bull. Soc. chim., 1932, [iv], 51, 74—80).—With gaseous H_2 in Et₂O rubrene affords about 70—95% of a mixture of two stereoisomeric dihydrorubrenes, needles, m. p. 241—242° (paraffin bath), 249—250° (block), and massive crystals, m. p. 224—225° (paraffin bath), 230—231° (block), together with some μ -rubrene. The needles, m. p. 241—242°, are converted into the massive crystals by heating with Na amyloxyde in amyl alcohol. Hydrogenation with Na and amyl alcohol similarly affords a mixture of the dihydrorubrenes together with three other substances, m. p. 214°, 241°, and 307°. The dihydrorubrenes were not further hydrogenated with H_2 at 150°; at 180° a small amount of substance, m. p. about 110°, was formed. Hydrogenation with Na in anhyd. media, e.g., xylene, also affords a mixture of the dihydrorubrenes on decomp. with H_2O . It is suggested that addition takes place in 1:4-positions, yielding two racemic diastereoisomerides. R. BRIGHTMAN.

Hydrocarbons, isomeric with rubrene obtained by reduction of 9:11-diphenyl-9:12:10:11-dibenzo-9:11-dihydronaphthac-

ene. M. BADOCHÉ (Compt. rend., 1932, 194, 891—892).—Decomp. of the Na additive compound (by Schlenk's method, A., 1914, i, 396) of the hydrocarbon $C_{42}H_{28}$ (I), obtained by dehydrogenation of rubrene, with H_2O , affords the hydrocarbon $C_{42}H_{28}$, $+ 2C_6H_6$, m. p. 155—156°, and solvent-free, m. p. 302—303°, and a (?) stereoisomeric form, $+ C_6H_6$, m. p. 216—217°, and solvent-free, m. p. 337—338°, isomeric with rubrene, which are oxidised by PbO to (I) and hence result from the normal addition of Na to the double linking. On the basis of Dufraisse and Enderlin's structure for (I) (this vol., 261) these two hydrocarbons are probably stereoisomeric forms of 9:11-diphenyl-9:12:10:11-dibenzo-9:10:11:12-tetrahydronaphthacene. J. W. BAKER.

Modified Curtius reaction. VI. Reaction with chaulmoogric and hydnocarpic acids and their dihydro-derivatives. C. NAEGELI and E. VOGT-MARKUS (Helv. Chim. Acta, 1932, 15, 60—75).—This reaction is readily applied to the acid chlorides derived from the above acids providing active NaN_3 (prep. described) is used. Chaulmoogryl chloride (best prepared from purified PCl_3 and the acid at 70—80°) (*p*-chaulmoogrylamidoazobenzene, m. p. 123°, sinters at 115°) thus affords μ -(Δ^2 -cyclopentenyl)-dodecylamine, b. p. 190°/15 mm., m. p. 18° (45% yield) [*Ac* derivative, m. p. 60°, $[\alpha]_D^{25} + 45.3^\circ$ in EtOH (45% yield), together with a substance, m. p. 81—92°; hydrochloride (78% yield), m. p. 151°, $[\alpha]_D^{25} + 55.0^\circ$ in EtOH], converted by $KNCO$ into the corresponding carbamide, m. p. 107°. Hydnocarpic acid (prep. from hydnocarpus oil described) is similarly converted into κ -(Δ^2 -cyclopentenyl)decylamine, b. p. 169—170°/12 mm., m. p. 5—6° [*Ac* derivative, m. p. 53—57° (together with the above substance, m. p. 80—90°); hydrochloride, m. p. 146°, $[\alpha]_D^{25} + 59.55^\circ$; chloroplatinate; picrate, m. p. 109°; carbamide, m. p. 112°]. Dihydrochaulmoogric acid (by reduction of chaulmoogric acid with PtO_2 and H_2 at 2—3 atm.) affords μ -cyclopentylidodecylamine, b. p. 187°/12 mm., m. p. 13.5—15° [*Ac* derivative, m. p. 73° (and substance, m. p. 80—90°); hydrochloride, m. p. 195° (previous softening); chloroplatinate; picrate, m. p. 110°; carbamide, m. p. 109°], whilst dihydrohydnocarpic acid gives κ -cyclopentyldecylamine, b. p. 187°/16 mm., m. p. 2—3.5° [*Ac* derivative (43% yield), m. p. 64° (and a substance, m. p. 83—87°); hydrochloride, m. p. 162° (and a substance, m. p. 85—88°); chloroplatinate; picrate, m. p. 124°; carbamide, m. p. 122.5°].

J. W. BAKER.

p-Toluenesulphonates as derivatives for the identification of aromatic amines. C. R. NOLLER and P. LIANG (J. Amer. Chem. Soc., 1932, 54, 670—673).—The *p*-toluenesulphonates of aromatic amines can, in general, be readily prepared in a pure state and are satisfactory derivatives for identification. The following *p*-toluenesulphonates are described, of which those of the italicised bases are new: NH_2Ph , m. p. 238.4° (all m. p. are corr.); *o*-, m. p. 189.7—190.5°; and *m*-toluidine, m. p. 174.6—176.1°; *p*-toluidine, m. p. 197.7—199.2°; *m*-4-xylydine, m. p. 180.4—181.3°; *o*-, m. p. 192.9—193.6°, and *p*-chloroaniline, m. p. 213—231°; *m*-chloroaniline, m. p. 209.8—210.3°; *o*-, m. p. 206.1—206.6°, *m*-, m. p. 204.1—205.0°, and *p*-

bromoaniline, m. p. 214.2—234.2°; *o*-, an oil, *m*-, m. p. 213.5—215.5°, and *p*-nitroaniline, m. p. 232.2—234.7°; *o*-, m. p. 224.7—226.2°, and *m*-aminophenol, an oil; *p*-aminophenol, m. p. 252.1—253.6°; *o*-, *m*-, and *p*-aminobenzoic acids, m. p. 224.1—224.6°, 255.9—256.5°, and 236.5—241.5°, respectively; *p*-aminoacetophenone, m. p. 177.8—179.3°; α -, m. p. 248.4—249.9°, and β - $C_{10}H_7NH_2$, m. p. 217.3—219.1°; *o*-, m. p. 194.1—195.6°, and *p*-aminodiphenyl, m. p. 253.8—254.9°; NH_2CH_2Ph , m. p. 184.5—185.5°; *di*-benzylamine, m. p. 158.3—159.3°; tribenzylamine, m. p. 205—207.7°; benzylaniline, m. p. 148.3—148.8°; dibenzylaniline, oil; *o*-, *m*-, and *p*-phenylenediamine, m. p. 267.3—268.8°, 296.8—297.8°, and above 340°, respectively; 2:4-diaminotoluene, m. p. 270.8—271.3°. C. J. WEST (b).

Ternary compounds of sulphur dioxide with ketones and amines. F. FEIGL and E. FEIGL (Z. anorg. Chem., 1931, 203, 57—63).—The following compounds are described: $C_{10}H_7NH_2SO_2COMe_2$ (decomp. 110—120°); $(C_6H_5)_3(NH_2)_2SO_2COMe_2$ (decomp. 108—110°); $(C_6H_5)_2(NH_2)_2SeO_2COMe_2$; $C_6H_5(NO_2)NH_2SO_2COMe_2$ (m. p. 108°); $C_6H_5MeNH_2SO_2COMe_2$ (m. p. 77—78°); $C_6H_5N(SO_2COMe_2)_2$ (m. p. 80—82°); $C_6H_5N(SO_2COMe_2)_2$ (m. p. 85—86°); $C_6H_5N(SO_2COMe_2)_2$; $NH_2MeSO_2COMe_2$; $CH_3PhNH_2SO_2COMe_2$; $Ph[CH_2]_3NH_2SO_2COMe_2$; $N(CH_2Ph)_3SO_2COMe_2$ (m. p. 118—119°); $NPhCHPhSO_2COMe_2$ (m. p. 112—113°); $C_{10}H_7NH_2SO_2COMeEt$ (m. p. 83—84°); $NH_2PhSO_2C_6H_5OMe$ (decomp. 110°) (from aniline and 2-methylcyclohexanone), $NH_2PhSO_2COPhMe$, and $C_6H_5MeNH_2SO_2COPhMe$ (m. p. 108—110°).

E. S. HEDGES.

Addition of cyclic amines to butenenitriles [allyl cyanide]. A. MEVIS (Bull. Soc. chim. Belg., 1931, 40, 726—736).—Allyl cyanide and NH_2Ph at 150—180° in presence of catalysts, best $CuCl$ or CuO , afford β -anilinobutyronitrile, m. p. 57—58°, b. p. 169—172°/13—14 mm. (*NO*-derivative), in 40% yield; hot, conc. HCl partly decomposes and partly hydrolyses this to the hydrochloride of β -anilinobutyric acid [*Et* ester, b. p. 160.8°/13.5 mm. (hydrochloride, m. p. 172—173°); anilide, m. p. 212—213°]. *p*- and (more slowly) *o*-toluidine give similarly β -*p*- and β -*o*-toluidinobutyronitrile, m. p. 67—68° and 78—79.5°, b. p. 176—178°/11.5 mm. and 173—176°/11.6 mm., respectively. $NHPh_2$ isomerises the cyanide to crotononitrile.

R. S. CAHN.

Analogy between the benzidine change and the dissociation of oxides of nitrogen. New reagent for the recovery of secondary bases from nitrosoamines and for purifying amines. E. C. S. JONES and J. KENNER (J.C.S., 1932, 711—715).—Objections to regarding the decomp. of hydrazobenzene into NH_2Ph and azobenzene and the benzidine change as due to dissociation into radicals are refuted. The reduction of nitrosoamines in strongly acid (HA) solution is regarded as preceded by dissociation into the radicals $NHPhRA$ and NO ; this view is supported by the smooth decomp. of the *NO*-derivatives of $NHPhMe$, $NHPhEt$ (I), $NHPh_2$, piperidine (II), and triacetoneamine by $CuCl$ in conc. HCl at room temp. into NO and the free base. The *NO*-derivatives of

(I) and (II) have b. p. 93°/0.5 mm. and 85°/0.5 mm., respectively. CuCl in EtOH-HCl forms colourless, complex salts (1 mol. of CuCl and 1 mol. of hydrochloride) with the following bases: NHPMc, m. p. 210—220° (decomp.); (I), m. p. 120—130° (decomp.); NH₂Ph, m. p. 150—160° (decomp.); *m*-toluidine, m. p. 131—140° (decomp.) *vic. m*-xylidine, m. p. 180—190° (decomp.). CuCl in conc. aq. HCl can be used to purify commercial samples of the last four bases. R. S. CAHN.

Molecular compounds of centralite [s-diphenyl-diethylcarbamide]. L. MÉDARD (Mém. Poudres, 1930—1931, 24, 174—210).—Anhyd. SnCl₄ (Cl-free) reacts with CO(NPhEt)₂ (C) to give a greyish-green complex, probably SnCl₄·2C, converted into a violet compound by Cl, but too unstable to isolate, since it is decomposed by all solvents. A similar additive compound is obtained with anhyd. HCl. Thermal analysis indicates the existence of additive compounds (all of type AC) of C with the following substances (A): PhOH, m. p. 41.8°; pyrogallol, pyrocatechol, m. p. 64.3°; resorcinol, m. p. 42°; β-naphthol, m. p. 49—50°; NHPH₂, dissociates at 37—38°; doubtful evidence of combination is obtained with *p*-cresol, and ββ-dinaphthol, whilst no compounds are formed with C₁₀H₈, anthracene, *m*-C₆H₄(NO₂)₂, borneol, cyclohexanol, Pr^oOH, Pr^oOH, α- and β-C₁₀H₇NH₂, NH₂Ph, NPhEt₃, glycerol di- or tri-nitrate, or trinitrotoluene. CO(NMePh)₂ similarly forms compounds with pyrogallol, m. p. 118—119°, and pyrocatechol, but not with NHPH₂. Hg(NO₃)₂ acts on carbonyl compounds to give the nitrate of the stronger oxonium base: Hg(NO₃)₂·H₂O + 2COR₂ → 2COR₂·HNO₃ + HgO and thus the oxonium nitrates of camphor, CHPh·CH·CHO, cineole, phenanthraquinone, and COMe₂ (cf. A., 1915, i, 257) are obtained. The nitrates of C and CO(NMePh)₂ are similarly obtained, but could not be separated from HgO, but with CO(NEtPh)(NEt·C₆H₄Me-*p*) centrifuging separates the liquid nitrate which is only slowly decomposed by H₂O. The action is sp. to salts of the weak base Hg(OH)₂ [salts of Cu(OH)₂ and Pb(OH)₂ do not so react], but evidence of perchlorate formation with the aid of Hg(ClO₄)₂ was obtained. J. W. BAKER.

Nitro- and amino-triphenylguanidines. E. DYER and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 777—787).—*p*-NO₂·C₆H₄·NCS and NH₂Ph in C₆H₆ give 97% of *p*-nitrodiphenylthiocarbamide (I), m. p. 160°; with *p*-NO₂·C₆H₄·NH₂ in C₆H₆ and a little pyridine, 94% of *pp'*-dinitrophenylthiocarbamide, m. p. 195—196°, results. BzNCS with *m*- and *p*-NO₂·C₆H₄·NH₂ in C₆H₆ give benzoyl-*m*- and *p*-nitrophenylthiocarbamide, m. p. 164—165° and 182°, respectively. (I) and MeI in MeOH afford 72% of the *S*-Me derivative (III), m. p. 121—122°, of *p*-nitrodiphenyl-*γ*-thiocarbamide, converted by NH₂Ph into β-*γ*-diphenyl-α-*p*-nitrophenylguanidine (IV), m. p. 172—173°, also formed from (I), NH₂Ph, and I in pyridine. β-Phenyl-α-*γ*-di-*p*-nitrophenylguanidine (V) (+EtOH), m. p. 168—169°, is obtained together with γ-phenyl-α-β-di-*p*-nitrophenylguanidine (VI) (+EtOH), m. p. 191—193°, from (II), NH₂Ph, and I in pyridine. (VI) is converted into (V) by conc. HCl at 100°, whilst (V) passes into (VI) at 170—175°/30 min. (V) is also

prepared in 40% yield from *p*-NO₂·C₆H₄·NH₂ and NPh·CCl₂, whilst (VI) results in 26% yield from (III) and *p*-NO₂·C₆H₄·NH₂. Tri-*p*-nitrophenylguanidine and (VI) are formed in equal amounts from (I) and *p*-NO₂·C₆H₄·NH₂. β-Phenyl-α-*γ*-di-*m*-nitrophenylguanidine, m. p. 175—176°, is prepared in 65% yield from NPh·CCl₂ and *m*-NO₂·C₆H₄·NH₂. αβ-*Tri-p*-nitrophenylguanidine, m. p. 244—245°, results from (II), *p*-NO₂·C₆H₄·NH₂, and I in pyridine. Catalytic reduction (PtO₂) of (IV) in AcOEt gives β-*γ*-diphenyl-α-*p*-aminophenylguanidine, m. p. 152—153°. β-Phenyl-α-*γ*-di-*p*-aminophenylguanidine, m. p. 167—168°, is prepared similarly from (V) or (VI). β-Phenyl-α-*γ*-di-*m*-aminophenylguanidine, m. p. 138—139°, and αβ-*tri-p*-aminophenylguanidine, m. p. 215°, are described. These NH₂-derivatives are inactive towards tubercle bacilli. C. J. WEST (b).

Aromatic thionylamines. L. ANSCHUTZ and Z. M. DELUSKI (Annalen, 1932, 493, 241—250).—3:5-Dichloro-*o*-toluidine and SOCl₂ in C₆H₆ at 80° give 3:5-dichloro-2-thionylaminotoluene, b. p. 139—140°/11 mm., m. p. 52°, which can be steam-distilled without appreciable decomp., and is more stable than 3:5-dibromo-2-thionylaminotoluene, b. p. 166—167.5°/10 mm., m. p. 64°. A Cl atom *ortho* to the ·N·S·O group has a stronger retarding effect on the reactivity than an *o*-Br atom; conversely, the Br-amine reacts more readily with SOCl₂ than the Cl-amine. 3:5-Dichloro-2-aminobenzoic acid and SOCl₂ in Et₂O give 3:5-dichloro-2-thionylaminobenzoyl chloride, b. p. 116—118°/0.02 mm., m. p. 87—89°. *o*-Thionylaminobenzoyl chloride (A., 1929, 696) and dry HCl in Et₂O afford *o*-aminobenzoyl chloride hydrochloride (I), sublimes partly at 35°/0.02 mm., and eliminates HCl at 40—100°, forming (probably) dianthranilide. *o*-Aminobenzoyl chloride could not be obtained from (I) by sublimation/high vac. in presence of MgO, Mg(OH)₂, MgCO₃, or HgO, or by treatment with NMe₃ or NPhMe₂ in Et₂O. (I) and MeOH (EtOH) give the hydrochloride of Me (Et) anthranilate, whilst with Mg acetylacetyl bromide, di-*o*-aminobenzoylacetylene, (*o*-NH₂·C₆H₄·CO·C≡C)₂, m. p. 161—162° (decomp.) after previous sintering, results. H. BURTON.

Dinaphthyl bases. I. Syntheses and properties. W. M. CUMMING and G. HOWIE (J.C.S., 1932, 528—534).—Reduction of 4:4', 3:3', and 2:2'-dinitro-1:1'-dinaphthyl is investigated. The 4:4' and 2:2'-dinitro-compounds afford in EtOH with (NH₄)HS and Na₂S, 4'-nitro-4-amino-1:1'-dinaphthyl, m. p. 195—196° (Ac derivative, m. p. 243—244°), and 2'-nitro-2-amino-1:1'-dinaphthyl, m. p. 251°, respectively. Reduction of each of the (NO₂)₂-isomerides with Zn dust and AcOH affords 4:4'-diamino-, m. p. 202° (lit. 198°) (Ac₂ derivative, m. p. 363—364°; Bz₂ derivative, m. p. 319—320°; picrate, m. p. 146—147°), 3:3'-diamino-, m. p. 270°, and 2:2'-diamino-, m. p. 191° [Ac₂ derivative, m. p. 235—236°; Bz₂ derivative, m. p. 235°; picrate, m. p. 185° (decomp.)], -1:1'-dinaphthyl, respectively. The 2:2'-diamino-compound suffers ring closure to give 2:2'-imino-1:1'-dinaphthyl (picrate, m. p. 218—219°). Reduction of 1:1'- and 3:3'-dinitro-2:2'-dinaphthyl is investigated. With NH₄HS and Na₂S, the 1:1'-dinitro-compound affords 1'-nitro-1-amino-2:2'-di-

naphthyl, m. p. 264°. 1:1'-Diamino-2:2'-dinaphthyl, m. p. 281° (lit. 253—259°) (*Ac*₂ derivative, m. p. 229—230°; *Bz*₂ derivative, m. p. 277—278°), gives, contrary to A., 1886, 245, on elimination of the NH_2 groups, 2:2'-dinaphthyl. By ring closure, the 1:1'-diamine affords 1:1'-imino-2:2'-dinaphthyl (*picrate*, m. p. 242—243°). 3:3'-Dinitro-2:2'-dinaphthyl on reduction with Zn and AcOH affords an unidentified compound, $\text{C}_{10}\text{H}_{16}\text{O}_3\text{N}_2$, m. p. about 350°, whereas 1-nitro-2:2'-dinaphthyl affords 1-amino-2:2'-dinaphthyl (*Ac* derivative, m. p. 225—226°). The NH_2 -bases described couple with azo-components to give colours unaffected by acids. The absorption spectra of many of these substances have been measured.

J. L. D'SILVA.

Perylene and its derivatives. XXXIII. Constitution of diaminoperylene. K. FUNKE (Monatsh., 1932, 59, 184—193).—Naphthidine (improved prep. given; cf. J.C.S., 1923, 123, 2464) or, better, its hydrochloride is converted by AlCl_3 (3 pts.) at 130° into a *diaminoperylene* (hydrochloride; $\text{NN}'\text{-Bz}_2$ and -Ac_2 derivatives, both not melted at 340°; *diurethane*, not melted at 340°), purified through its *dibenzylidene* derivative, m. p. 267—268° (corr.) (decomp.), and differing from the known (3:9 and 3:10) diamino-derivatives. The Friedel-Crafts reaction with perylene-3:10-dicarboxyl chloride and C_6H_6 gives an insol. product (formed by self-condensation of the chloride). No violanthrone was obtained.

H. BURTON.

Action of cyanogen on β -arylhydroxylamines. D. VOGLANDER, F. HOELKESKAMP, and P. GÜNTHER (Ber., 1932, 65, [B], 359—364).— $\text{NHPh}\cdot\text{OH}$ in Et_2O at 0° is converted by C_2N_2 into *dicyanophenylhydroxylamine*, $\text{OH}\cdot\text{NPh}\cdot\text{C}(\text{NH})\cdot\text{CN}$ or $\text{O}\cdot\text{NPh}\cdot\text{C}(\text{NH}_2)\cdot\text{CN}$, m. p. about 136° (decomp.) after darkening at 100—110° (hydrochloride; sulphate; Cu^{++} , Ni , Fe^{++} , Hg^{++} salts), converted by HCl in anhyd. Et_2O into (?) the *amide hydrochloride*, $\text{C}_8\text{H}_9\text{O}_2\text{N}_3\cdot\text{HCl}$, decomp. 180—190°. With H_2S the dicyano-compound in EtOH affords dithio-oxamide, whilst it is transformed by alkali into PhNO_2 and thence into azoxybenzene and alkali oxalate. Reduction with Zn dust and AcOH gives NH_2Ph . $\text{NHPh}\cdot\text{OH}$ and dicyanophenylhydroxylamine give a grey product, decomp. above 330°, probably formed to some extent as by-product of the prep. of the dicyano-compound. *Acetyl dicyanophenylhydroxylamine*, m. p. about 149° (decomp.) after darkening at 138°, is prepared by means of Ac_2O . With COMe_2 or COPhMe in presence of alkali, the dicyano-derivative gives products, $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3$, m. p. 139° and 134°, respectively. With dil. HCl, dicyanophenylhydroxylamine gives a blue dye not identical with indigotin; the COMe_2 compound behaves similarly. *Dicyano-o-tolylhydroxylamine*, m. p. about 169° (decomp.), its *Ac* derivative, m. p. about 178° (decomp.), and its compounds with COMe_2 and COPhMe , m. p. 177° and 96°, respectively, are described. *Dicyano-p-tolylhydroxylamine*, m. p. about 140° (decomp.), and its *Ac* derivative, m. p. about 151° (decomp.), have been prepared. H. WREN.

Dehydrogenation of amines and hydrazines by unsaturated compounds. L. A. PINCK and G. E. HILBERT (J. Amer. Chem. Soc., 1932, 54, 710—

716).—9-Amino-1-fluorene is dehydrogenated to fluorenoneimine by di(diphenylene)ethylene (I), benzylidenefluorene, azobenzene, indigotin, and methylene-blue in liquid NH_3 . Hydrazobenzene is similarly converted by (I) into azobenzene. Various non-reacting systems are given. These results favour Wieland's theory of dehydrogenation as a mechanism of biological oxidation. C. J. WEST (b).

Properties and reactions of phenylhydrazine. E. G. R. ARDAGH, B. KELLAM, F. C. RUTHERFORD, and H. T. WALSTAFF (J. Amer. Chem. Soc., 1932, 54, 721—727).—Details are given for the iodometric determination (cf. A., 1926, 189) of $\text{NHPh}\cdot\text{NH}_2$ in presence of EtOH. Pure $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$ is obtained by adding a solution of the distilled base in EtOH with continual stirring to an excess of HCl in EtOH; the reverse procedure often gives a product containing $\text{NH}_2\text{Ph}\cdot\text{HCl}$ and NH_4Cl . Optimum conditions for the prep. of the phenylhydrazones of COPhMe and COPh_2 are studied.

C. J. WEST (b).

Action of halogens on arylazoacetoacetates and related compounds. I. F. D. CHATTAWAY and R. J. LYE (Proc. Roy. Soc., 1932, A, 135, 282—299).—*Et 2:4:6-tribromobenzeneazoacetoacetate* (*Et $\alpha\beta$ -diketo-n-butylate- α :2:4:6-tribromophenylhydrazone*) (I), m. p. 123° (*Ac* derivative, m. p. 129—130°) (from diazotised tribromoaniline and Et acetoacetate), with Br (1 mol.) in AcOH containing a little H_2O or NaOAc gives *Et α -bromoglyoxylate-2:4:6-tribromophenylhydrazone* (II), m. p. 102°, but with Br (1 mol.) in AcOH alone at 100° gives *Et 2:4:6-tribromobenzene-azo- γ -bromoacetoacetate* (III), m. p. 160° (decomp.), and with Br (2 mols.) in AcOH alone at 100° affords *Et 2:4:6-tribromobenzeneazo- $\gamma\gamma$ -dibromoacetoacetate* (IV), m. p. 110°, whilst with excess of Br under similar conditions $\beta\omega$ -tribromo- α -ketopropaldehyde-2:4:6-tribromophenylhydrazone, dimorphic, m. p. 135—136°, is obtained. The last compound was also prepared from Br and α -ketopropaldehyde-2:4:6-tribromophenylhydrazone, m. p. 146° [obtained from diazotised tribromoaniline and Et acetoacetate or by hydrolysis of (I) by aq. alcoholic KOH], in hot AcOH. (II) with NH_3 in EtOH gives *Et α -aminoglyoxylate-2:4:6-tribromophenylhydrazone*, m. p. 137°. (III), also obtained from diazotised tribromoaniline and Et γ -bromoacetoacetate, best with KOAc in hot EtOH, affords *4-hydroxy-3-carbethoxy-1-(2':4':6'-tribromophenyl)pyrazole*, m. p. 160° (*Bz* derivative, m. p. 155°), whilst (IV) gives similarly *5-bromo-4-hydroxy-3-carbethoxy-1-(2':4':6'-tribromophenyl)pyrazole*, m. p. 208°. *Et 2:4:6-trichlorobenzeneazoacetoacetate*, m. p. 96° (*Ac* derivative, m. p. 122°), with Cl_2 in AcOH at room temp. gives *Et α -chloroglyoxylate-2:4:6-trichlorophenylhydrazone* (V), m. p. 74° (giving with NH_3 in EtOH the corresponding α -amino-compound, m. p. 136°), prepared also from diazotised trichloroaniline and Et γ -chloroacetoacetate, whilst with Cl_2 in dry CHCl_3 a mixture of (V) and *Et 2:4:6-trichlorobenzene- γ -chloroacetoacetate*, m. p. 106—107°, is obtained. The last compound with KOAc in EtOH affords *4-hydroxy-3-carbethoxy-1-(2':4':6'-trichlorophenyl)pyrazole*, m. p. 158—159° [*Bz* derivative, m. p. 150—151°; 5-Cl-derivative (VI), m. p. 178°]. The

following compounds were prepared by analogous methods: *Et* α -chloroglyoxylate-2:4:6-tribromophenylhydrazone, m. p. 108—109°; *Et* α -bromoglyoxylate-2:4:6-trichlorophenylhydrazone, m. p. 75—5°; *Et* 2:4:6-tribromobenzeneazo- γ -chloroacetoacetate [from diazotised tribromoaniline and *Et* γ -chloroacetoacetate or (I) and Cl_2], m. p. 170—171° (decomp.) [yielding (VI) with KOAc]; *Et* 2:4:6-trichlorobenzeneazo- γ -bromoacetoacetate, m. p. 112—113° (by both methods); *Et* 2:4:6-trichlorobenzeneazo- $\gamma\gamma$ -dibromoacetoacetate, m. p. 84—85°; *o*-bromo-4-hydroxy-3-carbethoxy-1-(2':4':6'-trichlorophenyl)pyrazole, m. p. 190—191° (*Bz* derivative, m. p. 147°); α -ketopropaldehyde-2:4:6-trichlorophenylhydrazone, m. p. 164—165°; $\beta\beta$ -tribromo- α -ketopropaldehyde-2:4:6-trichlorophenylhydrazone, m. p. 100—101°; 5-chloro-4-hydroxy-3-carbethoxy-1-(2':4':6'-trichlorophenyl)pyrazole, m. p. 195—197°.

R. S. CAHN.

Hydrogenation of cyclic compounds. II. G. ROBERTI (Annali Chim. Appl., 1932, 22, 3—10).—PhOH, cyclohexanol, and NH_2Ph were subjected to hydrogenation by methods described previously (B., 1931, 833). cyclohexanol was not obtained from PhOH nor cyclohexylamine from NH_2Ph ; these compounds may occur as intermediate products. From PhOH and NH_2Ph hydrocarbons resulting from the condensation of two rings are obtained. In all reactions cyclohexane and cyclohexene are formed, the latter in considerable amount in the fraction of light hydrocarbons obtained from NH_2Ph .

O. F. LUBATTI.

Replacement of bromine in bromophenols by the nitro-group. III. 2:3:4:6-Tetrabromophenol and 2:4:6-tribromo-3-iodophenol. Halogen effect in position 3. H. H. HONESON and E. W. SMITH (J.C.S., 1932, 503—505).—The influence of halogen in position 3 on the reactivity of the Br atoms towards HNO_3 in the 3-halogeno-2:4:6-tribromophenols is explained on current electronic theory. Nitration of 2:3:4:6-tetrabromophenol at room temp. gives a mixture of 2:3:4-tribromo-6-nitrophenol, m. p. 123° (lit., 121°), and 3:4:6-tribromo-2-nitrophenol. 3-Bromo-4-nitrophenol affords with Br 2:3:6-tribromo-4-nitrophenol, m. p. 151° (decomp.). Bromination of 3-iodophenol affords 2:4:6-tribromo-3-iodophenol, m. p. 91°, which when treated with HNO_3 at room temp. gives 2:6-dibromo-3-iodo-4-nitrophenol, m. p. 145°, identical with the Br_2 -derivative of 3-iodo-4-nitrophenol. 3-Iodo-6-nitrophenol gives with Br 2:4-dibromo-3-iodo-6-nitrophenol, m. p. 173°.

J. L. D'SILVA.

Nitration of *p*-tert.-butylphenol. O. H. SCHAAF (J. pr. Chem., 1932, [ii], 133, 173—176).—The action of cold HNO_3 - H_2SO_4 on *p*-tert.-butylphenol gives the (?) 2:6-(NO_2)₂-derivative, m. p. 96° (cf. A., 1881, 398); further nitration at -5° causes oxidation and tetranitro-*p*-isopropylphenol, m. p. 122°, and CO_2 are formed.

H. A. PIGGOTT.

Bromo-derivatives of *o*-anisidine. F. MADE-SANI (Gazzetta, 1932, 62, 51—62).—Aceto-*o*-anisidine reacts with 1 mol. of Br to give the Ac derivative, m. p. 159—160°, of 4-bromo-*o*-anisidine (*Bz* derivative, m. p. 108°; 5-bromo-2-methoxydiphenylthiocarbamide, m. p. 170°; 5-bromo-2-methoxy-2':4'-dinitrodiphenylamine,

m. p. 166—168°), which is also obtained by reduction of 4-bromo-*o*-nitroanisole, and with 2 mols. of Br to give the Ac derivative, m. p. 146°, of 3:4-dibromo-*o*-anisidine (I), m. p. 102—103° (hydrochloride, m. p. 210°; 5:6-dibromo-2-methoxydiphenylthiocarbamide, m. p. 156°; 5:6-dibromo-2-methoxy-2':4'-dinitrodiphenylamine, m. p. 154—155°). *o*-Anisidine reacts with 1 mol. of Br to give 3-bromo-*o*-anisidine (II), m. p. 65° [hydrochloride, m. p. 225° (decomp.)]; Ac derivative, m. p. 165°; *Bz* derivative, m. p. 90°; 6-bromo-2-methoxydiphenylthiocarbamide, m. p. 145°; 6-bromo-2-methoxy-2':4'-dinitrodiphenylamine, m. p. 180°] [bromination of the Ac derivative of (II) gives (I)], and with 2 mols. of Br to give 3:5-dibromo-*o*-anisidine, m. p. 20—25° (hydrochloride, m. p. 200°; Ac derivative, m. p. 185°; *Bz* derivative, m. p. 158°). 4:6-Dibromo-*o*-anisidine (A., 1883, 662) (oxalate, m. p. 148—150°; Ac derivative, m. p. 137°; *Bz* derivative, m. p. 118°; 3:5-dibromo-2-methoxydiphenylthiocarbamide, m. p. 155°) is obtained from *o*-nitrophenol. The results of this work support the views of Bargellin (A., 1930, 1282) as to the relative directing influences on halogen substitution of alkoxy-, NH_2 , and NHAc groups.

E. E. J. MARLER.

Sulphonation of *o*-anisidine and aceto-*o*-anisidine. R. CHILD (J.C.S., 1932, 715—720).—Sulphonation of *o*-anisidine with 20% oleum in H_2SO_4 gives 2-anisidine-4-sulphonic acid (I), decomp. about 300°, also obtained by reduction of 2-nitroanisole-4-sulphonic acid (modified prop.) with Sn and HCl. The NH_2 -acid yields (Sandmeyer) 2-chloroanisole-4-sulphonic acid [Na salt; amide, m. p. 130—131°; acid chloride (II), m. p. 81—82°]. *o*-Chloroanisole and ClSO_3H at 0° give (II) and 3:3'-dichloro-4:4'-dimethoxydiphenylsulphone, m. p. 165—166°, also obtained by chlorination of *pp'*-dimethoxydiphenylsulphone, m. p. 129°, in boiling AcOH . Aceto-*o*-anisidine and ClSO_3H at 50° give 2-acetamidoanisole-4-sulphonyl chloride (III), m. p. 152—153° (75% yield) (corresponding amide, m. p. 226°) [also prepared from the Na salt of (I)], which with Na_2SO_3 yields 2-acetamidoanisole-4-sulphonic acid (IV), $+\text{H}_2\text{O}$, m. p. 117—119° (decomp.). The Ag salt of (IV) with MeI affords 2-acetamidoanisyl-4-methylsulphone, m. p. 186°. Reduction of (IV) with SO_2 and HI gave 2-acetamidoanisyl 4-disulphoxide, m. p. 226°, and with Zn dust and alcoholic HCl, 2-acetamidoanisyl 4-mercaptan, m. p. 121—122° (4-Me sulphide, m. p. 109—110°), oxidised by FeCl_3 to 2:2'-diacetamidodianisyl 4:4'-disulphide, m. p. 153°, which with boiling conc. HCl gives the 2:2'-(NH_2)₂-compound, m. p. 105° [dihydrochloride, m. p. 268° (decomp.)] (could not be demethylated). Reduction of (III) by Zn dust and HCl gives impure disulphide, which is best purified by hydrolysis, crystallisation, and re-acetylation.

R. S. CAHN.

Reduction of Schiff bases. I. Reduction of methylene-*p*-aminophenol and its probable structure. E. C. WAGNER (J. Amer. Chem. Soc., 1932, 54, 660—669).—Reduction of *p*-OH-C₆H₄-N=CH₂, *M* 124—179 (in PhOH), 408 (in $\text{CMe}_3\text{-OH}$), with Zn and dil. H_2SO_4 gives a mixture (accounting for about 90% of the original substance) of *p*-NH₂-C₆H₄-OH, *p*-NHMe-C₆H₄-OH, and *p*-NMe₂-C₆H₄-OH; some of

the $p\text{-NH}_2\text{C}_6\text{H}_4\text{OH}$ is regenerated by hydrolysis. It is concluded that polymerised $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_3$ is a cyclic compound containing the 1:3-dimethinediazidine or a similar larger ring. C. J. WEST (b).

2:3:5:6-Tetrachloro-*p*-anisidine and its derivatives. E. BUREŠ and J. HUTTER (Časopis Českoslov. Lek., 1931, 11, 29—33, 57—62; Chem. Zentr., 1931, ii, 225).—The following were prepared: *p*-methoxyacetanilide, m. p. 128°; 2:3:5:6-tetrachloro-*p*-methoxyacetanilide, m. p. 230°; *p*-anisidine [sulphate; hydrochloride (decomp.)]; *p*-methoxydiacetanilide, m. p. 101°; *p*-methoxybenzanilide, m. p. 194°; *p*-anisylmethylamine, m. p. 93°; *p*-bromoanisole, m. p. 98°; *p*-iodoanisole, m. p. 62—63°; *p*-hydroxyanisole, m. p. 103—104°; *p*-anisole, m. p. 54°.

A. A. ELDRIDGE.

Organic peroxides. II. Reaction between perbenzoic acid or benzoyl peroxide and triphenylmethyl. S. S. MEDVEDEV and E. N. ALEXEEVA (Ber., 1932, 65, [B], 137—142).—Interaction of BzO_2H and C_6Ph_3 yields small amounts of BzOH and CPh_3 peroxide, a substance, $\text{C}_{38}\text{H}_{30}\text{O}$, m. p. (indef.) 232—234°, which gives a colourless solution in molten C_{10}H_8 and the isomeric *phenoxy-pentaphenylethane*, m. p. 236—238° (decomp.), which absorbs O_2 when exposed in solid or dissolved condition to the atm. and dissolves in C_{10}H_8 , yielding a solution of which the colour darkens with rise in temp. and fades as the temp. is reduced. When heated somewhat below its m. p. it gives CPh_3 and COPh_2 . Phenoxy-pentaphenylethane and the substance $\text{C}_{38}\text{H}_{30}\text{O}$ (above) are stable towards Br and are transformed by Ac_2O into the ether $(\text{CPh}_3\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4)_2\text{O}$, m. p. 255—260°. The substance $\text{C}_{38}\text{H}_{30}\text{O}$ yields CPh_3 when heated. When Bz_2O_2 and C_6Ph_3 (1:1) interact, a part of the former remains unchanged and CPh_3 peroxide is not produced. The sole products are COPh_2 , CPh_3 (products of the thermal decomp. of phenoxy-pentaphenylethane), and BzOH ; since the last-named substance is isolated mainly after treatment of the mixture with $\text{KOH}\text{--EtOH}$, it is probably present initially as Bz_2O .

H. WREN.

Derivatives of β -naphthol. A. WAHL and R. LANTZ (Compt. rend., 1932, 194, 464—467).—The following are prepared by heating the appropriate diamine or its derivative with 1-chloro- or 1-bromo- β -naphthol, using xylene or an excess of the base as solvent, at 100—140°; 1-*m*-aminophenylamino-, m. p. 161°; 1-4'-amino-2'-tolylamino- (?), m. p. 188° (hydrochloride) (from *m*-toluylenediamine); 1-*m*-dimethylaminoanilino-, m. p. 154°; and 1-*p*-aminoanilino- β -naphthol, m. p. 185—186° [*p*-N-Acderivative, m. p. 215—216° (from *p*-aminoacetanilide)].

H. A. PIGGOTT.

Isomeric 3-bromo-derivatives of dehydro- β -naphthol 1-sulphide. J. A. C. McCLELLAND and S. SMILES (J.C.S., 1932, 637—641).—The isomerides (I) and (II) are capable of independent existence, and attempts at interconversion failed. Dehydro- β -naphthol 1-sulphide with Br in CHCl_3 gives 3-bromodehydro- β -naphthol 1-sulphide (I), m. p. 155°, converted by AcI into $\alpha\beta\beta'\alpha'$ -dinaphthathioxin, m. p. 210°. The structure of (I) is proved (a) by its

reduction by Zn and H_2O to the isosulphide, cryst., whence 3-bromo- β -naphthol 1-sulphide, m. p. 192°,



also prep. from 3-bromo- β -naphthol and β -naphthol-1-bromothiols in CCl_4 , was obtained; (b) by the rules of substitution of β -naphthaquinones; (c) because it does not yield a phenylhydrazone, and (d) by bromination in CHCl_3 to 3:4-dibromodehydro- β -naphthol 1-sulphide, m. p. 204° (also obtained directly from dehydro- β -naphthol 1-sulphide), which with NH_2Ph yields 3-bromo-4-anilinodehydro- β -naphthol 1-sulphide, m. p. 240—241°. 3-Bromo- β -naphthol and S_2Cl_2 in CHCl_3 at 100° give 3:3'-dibromo- β -naphthol 1-sulphide, m. p. 192°, oxidised by warm alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ to 3:3'-dibromodehydro- β -naphthol 1-sulphide, m. p. 205° (no phenylhydrazone formed), converted by AcI in Ac_2O into 6:13-dibromo- $\alpha\beta\beta'\alpha'$ -dinaphthathioxin, m. p. 248°, and by boiling AcCl into a ?-Cl-derivative, m. p. 264°, of the latter. 3-Bromo- β -naphthol 1-sulphide, m. p. 192° (from 3-bromo- β -naphthol and β -naphthol-1-bromothiols), gives on oxidation a mixture containing 3'-bromodehydro- β -naphthol 1-sulphide (II), m. p. 172—173° (phenylhydrazone, m. p. 196°).

R. S. CAHN.

Mechanism of the action of phosphorus aryl-oxo- and alkoxy-dichlorides on pyrocatechol. L. ANSCHUTZ and H. WALBRECHT (J. pr. Chem., 1932, [ii], 133, 65—80).— $\text{o-C}_6\text{H}_4(\text{OH})_2$ reacts with P alkoxy- (or aryloxy-) dichlorides in C_6H_6 at room temp.—100° (bath) forming alkyl (aryl) *o*-phenylene phosphites (I), $\text{o-C}_6\text{H}_4\text{O}(\text{OR})_2\text{P}(\text{OR})_2$, together with

o-hydroxyphenyl *o*-phenylene phosphite, $\text{OH}\cdot\text{C}_6\text{H}_4\text{O}\cdot\text{P}(\text{OC}_6\text{H}_4)_2$, (II), m. p. 117—118° (cf. A., 1928, 880) (*O*-Ac derivative, b. p. 135°/0.02 mm.), and *o*-phenylene phosphite, $(\text{C}_6\text{H}_4)_3\text{P}(\text{O})_2$, (III). The reactions occurring are: (i) $\text{C}_6\text{H}_4(\text{OH})_2 + \text{OR}\cdot\text{PCl}_2 \rightarrow (\text{I}) + 2\text{HCl}$; (b) $(\text{I}) + \text{C}_6\text{H}_4(\text{OH})_2 \rightarrow (\text{II}) + \text{R}\cdot\text{OH}$; (c) $(\text{II}) + (\text{I}) \rightarrow (\text{III}) + \text{R}\cdot\text{OH}$. In accordance with (b), Et *o*-phenylene phosphite, $\text{o-C}_6\text{H}_4(\text{OH})_2$, and dry HCl give (II) and EtCl (from EtOH). The following alkyl and aryl *o*-phenylene phosphites are prepared: Me, b. p. 76—77°/15 mm.; Et, b. p. 83—84°/11 mm.; *n*-Pr, b. p. 100—102°/13 mm.; *n*-Bu, b. p. 116—117°/12 mm.; Ph (IV), b. p. 152°/11 mm.; *o*-, b. p. 159—160°/13 mm.; *m*-, b. p. 158—159°/11 mm., and *p*-tolyl, b. p. 164°/12 mm., m. p. 25°. Guaiacol and P pyrocatechyl chloride (loc. cit.) at 130° give *o*-methoxyphenyl *o*-phenylene phosphite, b. p. 137°/0.13 mm., 184°/13 mm., not obtainable by methylation of (II).

[By W. BROEKER.] (IV) is also prepared from $\text{o-C}_6\text{H}_4(\text{OH})_2$ and $\text{P}(\text{OPh})_2\text{Cl}$ in warm C_6H_6 or from PhOH and P pyrocatechyl chloride at 100°. Pyrocatechyl phenylphosphinate, $\text{Ph}\cdot\text{P}(\text{O})\text{O}\cdot\text{C}_6\text{H}_4\text{O}$, m. p. 124—125°, is obtained from $\text{o-C}_6\text{H}_4(\text{OH})_2$ and

Ph·POCl₂ at 160—180°. The following *aryl o-phenylene thiophosphates*, $\text{o-C}_6\text{H}_4\text{--}\langle\text{O}\rangle\text{P(S)·OAr}$, are prepared from the aryl *o*-phenylene phosphites and S at 180—190°: *Ph*, b. p. 186°/10 mm., m. p. 71—72°; *o*-, b. p. 197—200°/14 mm., m. p. 87—88°, and *p*-tolyl, b. p. 206—208°/12 mm., m. p. 71—72°; *o*-methoxyphenyl, m. p. 93—94°. H. BURTON.

Substitution in resorcinol derivatives. III. Molecular rearrangement during bromination. C. SRIKANTIA, M. S. IYENGAR, and K. SANTANAM (J.C.S., 1932, 524—527).—Nitration (I) of 2-hydroxy-4-methoxybenzaldehyde affords mainly the 5-nitro-aldehyde (of. A., 1925, i, 675), and in small quantity, 6-nitroresorcinol 3-Me ether [*monobromo*-derivative, m. p. 117—118°, identical with the product of nitration of 5-bromo-2-hydroxy-4-methoxybenzaldehyde; Br₂-derivative, m. p. 127—128°, identical with 2 : 4-dibromo-6-nitroresorcinol 3-Me ether (II)]. Bromination of 5-nitro-2-hydroxy-4-methoxybenzaldehyde affords first 3-bromo-5-nitro-2-hydroxy-4-methoxybenzaldehyde, m. p. 129—130°, oxidised by KMnO₄ to an acid, m. p. 212—214°, obtained by brominating 5-nitro-2-hydroxy-4-methoxybenzoic acid. Further bromination affords (II). Another product of (I) is 3-nitro-2-hydroxy-4-methoxybenzaldehyde, m. p. 146—147°, which on bromination first affords 5-bromo-3-nitro-2-hydroxy-4-methoxybenzaldehyde, m. p. 126°, identical with the product of nitration of 5-bromo-2-hydroxy-4-methoxybenzaldehyde. Further bromination affords (II). As 3-nitro-2-hydroxy-4-methoxybenzaldehyde and 5-nitro-2-hydroxy-4-methoxybenzaldehyde both yield (II) with excess of Br, it is suggested that an intramol. rearrangement involving the migration of a NO₂-group has occurred. J. L. D'SILVA.

Bactericidal properties of mono-ethers of dihydric phenols. II. E. KLARMANN and others. —See this vol., 308.

Action of benzoyl chloride on dimethylpyrogallol [pyrogallol 1 : 3-dimethyl ether]. F. MAUTHNER (J. pr. Chem., 1932, [ii], 133, 126—128).—Pyrogallol 1 : 3-Me₂ ether, BzCl, and AlCl₃ in PhNO₂ give 3 : 4-dihydroxy-5-methoxybenzophenone m. p. 168—169° (*oxime*, m. p. 169—170° after previous sintering). H. BURTON.

Quaternary ammonium halides of ephedrine. C. T. FENG (J. Amer. Pharm. Assoc., 1932, 21, 8—15).—Methylephedrine methiodide, m. p. 208—209°, [α]_D²⁰ — 32.3° in MeOH (*C* = 5.0), — 22.3° in H₂O, isolated during the prep. of methylephedrine, has been used for the prep. of methylephedrine methochloride, m. p. 245° (decomp.), [α]_D²⁰ — 45.2° in MeOH, — 31.2° in H₂O, and methylephedrine methobromide, m. p. 238.0°, [α]_D²⁰ — 37.9° in MeOH, — 25.8° in H₂O. The properties of these compounds and their reactions with K₂Cr₂O₇, H₂PtCl₆, HAuCl₄, and HgCl₂ are given. They give no biuret reaction, have equal mol. rotations, and form characteristic crystals. Bi can be detected by the methiodide in an aq. solution containing 0.001% of Bi(NO₃)₃. E. H. SHARPLES.

Chromic acid oxidation of sec.-cyclic alcohols. G. VAVON and C. ZAREMBA (Bull. Soc. chim., 1931,

[iv], 49, 1853—1860).—The oxidation of *sec.* cyclic alcohols by AcOH—CrO₃ in dil. (0.005*N*) solution is approx. of the second order, the reaction const., *K*, increasing towards the end of the reaction, due to oxidation of the ketone formed. In more conc. solutions (0.05*N*) the reaction is bimol. and the const. decreases towards the end of the reaction. The concn. of the AcOH is crit. and with 0.005*N*-cyclohexanol at 25° oxidation is 1000 times as fast in 100% as in 50% AcOH. For the 27 cyclanols studied the velocity of oxidation at 39° is 7 to 13 times as great in 75% as in 50% AcOH and similarly at 30° in 100% AcOH menthone is oxidised 50 times as fast as in 50% AcOH, and in 75% AcOH 6 times as fast. In eleven out of thirteen instances, the *cis*- is oxidised more rapidly than the *trans*-isomeride. The rate of oxidation increases with the mol. wt. of the alkyl group in the 2-position with respect to OH. Thus the 2-methylcyclohexanols are oxidised more slowly than the 2-ethyl-, propyl-, or -butyl-cyclohexanols and the 2-isopropylcyclohexanols more readily than the 2- or 4-Prⁿ derivatives. Ditert. butylcarbinol in 75% AcOH at 25° or 39° or in 50% AcOH at 39° is oxidised a little more rapidly than di-*n*-butylcarbinol, although with AcOH at 140° and Ac₂O in C₆H₆ at 100° it is esterified at 1/40 to 1/50 the rate of its isomeride. Similarly, ditert. butylmethyl phthalate is hydrolysed at 1/140 the rate of di-*n*-butylmethyl phthalate in aq. EtOH and 1/400 in H₂O. Neither dehydration nor CrO₃ oxidation is sensitive to steric hindrance. R. BRIGHTMAN.

αβ-Dicyclohexylethylene glycol. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1932, 54, 820—821).—αβ-Dicyclohexylethylene glycol, m. p. 194° (cf. A., 1931, 1294), is prepared by catalytic reduction of dodecahydrobenzoin. Hexahydromandelonitrile and hexahydromandelamide, b. p. 104°/0.7 mm., 121°/1.8 mm., do not react with Mg cyclohexyl bromide, whilst unimol. glyoxal gives iso-αβ-dicyclohexylethylene glycol, m. p. 153° (corr.). C. J. WEST (b).

Resorcylic alcohols. T. BOEHM and H. PARLASCA (Arch. Pharm., 1932, 270, 168—183).—The dicarbomethoxy-derivative [m. p. 94—95° (lit. 154—155°)] of 3 : 5-dihydroxybenzaldehyde (α-resorcylic aldehyde) [+H₂O, m. p. (anhyd.) 156—157° (lit. 145—146°)], when reduced catalytically (Pd—BaSO₄) in AcOH gives dicarbomethoxy-α-resorcylic alcohol, m. p. 75—76° (*p*-nitro- and *p*-bromo-benzoyl derivatives, m. p. 107—108° and 104—105°, respectively; α-naphthylurethane, m. p. 114—115°), hydrolysed by aq. alcoholic KOH in H₂ to the phenolic alcohol, which is stable to acids. Attempts to prepare 2 : 4-dihydroxybenzyl alcohol (β-resorcylic alcohol) (I) by catalytic reduction of the corresponding aldehyde failed. The dicarbomethoxy-derivative, m. p. 99° (*p*-nitrophenylhydrazone, m. p. 172—173°), of the latter is reduced catalytically to the dicarbomethoxy-derivative, an oil (*p*-nitrophenylhydrazone, m. p. 108°), of (I), whilst the Ac₂ derivative, m. p. 65—66° (*p*-nitrophenylhydrazone, m. p. 206—207°), affords similarly the Ac₂ derivative, b. p. 290—293°/768 mm., 172—173°/23 mm. (*p*-nitro- and 2 : 4-dinitro-benzoyl derivatives, m. p. 90—91° and 109°, respectively), of

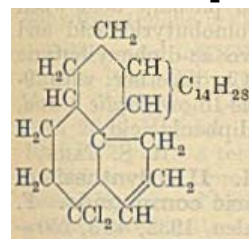
(I). Hydrolysis led, however, to red, amorphous polymerisation products, similar to "artopon." Resoreinol and CH_3O do not give 6-hydroxyfluorone (cf. A., 1925, i, 812).

R. S. CAIN.

Irradiation of cholesterol. W. B. S. BISHOP (Chem. Eng. Min. Rev., 1932, 24, 145—146).—X-Rays and Ra radiations have no effect on cholesterol dissolved in C_6H_6 and EtOH , but reduce its concn. in CHCl_3 and CCl_4 solutions. The last two solvents are, however, themselves affected by the radiations with liberation of Cl_2 , so that the reaction on the cholesterol may be indirect.

N. H. HARTSHORNE.

Constitution of cholesterol. VI. Reactions of cholesterol with phosphorus pentachloride. F.



PIRONE (Gazzetta, 1932, 62, 63—80).— PCl_5 with cholesterol under various conditions does not give H_3PO_4 derivatives as with indene etc. (A., 1930, 1050), but trichlorocholesterane, m. p. 106° , cholesteryl chloride, m. p. 96° , and 4:4-dichlorocholesterene (annexed formula), m. p. 92° (Br-derivative, m. p.

$108\text{--}109^\circ$); i.e., it appears to react not as $\text{PCl}_4^+\text{Cl}^-$, as predicted by the octet theory of Lewis and Langmuir, but as $\text{PCl}_3 + \text{Cl}_2$.

E. E. J. MARLER.

Cholesteryl esters. XV. E. MONTIGNIE (Bull. Soc. chim., 1931, [iv], 49, 1852—1853).—Cholesterol and acetylsalicylic acid at 150° for 2 hr. give cholesteryl acetylsalicylate, m. p. 105° (bromide, m. p. 108°), giving the Liebermann reaction. Cholesteryl cresotate, m. p. $158\text{--}159^\circ$, similarly obtained at 180° (dibromide, m. p. 112°), also gives the Liebermann reaction, but cholesteryl acetylcresotate, m. p. 102° (bromide, m. p. $118\text{--}119^\circ$), does not. Camphor-carboxylic acid at 130° similarly yields cholesteryl camphorcarboxylate, m. p. $178\text{--}179^\circ$ (phenylhydrazones, m. p. 184° ; oxime, m. p. 160°) (slow Liebermann reaction), together with a substance, m. p. $139\text{--}140^\circ$ (acetate, m. p. 110°).

R. BRIGHTMAN.

Crystalline form of anhydrous cholesterol. L. KOFLER and A. KOFLER (Z. physiol. Chem., 1932, 204, 211—213).—Anhyd. cholesterol crystallises in needles and sublimes in rectangular plates belonging to the rhombic system.

J. H. BIRKINSHAW.

Isomerisation of various ergosterol derivatives with hydrogen chloride. K. DITHMAR and T. ACHTERMANN (Z. physiol. Chem., 1932, 205, 55—64).— HCl in CHCl_3 converts ergostatrienone D (I) into ergostatrienone B₁ (II), m. p. $149\text{--}150^\circ$, $[\alpha]_D^{25} -57.5^\circ$ (oxime, m. p. $187\text{--}191^\circ$ (decomp.)). Hydrogenation of (II) with Na in EtOH yields ergostatrienol B₁, m. p. 148° , $[\alpha]_D^{25} -42.5^\circ$ (acetate, m. p. 140° , $[\alpha]_D^{25} -54.7^\circ$). Ergosterol B₁ prepared from (I) is identical with that from ergosteryl acetate and HCl . With Pt and H_2 its acetate yields *allo-α*-ergostanyl acetate (III) at 65° in presence of HCl and *α*-ergostenyl acetate (IV) at room temp. HCl in CHCl_3 converts ergostadienone I into ergostadienone III (V), m. p. 114° , $[\alpha]_D^{25} -5.1^\circ$ (oxime, m. p. $192\text{--}193^\circ$ (decomp.)). Hydrogenation of (V) with Na in EtOH affords dihydroergosterol III, m. p. 122° , $[\alpha]_D^{25} -16.7^\circ$ (acetate (VI), m. p. 108° ,

$[\alpha]_D^{25} -25.3^\circ$); treatment of (VI) with Pt and H_2 yields (III) at 65° (+ HCl) and (IV) at room temp.

u-Ergostatrienone with HCl in CHCl_3 gives *u*-ergostatrienone B (VII), m. p. 120° , $[\alpha]_D^{25} -49.1^\circ$ (oxime, m. p. $166\text{--}168^\circ$). With Na in EtOH , (VII) gives *u*-ergostatrienol B, m. p. $163\text{--}164^\circ$, $[\alpha]_D^{25} -49.3^\circ$ (acetate (VIII), m. p. 128° , $[\alpha]_D^{25} -35.5^\circ$). With Pt and H_2 in AcOH at 65° , (VIII) yields *u*-ergostanyl acetate. (All rotations in CHCl_3 .)

J. H. BIRKINSHAW.

Lumisterol. A. WINDAUS, K. DITHMAR, and E. FERNHOLZ (Annalen, 1932, 493, 259—271).—Acetylation of vitamin-D₁ (A., 1931, 1464) (convenient prep. given) with Ac_2O at 100° gives the acetate of vitamin-D₂ (this vol., 311) together with the acetate, m. p. 100° , $[\alpha]_D^{25} +130.5^\circ$ in COMe_2 , of lumisterol (I), $\text{C}_{27}\text{H}_{42}\text{O}$, m. p. 118° , $[\alpha]_D^{25} +191.5^\circ$ in COMe_2 . (I) absorbs 30 when titrated with BzO_2H , shows absorption maxima at 265 and 280 $\text{m}\mu$, eliminates 1 mol. of H_2O when heated with NaOEt at 200° , has no antirachitic action, is non-poisonous, is unaffected by heating to 190° , forms a mol. (1:1) compound (=vitamin-D₁) with vitamin-D₂, and is converted into vitamin-D₂ by irradiation of a solution in Et_2O with unfiltered light from a Mg arc. (I) is reduced by Na and EtOH to dihydrolumisterol (II), m. p. $138\text{--}139^\circ$, $[\alpha]_D^{25} +50.4^\circ$ in CHCl_3 (acetate, m. p. 142° , $[\alpha]_D^{25} +25.2^\circ$ in CHCl_3 ; benzoate, m. p. 130° , $[\alpha]_D^{25} +4.8^\circ$ in CHCl_3), converted by NaOEt at 200° into epidihydrolumisterol (III), m. p. 140° , $[\alpha]_D^{25} +43.3^\circ$ in CHCl_3 (acetate, m. p. 127° , $[\alpha]_D^{25} +48.6^\circ$ in CHCl_3 ; benzoate, m. p. 151° , $[\alpha]_D^{25} +35.7^\circ$ in CHCl_3), which is pptd. by digitonin. (II) and (III) form a 1:1-additive compound, m. p. 186° , $[\alpha]_D^{25} +47.8^\circ$ in CHCl_3 . (I) is converted by dry HCl in CHCl_3 at -10° into isolumisterol, m. p. 138° , $[\alpha]_D^{25} -103^\circ$ in C_6H_6 , $[\alpha]_D^{25} -125^\circ$ in CHCl_3 (acetate, m. p. 128°), isomerised by NaOEt at $150\text{--}200^\circ$ to epi-isolumisterol, m. p. 165° , $[\alpha]_D^{25} -123^\circ$ in COMe_2 (acetate, m. p. 117° , $[\alpha]_D^{25} -105.7^\circ$ in COMe_2), also pptd. by digitonin.

H. BURTON.

Spinasterol and some of its esters. M. C. HART and F. W. HEYL (J. Biol. Chem., 1932, 95, 311—315).—The crude unsaponifiable matter from spinach fat crystallised from EtOH gives spinasterol, m. p. $168\text{--}169^\circ$, $[\alpha]_D^{25} -1.8^\circ$, and from the mother-liquor cryst. Et_2O -insol. material, m. p. $102\text{--}103^\circ$, has been isolated. The following esters of spinasterol have been obtained: acetate, m. p. $183\text{--}185^\circ$, $[\alpha]_D^{25} -4.7^\circ$; benzoate, m. p. $201\text{--}202^\circ$, $[\alpha]_D^{25} +2.25^\circ$; phenylurethane, m. p. $173\text{--}174^\circ$, $[\alpha]_D^{25} -2.25^\circ$; p-nitrobenzoate, m. p. $217\text{--}218^\circ$, $[\alpha]_D^{25} +4.5^\circ$; trichloroacetate, m. p. $167\text{--}169^\circ$, $[\alpha]_D^{25} -3.5^\circ$; propionate, m. p. $152\text{--}153^\circ$, $[\alpha]_D^{25} -5.0^\circ$; and butyrate, m. p. $131\text{--}132^\circ$, $[\alpha]_D^{25} -4.0^\circ$. With $\text{CH}_2\text{Cl}\text{--COCl}$ in absence of $\text{C}_2\text{H}_5\text{N}$, isospinasteryl chloroacetate, m. p. $155\text{--}156^\circ$, $[\alpha]_D^{25} -6.0^\circ$, is formed, hydrolysed to isospinasterol, m. p. $148\text{--}150^\circ$, $[\alpha]_D^{25} +5.2^\circ$. Colorimetric tests indicate the absence of the $\Delta^{1:2}$ (or $\Delta^{1:3}$) and the inactive $\Delta^{10:19}$ linkings in spinasterol.

F. R. SHAW.

Action of selenium oxide on sterols. E. MONTIGNIE (Bull. Soc. chim., 1932, [vi], 51, 154).—In EtOH solution at 95° with 10% aq. SeO_2 ergosterol gives a red coloration or ppt. of Se-red after boiling for 1—2 min. Other sterols, particularly cholesterol,

stigmasterol, and phytosterols, do not give the reaction, and ergosterol derivatives give the reaction less readily, e.g., the acetate and γ -dihydroergosterol are about 2–3 times less sensitive. The limit of the reaction is about 0.0006 g. of ergosterol. The sensitivity decreases on irradiation in proportion to the time of irradiation and resin formation. R. BRIGHTMAN.

Action of hydrogen selenide on acid chlorides.

I. Hydrogen selenide and benzoyl chloride. I. SZPERL and W. WIOROGÓRSKI (Rocz. Chem., 1932, 12, 71–78).— H_2Se yields CH_3Ph selenobenzoate (an oil) with BzCl in boiling xylene solution; in the presence of AlCl_3 at room temp. the products are Bz_2Se , m. p. 61–62°, Bz_2Se_2 , m. p. 129–130°, and benzylidene diselenobenzoate, m. p. 149–150°. The above compounds readily decompose in the presence of light and H_2O , with the liberation of Se . R. TRUSZKOWSKI.

Reaction of phenylacetonitrile. J. A. NIEUWLAND and L. H. BALDINGER (J. Amer. Chem. Soc., 1932, 54, 828).— $\text{C}_6\text{H}_5\text{Ph}\cdot\text{CN}$ (1 mol.) and Na (1 mol.) in liquid NH_3 form a salt, converted by EtBr (in liquid NH_3) into $\text{CHPhEt}\cdot\text{CN}$; the H atom in this nitrile can be replaced by Na and the resulting salt reacts with a second mol. of alkyl bromide.

C. J. WEST (b).

Pinacolin deamination. I. Action of nitrous acid on amino-alcohols derived from α -aminohydratropic acid. A. MCKENZIE and J. R. MYLES (Ber., 1932, 65, [B], 209–218).— α -Amino- α -phenylpropionic acid is converted by EtOH and HCl into the *Et* ester, b. p. 135–136°/15 mm. (hydrochloride, m. p. 121–123°), transformed by MgPhBr into *r*- β -amino- $\alpha\beta$ -triphenylpropan- α -ol, m. p. 114–115° (hydrochloride, m. p. 212–213°). Treatment of the NH_2 -alcohol in dil. AcOH with NaNO_2 affords $\alpha\alpha$ -diphenylpropionophenone, m. p. 91–92°, which does not yield an oxime, semicarbazone, or *p*-nitrophenylhydrazone, does not react with MgPhBr , but is converted by boiling 10% KOH - EtOH into $\alpha\alpha$ -diphenylethane. ($\alpha\alpha$ -Diphenylpropionyl chloride, m. p. 40–41°, from the acid and SOCl_2 , is converted by C_6H_6 , AlCl_3 , and CS_2 into a substance, m. p. 139–140°.) Deamination yields smaller quantities of $\alpha\alpha\beta$ -triphenylpropylene oxide, m. p. 63–64°, converted by conc. H_2SO_4 into CPh_3Ac , m. p. 138–138.5°, which, with KOH - EtOH , gives CHPh_3 and KOAc (CHPh_3 is formed by the action of MgMeI on $\text{CPh}_3\cdot\text{CN}$). Dehydration of $\alpha\alpha\beta$ -triphenylpropane- $\alpha\beta$ -diol with conc. H_2SO_4 at room temp. or boiling dil. H_2SO_4 yields acetyltriphenylmethane. (+)- α -Formamido- α -phenylpropionic acid is hydrolysed by *N*- HBr to (+)- α -amino- α -phenylpropionic acid hydrobromide, $[\alpha]_D^{25} +69.7^\circ$ in EtOH [(–)-isomeride, $[\alpha]_D^{25} -69.1^\circ$ in EtOH], which yields *Et* (+)- α -amino- α -phenylpropionate, $[\alpha]_D^{25} +24.70^\circ$ [(–)-isomeride, $[\alpha]_D^{25} -25.5^\circ$]. The (+)-ester is converted into (+)- β -amino- $\alpha\alpha\beta$ -triphenylpropan- α -ol, m. p. 118–119°, $[\alpha]_D^{25} +69.4^\circ$ in EtOH , deaminated to $\alpha\alpha$ -diphenylpropionophenone and a product, $[\alpha]_{5461} -13.5^\circ$ in COMe_2 , consisting of (–)- $\alpha\alpha\beta$ -triphenylpropylene oxide possibly containing a little $\alpha\alpha$ -diphenylpropionophenone. *r*- β -Amino- β -phenyl- $\alpha\alpha$ -di-*p*-tolylpropan- α -ol, m. p. 107–108°, is converted by HNO_2 into *p*-tolyl α -phenyl- α -p-tolylethyl ketone, m. p. 77–78°, and (?) 2-phenyl-1-*p*-

tolyl-5-methylindene, m. p. 145–146°. The pinacolin is transformed by KOH - EtOH into *p*-toluic acid and α -phenyl- α -p-tolylethane. H. WREN.

Condensation of $\alpha\beta$ -dibromocarboxylic acids with benzene in presence of aluminium halides. J. C. EARL and C. H. WILSON (J. Proc. Roy. Soc. New South Wales, 1932, 65, 178–184).— $\alpha\beta$ -Dibromo- β -phenylpropionic acid and C_6H_6 in presence of AlBr_3 or FeCl_3 give $\alpha\beta\beta$ -triphenylpropionic acid, but using AlCl_3 afford 9-phenyl-9:10-dihydrophenanthrene-10-carboxylic acid, m. p. 148° (*Et* ester, m. p. 116°), yielding 9-phenyl-9:10-dihydrophenanthrene, m. p. 121.5°, when distilled with soda-lime, a substance, $\text{C}_{20}\text{H}_{14}\text{O}_2$, m. p. 105–106°, when treated with CrO_3 in AcOH , and BzOH and phthalic acid when oxidised by KMnO_4 . $\alpha\beta$ -Dibromobutyric acid and C_6H_6 in presence of AlBr_3 give $\alpha\beta$ -diphenylbutyric acid, also obtained using AlCl_3 together with 9-methyl-9:10-dihydrophenanthrene-10-carboxylic acid, m. p. 127°, oxidised (CrO_3) to diphenic acid.

R. S. CAHN.

Constitution of cannabinalol. II. Synthesis of cannabinalactone and isomeric compounds. F. BERGEL and K. VOGEL (Annalen, 1932, 493, 250–258).—3-Methylphthalic anhydride (1 mol.) and MgMeI (2 mols.) give probably 3-methyl- $\alpha\alpha$ -dimethylphthalide, b. p. 80–85°/0.01 mm., m. p. 58.5°, oxidised by alkaline KMnO_4 to $\alpha\alpha$ -dimethylphthalide-3-carboxylic acid (I), m. p. 178.5° (*Et* ester, m. p. 146.5°), not identical but isomeric with cannabinalactonic acid (II). Fusion of (I) with KOH at 290–300° gives *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, which probably results from a rearrangement of *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. MgMeI and 4-methylphthalic anhydride give a mixture, b. p. 106°/0.5 mm., m. p. 89°, of 4- and 5-methyl- $\alpha\alpha$ -dimethylphthalides; oxidation of the mixture and extraction of the mixed acids with Et_2O affords impure $\alpha\alpha$ -dimethylphthalide-4-carboxylic acid (III) as the more sol. acid. *p*-Cymene-3-carboxylic acid is oxidised by CrO_3 in AcOH - KHSO_4 to 4-isopropylisophthalic acid, thymoquinone, and 4-methyl- $\alpha\alpha$ -dimethylphthalide (cannabinalactone) (IV). (IV) is oxidised by alkaline KMnO_4 to (III), m. p. 203–204° (*Et* ester, m. p. 103–104°), which is identical with (II).

H. BURTON.

3-Methylgallic acid. F. MAUTHNER (J. pr. Chem., 1932, [ii], 133, 120–125).—4:5-Dihydroxy-3-methoxybenzoic (3-*O*-methylgallic) acid (*Me* ester, m. p. 112–113°) and $\text{Cl}\cdot\text{CO}_2\text{Me}$ in *N*- NaOH give 3-methoxy-4:5-di(carbomethoxyoxy)benzoic acid, m. p. 149–150°, the acid chloride, m. p. 101–102°, of which is reduced catalytically ($\text{Pd}\cdot\text{BaSO}_4$) in PhMe to the 4:5-di-*O*-carbomethoxy-derivative (not characterised) of 4:5-dihydroxy-3-methoxybenzaldehyde, m. p. 130–131° (*p*-nitrophenylhydrazone).

H. BURTON.

Esters of gallic acid. B. HEPNER and L. ZYTO (Rocz. Chem., 1932, 12, 100–102).—*Pr*^a, m. p. 150°, *Bu*^a, m. p. 143–144°, and *Bu*^b, m. p. 130–131°, gallates have been prepared. R. TRUSZKOWSKI.

Rotenone, the active constituent of derris root. XI. Synthetical experiments with 2-hydroxy-4:5-dimethoxybenzoic acid and rissic acid. Partial synthesis of derrissic acid and dehydro-

rotenone from derritol. S. TAKEI, S. MIYAJIMA, and M. ONO (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 304—318; cf., this vol., 400).—3-Nitro-2:5-dimethoxybenzoic acid has m. p. 169°, and 2:5-dimethoxymandelic acid, m. p. 98—103° (cf. A., 1931, 1415). 4-Hydroxyveratrole (I), m. p. 78°, gives 3:4-dimethoxyphenoxycetic acid, m. p. 116° (NO₂-derivative, m. p. 209°), identical with decarboxyric acid. (I) led to 2-hydroxy-4:5-dimethoxybenzoic acid, m. p. 202° (Me ester, m. p. 92°; Me ether, m. p. 143°, identical with asaronic acid), identical with the product from dehydrorotenone, and thence to 2-carboxy-4:5-dimethoxyphenoxycetic acid, m. p. 255° (Me₂ ester, m. p. 85°), identical with ricissic acid. Alkali fusion of hydroxyquinol or its Ac₃ derivative gives some quinol. In the prep. of derritol from derrissic acid some dehydrorotenone is also formed. R. S. CAHN.

Bile acids. XXXIII. M. SCHENCK (Z. physiol. Chem., 1932, 205, 76—82; cf. this vol., 159).—The α -acid, C₂₄H₃₆O₁₀N₂ (A., 1930, 915), loses NH₃ on boiling with 20% HCl for 1 hr. Boiling for 20 min. with 10% HCl yields a tetrabasic acid, C₂₄H₃₃O₁₁N₂, m. p. 226° (decomp.), probably an acid amide, since it loses NH₃ on acid hydrolysis. The α -acid is probably a substituted malonic acid (rupture of ring III) with the supposed nitro-N present as a CN group.

J. H. BIRKINSHAW.

New synthesis of aromatic aldehydes. H. WUYTS, L. BERMAN, and (Miss) A. LACOURT (Bull. Soc. chim. Belg., 1931, 40, 665—672).—Dithiocarboxylic acids, R-CS₂H, with semicarbazide hydrochloride, best in aq. pyridine, give the semicarbazones of the aldehydes, R-CHO, readily hydrolysed after removal of most of the free S. The following were thus prepared: PhCHO, *o*- and *p*-tolu-, *p*-bromobenz-, α - and β -naphth-aldehyde. R. S. CAHN.

Distyryl ketone and triphenylmethane. XIV. α -Methoxybenzyl chloride and α -methoxycinnamyl chloride. F. STRAUS and H. HEINZE (Annalen, 1932, 493, 191—217).—CHPh(OMe)₂ (0.5 mol.) with AcCl (1.1 mols.) containing a little SOCl₂, first at 55° and then at room temp., gives 80% of not quite pure α -methoxybenzyl chloride (α -chlorobenzyl Me ether) (I), b. p. 71—72°/0.1 mm., m. p. about -24°, hydrolysed readily by H₂O to PhCHO, MeOH, and HCl, converted by NaOMe into CHPh(OMe)₂, and decomposed at 110° to PhCHO and MeCl. Impure α -methoxycinnamyl chloride (II) is similarly prepared from cinnamaldehyde dimethylacetal. (I) and HgCl₂ in Et₂O give a complex containing 5—6 mols. of HgCl₂, whilst (II) similarly affords the mercurichloride, [CHPh:CH-CH(OMe)]Cl₂HgCl₂ (III), which, like (I) and (II), is extremely sensitive to moisture. (I) and CPhMe give Ph styryl ketone; with COMe₂, distyryl ketone [dimethylacetal, m. p. 63—63.5° (corr.) (lit. 55—56°)] and styryl Me ketone are produced. (I) and MeCHO in absence or presence of Et₂O afford PhCHO and paracetaldehyde, but in presence of Et₂O-HgCl₂, (III) is gradually produced. Mol. quantities of (I) and cinnamaldehyde or of (II) and PhCHO give after about 20 hr., an equilibrium mixture of about 59% of (I) and 41% of (II), indicating the reversible reaction, CHPhCl-OMe + CHPh:CH-CHO \rightleftharpoons CHPh:CH-CHCl-OMe + PhCHO.

In presence of 1 mol. of HgCl₂ (and Et₂O), equilibrium is displaced to the right and (III) results; this is the most convenient method of prep. of (III). (III) is also produced by the prolonged interaction of (I) and Et₂O-HgCl₂ in presence of air, owing to the oxidation of Et₂O to MeCHO. The reversible reaction, (I) + PhCHO \rightleftharpoons PhCHO + CHPhCl-OMe (to be described later), also occurs; prolonged interaction leads to other condensation products. (I), Ph styryl ketone (IV), and HgCl₂ in Et₂O give a compound, convertible by NaOMe into the dimethylacetal of (IV). PhCHO and CH₂Cl-OMe give (after treatment with NaOMe) a mixture of CHPh(OMe)₂ and α -methoxybenzyl methoxymethyl ether (V), b. p. 109—110°/12 mm.; the amount of (V) produced rises (up to 39.4%) with increased (initial) reaction time. (V) decomposes readily in air to CH₂O and PhCHO. The production of (V) involves the addition of Cl and -CH₂-OMe across the C=O group of PhCHO; a similar reaction does not occur with PhCHO and MeCl. CPh₂(OMe)₂ and PCl₅ in C₆H₆ afford impure CPh₂Cl-OMe, which when heated gives MeCl and CPh₂, and with NaOMe yields CPh₂(OMe)₂.

H. BURTON.

Syntheses with diazomethane. VII. Reaction of aldehydes and ketones. F. ARNDT, J. AMENDE, and W. ENDER (Monatsh., 1932, 59, 202—219; cf. A., 1929, 328).—OH-Compounds (e.g., MeOH) catalyse the reaction between diazomethane and RCHO (especially when R is positive) in Et₂O and the subsequent formation of CH₂R-CHO (from the hypothetical intermediate CHR<O-CH₂), which results, together with COMeR, when R is an (electrically) indifferent group. When R is positive, ethylene oxide production is favoured. CH₂R-CHO reacts in the same ways as RCHO, but a positive R now favours the formation of CH₂R-COMe. COMeR also reacts similarly; a positive R promotes the formation of an ethylene oxide and COEtR (catalysed by OH-compounds). Compounds of the type RSO₂-CH₂-COR react readily with diazomethane to give RSO₂-CH₂CR-OMe.

p-NO₂-C₆H₄-CHO and Et₂O-diazomethane (I) in presence of a little MeOH give (contrary to previous findings) practically no *p*-NO₂-C₆H₄-CH₂-COMe, but somewhat better yields of *p*-NO₂-C₆H₄-COMe and *p*-nitrophenylethylene oxide (cf. loc. cit.). The yield of *o*-NO₂-C₆H₄-COMe from *o*-NO₂-C₆H₄-CHO and (I) is improved by a little, and decreased by much MeOH; the amount of *o*-nitrophenylethylene oxide remains more or less const. in both cases. 2:4:6-(NO₂)₃C₆H₂-CHO and (I) give a product, decomp. 80—90°, which is not 2:4:6-(NO₂)₃C₆H₂-COMe (cf. Sonn and Bülow, A., 1925, i, 1267). CH₂Cl-COMe and (I) give an additive compound converted by evaporation into N₂ and α -chloroisobutylene oxide, CH₂>CMe-CH₂Cl, b. p. 124° (main product); the oxide and conc. HCl give OH-CMe(CH₂Cl)₂. Similarly, CCl₃-COMe affords $\alpha\alpha$ -trichloroisobutylene oxide, CH₂>CMe-CCl₃, b. p. 51°/10 mm., m. p. 53—54°, converted by conc. HCl into impure methylchloromethyltrichloromethylcarbinol, b. p. 93—95°/12 mm.

*epi*Chlorohydrin is not obtained from $\text{CH}_2\text{Cl}\cdot\text{CHO}$; reaction appears to proceed by way of $\text{CH}_2\text{Cl}\cdot\text{COME}$. Phenanthraquinone and (I) react slowly and incompletely; in presence of a little MeOH , *spirophe-*

thrylethylene oxide, $\text{C}_{12}\text{H}_8\text{C}(\text{CH}_3)_2\text{O}$, m. p. 166° [converted by $\text{MeOH}\cdot\text{HCl}$ into a *chlorohydrin*, m. p. 117° (*benzoate*, m. p. 168°)], results, whilst with 20% of MeOH the CH_2 ether described by Biltz and Paetzold (A., 1923, i, 1233) is obtained. Benzil is converted into $\alpha\alpha'$ -methylenedioxy stilbene under all the conditions tried. 1-Hydroxyisatin and 1 mol. of (I) give 3-hydroxy-1-methoxycarbostyryl, m. p. 203°; with 2 mols. of (I), 1:3-dimethoxycarbostyryl, m. p. 128—129°, results.

The reaction between solid $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and (I) (cf. *loc. cit.*; Meerwein *et al.*, A., 1929, 681) depends on the immediate decomp. of the additive compound at the crystal surface. The additive compound from $\text{CCl}_3\cdot\text{CHO}$ and (I) is decomposed by $\text{Et}_2\text{O}\cdot\text{BzOH}$ after several min.; in presence of porous earthenware decomp. occurs immediately.

H. BURTON.

Action of acetic anhydride on benzylideneanilines. J. B. EKELEY, M. C. SWISHER, and C. C. JOHNSON (Gazzetta, 1932, 62, 81—84).—Previous work by Ekeley and collaborators on the condensation of Ac_2O with substituted benzylideneanilines is discussed and the experimental conditions are described (cf. A., 1922, i, 934). E. E. J. MARLER.

Symmetrical triad prototropic systems. VIII. Analogy between symmetrical triad systems and aromatic side-chain reactivity, and the effect of *m*-substitution on mobility and equilibrium in the $\alpha\gamma$ -diphenylmethylenazomethine system. C. W. SHOPPEE (J.C.S., 1932, 696—711; cf. A., 1931, 834).—*m*-Chloro-, -bromo-, -iodo-, -nitro-, and -dimethylamino-benzaldehyde, *m*-anisaldehyde, and *m*-tolualdehyde (from *m*-toluanilide, m. p. 126°) give cryst. H sulphite compounds. Reduction of *m*-tolualdoxime, m. p. 60°, b. p. 137°/17 mm., by 3% Na amalgam in AcOH affords *m*-methylbenzylamine, b. p. 96°/20 mm. [*picrate*, m. p. 198° (decomp.); *benzoate*, m. p. 150—150.5°; *carbamido*-derivative, m. p. 148°]. The following substituted benzylamines were prepared: *m*-chloro-, b. p. 111—112°/18 mm. [*picrate*, m. p. 204° (decomp.); *carbamido*-derivative, m. p. 129°] (from *m*-chlorobenzaldoxime, m. p. 70°); *m*-bromo-, b. p. 126—127°/18 mm. [*picrate*, m. p. 205° (decomp.); *benzoate*, m. p. 135.5°; *carbamido*-derivative, m. p. 132°; hydrochloride, m. p. 216—217°] (from *phthal*-*m*-bromobenzylimide, m. p. 138—139°, by $\text{N}_3\text{H}_4\cdot\text{H}_2\text{O}$); *m*-iodo-, b. p. 132°/8 mm. [*picrate*, m. p. 210° (decomp.); *benzoate*, m. p. 132°; *Ac* derivative, m. p. 114.5°; *carbamido*-derivative, m. p. 170—171°] [from *phthal*-*m*-iodobenzylimide, m. p. 143.5°, which, with a substance, m. p. 228°, was prepared from *m*-iodobenzyl bromide, m. p. 49—49.5° (obtained from *m*-iodotoluene and Br at 180°)]; *m*-methoxy-, b. p. 103—104°/6 mm. [*picrate*, m. p. 181°; *benzoate*, m. p. 95°; *p*-nitrobenzoyl derivative, m. p. 124°] (from *m*-anisaldoxime, b. p. 170°/26 mm., and, less well, by electrolytic reduction of *m*-methoxybenzamide, m. p. 133°); *m*-dimethylamino-, b. p.

134—135°/10 mm. [*monopicrate*, m. p. 206° (decomp.); *dipicrate*, m. p. 170°; *benzoate*, m. p. 111.5°] (from the oxime); *m*-nitro- (*picrate*, m. p. 202°) (from the phthal-derivative, m. p. 160.5°). Reduction of (a) *m*-bromo- and (b) *m*-iodo-benzaldoxime by 3% Na amalgam and AcOH gives benzylamine in (a) 34—35% and (b) 100% yield. The following were prepared: *m*-methyl-, b. p. 187°/12 mm.; *m*-chloro-, b. p. 190°/10 mm.; *m*-bromo-, b. p. 200°/10 mm., m. p. 38°; *m*-iodo-, m. p. 73°; *m*-methoxy-, b. p. 206°/15 mm.; *m*-dimethylamino-, b. p. 233°/10 mm. *benzyliden*-benzylamines; also *benzylidene*-*m*-methyl-, b. p. 170°/7 mm.; *m*-chloro-, b. p. 175°/5.5 mm.; *m*-bromo-, b. p. 217—218°/15 mm.; *m*-iodo-, b. p. 220—221°/12 mm.; *m*-methoxy-, b. p. 186°/6 mm., m. p. 37°; *m*-dimethylamino-, b. p. 200°/5 mm.; and *m*-nitro-benzylamine, m. p. 32.5—32.7° (lit. 42°). ω -Benzylimino- (I) and ω -benzylideneamino (II) *m*-tolyltrimethylammonium iodide have m. p. 128—129° and 145—146°, respectively. The above compounds with *p*-nitrophenylhydrazine (III) yield the following substituted benzaldehyde-*p*-nitrophenylhydrazones: *m*-methyl-, m. p. 157°; *m*-chloro-, m. p. 214°; *m*-bromo-, m. p. 220.5°; *m*-iodo-, m. p. 208°; *m*-methoxy-, m. p. 171°; *m*-dimethylamino-, m. p. 190°; *m*-nitro-, m. p. 248°. (I) and (II) are stable to 0.145N-NaOEt at 82°; with (III), followed by H_2PtCl_6 , (I) gives the impure salt $[(p)\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2(m)]_2\text{PtCl}_6$, m. p. 207—208° (decomp.). Interconversion of the above tautomerides by 0.145N-NaOEt at 82° and thermal analysis of the hydrazones obtained on treating the resulting mixture with (III) indicates the following sequence for *m*-substituents, the figures in parentheses representing the mobilities conferred by the substituent, and those in brackets the percentage of isomeride $\text{C}_6\text{H}_4\text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\text{Ph}:\text{NMe}_2$ (0.606) [63], Me (1.10) [60], OMe (2.51) [54.7], I (7.33) [42.5], Br (9.47) [36.5], Cl (10.7) [35.5], NO_2 (147) [68]. The relation between these results and those in the *p*-series and dipole moments is discussed in the light of current electronic theories. *m*-Bromobenzaldehyde-semicarbazone has m. p. 228° (decomp.).

R. S. CAHN.

Alkoxyaldehydes. S. SABETAY and D. N. MIRA (Compt. rend., 1932, 194, 617—620).—By the action of the appropriate halogenoacetal, in the presence of Cu, on the Na or K derivatives of various alcohols and subsequent hydrolysis of the product with 15% H_2SO_4 in AcOH , the following alkoxyaldehydes are obtained (cf. A., 1930, 323): *benzyloxy*-, b. p. 110—112°/13 mm. (*acetal*, b. p. 143—144°/15 mm.; *semicarbazone*, m. p. 118°); β -phenylethoxy-, b. p. 119—121°/13 mm. (*acetal*, b. p. 153—154°/16 mm.; *semicarbazone*, m. p. 88°); and *cinnamyloxy*-, b. p. 139—141°/16 mm. (*acetal*, b. p. 155—157°/16 mm.; *semicarbazone*, m. p. 120°), *acetaldehyde*.

J. W. BAKER.

Preparation of 3:4:5-trimethoxybenzaldehyde. K. H. SLOTTA (J. pr. Chem., 1932, [ii], 133, 129—130).—3:4:5-Trimethoxybenzaldehyde is prepared in 80% yield by reduction of carefully purified 3:4:5-trimethoxybenzoyl chloride (from the acid and PCl_5 , not SOCl_2) with H_2 and Pd-BaSO₄ in dry xylene (cf. A., 1925, i, 951; 1931, 213). H. A. PIGGOTT.

Nitro-derivatives of dehydrodivanillin. J. M. GULLAND and G. U. HOPKIN (J.C.S., 1932, 439—443).—Dehydrodivanillin, m. p. 312° (lit., m. p. 305°), with Me_2SO and NaOH affords the Me_2 ether and sometimes also *dehydrodivanillin Me ether*, m. p. 196°. Nitration of the Me_2 ether with cold HNO_3 (d 1.42) affords 3:3'-dinitro-5:6:5':6'-tetramethoxydiphenyl, m. p. 215°, whilst with mixed H_2SO_4 and fuming HNO_3 at -18° it affords 2:3:2':3'-tetranitro-5:6:5':6'-tetramethoxydiphenyl (I), m. p. 242°, which, after reduction to the $(\text{NH}_2)_4$ -compound, condenses with phenanthraquinone to give 5:6:5':6'-tetramethoxydiphenyl-2:3:2':3'-bisphenanthraphenazine, m. p. above 300°. The strong violet fluorescence of the phenazine in C_6H_6 supports the structure assigned to the $(\text{NO}_2)_4$ -compound. Contrary to Elbs and Lerch (A., 1916, i, 315), diacetyldehydrodivanillin and HNO_3 (d 1.5) at -18° affords 4:4'-dinitrodiacetyldehydrodivanillin, m. p. 168—169° (+2.5EtOH, m. p. 85—90°), which on alkaline hydrolysis affords 4:4'-dinitrodehydrodivanillin, m. p. 230° (decomp.) [Me_2 ether, m. p. 176—177°]. Nitration of this Me_2 ether with HNO_3 (d 1.48) and H_2SO_4 at 50° affords 2:3:4:3':4'-pentanitro-5:6:5':6'-tetramethoxydiphenyl, m. p. 175°, but at 0°, the product is 3:4:3':4'-tetranitro-5:6:5':6'-tetramethoxydiphenyl, m. p. 197°, isomeric with (I).

J. L. D'SILVA.

Thiolacetic acid lignin of pine wood. VI. B. HOLMBERG [with S. HAGLUND] (Svensk Pappers-Tidn., 1930, 33, 679—686; Chem. Zentr., 1931, ii, 420—421).—The aq. extract, after evaporation, was treated with thiolacetic acid in 2N-HCl, affording lignothiolacetic acid; 17 samples of pine wood were so treated, the results being tabulated. Purified samples of lignothiolacetic acid contained (1) C 53.16, H 5.20, S 13.27%, corresponding with the formula $\text{C}_{40}\text{H}_{38.81}\text{O}_{10.50}\cdot 4.60\text{HS}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$; (2) C 55.29, H 5.27, O 24.49, S 9.95, OMe 11.46, corresponding with $\text{C}_{40}\text{H}_{40.01}\text{O}_{21.25}\cdot 3.11\text{HS}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$; (3) C 55.00, H 5.34, S 9.98, OMe 11.56%. A. A. ELDRIDGE.

Preparation of cyclopentanone and glutaric acid. M. E. BÆDTKER (J. Pharm. Chim., 1932, [viii], 15, 225—228).—A detailed account of the prep. of cyclopentanone by distillation of Ba adipato (yield 94% of theory) and its oxidation to glutaric acid by boiling aq. HNO_3 (d 1.084). Adipic acid has b. p. 320°/752 mm. (corr.; slight decomp.).

H. A. PIGGOTT.

Additive reactions of phenyl vinyl ketone. II. Deoxybenzoin. C. F. H. ALLEN and W. E. BARKER (J. Amer. Chem. Soc., 1932, 54, 736—748; cf. A., 1929, 1071).— α -Diketo- $\alpha\beta\epsilon$ -triphenylpentane (I), m. p. 95° (monoxime, m. p. 131°; dioxime, m. p. 162°); mono-2:4-dinitrophenylhydrazone, m. p. 221°; prepared from Ph β -chloroethyl ketone, deoxybenzoin, and KOAc in MeOH-NaOMe, gives with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in MeOH 2:3:6-triphenylpyridine, m. p. 115° (picrate, m. p. 163°), and with Ac_2O and FeCl_3 the pyrylium salt, $\text{C}_{23}\text{H}_{17}\text{OCl}_2\text{Fe}$, m. p. 189°. $\alpha\epsilon$ -Diketo- $\beta\epsilon$ -diphenyl- α -p-diphenylpentane (II), m. p. 104° (dioxime, m. p. 79—80°), prepared similarly, gives a pyrylium salt, $\text{C}_{23}\text{H}_{17}\text{OCl}_2\text{Fe}$, m. p. 191—193°, and 2:3-diphenyl-6-p-diphenylpyridine, m. p. 193°, whilst $\alpha\epsilon$ -diketo- $\alpha\beta\epsilon$ -

diphenyl- ϵ -p-diphenylpentane (III), m. p. 115° (dioxime, m. p. 214—215°), affords a pyrylium salt, m. p. 203°. Monobromination of (I) gives (probably) the δ -Br derivative, m. p. 152° (50—55% yield); a stereoisomeride, m. p. 150°, of this is produced during the dibromination of (I), whereby two Br_2 derivatives, probably the $\beta\delta$ -stereoisomerides (not interconvertible), m. p. 127° and 180°, are produced. Bromination of both Br compounds gives the Br_2 derivative, m. p. 127°, converted by Hg and aq. NaOH-KI into 1:2-dibenzoyl-1-phenylcyclopropane (IV), m. p. 123°; the less fusible Br_2 derivative is unchanged by this treatment. (IV) is converted by 1% EtOH-KOH into an isomeride (V), m. p. 126°, also formed from the Br derivative, m. p. 150°, and 8—10% EtOH-KOH. (IV) and (V) give the same dioxime, m. p. 212°, and the same monophenylhydrazone, m. p. 169°. (IV) is much more reactive than (V); (IV) is reduced by Zn and EtOH or AcOH to (I), whilst (V) is unaffected by Zn and EtOH. (IV) and HBr give the Br derivative, m. p. 152°, whilst (V) is unaffected. (IV) and Br give mainly the Br_2 compound, m. p. 127°, and a little of its isomeride [also formed in small amount by prolonged treatment of (V)]. (IV) and MgPhBr give 40% of 1-phenyl-1:2-di(hydroxydiphenylmethyl)-cyclopropane, m. p. 168°; with MgMeI , 1-phenyl-1:2-di(α -hydroxy- α -phenylethyl)cyclopropane, m. p. 196° (45% yield), results. In all reactions involving opening of the cyclopropane ring, fission occurs in the 1:2-position (i.e., the point of ring closure), regardless of the nature of the reagent. C. J. WEST (b).

Abnormal reactions of magnesium benzyl chloride. P. R. AUSTIN and J. R. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 647—660).— $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ (I) and ClCO_2Et give mainly o -Me- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ and $\text{C}(\text{CH}_2\text{Ph})_3\cdot\text{OH}$; it is suggested that the formation of these products depends on a selective action of the Grignard reagent on the initial products of the reaction. ClCO_2Me gives an ester fraction from which o -Me- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is obtained; $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ could not be isolated, but microscopical examination showed its presence. The main product from (I) and Et_3CO_3 is $\text{C}(\text{CH}_2\text{Ph})_3\cdot\text{OH}$, whilst o -Me- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ and (I) give (probably) o -Me- $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, b. p. 225—227°/7 mm. (I) and solid CO_2 give 40% of $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, whilst o -Me- $\text{C}_6\text{H}_4\cdot\text{MgBr}$ (II) affords similarly 62% of o -Me- $\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. (II) and $\text{CO}(\text{CH}_2\text{Ph})_2$ give a compound, $\text{C}_{30}\text{H}_{30}\text{O}_2$ (?), m. p. 157—158°, which may be tetrabenzylethylene glycol. (I) and Ac_2O afford 30% of o -Me- $\text{C}_6\text{H}_4\text{Ac}$; with $(\text{CH}_2\text{Cl}\cdot\text{CO})_2\text{O}$, 42% of o -tolyl chloromethyl ketone, b. p. 129—130°/11 mm. (semicarbazone, m. p. 103—105°), results. o -Me- $\text{C}_6\text{H}_4\text{Ac}$ (24%) and o -Me- $\text{C}_6\text{H}_4\cdot\text{COPh}$ are obtained from (I) and AcCl and BzCl , respectively. (I) reacts normally with paracetaldehyde, alkyl and aryl ketones, acetals, Et orthoformate, AcOEt , BzOEt , Et_2CO , CO_2 , epichlorohydrin, ClCH_2Ac , allyl iodide, HgCl_2 , PhNCO , and alkyl p -toluenesulphonates. o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{MgCl}$ and CO_2 (gas) give o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (also formed using ClCO_2Me); with Ac_2O or AcCl , a ketone, oxidised to 6-chloro- o -toluic acid, is produced. The Grignard reagent from 2:6-dichlorobenzyl chloride, b. p. 135°/25 mm., m. p. 39—40°, and CO_2 or ClCO_2Me give 2:6-dichloro-

phenylacetic acid, m. p. 156—157°; with Ac_2O , a product containing 2:6-dichlorophenylacetone is produced, whilst with AcCl , a product containing 3:5-dichloro-4-methylacetophenone results. The mechanism of the rearrangement process in abnormal reactions of (I) is discussed. C. J. WEST (b).

Structure of metal ketyls. C. B. WOOSTER (J. Amer. Chem. Soc., 1932, 54, 834—835).—The metal ketyl from COPh_2 conducts an electric current in liquid NH_3 , suggesting that $\text{CPh}_2\cdot\text{ONa}$ is ionised to Na^+ and CPh_2O^- . The constitution of metal ketyls is being studied. C. J. WEST (b).

Condensation of benzanilides and *p*-dialkylanilines with phosphoryl chloride as condensing agent. Mechanism of the reaction. R. C. SHAH, R. K. DESHPANDE, and J. S. CHAUBAL (J.C.S., 1932, 642—650).— NPhPhBz and POCl_3 , when heated, give HCl and undistillable P compounds, which with NPhMe_2 (I) at 100° yield *p*-dimethylaminobenzophenone (II). Benzanilide imidochloride (III) does not react with (I) at 100° and is thus not, as hitherto assumed, an intermediate in the formation of (II). (III) and (I) at 160—180° give a base, m. p. 148—150° [hydrochloride, m. p. 282° (decomp.); picrate, m. p. 218°], believed to be a stereoisomeride of diphenyl-*N*-methylbenzamidine, an oil (hydrochloride, m. p. 250°; picrate, m. p. 189—190°) [prepared from (III), NPhMe , and NPhEt_2 (IV) at 100°]. (III) and (IV) similarly yield a base, m. p. 150° [hydrochloride, m. p. 289—290° (decomp.)], believed to be stereoisomeric with diphenyl-*N*-ethylbenzamidine, m. p. 81° (hydrochloride, m. p. 189—190°) (similarly prepared). NPhMeBz , (I), and POCl_3 at 100° give (II) and NPhMe . The first stage of the above reactions is considered to be formation of $\text{CPh}(\text{NPhR})\cdot\text{OCl}\cdot\text{O}\cdot\text{POCl}_2$ ($\text{R}=\text{Me}$ or H), which on further heating loses HCl if $\text{R}=\text{H}$, or with (I) gives $\text{CClPh}(\text{NRPh})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, which is subsequently hydrolysed. The following benzophenones were prepared by heating the appropriate anilide with the necessary alkylaniline and POCl_3 at 100°: 4-dimethylamino-2'-methoxy-, m. p. 74°; *p*-diethylamino- (oxime, m. p. 143—144°); *p*-dimethylamino-, m. p. 92—93° (lit. 90°) (oxime, m. p. 152°); 4'-bromo-4-dimethylamino-, m. p. 128—129° (oxime, m. p. 185°); 2'-chloro-2-diethylamino-, m. p. 79°; 4-dimethylamino-3'-methoxy-, m. p. 72—73° (lit. 67°) (oxime, m. p. 185°); 4-dimethylamino-4'-methoxy-, m. p. 92°; 4-dimethylamino-3'-hydroxy-, m. p. 185—187°; 4-dimethylamino-4'-hydroxy-, m. p. 199—200° (from *p*-methylcarbonatobenzanilide, m. p. 179—181°). The following were similarly prepared at 110—115°: 3'-nitro-4-diethylamino-, m. p. 84°; 4'-nitro-4-dimethylamino-, m. p. 206—207°; 4'-nitro-4-diethylamino-, m. p. 116—117° (oxime, m. p. 156°), and 2'-nitro-4-dimethylamino-benzophenone (prepared by long heating at 60°), m. p. 251—253°, accompanied by a substance, m. p. 93°. *p*-Dimethylaminophenyl I- and 2-naphthyl ketone, new m. p. 115—116° and 128—129°, respectively, were similarly prepared at 100°. The following *N*-methyl-diphenylbenzamidines were prepared (m. p. of the hydrochloride in parentheses): *o*- [m. p. 141° (m. p. 225—227°)], *m*- [an oil (m. p. 230°)], and *p*- [m. p. 94° (m. p. 213°)] -nitro-

m-methoxy-, m. p. 83° (m. p. 214—215°); *o*-chloro-, m. p. 106° (m. p. 230—235°); *p*-bromo-, m. p. 121—123° (m. p. 290—295°). The following *N*-ethyl-diphenylbenzamidines were prepared: *o*- [m. p. 99—100° (m. p. 160—161°)], *m*- [m. p. 174—175° (m. p. 247°)], and *p*- [m. p. 112° (m. p. 179—180°)] -nitro-; *m*-methoxy-, m. p. 175° (m. p. 248°); *o*-chloro-, m. p. 70—71° (m. p. 250°). R. S. CAHN.

Direct synthesis of *p*-dialkylaminobenzophenones. R. C. SHAH and J. S. CHAUBAL (J.C.S., 1932, 650—652).—By condensing NPhMe_2 or NPhEt_2 with the appropriate benzanilide imidochloride in cold CS_2 in presence of AlCl_3 the following benzophenone derivatives were prepared in good yield: *p*-dimethyl- (I) and -diethyl-amino-; 4'-nitro-4-dimethyl- and -diethyl-amino-; 4'-bromo-4-dimethylamino-; 4'-bromo-4-diethylamino-, m. p. 99—100°; 2'-chloro-4-dimethylamino-, m. p. 68°. *p*-Bromobenzanilide imidochloride has m. p. 85—86°; the corresponding *o*-chloro-compound is an oil, b. p. 182—183°/10 mm. NPhMe_2 , BzCl , and AlCl_3 in hot CS_2 give a poor yield of (I). R. S. CAHN.

4'-Dimethylaminobenzophenone-2-sulphonic acid. R. T. K. CORNWELL (J. Amer. Chem. Soc., 1932, 54, 819—820).—*o*-Sulphobenzoic anhydride (1 mol.) and NPhMe_2 (3 mols.) at 110° give 43% of 4'-dimethylaminobenzophenone-2-sulphonic acid (+2 H_2O), decomp. slowly at 230—235° to a green liquid [Ba (+3 H_2O) and NH_4 salts]. An Ac derivative could not be prepared. C. J. WEST (b).

Preparation of substituted fluorenones. E. H. HUNTRESS and I. S. CLIFF (J. Amer. Chem. Soc., 1932, 54, 826—828).—Langecker's statement (this vol., 163) that nitration of 9-acetamidofluorene gives 2-nitrofluorenone as the only recognisable product is confirmed; more vigorous nitration affords 30% of the 2:7- and 13% of a new (NO_2)₂-derivative, m. p. 213—214°. 2-Nitrofluorenoneoxime is described with m. p. 249° (loc. cit.) and 262.5—263° (A., 1927, 1201); these may be stereoisomeric forms. C. J. WEST (b).

Beckmann rearrangement. VI. Unsaturated ketoximes. II. K. VON AUWERS and H. BRINK (Annalen, 1932, 493, 218—240).—In part a reply to Blatt (A., 1931, 621; this vol., 163). Oximation of Ph *o*-methoxystyryl ketone (dibromide, m. p. 132°) in acid solution (cf. A., 1931, 223) gives mainly the oxime (I), m. p. 135—145° (*Bz* derivative, m. p. 133—134°), and a little 3-phenyl-5-*o*-methoxyphenylisoxazoline (II), m. p. 103—104°. (I) is unaffected by boiling NaOH , is probably sulphonated by conc. H_2SO_4 , and is converted by PCl_5 in Et_2O into *o*-methoxycinnamanilide, m. p. 161—162°. Oximation of the ketone in aq. NaOH (cf. loc. cit.) gives mainly (II) and an alkali-sol. hydroxylamino-oxime. Ph *m*-methoxystyryl ketone is oximated in acid or alkaline solution to the oxime, m. p. 75—95° (small yield in alkali) (*Bz* derivative, m. p. 144—145°, hydrolysed in one case to the oxime, m. p. 94—97°), rearranged to *m*-methoxycinnamanilide, m. p. 107—108°, and converted by conc. H_2SO_4 into a sulphonyl-derivative, m. p. 169—170°. Ph *p*-methoxystyryl ketone affords mainly 3-phenyl-4-anisylisoxazoline (III), m. p. 103—104° (oxidised by CrO_3 in AcOH to the isoxazole), and a little

oxime(?) in acid, whilst in alkali, (III), a substance, m. p. 184—186° (decomp.), and (mainly) a *hydroxylamino-oxime*, $C_{16}H_{18}O_3N_2$, m. p. 118—119° (decomp.), are produced. *o*-Methoxyphenyl styryl ketone, b. p. 226°/11.5 mm., prepared from *o*-OMe- C_6H_4 Ac and PhCHO in aq. EtOH-NaOH, is oxidized in acid to the *oxime*, m. p. 135—145° (Bz derivative, m. p. 140—141°), rearranged to *cinnam-o-anisidide*, m. p. 136—138°, and sulphonated by conc. H_2SO_4 at room temp. Oximation in alkali gives (mainly) a *hydroxylamino-oxime*, m. p. 162°, and small amounts of the *oxime* and *o*-phenyl-3-*o*-methoxyphenylisooxazoline, m. p. 50—52°. *m*-Methoxyphenyl styryl ketone, b. p. 236—238°/12 mm., m. p. 41—43°, is oxidized in acid to the *oxime*, m. p. 132—137° (Bz derivative, m. p. 127—128°), rearranged to *cinnam-m-anisidide*, m. p. 121—122°, and unaffected by conc. H_2SO_4 ; in alkaline solution, a *hydroxylamino-oxime*, m. p. 127—128° (about 66%), and a *dioxime*, $C_{16}H_{16}O_3N_2$, m. p. 156—158° (about 33%), are produced. These results afford no evidence for the configurations of the various oximes. The position of the OMe group in the ketones studied does exert some influence on the oximation [but not in the manner indicated by the work of Meisenheimer *et al.* (A., 1928, 1136)], but has no influence on the Beckmann rearrangement (since a derivative of cinnamic acid is produced in each case). None of the above oximes is converted by conc. H_2SO_4 into an isooxazoline as are the oximes of Ph and anisyl styryl ketones (cf. *loc. cit.*).

Oximation of Ph β -chloro- β -phenylethyl ketone (IV) in acid solution gives Ph styryl ketoxime, the dibromide of which undergoes the Beckmann rearrangement yielding *r*- α - β -chloro- β -phenylpropionanilide. Prolonged interaction of (IV) and NH_2OH in MeOH-AcOEt at room temp. affords 3:5-di-phenylisooxazoline as the main product.

H. BURTON.

Beckmann rearrangement. VII. **Unsaturated ketoximes.** III. K. VON AUWERS and H. BRINK (J. pr. Chem., 1932, [ii], 133, 154—172).—Distyryl ketoxime (A., 1898, i, 194; 1900, i, 237) is unchanged by hot 20% NaOH, but is converted by cold conc. H_2SO_4 into 5-phenyl-3-styrylisooxazoline, m. p. 110—111° (*loc. cit.*), identified by oxidation with CrO_3 in AcOH to 5-phenylisooxazole-3-carboxylic acid, m. p. 162°, and $BzOH$; formation of the isooxazoline is regarded as due to addition of H_2SO_4 at the double linking and subsequent elimination. 5-Phenyl-3-styrylisooxazole, m. p. 144°, is obtained by the action of NH_2OH and NaOH on distyryl ketone dibromide or on α -bromodistyryl ketone; it was not formed by oxidation of the isooxazoline. Rearrangement of distyryl ketoxime with PCl_5 gives *cinnamostyrylamide*, m. p. 213°, identified by hydrolysis with 25% H_2SO_4 to $CHPh:CH:CO_2H$, NH_3 , and $CH_2Ph:CHO(?)$. Styryl Me ketone yields the *oxime*, m. p. 116° (Bz derivative, m. p. 145—147°), both under acid (NH_2OH, HCl and EtOH) and alkaline (aq.) conditions, and, although obtained purer in the latter case, no isomeride was isolated in the former. The *oxime* with HCl in Et_2O , AcOH, or C_6H_6 gives the *hydrochloride*, m. p. 140—145°, which is slowly isomerised in EtOH to the *hydrochloride*, m. p. 157—160°, of an oximo, m. p. 75—88° (crude) (Bz deriv-

ative, m. p. 94—96°). A Beckmann rearrangement of the *oxime*, m. p. 116°, gives β -acetostyrylamide, m. p. 105—106°, identified by its non-identity with cinnamomethylamido, its hydrolysis by 25% H_2SO_4 to AcOH, NH_3 , NH_2Me , and $CH_2Ph:CHO(?)$, and its synthesis from β -acetoxystyrene and NH_2Ac or, better, from $CH_2Ph:CHO$ and NH_2Ac . Styryl Me ketone dichloride (I) gives no definite product with NH_2OH, HCl in acid solution; in alkaline medium α -chlorostyryl Me ketoxime, m. p. 132—133°, and 5-phenyl-3-methylisooxazole, m. p. 64°, are formed, the former in preponderating amount in low concn. of alkali. α -Chlorostyryl Me ketone, b. p. 140°/11 mm., is prepared by action of NaOAc on (I) in anhyd. EtOH, and is converted into its *oxime* in acid medium; this is stable to NaOAc in anhyd. EtOH, and does not give an isooxazoline with H_2SO_4 . The product of the action of PCl_5 on this oximo is a viscous yellow oil which continuously evolves HCl on keeping and forms *acetophenylacetamide*, $CH_3Ph:CO:NHAc$, m. p. 129—130°, hydrolysed by NaOH in EtOH to NH_3 , AcOH, and $CH_2Ph:CO_2H$. α -Bromostyryl Me ketone, b. p. 152°/11 mm. (hitherto incorrectly designated " β ," cf. J.C.S., 1904, 85, 464), and its *oxime*, m. p. 130—131°, are similarly prepared, and the latter behaves on rearrangement with PCl_5 analogously to the Cl-compound.

H. A. PRAGOTT.

Isomerisation of aldehydes to ketones. (MME.) P. RAMART-LUCAS and J. P. GUERLAIN (Bull. Soc. chim., 1931, [iv], 49, 1860—1874).—In confirmation of previous work (A., 1929, 815, 1166; 1930, 86) it has now been shown that α -disubstituted aldehydes, $CHRAr:CHO$ ($R=alkyl$), isomerise to ketones, $CH_2Ar:CO:R$ under the influence of heat, in presence of kieselguhr, but at higher temp. than with the diarylacetaldehydes. The isomeric ketone $Ar:CO:CH_2R$ is not formed, and it is concluded that either the two ketones cannot be transformed one into the other or the temp. of isomerisation is higher than that of dissociation. The aldehydes are accordingly considered the intermediate stage in the conversion of glycols or ethylene oxides into ketones and in the dehydration of hydrobenzoin glycols the proportions of isomeric ketones formed can be varied only by varying the temp. or concn. of the acid if both ketones are formed and can be isomerised.

α -p-Tolyl-n-valeraldehyde, b. p. 132—133° (semicarbazone, m. p. 150—151°), obtained in 45% yield by distilling *p*-tolylpropylglycidic acid, with kieselguhr at 450°/10 mm. is converted into *p*-tolylmethyl *Pr^a* ketone (semicarbazone, m. p. 145°). α -p-Tolyl- γ -methylvaleraldehyde, b. p. 138—139°/15 mm. (semicarbazone, m. p. 230°), similarly obtained (yield 65%) is similarly converted at 450°/15 mm. into *p*-tolylmethyl *Bu^{\beta}* ketone (semicarbazone, m. p. 160°). $CH_2Ph:CO:Me$ and $CH_2Ph:CO:Et$ are obtained in 60% and 40% yields, respectively, from $CHPh_2:CN$ and $MgMeI$ or $MgEtI$, but *p*-tolylacetonitrile does not afford the homologous ketones. *p*-Tolyl isoamyl ketone, b. p. 156—157°/14 mm. (semicarbazone, m. p. 178—179°), is obtained from isobutylacetic acid, b. p. 185—190°, by condensing the chloride with $PhMe$. $CHPhMe:CHO$ in presence of kieselguhr at 600°/15 mm. affords about 60% of $CH_2Ph:CO:Me$; α -phenyl-

butaldehyde similarly yields $\text{CH}_2\text{Ph}\cdot\text{COEt}$, and α -*p*-tolylbutaldehyde at 500/15 mm. yields *p*-methylbenzyl Et ketene.

The ultra-violet absorption spectra of the aldehydes and ketones are described. R. BRIGHTMAN.

Synthesis of chalkone homologues and related compounds. I. Methoxyacetophenone, methoxychalkone, and some related compounds. (Miss) C. KURODA and (Miss) T. MATSUKUMA. **II. Some homologues of methoxychalkone and their related compounds.** (Miss) C. KURODA and (Miss) T. NAKAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 51—60, 61—76).—I. Careful addition of AlCl_3 to PhOMe or the appropriate polymethoxybenzene in cold AcCl gives the following acetophenone derivatives (m. p. in parentheses), which with anisaldehyde and KOH in MeOH at 50—60° yield the chalkones (m. p. in brackets): 4-methoxy- (I) [m. p. 100°]; 2:4 (II) [m. p. 80—81°], 3:6 (oxime, m. p. 106°) [m. p. 93°]-dimethoxy-; 2:3:4 (an oil; oxime, m. p. 91°) [94—95°], 1:2:4 (m. p. 99°), 1:3:5 [m. p. 119°]-trimethoxy-. In the prep. of (I) and (II) substances, m. p. 135° and 145°, respectively, were also obtained. The prep. of 4:5-dinitro- and -diamino-veratrole is modified. Halochromy in 30% HCl , conc. H_2SO_4 , and 90% H_3PO_4 increases with increasing no. of MeO groups. Anisaldehyde, but not *p*-hydroxy-, *p*-hydroxy-*m*-methoxy-, or *m*-methoxy-*p*-ethoxy-benzaldehyde, shows halochromy. The above method of synthesis failed with 1:2:4:5-tetramethoxybenzene.

II. Thymol Mo ether gives (above method) 4-methoxy-2-methyl-5-isopropylacetophenone, b. p. 236°, 157—158°/8 mm. (oxime, m. p. 157°; semicarbazone, m. p. 113°), which yields 4-methoxy-2-methyl-5-isopropylchalkone, m. p. 70°, and the following derivatives of the last substance: 2'- (m. p. 138°), 4'- (m. p. 163°)-hydroxy-; 4'-methoxy-, m. p. 77°; 3'-methoxy-4'-ethoxy-, m. p. 94—96°; 3':4'-methylenedioxy-, m. p. 97°; 3':4'-dimethoxy-6'-methyl-, m. p. 119°. The same method yields also the following chalkone derivatives: 3:4:3':4'-tetramethoxy-6:6'-dimethyl-, m. p. 132°; 3-hydroxy-4:3':4'-trimethoxy-6:6'-dimethyl-, m. p. 197—198°; 4:3':4'-trimethoxy-6'-methyl-, m. p. 169°; 2-hydroxy-3':4'-dimethoxy-6'-methyl-, m. p. 150—151°; 2:3:4:6:3':4'-hexamethoxy-6'-methyl-, m. p. 132°; 4'-hydroxy-3:4-dimethoxy-6:3'-dimethyl-, m. p. 144—145°; 3:4:3'-trimethoxy-4'-ethoxy-6-methyl-, m. p. 136°; 2:3:4:6:2':3':4':6'-octamethoxy-, m. p. 96—97°. 2:3:4:6-Tetramethoxyacetophenone with alkaline KMnO_4 affords 2:3:4:6-tetramethoxybenzoylformic acid, decomp. 126°, the $\text{NLi}\cdot\text{Ph}$ salt (m. p. 96°) of which in boiling xylene affords 2:3:4:6-tetramethoxybenzanil, m. p. 86° after softening at 83°, hydrolysed to the corresponding aldehyde, m. p. 86.5—87°. Pyrogallol Me_3 ether gives gallacetophenone, b. p. 140°/10 mm., which led similarly to 2:3:4-trimethoxybenzoylformic acid, m. p. 136° (NH_2Ph salt), and 2:3:4-trimethoxybenzanil, m. p. 76° after sintering at 74°. R. S. CAHN.

Affinity capacity and migratory power. II. Mechanism of dehydration of glycols and their transformation into aldehydes or ketones; reality of the semipinacolic transformation and

vinyl dehydration; non-necessity of intermediate aldehyde-ketone transposition. M. TIFFENEAU, (MME.) J. LÉVY, and P. WEILL (Bull. Soc. chim., 1931, [iv], 49, 1606—1617).—From a review of the transformations of di-*tert.* and di-*sec.* glycols and of *sec.-tert.*-glycols the following evidence is advanced in support of actual semipinacolic transformation in the dehydration of arylalkylethylene glycols, and against aldehyde formation as an intermediate stage: (1) the non-identity of the ketones obtained by dehydration with H_2SO_4 of *o*- and *m*-anisyl-dimethyl- and of *p*-anisylmethyl-ethyl-ethylene glycol with those similarly obtained from the corresponding trisubstituted acet-aldehydes: (2) the formation of active $\alpha\gamma\delta$ -triphenylbutan- β -one by dehydration of active phenyldibenzyl-ethylene glycol with cold H_2SO_4 , when the formation of an inactive intermediate aldehyde must lead to an inactive ketone; and (3) differences produced by varying experimental conditions, e.g., concn. of H_2SO_4 , and temp., on the dehydration of arylalkylethylene glycols and the isomerisation of arylalkyl-acetaldehydes. Thus whilst numerous glycols yield only ketones on distillation, most of the corresponding trisubstituted aldehydes are unchanged at the same temp. and isomerise only at higher temp. α -Anisyl- α -methylbutaldehyde is converted into the ketone at 450° only in presence of kieselguhr, but the latter is readily obtained by dehydration of anisylmethyl-ethylene glycol at 260°. The occurrence of vinyl dehydration is similarly established by the conversion of di-*p*-anisylpropylene glycol with H_2SO_4 into anisyl-anisylethane by vinyl dehydration without transposition, whilst α -di-*p*-anisylpropaldehyde is similarly converted by aldehyde-ketone isomerisation with migration of Me into α -di-*p*-anisylpropan- β -one. Accordingly, it is concluded that comparisons of the affinity capacity of cyclic radicals can safely be based on their migratory powers. R. BRIGHTMAN.

Affinity capacity and migratory power. III. General study of affinity capacity. M. TIFFENEAU and (MME.) J. LÉVY (Bull. Soc. chim., 1931, [iv], 49, 1617—1661).—Since "affinity capacity" is directly proportional to the effect of the radicals on various additive or elimination reactions, it is considered to be of use in interpreting the mechanism of reactions or in predicting their course. The following conclusions are reached from direct and indirect comparisons of the radicals by dehydration of glycols, isomerisation of the corresponding ethylene oxides, or addition of HOI to the analogous olefines, in the types $\text{CHR}\cdot\text{CH}_2$, $\text{CRR}\cdot\text{CH}_2$, $\text{CHR}\cdot\text{CHR}'$, $\text{CRR}\cdot\text{CHR}'$, and $\text{CRR}\cdot\text{CR}\cdot\text{R}'$: the affinity capacities of the aryl radicals are without exception higher than those of alkyl groups or than that of H , being approx. equal to that of two alkyl radicals. The affinity capacity of the Ph radical is slightly less than that of two Me groups, but is approx. equal to that of $\text{Me}+\text{Et}$ or $\text{Me}+\text{Pr}$ and is greater than $\text{Me}+\text{CH}_2\text{Ph}$. The radicals are thus classified in two broad groups of strong and weak affinity capacity, within which groups minor variations exist. The aryl groups may be arranged in the following order of decreasing affinity capacity: *p*-anisyl > piperonyl, *p*-tolyl, *o*-anisyl > *m*-anisyl > Ph . The effect of Me is not identical with that of OMe

substitution and for the tolyl groups the order of affinity capacity is $o > p > m$. For the alkyl groups the order is: $\text{Me} > \text{Pr}^a > \text{Bu} > \text{Et}$, the affinity capacity being generally greater than that of H, especially for Me, amyl, and isoamyl. Pr^a and Pr^b approx. to, and CH_2Ph is lower than, H. R. BRIGHTMAN.

Affinity capacity and migratory power. IV. General study of migratory powers. M. TIFFENEAU and (MME.) J. LEVY (Bull. Soc. chim., 1931, [iv], 49, 1661—1709).—From mol. transpositions which occur in the dehydration of α -glycols, isomerisation of the corresponding ethylene oxides, dehalogenation of the glycol iodohydrins, and the deamination of NH_2 -alcohols, derived from the types, $\cdot\text{CHR}\cdot\text{CHR}'$, $\cdot\text{CRR}'\cdot\text{CH}_2$, $\cdot\text{CRR}'\cdot\text{CHR}''$, $\cdot\text{CRR}'\cdot\text{CRR}'$, $\cdot\text{CRR}'\cdot\text{CRR}''$, and $\text{CRR}\cdot\text{CR}'\text{R}''$, the following general conclusions are reached. For aryl radicals the migratory powers are generally but not rigorously, parallel with the affinity capacities, and except in the dehydration of p -tolylhydrobenzoin when Ph migrates in place of p -tolyl, and the deamination of the NH_2 -alcohols $\text{C}(\text{Ar})(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$, when Ph has a greater migratory power than anisyl, C_{10}H_7 , or p -tolyl, the comparative migratory powers of aryl groups are relatively const. and the radicals can be arranged in the following groups of decreasing migratory power: (1) p -anisyl, p -tolyl, p -diphenyl, α -naphthyl, 3:4-veratryl, 2:4-veratryl, (2), p -ethoxyphenyl, p -isopropylphenyl, p -ethylphenyl, p -fluorophenyl, (3) Ph, p -iodophenyl, o -anisyl, o -ethoxyphenyl, (4) m -tolyl, m -anisyl, 2:5-veratryl, o -, m -, and p -chloro- and -bromo-phenyl. Normally p -substituted Ph groups, including 2:4-dimethoxy- and 3:4-dimethoxy-phenyl as well as α - and β - C_{10}H_7 , are markedly greater in migratory power than Ph, whilst m -substituted Ph groups are definitely greater. Aryl groups are invariably above H and alkyl groups in migratory power, H is above Me and about equal to CH_2Ph and Et. The migratory power of the alkyl groups varies inversely with their affinity capacity, and the radicals can be arranged in the following order of decreasing migratory power: Bu^a and CH_2Ph (fairly strong); Et and isoamyl; Pr^a and Me (weak); Bu^b and Pr^b afford an exception to the general rule that affinity capacity and migratory power vary universally. In aldehyde-ketone transposition the migration of radicals is irregular and no rules have been established.

R. BRIGHTMAN.

Affinity capacity and migratory power. V. Affinity capacity of the anisyl radical from the dehydration of anisylalkyl glycols and isomerisation by heat of the corresponding ethylene oxides. M. TIFFENEAU, (MME.) J. LEVY, and P. WEILL (Bull. Soc. chim., 1931, [iv], 49, 1709—1721).—Since the action of dry KOH on the iodohydrin of α -anisyl- β -dimethylethylene affords α -anisyl- α -methylpropaldehyde, b. p. 140—145°/18 mm. (oxime, m. p. 104—105°, converted into anisyl dimethylacetoneitrile, b. p. 165—170°/20 mm. by Ac_2O), and not β -anisylbutan- γ -one (cf. A., 1926, 818), whilst isomerisation of α -anisyl- β -methyl- $\alpha\beta$ -propylene oxide yields β -anisylbutan- γ -one, also obtained by dehydration of the glycol, the affinity capacity of anisyl is greater than that of two Me groups and consequently than that of Ph.

Similarly α -anisyl- β -ethyl- $\alpha\beta$ -butylene oxide, b. p. 156—158°/16 mm., obtained from α -anisyl- β -ethyl- Δ^a -butylene, b. p. 134°/15 mm., d_4^{20} 0.98 (from Mg anisyl bromide and α -ethylbutaldehyde, and dehydration), on distillation in presence of kieselguhr etc., affords only α -anisyl- n -propyl Et ketone (I), b. p. 160—162°/22 mm., d_4^{20} 1.034 (semicarbazone, m. p. 138°), also obtained in 40% yield from EtBr and α -anisylbutan- β -one in Et₂O in presence of NaNH_2 . Dehydration of α -anisyl- β -diethylethylene glycol similarly yields (I). α -Anisyl- β -propyl- $\alpha\beta$ -amylene oxide, d_4^{20} 0.995, b. p. 162—165°/13 mm., from BzO_2H and α -anisyl- β -propyl- Δ^a -amylene, b. p. 162—165°/16 mm., d_4^{20} 0.953 (by dehydration of α -anisyl- β -propylpentan- α -ol at 160° in presence of sulphuric-pumice), on distillation in presence of kieselguhr etc. similarly yields α -anisyl- n -butyl Pr^a ketone, b. p. 278—282°, d_4^{20} 0.986, also obtained from PrBr, NaNH_2 , and α -anisylbutan- β -one, or by dehydration of α -anisyl- β -propylpentan- $\alpha\beta$ -diol, m. p. 93—94° (obtained in 50% yield from MgPrBr and Et anisylglycolate), at 280—290° or with 50% H_2SO_4 . γ -Phenyl- α -anisyl- β -benzyl- $\alpha\beta$ -propylene oxide, similarly obtained from γ -phenyl- α -anisyl- β -benzyl- Δ^a -propene, b. p. 250—260°/40 mm., isomerises to benzyl β -phenyl- α -anisylethyl ketone, m. p. 75° (oxime, m. p. 95° [Ac derivative, m. p. 61—62°, yielding on distillation a substance (? the amide), m. p. 134—135°], oximino-derivative, m. p. 153—154°), which with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ affords α -anisyl- $\beta\beta$ -tribenzylethyl alcohol, and is also obtained by dehydration of α -anisyl- $\beta\beta$ -dibenzylethylene glycol. $\omega\omega$ -Dibenzyl- p -methoxyacetophenone, m. p. 93—95° (semicarbazone, m. p. 179—180°), is obtained from p -methoxyacetophenone and CH_2PhCl in presence of K. R. BRIGHTMAN.

Affinity capacity and migratory power. VI. Affinity capacity of o - and m -methoxyphenyl radicals compared with that of two methyl radicals. (MME.) J. LEVY and R. PERNOT (Bull. Soc. chim., 1931, [iv], 49, 1721—1730).—In the isomerisation of the ethylene oxides by

distillation with kieselguhr, the oxide ring is ruptured on the side of the Ar group when $\text{Ar} = o$ -anisyl and on the Me₂ side when $\text{Ar} = m$ -anisyl. Similarly, addition of HOI to $\text{CHAr}\cdot\text{CMe}_2$ yields $\text{CHArI}\cdot\text{CMe}_2\cdot\text{OH}$ when $\text{Ar} = o$ -anisyl and $\text{OH}\cdot\text{CHAr}\cdot\text{CMe}_2\text{I}$ when $\text{Ar} = m$ -anisyl. Accordingly it is concluded that in affinity capacity o -anisyl is superior to m -anisyl and approximates to p -anisyl, whereas m -anisyl is only slightly superior to Ph. The dehydration of the glycols, $\text{OH}\cdot\text{CHAr}\cdot\text{CMe}_2\cdot\text{OH}$, with H_2SO_4 did not indicate differences in affinity capacity between o - and m -anisyl, but showed that they were inferior to p -anisyl.

α - o -Anisyl- β -methylpropan- α -ol has b. p. 133°/14 mm., α - o -anisyl- β -methyl- Δ^a -propylene, b. p. 109°/14 mm. (dimeride, b. p. 212—215°/14 mm.; oxide, b. p. 115°/14 mm.); α - m -anisyl- β -methylpropan- α -ol, b. p. 130°/12 mm., and α - m -anisyl- β -methyl- Δ^a -propylene, b. p. 110°/12 mm. (oxide, b. p. 127°/17 mm.); α - o -anisyl- β -methyl- $\alpha\beta$ -propylene glycol, b. p. 162—164°/14 mm. (yield 70—80% from Et o -anisylglycolate, b. p. 168°/14 mm.), on dehydration by heat or H_2SO_4 affords α - o -anisylethyl Me ketone, b. p. 127—128°/14 mm. (semicarbazone, m. p. 222°); with boiling 20%

H_2SO_4 , α -*o*-anisyl- α -methylpropaldehyde, b. p. 125—126°/14 mm. (semicarbazone, m. p. 192°), is obtained together with (probably) a little diethylene oxide. α -*m*-Anisyl- β -methyl- α -propylene glycol, b. p. 129—130°/14 mm. (from Et *m*-anisylglycollate, b. p. 169°/14 mm.), similarly yields on distillation at 15 mm. α -*m*-anisyl- α -methylpropaldehyde, b. p. 128—129°/14 mm. (semicarbazone, m. p. 162°), together with resinous products; with 20% sulphuric acid a substance, b. p. 222—228°/13 mm., probably the diethylene oxide which in presence of sulphuric-pumice is converted into α -*m*-anisyl- α -methylpropaldehyde is also produced. With H_2SO_4 , d 1.84, α -*m*-anisylethyl Me ketone, b. p. 135—136°/16 mm. (semicarbazone, m. p. 145°), is obtained. *o*-Anisyl Pr^{β} ketone has b. p. 125—126° (? at 12 mm.) (semicarbazone, m. p. 118°), and *m*-anisyl Pr^{β} ketone, b. p. 130°/12 mm. (semicarbazone, m. p. 112°). R. BRIGHTMAN.

Affinity capacity and migratory power. VII. Migratory powers of *o*- and *m*-methoxyphenyl compared with those of phenyl and anisyl radicals. (MME.) J. LEVY and R. PERNOT (Bull. Soc. chim., 1931, [iv], 49, 1730—1738).—The elimination of HI from the iodohydrin of α -phenyl- α -*o*-anisylethylene, m. p. 37°, d₄²⁰ 1.08, with AgNO_3 yields Ph *o*-methoxybenzyl ketone, b. p. 207—210°/16 mm., 1.13 (semicarbazone, m. p. 179—180°), by migration of the *o*-anisyl group; the iodohydrin of α -phenyl- α -*m*-methoxyphenylethylene, b. p. 169—170°/12 mm., d₄²⁰ 1.08, yields *m*-methoxyphenyl CH_2Ph ketone, b. p. 208—212°/16 mm. (semicarbazone, m. p. 141°), the iodohydrin of α -*o*-anisyl- α -*p*-anisylethylene, m. p. 75°, b. p. 198°/14 mm., yields *p*-anisyl *o*-methoxybenzyl ketone, b. p. 230—232°/13 mm. (semicarbazone, m. p. 180°), by migration of the *o*-anisyl group; and α -*m*-anisyl- α -*p*-anisylethylene, b. p. 215—216°/19 mm., d₄²⁰ 1.10, yields *m*-anisyl *p*-methoxybenzyl ketone (I), m. p. 61° (semicarbazone, m. p. 145—146°), by migration of the anisyl group. (I) with MeI or CH_3PhCl in NaOEt affords *m*-anisyl α -*p*-anisylethyl ketone, b. p. 222—224° (semicarbazone, m. p. 185—186°; oxime, m. p. 82—83°), and *m*-anisyl β -phenyl- α -*p*-anisylethyl ketone, m. p. 109—110°. Accordingly, the four radicals are arranged in the following order of decreasing migratory power: *o*-anisyl, *p*-anisyl, Ph, *m*-anisyl, whereas the affinity capacities are in the decreasing order: *p*-anisyl, *o*-anisyl, *m*-anisyl, Ph. α -Phenyl- α -*o*-anisylethylene is obtained from MgMeI and *o*-methoxybenzophenone, m. p. 79°, by distillation of the α -phenyl- α -*o*-anisylethanol, m. p. 76°, first formed. 2:4'-Dimethoxybenzophenone, m. p. 99° (yield 30%), and α -*o*-anisyl- α -*p*-anisylethanol, m. p. 99°, are similarly obtained. *m*-Methoxybenzophenone, m. p. 37°, and 3:4'-dimethoxybenzophenone, m. p. 54—55°, obtained from *m*-methoxybenzoyl chloride in presence of AlCl_3 , yield the ethylene direct with MgMeI. α -*o*-Anisyl- α -*p*-anisylethylene and α -*m*-anisyl- α -*p*-anisylethylene react violently with BzO_2H , but at low temp. the latter gives 80% of a substance, m. p. 99°, probably α -*m*-anisyl- α -*p*-anisylethylene glycol monobenzoate, since on distillation it affords BzOH and 3:4'-dimethoxydiphenylacetaldehyde, b. p. 216—222°/19 mm. (semicarbazone, m. p. 130°). Phenyl-*o*-anisylacetaldehyde, b. p. 202—206°/16 mm. (semicarbazone, m. p. 167—

168°), phenyl-*m*-anisylacetaldehyde, b. p. 205—208° (semicarbazone, m. p. 181°), and 2:4'-dimethoxydiphenylacetaldehyde, b. p. 230—234°/14 mm. (semicarbazone, m. p. 183°), similarly obtained by isomerisation of the ethylene oxides or glycol benzoates, are readily resinified on distillation even under reduced pressure. R. BRIGHTMAN.

Affinity capacity and migratory power. VIII. Relative affinity capacities of *p*-tolyl and piperonyl radicals in direct or indirect comparison with other aryl radicals. M. TIEFFENAU and (MME.) J. LEVY (Bull. Soc. chim., 1931, [iv], 49, 1738—1753).—Direct comparison of the affinity capacity of *p*-tolyl and piperonyl with that of other aryl groups in the type $\text{CHR}:\text{CHPh}$ yields no definite conclusions, except that, since *o*-phenylpiperonyl-ethylene oxide is ruptured on the side of the piperonyl group, the piperonyl radical has a higher affinity capacity than Ph. The other ethylene oxides isomerise to the disubstituted aldehydes and dehydration of the glycols yields the same products. Indirect comparison, by isomerisation of the ethylene oxides.

$\text{CHR}:\text{CMe}_2 > \text{O}$, in which, when $\text{R} = \textit{p}$ -tolyl or piperonyl, rupture occurs on the side of the cyclic radical, indicates that *p*-tolyl and piperonyl, like *p*- and *o*-anisyl, are superior in affinity capacity to Ph and *m*-anisyl. Similarly, addition of HOI to the corresponding ethylenes yields $\text{OH}:\text{CHR}:\text{CMe}_2\text{I}$ when $\text{R} = \textit{p}$ -tolyl and piperonyl, and dehydration of the glycols yields $\text{CRMe}_2:\text{CHO}$, also indicating that *p*-tolyl and piperonyl are superior to two Me groups in affinity capacity. Since under the same conditions (dil. H_2SO_4) when $\text{R} = \textit{p}-anisyl the ketone, $\text{CHRMe}:\text{COMe}$, is obtained, it is concluded that the order of decreasing affinity capacity is *p*-anisyl; *o*-anisyl, *p*-tolyl, and piperonyl; *m*-anisyl; Ph.$

The following are described: β -phenyl- α -*p*-tolylethanol, m. p. 107—108° [from *p*-tolyl benzyl ketone, m. p. 107.5° (oxime, m. p. 131°)], giving on distillation or dehydration with 20% H_2SO_4 , β -phenyl- α -*p*-tolylethylene, m. p. 69°, converted by BzO_2H in CHCl_3 into the oxide, m. p. 59—60°, b. p. 190—192°/22 mm., isomerising in presence of ZnCl_2 to phenyl-*p*-tolylacetaldehyde, b. p. 180—185°/14 mm. (semicarbazone, m. p. 157—158°), and Ph *p*-methylbenzyl ketone, m. p. 94—95° (semicarbazone, m. p. 128—129°; oxime, m. p. 109°). β -Phenyl- α -piperonylethanol, m. p. 156—157° (in 90% yield from $\text{CH}_3\text{Ph}:\text{MgCl}$ and piperonal), and β -phenyl- α -piperonylethylene, m. p. 93—94°, yielding the oxide (in Et_2O) isomerised to Ph piperonylmethyl ketone, m. p. 70° (semicarbazone, m. p. 187°), and phenylpiperonylacetaldehyde, b. p. 214—215°/14 mm. (semicarbazone, m. p. 172—173°), are similarly obtained. Piperonyl CH_2Ph ketone has m. p. 91—92°, b. p. 222—223° (semicarbazone, m. p. 172°). α -Phenyl- β -*p*-tolylethylene glycol, m. p. 94—95° and 128—129°, is obtained in two stereoisomeric forms by converting the corresponding dibromide, m. p. 173—174°, into the stereoisomeric diacetates, liquid and m. p. 79—80°, and hydrolysis, both of which on dehydration with 20% H_2SO_4 afford phenyl-*p*-tolylacetaldehyde. β -Phenyl- α -piperonylethylene glycol, m. p. 92—93°, similarly obtained from

the corresponding dibromide, b. p. 185—187°, and diacetate, b. p. 235—242°/23 mm., yields phenylpiperonylacetalddehyde and ω -piperonylacetophenone on dehydration. Dehydration of α -p-tolyl- β -methylpropyl- α -ol, b. p. 145—147°/35 mm., by distillation alone or in presence of sulphuric-pumice, affords α -p-tolyl- β -methyl- Δ^2 -propylene, b. p. 208—210°, giving an oxide, b. p. 120—125°/17 mm., which isomerises only in presence of ZnCl_2 , yielding α -p-tolylethyl Me ketone, b. p. 114—118°/15 mm. (semicarbazone, m. p. 183—184°; oxime, m. p. 58—70°), which yields an iodohydrin converted by AgNO_3 into α -p-tolyl- α -methylpropalddehyde (I), b. p. 192°/14 mm. (semicarbazone, m. p. 171—172°). α -p-Tolyl- β -methyl- α -propylene glycol, m. p. 55—60°, obtained in 60—80% yield from Et p-tolylglycolate, m. p. 76°, b. p. 155—158°/18 mm., and 4 mols. of MgMeI , on dehydration with 20% H_2SO_4 affords (I), and a substance, m. p. 62°, b. p. 180°/20 mm., probably the diethylene oxide, since H_2SO_4 converts it into β -p-tolylbutan- γ -one; the latter is also obtained by dehydration of the glycol with H_2SO_4 , d 1.84, at 0—5°. α -Piperonyl- β -methylpropyl alcohol, α -piperonyl- β -methyl- Δ^2 -propylene, b. p. 134—135°/10 mm. (dimeride, m. p. 127—128°; oxide, b. p. 140—145°/12 mm.), Et piperonylglycolate, m. p. 70—71°, and α -piperonyl- β -methyl- α -propylene glycol, m. p. 107—108°, are similarly obtained, the last-named yielding with 20% H_2SO_4 α -piperonyl- α -methylpropalddehyde, b. p. 148—150°/12 mm. (semicarbazone, m. p. 184—185°; oxime, m. p. 90—91°), together with a substance, b. p. 250—260°/12 mm., converted into α -piperonylethyl Me ketone (II), b. p. 150°/12 mm. (semicarbazone, m. p. 179—180°), on distillation. With H_2SO_4 , d 1.84, even at -20°, piperonylmethylpropylene glycol is resinified. Isomerisation of the ethylene oxide by distillation at the ordinary pressure also affords (II), which is also obtained by oxidation of isosafrole in CHCl_3 with BzO_2H , and methylation of the piperonylacetone, b. p. 158°/15 mm. (semicarbazone, m. p. 157°), in Et_2O with NaNH_2 . Further methylation affords α -piperonyl- α -methyllethyl Me ketone, b. p. 164°/17 mm. (semicarbazone, m. p. 217°), also obtained directly from piperonylacetone. The iodohydrin of α -piperonyl- β -methyl- Δ^2 -propylene with AgNO_3 is converted into α -piperonyl- α -methylpropalddehyde, elimination of HI being thus accompanied by migration of piperonyl. p -Tolyl Pr² ketone has m. p. 235—236° (oxime, m. p. 92°). p -Tolylglycollic acid, m. p. 144—145°, is obtained together with a substance, m. p. 75—77°, in 40—45% yield by Na_2CO_3 hydrolysis of p -tolyltrichloromethylcarbinol (acetate, m. p. 107°), obtained in 12—15% yield from chloral, PhMe, and AlCl_3 . Et piperonylglycolate is obtained from piperonal cyanohydrin through the NH_2 -ester hydrochloride obtained with HCl in Et_2O -EtOH solution.

R. BRIGHTMAN.

Affinity capacity and migratory power. IX. Migratory power of cyclic radicals deduced from the dehydration reactions of pinacols. A. ORÉKHOV and M. ROGER (Bull. Soc. chim., 1931, [iv], 49, 1754—1756).—Since the pinacols, $(\text{OH}\cdot\text{CPhR})_2$, where R=veratryl or 3:4-dimethoxyphenyl, with 20% alcoholic KOH yield the pinacols, $\text{CPhR}\cdot\text{COPh}$, it is concluded that the migratory powers of 2:4-

or 3:4-dimethoxyphenyl are superior to that of Ph. Reduction of 2:4-dimethoxybenzophenone affords $\alpha\beta$ -2:4:2':4'-tetramethoxydiphenyl- $\alpha\beta$ -diphenylethylene glycol, m. p. 192—193°, also obtained from benzyl and Mg 2:4-dimethoxyphenyl iodide, and Ph 2:4:2':4'-tetramethoxytriphenylmethyl ketone, m. p. 148—149°, the latter being obtained by dehydration of the pinacol, and yielding on scission 2:4:2':4'-tetramethoxytriphenylmethane, m. p. 122°. Reduction of 3:4-dimethoxybenzophenone affords only Ph 3:4:3':4'-tetramethoxytriphenylmethyl ketone, m. p. 120—121°, yielding on scission 3:4:3':4'-tetramethoxytriphenylmethane, m. p. 121—124°. 2:4-Dimethoxytriphenylmethane has m. p. 124°.

R. BRIGHTMAN.

Affinity capacity and migratory power. X. Comparative migratory powers of cyclic radicals deduced from the deamination of amino-alcohols. M. TIFFENEAU, A. ORÉKHOV, and M. ROGER (Bull. Soc. chim., 1931, [iv], 49, 1757—1765).—The comparative migratory powers of o - and p -anisyl, o - and p -ethoxyphenyl, and 2:4-, 2:5-, and 3:4-dimethoxyphenyl have been compared with that of Ph by observing the structure of the ketone $\text{COPh}\cdot\text{CH}_2\text{R}$ or $\text{COR}\cdot\text{CH}_2\text{Ph}$ produced by the action of 50% NaNO_2 on the NH_2 -alcohols, $\text{OH}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{NH}_2$, in AcOH. 2:5-Dimethoxyphenyl migrates less readily than Ph or o -anisyl, but the other radicals examined migrate more readily than Ph. In opposition to the results of Lévy and Pernot for o - and p -anisyl, o -anisyl migrates in preference to p -anisyl, although p -anisyl migrates in preference to Ph, and Ph and o -anisyl appear equal in migrating power. Accordingly, it is concluded that the migratory power of a radical is not invariable for different reactions.

β -Hydroxy- β -phenyl- β - p -anisylethylamine, m. p. 134—135° (hydrochloride, m. p. 164—165°), affording ω - p -anisylacetophenone, m. p. 98—99°, on deamination, is obtained from MgPhBr and ω -amino- p -methoxyacetophenone hydrochloride, m. p. 195—196°, prepared by reduction of oximino- p -methoxyacetophenone. β -Hydroxy- β -phenyl- β - p -ethoxyphenylethylamine, m. p. 135—136° (hydrochloride, m. p. 170—175°), similarly obtained from ω -amino- p -ethoxyacetophenone hydrochloride, m. p. 194—195°, affords a mixture of p -ethoxyphenyl CH_2Ph ketone, m. p. 103—104° (semicarbazone, m. p. 156°; oxime, m. p. 103—104°), and (mainly) Ph p -ethoxybenzyl ketone, m. p. 110—111.5° (oxime, m. p. 121—122°); β -hydroxy- β -phenyl- β -veratrylethylamine, m. p. 93—94°, from ω -amino-3:4-dimethoxyacetophenone hydrochloride, m. p. 212°, yields Ph 3:4-dimethoxybenzyl ketone, m. p. 61.5—62.5° (oxime, m. p. 105—106°), and β -hydroxy- β - p -anisyl- β - o -anisylethylamine, m. p. 109—110° (hydrochloride, m. p. 182°), o -anisyl p -methoxybenzyl ketone, m. p. 178°. β -Hydroxy- β -phenyl- o -anisylethylamine, m. p. 107—108° (hydrochloride, m. p. 175—176°), similarly obtained from Mg ω -anisyl halide and ω -aminoacetophenone in HCl, on deamination yields a mixture of o -anisyl CH_2Ph ketone, b. p. 198—202°(?) / 14 mm. (semicarbazone, m. p. 214°), and Ph o -methoxybenzyl ketone, b. p. 198—202°/14 mm. (semicarbazone, m. p. 183°), on deamination. β -Hydroxy- β -phenyl- β - o -ethoxyphenyl-

ethylamine, m. p. 124—125° (hydrochloride, m. p. 183°), yields a mixture of *o*-ethoxyphenyl CH_2Ph ketone, b. p. 197—198°/14 mm. (semicarbazone, m. p. 118—119°), and mainly *Ph o*-ethoxybenzyl ketone, m. p. 110—111.5° (semicarbazone, m. p. 172°); β -hydroxy- β -phenyl- β -2:4-dimethoxyphenylethylamine, m. p. 108—109° (hydrochloride, m. p. 198°), yields a mixture of 2:4-dimethoxyphenyl CH_2Ph ketone, m. p. 47—48° (oxime, m. p. 120—121°), and mainly *Ph* 2:4-dimethoxybenzyl ketone, m. p. 99—100° (oxime, m. p. 92—93°); and β -hydroxy- β -phenyl- β -2:5-dimethoxyphenylethylamine, m. p. 131—132° (hydrochloride, m. p. 141°), yields 2:5-dimethoxyphenyl CH_2Ph ketone, m. p. 40° (oxime, m. p. 93°). 3:4-Dimethoxyphenyl CH_2Ph ketone has m. p. 91—93° (oxime, m. p. 128—129°; CH_2Ph derivative, m. p. 78—79°).

R. BRIGHTMAN.

Affinity capacity and migratory power. XI. Comparative affinity capacities of aryl and alkyl radicals. (MME.) J. LEVY and (MME.) DVOLETTZKA-GOMBINSKA (Bull. Soc. chim., 1931, [iv], 49, 1765—1776).—Dehydration of the glycols $\text{OH}\cdot\text{CHAr}\cdot\text{CHR}\cdot\text{OH}$, where $\text{Ar}=\text{Ph}$ or *p*-anisyl and $\text{R}=\text{Me}$, Et , Pr^a , Pr^b , CH_2Ph , with 20% H_2SO_4 , and isomerisation of the corresponding oxides always yields the ketone $\text{CH}_2\text{Ar}\cdot\text{CO}\cdot\text{R}$, and accordingly the affinity capacity of the aryl groups is superior to that of the alkyl or aralkyl. Similarly, addition of HOI to the corresponding ethylenes always yields $\text{OH}\cdot\text{CHAr}\cdot\text{CHRI}$, but in the elimination of HI with AgNO_3 the semihydrobenzoin transposition is accompanied by vinyl dehydration with migration of H , affording $\text{Ar}\cdot\text{CO}\cdot\text{CH}_2\text{R}$ to an extent depending on the nature of Ar and R . When $\text{Ar}=\text{anisyl}$ and $\text{R}=\text{Et}$, the aldehyde, $\text{CH}_2\text{Ar}\cdot\text{CHO}$, is exclusively formed, but $\text{Ar}\cdot\text{CO}\cdot\text{CH}_2\text{R}$, alone is formed when $\text{Ar}=\text{Ph}$ and $\text{R}=\text{Et}$ or Pr^b . The two reactions are simultaneous when $\text{Ar}=\text{anisyl}$ and $\text{R}=\text{Me}$ or Pr^a and when $\text{Ar}=\text{Ph}$ and $\text{R}=\text{CH}_2\text{Ph}$. Hence the elimination of HI is influenced by the nature of both the aryl and alkyl radicals. With HgO α -phenyl- Δ^a -butylene iodohydrin is converted into COPhPr^a . α -Phenyl- Δ^a -amylene iodohydrin with AgNO_3 affords α -phenylacetaldehyde, b. p. 122—123°/28 mm. (semicarbazone, m. p. 108°), and α -phenyl- γ -methyl- Δ^a -butylene iodohydrin (with HgO), COPhBu^b . $\alpha\gamma$ -Diphenyl- Δ^a -propylene iodohydrin similarly affords phenylbenzylacetaldehyde, b. p. 186—188°/23 mm., and *Ph* β -phenylethyl ketone; α -anisyl- Δ^a -propylene iodohydrin, α -anisylpropaldehyde, and a little anisyl Et ketone; α -anisyl- Δ^a -amylene iodohydrin, anisyl Bu^a ketone, and α -anisylacetaldehyde, b. p. 157—158°/17 mm. (semicarbazone, m. p. 97°), and α -anisyl- Δ^a -butylene iodohydrin, α -anisylbutaldehyde, b. p. 145—146°/17 mm. (semicarbazone, m. p. 147°).

α -Phenyl- Δ^a -propylene oxide, b. p. 87—90°/13 mm., in presence of 50% H_2SO_4 or ZnCl_2 isomerises to $\text{CH}_2\text{Ph}\cdot\text{COMe}$; α -phenyl- Δ^a -butylene oxide, b. p. 110—111°/21 mm., similarly yields $\text{CH}_2\text{Ph}\cdot\text{COEt}$; α -phenyl- Δ^a -amylene oxide, b. p. 114—115°/13 mm., $\text{CH}_2\text{Ph}\cdot\text{COPr}^a$, and α -phenyl- γ -methyl- Δ^a -butylene oxide, b. p. 108—110°/17 mm., $\text{CH}_2\text{Ph}\cdot\text{COPr}^b$. α -Diphenyl- Δ^a -propylene oxide, b. p. 162—165°/6 mm., commences to isomerise when distilled under reduced pressure, affording $\text{CO}(\text{CH}_2\text{Ph})_2$, m. p. 34—35°. The ethylene

oxides containing the anisyl radical are unstable and isomerise during distillation or in preparation, affording *p*-methoxybenzyl Me ketone, *p*-methoxybenzyl Et ketone, b. p. 265—270° (semicarbazone, m. p. 131—132°), and *p*-methoxybenzyl Pr^a ketone, b. p. 280—285° (semicarbazone, m. p. 142°). α -Phenyl- $\alpha\beta$ -propylene glycol has m. p. 52—53° (α -) and 92—93° (β -form), α -phenyl- $\alpha\beta$ -butylene glycol, m. p. 40—41° (α) and b. p. 205—208°/72 mm. (β); α -phenyl- $\alpha\beta$ -amylene glycol, b. p. 160—170°/14 mm. (α), and m. p. 36—38° (β); α -phenyl- γ -methyl- $\alpha\beta$ -butylene glycol, m. p. 81—82° (α), m. p. 108° (β); $\alpha\gamma$ -diphenyl- $\alpha\beta$ -propylene glycol, m. p. 63—64°, α -anisyl- $\alpha\beta$ -propylene glycol, m. p. 116°, α -anisyl- $\alpha\beta$ -butylene glycol, m. p. 75—76° (α) and 220—240° (β), and α -anisyl- $\alpha\beta$ -amylene glycol, m. p. 42—43°.

R. BRIGHTMAN.

Affinity capacity and migratory power. XII. Isomerisation of phenyldialkylethylene oxides.

(a). Affinity capacity of phenyl compared with that of two acyclic radicals. (b) Comparative migratory power of some acyclic radicals. (MME.) J. LEVY and A. TABART (Bull. Soc. chim., 1931, [iv], 49, 1776—1788).—In the $\beta\beta$ -dialkylstyrene

oxides, $\frac{\text{CHPh}}{\text{CRR}'} > \text{O}$, when R and $\text{R}'=\text{Me}$, on isomerisation by heat, the O -linking is ruptured on the side of Me ; when R and $\text{R}'=\text{CH}_2\text{Ph}$, the rupture occurs on the Ph side. Accordingly, the affinity capacity of Ph is inferior to that of two Me groups, but superior to two CH_2Ph groups. Similarly, when $\text{R}=\text{CH}_2\text{Ph}$ and $\text{R}'=\text{Me}$, Et , Pr^a , or Pr^b , the ketone, $\text{CHPhR}\cdot\text{COR}'$, alone is produced, whereas when $\text{R}=\text{Me}$ and $\text{R}'=\text{Et}$ or Pr^a and when R and $\text{R}'=\text{Et}$, a mixture of aldehyde and ketone is obtained. Thus whilst the affinity capacity of $\text{Ph}+\text{H}$ is approx. equal to that of two Et groups, $\text{Me}+\text{Et}$, or $\text{Me}+\text{Pr}^a$, it is superior to that of CH_2Ph and any other radical. Since, moreover, when $\text{R}=\text{Me}$ and $\text{R}'=\text{Et}$, the Et group alone migrates, whilst when $\text{R}'=\text{Pr}^a$ Me migrates, the order of decreasing migratory power is Et , Me , Pr^a , observations when $\text{R}=\text{CH}_2\text{Ph}$, including $\text{R}'=\text{Pr}^b$, similarly indicating that CH_2Ph is superior to Et and Pr^a about equal to Pr^b .

$\beta\beta$ -Diethylstyrene, b. p. 216—218° (oxide, b. p. 113—114°), is obtained by dehydration of α -phenyl- β -ethylbutan- α -ol by distillation at 760 mm., or in presence of sulphuric-pumice, or of α -phenyl- β -ethylbutan- β -ol, b. p. 135—136°/15 mm., obtained in 80—90% yield from Et phenylacetate and MgEtX . When heated to its b. p. the oxide isomerises to a mixture of α -phenyl- α -ethylbutaldehyde, b. p. 119—121°/14 mm. (semicarbazone, m. p. 181°), and α -phenyl-propyl Et ketone, b. p. 114—116°/13 mm. (semicarbazone, m. p. 144°). *Ph* α -ethyl- n -propyl ketone has b. p. 246—247° (semicarbazone, m. p. 172—173°). The following dialkylstyrenes, similarly obtained by dehydration of the appropriate *tert*-alcohols, are converted into oxides in 70—90% yield with BzO_2H in CHCl_3 or Et_2O at 18—20°: α -phenyl- β -methyl- Δ^a -butylene, b. p. 201—202° [oxide, b. p. 137—138°/33 mm., affording when heated α -phenyl- α -methylbutaldehyde, b. p. 228—230° (semicarbazone, m. p. 152°), and α -phenylethyl Et ketone, b. p. 225—228° (semicarbazone, m. p. 136°), but only the latter with H_2SO_4 , from

α -phenyl- β -methylbutan- β -ol, b. p. 115°/14 mm.; α -phenyl- β -methyl Δ^{α} -pentene, b. p. 212—215°/768 mm. [oxide, b. p. 131—132°/27 mm., isomerising by heat to α -phenyl- α -methylvaleraldehyde, b. p. 235—240° (semicarbazone, m. p. 136—137°), and α -phenylethyl Pr^{α} ketone, b. p. 235—236° (semicarbazone, m. p. 129—130°), by heat and polymerising with H_2SO_4], from α -phenyl- β -methylpentan- β -ol; $\alpha\gamma$ -diphenyl- β -methyl- Δ^{α} -propylene, b. p. 175—177°/20 mm. [oxide, b. p. 165—166°/8 mm., isomerising to CH_2Ph α -phenylethyl ketone, b. p. 205—206°/40 mm. (semicarbazone, m. p. 143—145°)], from α -phenyl- β -benzylpropan- β -ol, b. p. 197—198°/20 mm.; α -phenyl- β -benzyl- Δ^{α} -butylene, b. p. 183—185°/14 mm. [oxide, b. p. 163—164°/6 mm., isomerising to $\alpha\beta$ -diphenyldiethyl ketone, b. p. 190—192°/13 mm. (semicarbazone, m. p. 212—213°), by heat, and to a mixture of this and CH_2Ph α -phenyl- n -propyl ketone, b. p. 195—198°/25 mm. (semicarbazone, m. p. 144—145°), with H_2SO_4], from α -phenyl- β -benzylbutan- β -ol, b. p. 208—215°/12 mm.; α -phenyl- β -benzyl- Δ^{α} -pentene, b. p. 315—317° [oxide, b. p. 195—197°/8 mm., isomerising to $\alpha\beta$ -diphenylethyl Pr^{α} ketone, b. p. 210—212° (semicarbazone, m. p. 183°)], from α -phenyl- β -benzylpentan- β -ol, b. p. 203—204°/16 mm.; and α -phenyl- β -benzyl- γ -methyl- Δ^{α} -butylene, b. p. 315—317° [α -oxide, b. p. 188—189°/14 mm., β -oxide, m. p. 88—90°, both isomerising with H_2SO_4 to $\alpha\beta$ -diphenylethyl Pr^{α} ketone, b. p. 187—200°/27 mm. (semicarbazone, m. p. 122—123°)], from α -phenyl- γ -methyl- β -benzylbutan- β -ol, b. p. 200—201°/20 mm. α -Phenyl- β -methyl- $\alpha\beta$ -propylene oxide, b. p. 87—90°/15 mm., does not isomerise on distillation at atm. pressure, but in presence of kieselguhr yields α -phenyl- α -methylpropaldehyde; in presence of $ZnCl_2$ or with H_2SO_4 at 0°, α -phenylethyl Me ketone is obtained. $COPhPr^{\beta}$ has b. p. 91.5—92.5°/10 mm. (semicarbazone, m. p. 167—168°); Ph isoamyl ketone, b. p. 246—247° (semicarbazone, m. p. 172—173°); α -phenyl- n -propyl Me ketone, b. p. 220—225° (semicarbazone, m. p. 189—200°); α -phenyl- n -butyl Me ketone, b. p. 240—242° (semicarbazone, m. p. 148—149°). α -Phenyl- α -methylbutaldehyde and α -phenyl- α -methylvaleraldehyde are obtained by dehydration of the corresponding *sec. tert.*-glycols with 8% H_2SO_4 . α -Phenyl- α -benzylbutaldehyde, b. p. 220—235°/35 mm. (semicarbazone, m. p. 175—176°), and α -phenyl- α -benzylvaleraldehyde, b. p. 195—200°/15 mm. (semicarbazone, m. p. 192°), are obtained by oxidation of the corresponding alcohols with CrO_3 in acetic acid. The following are obtained by reduction of the corresponding amides with Na and EtOH, the amides being obtained by hydrolysis of the nitriles with 85% H_2SO_4 : β -phenyl- β -methyl- n -amylalcohol, b. p. 159—160°/22 mm., from α -phenyl- α -methylvaleronitrile, b. p. 155—156°, and amide, b. p. 196—197°/21 mm.; and β -phenyl- β -benzylpentan- α -ol, b. p. 207—210°/15 mm., from α -phenyl- α -benzylvaleronitrile, m. p. 63°, and amide, m. p. 110°. α -Phenyl- α -benzylpropionitrile (b. p. 194—195°) and α -propionamide (m. p. 108°) are described.

R. BRIGHTMAN.

Affinity capacity and migratory power. XIII. Comparative migratory powers of acyclic radicals deduced from the dehydration of phenyldialkyl glycols. M. Tiffeneau, (MME.) J. Levy,

and P. Jullien (Bull. Soc. chim., 1931, [iv], 49, 1788—1795).—Dehydration by H_2SO_4 , d 1.84, at 0°, of the glycols, $OH\cdot CHPh\cdot CRR'\cdot OH$, where $R=Me$ and $R'=Et, Pr^{\alpha}, Pr^{\beta}, Bu^{\alpha}, Bu^{\beta}$, or CH_2Ph affords the ketone $CHPhR'\cdot COMe$ when $R'=Et, Pr^{\alpha}, Bu^{\alpha}$, or CH_2Ph , indicating that these radicals are superior in migratory power to Me; when $R'=Pr^{\beta}$, the ketone, $CHMePh\cdot COR'$, is also formed and exclusively when $R'=Bu^{\beta}$. When $R=Et$ and $R'=Me, Pr^{\alpha}, Pr^{\beta}$, and Bu^{β} , migration of Et alone occurs; with $R'=CH_2Ph$ migration of CH_2Ph preponderates and with $R'=Bu^{\alpha}$ the latter exclusively migrates. The order of migratory power given by these experiments is $CH_2Ph > Bu^{\alpha} > Et > Pr^{\beta} > Me, Pr^{\alpha} > Bu^{\beta}$, i.e., inversely as their affinity capacities. The following are described: α -phenyl- β -methylpentan- $\alpha\beta$ -diol, m. p. 59—60° (β); α -phenyl- β -methylhexan- $\alpha\beta$ -diol, m. p. 49—50° (β), affording α -phenyl- n -amyl Me ketone, b. p. 250—251° (semicarbazone, m. p. 156—158°); α -phenyl- $\beta\delta$ -dimethylpentan- $\alpha\beta$ -diol, m. p. 87—88° (β); α -phenyl-methyl Bu^{β} ketone, b. p. 237—240° (semicarbazone, m. p. 147.5—148°); α -phenylisobutyl Me ketone, b. p. 115—118°/28 mm. (semicarbazone, m. p. 153—154°); $\alpha\gamma$ -diphenyl- β -methylpropan- $\alpha\beta$ -diol, m. p. 96—97° (α); $\alpha\beta$ -diphenylethyl Me ketone, b. p. 188—189°/20 mm. (semicarbazones, m. p. 144—145° and 168°); α -phenyl- β -benzyl- β -ethylethylene glycol, m. p. 115—116° (α); α -phenyl- β -benzyl- n -butan- $\alpha\beta$ -diol, m. p. 126—127° (α); α -phenyl- β -benzyl- γ -methyl- n -butan- $\alpha\beta$ -diol, m. p. 90° (α), giving $\alpha\beta$ -diphenylethyl Pr^{β} ketone, b. p. 195—200°/27 mm. (semicarbazone, m. p. 205—206°), and a substance, m. p. 37°; α -phenyl- n -propyl Pr^{β} ketone, b. p. 253—254° (semicarbazone, m. p. 158—159°); α -phenyl- n -amyl Et ketone, b. p. 147—150°/16 mm. (semicarbazone, m. p. 104—105°); α -phenyl- n -propyl Bu^{α} ketone, b. p. 242° (semicarbazone, m. p. 141—142°); α -phenyl- n -amyl Pr^{α} ketone, b. p. 275—279° (semicarbazone, m. p. 100—101°).

R. BRIGHTMAN.

Affinity capacity and migratory power. XIV. Affinity capacity of anisyl and migratory power of Et compared with those of Me and Pr^{α} in molecular transpositions of anisyldialkyl glycols. P. Weill (Bull. Soc. chim., 1931, [iv], 49, 1795—1806).—Dehydration of the glycols, $OH\cdot CHAr\cdot CRR'\cdot OH$ or isomerisation of the corresponding oxides, when $Ar=anisyl, R=Et, R'=Me$ or Pr^{α} , affords the ketone, $CHArR'\cdot CO\cdot R'$ or $CHArR'\cdot CO\cdot R$, rupture of the oxide ring occurring on the side of the anisyl group. Accordingly, the affinity capacity of anisyl is superior to that of two acyclic groups. When $R'=Me$, the Et radical alone migrates, yielding $CHArEt\cdot COMe$, indicating that Et has a greater migratory power than Me, but when $R'=Pr^{\alpha}$, the ketone $CHArPr^{\alpha}\cdot COEt$ is alone obtained, the alkyl group of stronger affinity capacity migrating.

α -Anisyl- β -methylbutan- $\alpha\beta$ -diol, obtained in an α -form from α -anisylpropan- α -ol- β -one, b. p. 135—140°/25 mm. (from $MgMeI$ and anisylglycollamide), and a β -form from α -anisylbutan- α -ol- β -one, on dehydration affords only γ -anisylpentan- β -one, also obtained by isomerisation of α -anisyl- β -methyl- $\alpha\beta$ -butylene oxide, b. p. 135—140°/14 mm., from the α -anisyl- β -methyl- Δ^{α} -butylene, b. p. 248°, obtained by dehydrating α -anisyl- β -methyl- n -butyl alcohol, b. p. 155—165°/35

mm. α -Anisyl- β -methyl- $\alpha\beta$ -butylene iodohydrin with KOH yields 35% of α -anisyl- α -methyl- n -butaldehyde, b. p. 145°/12 mm. (semicarbazone, m. p. 144°; oxime, m. p. 87°, affording on dehydration 76% of α -anisyl- α -methylbutyronitrile, b. p. 135–136°/6 mm.), converted into α -anisylethyl Et ketone, b. p. 262–265°/4 mm. (semicarbazone, m. p. 116–117°; oxime, m. p. 69–70°), with H_2SO_4 at -10° . γ -Anisylpentan- γ -ol, b. p. 147–148°/20 mm. (yield 85% from Et anisate), in presence of sulphuric-pumice below 100° yields γ -anisyl- Δ^2 -pentene, b. p. 235°. The α -form of α -anisyl- β -ethylpentane- $\alpha\beta$ -diol, m. p. 91–92°, is obtained from $MgPr^aBr$ and anisylbutan- α -ol- β -one; the β -isomeride, m. p. 79–80°, is similarly obtained from α -anisylpentan- α -ol- β -one, b. p. 178°/12–13 mm. On dehydration both yield α -anisyl- n -butyl Et ketone, b. p. 273° (semicarbazone, m. p. 129°), also obtained by isomerisation with H_2SO_4 of the oxide, b. p. 285°/760 mm., of α -anisyl- Δ^2 -heptene, b. p. 260°. The iodohydrin of the last with KOH yields α -anisyl- n -propyl Pr^a ketone. R. BRIGHTMAN.

Affinity capacity and migratory power. XV. Migratory power of the phenyl radical. Dehalogenation of the iodohydrins of methylhydrobenzoin; semihydrobenzoin and semipinacolic transpositions. M. Tiffeneau and (MME.) J. Lévy (Bull. Soc. chim., 1931, [iv], 49, 1806–1811).—The iodohydrin of methylhydrobenzoin, $CPhMeI \cdot CHPh \cdot OH$, with $AgNO_3$ affords $\alpha\alpha$ -diphenylpropaldehyde, also obtained by dehydration of methylhydrobenzoin or isomerisation of α -methylstilbene oxide, m. p. 45–46°. Similarly, the iodohydrin, $OH \cdot CMePh \cdot CHPhI$, obtained from HOI and α -methylstilbene, affords $\alpha\alpha$ -diphenylpropan- β -one, m. p. 61°, also formed by the dehydration of alkylhydrobenzoins but not hydrobenzoin. These reactions demonstrate the reality of the semipinacolic transposition and indicate that it applies in the dehydration of the alkylhydrobenzoins. The migration of Ph in the second case confirms the superior migratory power of Ph over Me. R. BRIGHTMAN.

Affinity capacity and migratory power. XVI. Comparative migratory powers of different alkyl radicals and of these and aryl radicals. Influence of the anisyl radical on the dehydration of diaryl-alkyl glycols and on the isomerisation of the corresponding oxides. P. Weill (Bull. Soc. chim., 1931, [iv], 49, 1811–1823).—The semipinacolic dehydration of β -phenyl- α -anisylbutane- $\alpha\beta$ -diol affords α -anisylbenzyl Et ketone and accordingly the sum of the affinity capacities of anisyl and H is greater than that of Ph and Et, and the migratory power of Ph is superior to that of Et. In the dianisyl glycols, $OH \cdot CHAr \cdot CRAr \cdot OH$, where Ar=anisyl and R=Me and Et, semihydrobenzoin, semipinacolic, or vinylic transposition can occur according to the conditions of dehydration. The anisyl group diminishes the stability of a sec. OH group much less in presence of a second anisyl group near the tert. OH group. The substitution of anisyl for Ph thus affects the mode of dehydration by increasing the stability of the sec. CH·OH group and by modifying the transposition, which leads to elimination of the tert. OH group. The presence of Me is sufficient to determine vinylic

transposition in presence of H_2SO_4 . Rupture of the O ring in the three oxides always takes place on the side of the two aryl groups and the replacement of Ph by anisyl in oxides already containing an anisyl group does not affect the mechanism of isomerisation. Migration of H is exclusive only in oxides containing at least one anisyl group.

$\alpha\beta$ -Dianisylbutane- $\alpha\beta$ -diol, m. p. 111–112° (β -form; liquid α -form), when dehydrated with 20% or 50% H_2SO_4 or by heat, affords mainly $\alpha\alpha$ -dianisylbutaldehyde, b. p. 190–191°/2 mm. (semicarbazone, m. p. 182°), and a little dianisylmethyl Et ketone (I), m. p. 51° (semicarbazone, m. p. 192–193°; oxime, m. p. 99°), also obtained from the aldehyde with H_2SO_4 at -5° . With H_2SO_4 , d 1.84, (I) alone is formed. Anisyl α -anisyl- n -propyl ketone, b. p. 180–200°/17 mm. (semicarbazone, m. p. 150°), is obtained from $\alpha\alpha$ -dianisyl- Δ^2 -butylene, b. p. 225°/18 mm. (from α -dianisylbutyl alcohol, m. p. 138°), by treating the iodohydrin with $AgNO_3$. $\alpha\beta$ -Dianisyl- Δ^2 -propylene glycol, b. p. 190°/3 mm. (β -isomeride), when dehydrated by heat or by 20% or 50% H_2SO_4 , yields $\alpha\alpha$ -dianisylpropaldehyde, b. p. 170–172°/2 mm. (semicarbazone, m. p. 184°; oxime, m. p. 125°), converted by H_2SO_4 into $\alpha\alpha$ -dianisylacetone, m. p. 71° (semicarbazone, m. p. 110–157°; oxime, m. p. 125°), and by H_2SO_4 , d 1.84, at -5° , into anisyl α -anisylethyl ketone, b. p. 222°/14 mm. (semicarbazone, m. p. 162–163°), also obtained from $\alpha\alpha$ -dianisyl- Δ^2 -propylene, m. p. 100–101°, by treating the iodohydrin with $AgNO_3$. α -Phenyl- α -anisyl- Δ^2 -butylene, b. p. 220–222°/30 mm. (oxide isomerising to α -anisylbenzyl Et ketone), is obtained from α -phenyl- α -anisylbutyl alcohol, m. p. 59–60°. $\alpha\alpha$ -Dianisylbutylene oxide affords α -dianisylmethyl Et ketone, and $\alpha\alpha$ -dianisylpropylene oxide gives $\alpha\alpha$ -dianisylacetone. R. BRIGHTMAN.

Affinity capacity and migratory power. XVII. Radicals, $Ph \cdot [CH_2]_n$, compared with hydrogen.

Isomerisation of oxides, $\begin{smallmatrix} CHR_2 \\ | \\ CH_2 \end{smallmatrix} > O$. (MME.) J.

Lévy and J. Sfiras (Bull. Soc. chim., 1932, [iv], 49, 1823–1830).— γ -Phenyl- $\alpha\beta$ -propylene oxide, b. p. 98–100°/17 mm., in presence of $ZnCl_2$ or when passed over Al_2O_3 at 260°, yields benzyl Me ketone; with aq. NH_3 , 7% of di-(hydrochloride, m. p. 140°) and 48% of tri-(β -hydroxy- γ -phenylpropyl)amine (hydrochloride, m. p. 160–161°) and with $NHMe_3$ in C_6H_6 , dimethyl- β -hydroxy- γ -phenylpropylamine, b. p. 140°/22 mm. (hydrochloride, m. p. 95°; benzoate hydrochloride, m. p. 155–156°), are formed. δ -Phenyl- $\alpha\beta$ -butylene oxide, b. p. 106–109°/14 mm., similarly affords β -phenylethyl Me ketone, di-(hydrochloride, m. p. 137–139°), 1%, tri-(β -hydroxy- δ -phenylbutyl)amine (hydrochloride, m. p. 136°), 32%, and dimethyl- β -hydroxy- δ -phenyl- n -butylamine, b. p. 145°/14 mm. (benzoate hydrochloride, m. p. 155°); ϵ -phenylpentene $\alpha\beta$ -oxide, b. p. 122°/16 mm., yields γ -phenyl- n -propyl Me ketone, b. p. 132–135°/17 mm. (semicarbazone, m. p. 127–128°; oxime, m. p. 52°), tri-(β -hydroxy- ϵ -phenyl- n -amylamine (hydrochloride, m. p. 148°) (yield, 23%), and dimethyl- β -hydroxy- ϵ -phenyl- n -amylamine (benzoate hydrochloride, m. p. 136°); ϵ -phenylhexene $\alpha\beta$ -oxide, b. p. 136–139°/13 mm., yields δ -phenyl- n -butyl Me ketone, b. p. 150–153°/17 mm. (semicarbazone, m. p. 127–128°; oxime, m. p. 52°).

azone, m. p. 136—137°; tri-(β -hydroxy- ϵ -phenyl-n-hexyl)amine (yield 15%) (hydrochloride, m. p. 78°), and dimethyl- β -hydroxy- ϵ -phenyl-n-hexylamine, b. p. 171°/17 mm. (hydrochloride, m. p. 104°; benzoate hydrochloride, m. p. 126°).

The course of these isomerisations shows that the affinity capacities of the radicals $\text{Ph}\cdot[\text{CH}_2]_n$ are lower than that of H, whilst that of Ph is greater. The benzoates of the above NH_2 -alcohols are local anaesthetics. R. BRIGHTMAN.

Affinity capacity and migratory power. XVIII. Isomerisation of phenylcyclohexene and of 1-phenyl-4-methylcyclohexene oxide. Molecular transposition with change from a six- to a five-membered ring. (MME.) J. LEVY and J. SEFRAS (Bull. Soc. chim., 1931, [iv], 49, 1830—1838).—When phenylcyclohexene oxide, b. p. 136°/15 mm., is distilled at atm. pressure or heated with ZnCl_2 or sulphuric-pumice, 60% of 2-phenylcyclohexanone, m. p. 61° (semicarbazone, m. p. 196°; oxime, m. p. 169°), and 9% of 1-phenylcyclopentane-1-aldehyde, b. p. 134°/15 mm. (semicarbazone, m. p. 196·5°), is obtained. Similarly, 1-phenyl-4-methylcyclohexene oxide, b. p. 140—141°/15 mm., m. p. 36°, yields 55% of 2-phenyl-5-methylcyclohexanone, m. p. 62° (semicarbazone, m. p. 217°), and 2% of 1-phenyl-4-methylpentane-1-aldehyde (semicarbazone, m. p. 172°). Thus rupture of the oxide ring occurs on the side of the Ph group, indicating the stronger affinity capacity of Ph, but since the yields of cyclopentane derivative are lower than those in the dehalogenation of cyclohexene iodohydrins (10—20%), it is concluded that the presence of Ph decreases the migratory power of the CH_2 chain, a Me group in 4-position having a further adverse effect. A similar mechanism is suggested for the formation of the cyclopentane ring by dehalogenation. With NH_3 at 150° for 10 hr. 1-phenylcyclohexene 1:2-oxide yields 25% of 2-amino-1-phenylcyclohexan-1-ol, m. p. 105° (hydrochloride, m. p. 140°), with traces of a sec.-amine, and with NHMe_2 in C_6H_6 at 160°, 2-dimethyl-amino-1-phenylcyclohexan-1-ol, b. p. 172—173°/18 mm. (hydrochloride, m. p. 174°; benzoate hydrochloride, m. p. 154°). 1-Phenyl-4-methylcyclohexene oxide similarly gives 25% of 2-amino-1-phenyl-4-methylcyclohexan-1-ol, b. p. 185°/17 mm. (hydrochloride, m. p. 135°), and 5% di-(2-hydroxy-2-phenyl-5-methylcyclohexyl)amine, b. p. 220—230°/15 mm. (hydrochloride, m. p. 156°), and 2-dimethylamino-1-phenyl-4-methylcyclohexan-1-ol, m. p. 103° (hydrochloride, m. p. 187°; benzoate hydrochloride, m. p. 187°). R. BRIGHTMAN.

Affinity capacity and migratory power. XX. Benzyl radical. Dibenzyl glycol and the corresponding ethylene oxide. M. TIFFENEAU, A. ORÉKHOV, and (MME.) J. LEVY (Bull. Soc. chim., 1931, [iv], 49, 1840—1846).— γ -Phenyl- β -benzylprop-ane- β -diol, m. p. 100—101°, b. p. 359—360°, when distilled over kieselguhr yields traces of a substance, b. p. 305—310°; with H_2SO_4 at 0° resinous products only are obtained, and with 20% H_2SO_4 or anhyd. $\text{H}_2\text{C}_2\text{O}_4$, γ -phenyl- β -benzyl- $\alpha\beta$ -propylene oxide, m. p. 70, is formed, all attempts to isomerise which failed. view of the stability of the oxide and its direct

formation from the glycol, it is concluded that the affinity capacities of CH_2Ph and of H are very nearly the same. β -Phenyl- α -benzylpropaldehyde has b. p. 217—218°/20 mm. (semicarbazone, m. p. 122—123°; oxime, m. p. 70—71°); benzyl β -phenylethyl ketone, m. p. 42—43° (semicarbazone, m. p. 130—131°; α -oxime, m. p. 120—121°; β -oxime, m. p. 80—85°).

R. BRIGHTMAN.

Affinity capacity and migratory power. XXI. Deamination of phenylaminoalcohols. $\text{OH}\cdot\text{CHPh}\cdot\text{CHR}\cdot\text{NH}_2$. Intermediate formation of vinyl alcohols. Formation of acylbenzenes without transposition. M. TIFFENEAU and (MME.) J. LEVY (Bull. Soc. chim., 1931, [iv], 49, 1847—1851).—Deamination of four phenylamino-alcohols, $\text{OH}\cdot\text{CHPh}\cdot\text{CHR}\cdot\text{NH}_2$, when $\text{R}=\text{Et}$, Pr^i , Pr^n , or Bu^n , with NaNO_2 in AcOH , yields the ketone $\text{COPh}\cdot\text{CH}_2\text{R}$, and not $\text{CH}_2\text{Ph}\cdot\text{COR}$. Accordingly, the glycols and ethylene oxides are not intermediate products, since these would yield $\text{CH}_2\text{Ph}\cdot\text{COR}$, and it is concluded that intermediate formation of the vinyl alcohol, $\text{OH}\cdot\text{CPh}\cdot\text{CHR}$, is most probable. The following amino-alcohols are obtained by reduction of the oximes of the ketols $\text{OH}\cdot\text{CHPh}\cdot\text{COR}$ with Na and EtOH , Na-Hg in 95% EtOH , or H_2 and Ni in EtOH : β -amino- α -phenyl-n-butyl, b. p. 120—130°/23 mm. (hydrochloride, m. p. 225—226°; chloroaurate, m. p. 157°); β -amino- α -phenyl-n-amyl (hydrochloride, m. p. 170°); β -amino- α -phenyl- γ -methyl-n-butyl (hydrochloride, m. p. 159—160°), and β -amino- α -phenyl-n-hexyl (hydrochloride, m. p. 140—141°) alcohol.

R. BRIGHTMAN.

Orientation of α -chloroanthrones. E. DE B. BARNETT and C. L. HEWETT (J.C.S., 1932, 506—509).—The view that only Cl atoms o- to a carbonyl group in the chloroanthraquinones can be replaced by CN on treatment with $\text{Cu}_2(\text{CN})_2$ and $\text{CH}_2\text{Ph}\cdot\text{CN}$ receives strong support from the inactivity of 2-chloro-anthraquinone. Reaction should occur with 1-chloro- and 1:8-dichloro-anthrone, but not with 4-chloro- or 4:5-dichloro-anthrone. Owing to the enolic properties of these compounds, resinification occurs and no nitrile is isolable. 1-Chloro-10:10-dibenzylanthrone cannot enolise and reacts with $\text{Cu}_2(\text{CN})_2$ and $\text{CH}_2\text{Ph}\cdot\text{CN}$ to give 1-cyano-10:10-dibenzylanthrone, m. p. 276°, thus providing evidence that the orientation of 1-chloroanthrone is correct. 4-Chloroanthrone gives only resinous products with benzyl chloride and alkali. 1:8-Dichloro-10:10-di-o-chlorobenzylanthrone affords 1:8-dicyano-10:10-di-o-chlorobenzylanthrone, m. p. 264°, in contrast to 1:8-dichloro-10-benzylanthrone, which affords resinous products. Both 1:4- and 1:5-dichloro-10-benzylanthrone react with $\text{Cu}_2(\text{CN})_2$ yielding 1-chloro-, m. p. 208°, and 5-chloro-1-cyano-10-benzylanthrone, m. p. 234°, respectively. Bromination of 1:8-dichloro-10-phenylanthrone affords 1:8-dichloro-10-bromo-10-phenylanthrone, m. p. about 224°, which by prolonged boiling with MeOH and CaCO_3 affords 1:8-dichloro-10-methoxy-10-phenylanthrone, m. p. 237°. Reaction of C_6H_6 with the above bromo-anthrone and AlCl_3 affords 1:8-dichloro-10:10-diphenylanthrone, m. p. above 310°, which when warmed with NPhMe_2 affords 1:8-dichloro-4'-dimethylamino-10:10-diphenylanthrone, m. p. 308°.

J. L. D'SILVA.

with KOH-EtOH into rhizonic acid Me ether, m. p. 105°, traces of isorhizonic acid, and Me isorhizonate (hydrolysed to the acid by further action of KOH-EtOH).
H. WREN.

Constitution of mangostin. I. S. YAMASHINO (Bull. Chem. Soc. Japan, 1932, 7, 1-8).—Mangostin (I), $C_{20}H_{22}O_5$ (cf. A., 1924, i, 1332), m. p. 176.5–177°, with Me_2SO_4 and KOH gives methylmangostin (II), m. p. 120.5–121° (Ac derivative, m. p. 191–191.5°), and a substance, m. p. 171–171.5°, converted by further methylation into (II). (II) with Br in C_6H_6 gives a Br_3 -derivative, decomp. about 160°, unstable to H_2O and light. Alkali fusion of (I) yields AcOH, isovaleric and oxalic acid, phloroglucinol, an acid, m. p. 373°, a phenolic substance, m. p. 212°, and probably amyl alcohol. The phenol, when further fused with alkali, gives isovaleric acid, phloroglucinol, and probably amyl alcohol. (I) is thus not a lapachol derivative.
R. S. CARR.

Saponins. M. KOTAKE (Proc. Imp. Acad. Tokyo, 1932, 8, 12–15).—The sapogenin from *Panax repens*, m. p. 304° [Ac derivatives, m. p. 263°, 207–210°, and 306–312°; $(NO_2)_2$ -derivatives, m. p. 240–242° and 211–213°; Br-derivative, m. p. 223–224°; yields with HI substances, $C_{29}H_{48}O_3$ (?), m. p. 337–338°, and $C_{29}H_{46}O_2$, m. p. 247–249°], is identical with that from *Aralia Chinensis*, L., and is $C_{29}H_{48}O_3$ or $C_{30}H_{52}O_3$ (lit. $C_{31}H_{52}O_5$ etc.). The sapogenin from *Kalopanax ricinifolius*, $C_{30}H_{48}O_4$, m. p. 330–332°, is identical with hederagenin. Dry distillation of a sapogenin yields CH_4O , H_2O , oils resembling terpenes, b. p. 95–96.5°, 104.5°, and 115–116.5°/16 mm. (mol. wt. about 190) (giving reduction products, b. p. 235–237°, 241–244°, and 255–258°/760 mm., respectively), and substances, $C_{21}H_{36}$, m. p. 246–248°, and $C_{25}H_{40}$, m. p. 306–308°. These substances are considered to be more closely related to the sapogenins than the products obtained by means of S and Se.
R. S. CARR.

Toad poisons. VI. Degradation of bufotalin to a cholanic acid. H. WIELAND, G. HESSE, and H. MEYER (Annalen, 1932, 493, 272–280).—Acetylbufotalien (A., 1922, i, 784) and H_2 (Pd-black) in AcOH give acetylbufotalan and a small amount of an *acetorycholanic acid* (I), $C_{26}H_{42}O_2$, m. p. 148°. Hydrolysis of (I) with 2N-MeOH-KOH gives the *hydroxy-cholanic acid*, m. p. 161° (slight previous sintering), also formed in small amount during the catalytic reduction of bufotalien, which at 300° gives H_2O and a *cholanic acid*, $C_{24}H_{38}O_2$, m. p. 169–170°. This is reduced catalytically (as above) to the *cholanic acid* (termed *isobufocholanic acid*), $C_{26}H_{42}O_2$, m. p. 179°, $[\alpha]_D^{25} + 50.5^\circ$ in EtOH.

Acetylbufotalan and 2N-MeOH-KOH give bufotalanic acid, m. p. 153–154°, which when heated, or dissolved in cold EtOH, passes into bufotalan, m. p. 199°. Bufotalan is converted by conc. HCl into *bufotalienone*, $C_{24}H_{38}O_3$, m. p. 158°, whilst bufotalan is oxidised by CrO_3 in cold AcOH to *bufotalanone*, $C_{24}H_{36}O_3$, m. p. 196°. Acetylbufotalan is not oxidised by CrO_3 , but is converted by conc. HCl into acetylbufotalien; it contains, therefore, a *tert*-OH group and a $>CH\cdot OAc$ residue.

Toad poisons. IV. Bufagin and cinobufagin. H. JENSEN (Science, 1932, 75, 53–54).—Revised formulæ, viz., cinobufagin, $C_{25}H_{32}O_6$, and bufagin, $C_{24}H_{32}O_5$, are proposed. The reactions described indicate that the former contains a lactone, an OAc, a *sec*- and a *tert*-OH group, and the latter a lactone, a CHO, and a *tert*-OH group. Catalytic reduction yields tetrahydro-cinobufagin and -bufagin, respectively. Both compounds resemble the plant cardiac aglucones in their chemical behaviour, the principles of the toad poisons being coupled with AcOH or HCO_2H instead of with carbohydrates.

L. S. THEOBALD.

Elemic acid from Manila elemi resin. III. Elemic acid, its reduction product, and bromohydroelemic acid. IV. Dihydroelemic acid and its derivatives. M. MLADENOVIC (Monatsh., 1932, 59, 7–15, 228–237).—III. Oxidation of elemic acid with CrO_3 in AcOH gives elemic acid (I), $C_{30}H_{46}O_3$, m. p. 274°, $[\alpha]_D^{25} - 66.82^\circ$ in $CHCl_3$ (not $C_2H_5O_3$; cf. A., 1924, i, 1312; 1931, 1067), and a smaller quantity of another acid (details to be published later). The derivatives of (I) also support the C_{30} formula. (I) is reduced by H_2 and Pd in AcOH at 100° to *tetrahydroelemic acid*, $C_{30}H_{50}O_3$, m. p. 293°, $[\alpha]_D^{25} - 54.69^\circ$ in $CHCl_3$, and converted by HBr in cold $CHCl_3$ into *bromohydroelemic acid*, $C_{30}H_{47}O_3Br$, m. p. 262°, $[\alpha]_D^{25} - 10.8^\circ$ in $CHCl_3$, which with MeOH-KOH regenerates (I).

IV. Catalytic reduction of elemic acid by the method previously described (A., 1931, 960) (in AcOH) gives dihydroelemic acid (II), m. p. 238° [K salt (+3H₂O)], and its Ac derivative (III), m. p. 248.5° (corr.), $[\alpha]_D^{25} - 38.94^\circ$ in EtOH, also prepared by acetylation of (II) with Ac_2O in pyridine and by catalytic reduction (Pd) of acetyelemic acid. (III) is hydrolysed by MeOH-KOH to (II). Analyses of the compounds support the C_{30} formula for elemic acid (cf. *loc. cit.*). The dihydroelemic acid of Ruzicka *et al.* (A., 1931, 1067) is probably impure (III).
H. BURTON.

Saponin series. I. Glucoside of *Panax ginseng*, C. A. MEYER. M. KOTAKE. II. Saponins of *Kalopanax ricinifolius*. M. KOTAKE and K. TAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 1–4, 5–11).—I. The roots of *P. ginseng* contain a bitter glucoside (hydrolysed to a brown amorphous substance) and a bitter-sweet, non-haemolytic saponin (possibly identical with ginsenin), which with H_2SO_4 in hot MeOH gives *parrazin*, $C_{36}H_{66}O_{12}$ or $C_{35}H_{68}O_{12}$, m. p. 246–248° (decomp.), hydrolysed by cold conc. HCl to CO_2 , glucose, an amorphous substance, and *parrazigenin chloride*, $C_{36}H_{63}O_2Cl$, m. p. 209–211°, whence hot alcoholic KOH liberates *parrazigenin*, $C_{30}H_{52}O_3$, m. p. 256–258° (Ac derivative, m. p. 112–114°).

II. *K. ricinifolius* contains *kalosaponin* (I), amorphous, and *kalotoxin* (II), $C_{43}H_{70}O_{14}$, m. p. 260–261°. (I) with hot 10% NaOH gives *isokalotoxin* (III), $C_{45}H_{70}O_{14}$, m. p. 258°. (II) or (III) with cold, conc. HCl, or (I), (II), or (III) with HCl in hot MeOH gives *kalosapogenin*, $C_{30}H_{48}O_4$ or $C_{31}H_{50}O_4$, m. p. 330° [Ac derivative, m. p. 167°; $(NO_2)_3$ -derivative, m. p. 229–230° (transformed by Zn and HCl in AcOH into a substance, $C_{30}H_{42}O_5$, m. p. 320°)], which yields with hot

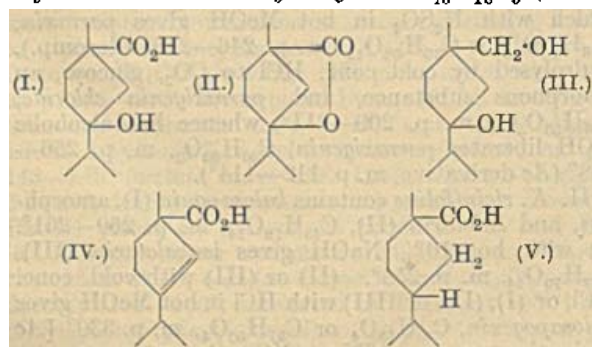
HCO_2H formylanhidrokalosapogenin, $\text{C}_{31}\text{H}_{46}\text{O}_4$, m. p. 161–5—162–5°, or a substance, $\text{C}_{33}\text{H}_{48}\text{O}_6$, m. p. 269—270–5°, and with HI and red P in hot AcOH a substance, $\text{C}_{34}\text{H}_{52}\text{O}_6$ or $\text{C}_{35}\text{H}_{54}\text{O}_6$, m. p. 258—260°, and a substance, $\text{C}_{30}\text{H}_{48}\text{O}_4$, m. p. 320°. The occurrence of the isomeric sapogenins is inexplicable.

R. S. CAHN.

Oxidation of caoutchouc, gutta-percha, and balata with hydrogen peroxide. J. A. MAIR and J. TONN (J.C.S., 1932, 386—399).—Oxidation of caoutchouc with H_2O_2 in CHCl_3 -AcOH gave alcohol CI, viz., $\text{C}_{50}\text{H}_{76}(\text{OH})_{16}$ (OH by Zerevitinov), presumably formed by direct addition of OH to the double linkings of the hydrocarbon. This with CrO_3 in AcOH gave aldehyde CII, viz., $\text{C}_{48}\text{H}_{86}\text{O}_{14}(\text{CHO})_2$, which on oxidation with 30% HNO_3 gave acid CII, viz., $\text{C}_{48}\text{H}_{86}\text{O}_{14}(\text{CO}_2\text{H})_2$; it is therefore presumed to contain two $\text{CH}_2\text{-OH}$ groups. The action of Ac_2O and NaOAc on alcohol CI led to dehydration in addition to acetylation and gave acetate CI, $\text{C}_{50}\text{H}_{76}\text{O}_6(\text{OAc})_4$, the alcohol CIA from which was in its turn oxidised to aldehyde CII and acid CII, $\text{C}_{48}\text{H}_{86}\text{O}_8(\text{CO}_2\text{H})_2$. Further H_2O_2 oxidation of acetate CI gave acetate CII, $\text{C}_{50}\text{H}_{56}\text{O}_{16}(\text{OH})_8(\text{OAc})_4$, which was hydrolysed to the saturated alcohol CII, $\text{C}_{50}\text{H}_{56}\text{O}_{16}(\text{OH})_{12}$. Guttapercha and balata gave a similar series of products, but of somewhat different composition owing to their greater initial ease of oxidation, e.g., alcohol GI (gutta-percha), $\text{C}_{50}\text{H}_{78}\text{O}_4(\text{OH})_{20}$, BI (balata), $\text{C}_{50}\text{H}_{72}\text{O}_4(\text{OH})_{16}$; acid GI, $\text{C}_{48}\text{H}_{82}\text{O}_{22}(\text{CO}_2\text{H})_2$, BI, $\text{C}_{48}\text{H}_{82}\text{O}_{18}(\text{CO}_2\text{H})_2$; acetate GI, $\text{C}_{50}\text{H}_{68}\text{O}_{10}(\text{OAc})_8$, BI, $\text{C}_{50}\text{H}_{72}\text{O}_8(\text{OAc})_8$; acid GII, $\text{C}_{48}\text{H}_{70}\text{O}_{18}(\text{CO}_2\text{H})_2$, BII, $\text{C}_{48}\text{H}_{74}\text{O}_{14}(\text{CO}_2\text{H})_2$; and acetate GII, $\text{C}_{50}\text{H}_{56}\text{O}_{15}(\text{OH})_4(\text{OAc})_8$, BII, $\text{C}_{50}\text{H}_{56}\text{O}_{16}(\text{OH})_4(\text{OAc})_8$. The aldehydes were characterised (for analysis) as semicarbazones, and the acids as Pb or Ag salts. Corresponding products in the three series had very similar properties, and in each case the final saturated alcohols CII, GII, and BII had the same empirical composition. Attempts at determination of the mol. wt. of alcohol CI gave variable results.

H. A. PIGGOTT.

Autoxidation of $\alpha\beta$ -unsaturated ketones. IV. Autoxidation of carvenone and constitution of carvenolenic acid. W. TREIBS (Ber., 1932, 65, [B], 163—168; cf. A., 1931, 1421).—Oxidation of carvenone by O_2 or H_2O_2 in alkaline EtOH closely resembles that of piperitone (loc. cit.), yielding isobutyric acid and the hydroxy-acid $\text{C}_{10}\text{H}_{18}\text{O}_3$ (cf. I),



m. p. 79—80°, which is stable towards cold KMnO_4 , but readily transformed into the lactone (cf. II), m. p.

4—5°, rather difficultly hydrolysed by alkalis, but reduced by Na and MeOH to the glycol, $\text{C}_{10}\text{H}_{20}\text{O}$, (cf. III), b. p. 150°/14 mm. The hydroxy-acid or the lactone is transformed by boiling dil. H_2SO_4 into carvenolenic acid (cf. IV), b. p. 250—252° (Me ester). Oxidative degradation of Me carvenolenate affords little insight into its constitution, which is established by hydrogenation in presence of Pd and MeOH to Me carvenolate (Me piperitolate is described). Hydrolysis of the ester affords carvenolenic acid, b. p. 255—257° (cf. V), the identity of which with fencholic acid is proved by conversion through the chloride into fencholamide, m. p. 96—97°. Dihydroxycarvenolactone, $\text{C}_{10}\text{H}_{18}\text{O}_3$, m. p. 138—139°, is isolated from that portion of the product of autoxidation which is not volatile with steam.

H. WREN.

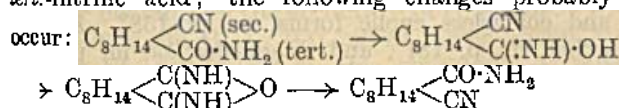
Racemisation phenomena with camphene and their reaction mechanism. I. P. LIPP and G. STUTZINGER (Ber., 1932, 65, [B], 241—250).—Re-examination of the action of NH_2Ph on active bornyl chloride confirms the production of the compound designated "bornylaniline" by Ullmann and Schmid (A., 1911, i, 70). Attempts to establish its secondary nature lead to the isolation of the nitronitroamine, $\text{C}_{16}\text{H}_{21}\text{O}_4\text{N}_3$, m. p. 158°. The formation of "bornylaniline" by catalytic hydrogenation of camphoranil in presence of Pt-black and by addition of NH_2Ph in presence of $\text{NH}_2\text{Ph.HCl}$ to camphene shows the compound to be isobornylaniline. The following data are incidentally recorded: isobornylaniline, b. p. 173—175°/14 mm., d^{25}_D 1.021, $[\alpha]^{25}_D$ —89.07° (hydrochloride, decomp. 187°; perchlorate; Bz derivative, m. p. 142—143° (corr.); camphoranil, d^{25}_D 0.99617, $[\alpha]^{25}_D$ +9.61°; camphor-p-toluid, b. p. 154—156°/13 mm., d^{25}_D 0.9808, $[\alpha]^{25}_D$ +25.89°; fenchoneanil, b. p. 154—156°/11 mm., d^{25}_D 0.99583. The mechanism of the formation of camphene from pinene hydrochloride and NH_2Ph and the accompanying slow racemisation are explained as follows. Camphene production occurs initially through isobornyl chloride and camphene hydrochloride. The "primary camphene" adds NH_2Ph under the influence of $\text{NH}_2\text{Ph.HCl}$ formed in the first phase immediately in the 2-a position. Thence the production of isobornylaniline takes place directly or, under the influence of $\text{NH}_2\text{Ph.HCl}$, accompanied by a Nametkin transformation (cf. A., 1928, 182). The first change with short period of action leads to the active base, whereas the second, of longer duration, proceeds through mirror-image formation to the racemic variety. During the dry distillation of the reaction mixture, the isobornylaniline is converted into NH_2Ph and a secondary camphene. Small amounts of camphene are present in the product before decomp. of the isobornylaniline; these must be regarded as primary camphene and are found to be optically active if removed from the racemising action of $\text{NH}_2\text{Ph.HCl}$ by suitable interruption of the change and modified method of isolation. The isolation of optically active camphene from bornyl chloride by other agents which remove HCl , e.g., KOPh , is explained by the inability of camphene to add the phenoxide and to a definite acidity of the solution necessary for the santene displacement.

H. WREN.

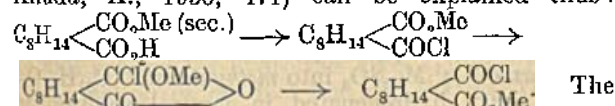
Constitution of camphoric acid and its esters. Historical. J. BREDT (J. pr. Chem., 1932, [ii], 133, 92—94).

Stereoisomeric camphornitrilic acids and *cis*- and *cis-trans*-camphoric acid dinitriles and their reduction products: *cis*- and *cis-trans*-di(aminomethyl)camphoceanes. J. BREDT and M. DE SOUZA (J. pr. Chem., 1932, [ii], 133, 84—87).—*cis*-Camphor-*sec*-nitrilic acid amide (A., 1925, i, 254) and PCl_5 give *cis*-camphoric acid dinitrile (I), m. p. 160°, reduced by Na and EtOH to *cis*-di(aminomethyl)camphoceanes, $\text{C}_8\text{H}_{14}(\text{CH}_2\text{NH}_2)_2$, b. p. 135—136°/14 mm., $[\alpha]_D^{25} -6.5^\circ$ (chloroplatinate). *trans*-Camphoric acid amide and PCl_5 afford *trans*-camphoric acid dinitrile, m. p. 144—145°, similarly reduced to *trans*-di(aminomethyl)camphoceanes, b. p. 135—136°/14 mm., $[\alpha]_D^{25} -20.8^\circ$ (chloroplatinate). (I) and conc. H_2SO_4 at room temp. give the amide, m. p. 197—198°, of *cis*-camphor-*tert*-nitrilic acid, convertible by successive treatment with H_2SO_4 and HNO_2 into *cis*-camphoric acid. H. BURTON.

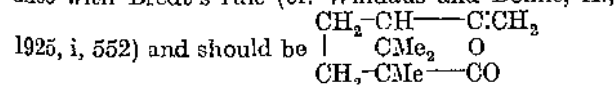
Mechanism of the rearrangement of carboxy-derivatives of camphoric acid. I. Transformation of *cis*-camphor-*sec*-nitrilic acid amide into *cis*-camphor-*tert*-nitrilic acid amide. II. Transformation of *sec*-(*ortho*)-methyl hydrogen camphorate into *tert*-(*allo*)-methyl hydrogen camphorate. J. BREDT (J. pr. Chem., 1932, [ii], 133, 87—91).—I. The amide of *cis*-camphor-*sec*-nitrilic acid is converted by conc. H_2SO_4 at room temp. during 5—7 days into the amide of *cis*-camphor-*tert*-nitrilic acid; the following changes probably occur:



II. The conversion of *ortho*-Me H camphorate into the chloride of *allo*-Me H camphorate (Qudrat-i-Khuda, A., 1930, 471) can be explained thus:



The structure assigned by Qudrat-i-Khuda (*loc. cit.*) to the unsaturated lactone from 5-acetyl-1:1:2-trimethylcyclopentane-2-carboxylic acid is not in accordance with Bredt's rule (cf. Windaus and Bohne, A.,



H. BURTON.

β -Homocamphoric acid. Formation of β -camphor [epicamphor]. F. SALMON-LEGANEUR (Compt. rend., 1932, 194, 467—469).—Interaction of β -homocamphor (A., 1931, 626) with NaNH_2 and amyl nitrite gives an *oximino*-derivative,

$\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \diagup \\ \text{CH} \end{array} \text{C=N-OH}$, m. p. 174—175°, which is converted by SOCl_2 (preferably in large excess) and subsequent treatment with H_2O into β -homocamphoro- β -nitrile, m. p. 154—156°; this with 85% H_2SO_4 gives β -homocamphoramic acid, m. p. 256°, hydrolysed by aq. (?) KOH to β -homocamphoric acid, m. p. 220—222°, $[\alpha]_D^{25} +27.3^\circ$ in EtOH. Direct oxid-

ation of β -homocamphor with HNO_3 gives a little β -homocamphoric acid and much dinitro- β -homocamphor, m. p. 80—82°; distillation of Pb β -homocamphorate gives β -camphor. H. A. PRIGGOTT.

Resolution of racemates with the help of additive compounds. R. WEISS and A. ABELES (Monatsh., 1932, 59, 238—240).—*d*-3-Naphthyleamphylamine (1 mol.) and 2 mols. of dl-2:4:6-trinitro-*sec*-butylaniline (I), m. p. 78—80° (prepared from picryl chloride and $\text{NH}_2\cdot\text{CHMeEt}$ in EtOH), in EtOH give an additive (1:1) compound, m. p. 110—111°; part of the excess of (I) separates from the mother-liquors with m. p. 81—85°, $[\alpha]_D^{25} -2.6^\circ$ in CHCl_3 , after crystallisation from EtOH. H. BURTON.

Sclareol from the so-called "absolute" extract of *Salvia Sclarea*, L. M. JANOT (Ann. Chim., 1932, [x], 17, 5—127).—A detailed account of investigations some of which have previously been published (A., 1931, 94, 737). The conclusion that sclareol, $\text{C}_{30}\text{H}_{48}\text{O}_2$ (Br_2 -compound, $\text{C}_{30}\text{H}_{34}\text{OBr}_2$), is a diterpeno di-*tert*-alcohol related in type to *d*-pimaric acid is confirmed. Although it could not be separated from hydrocarbons formed by dehydration, sclareol yields an allopahanate. Dehydration with naphthalene-2-sulphonic acid affords a mixture, difficult to separate, of isomeric sclarenes, $\text{C}_{30}\text{H}_{32}$ (dicyclic, F_3), b. p. 125—128°/0.20 mm., and cyclosclarenes (tricyclic, F_2), b. p. 119—122°/0.10 mm., the proportion of the latter being increased when HCO_2H is employed. Dihydro-sclareol, m. p. 114—115°, is similarly dehydrated to a mixture of dihydro-sclarenes and dihydrocyclosclarenes. Dehydrogenation of cyclosclarene with Se gives a mixture of hydrocarbons from which a dimethylphenanthrene, $\text{C}_{16}\text{H}_{16}$, is isolated as its *picrate*, m. p. 136°, some evidence of the presence of a trimethylphenanthrene also being obtained. Further evidence relating to the oxidation products of sclareol is recorded. Ozonolysis affords, in addition to CH_2O , a neutral substance, $\text{C}_{18}\text{H}_{30}\text{O}$, b. p. 138—142°/0.40 mm. (dihydro-derivative), in which the O is present as a C-O-C group. Oxidation with KMnO_4 in COMe , gives a neutral substance, $\text{C}_{18}\text{H}_{30}\text{O}$, b. p. 142—146°/0.80 mm., m. p. 42° (reduced by PtO and AcOH to a dihydro-compound, m. p. 52°), and an aldehydic or ketonic substance, $\text{C}_{18}\text{H}_{34}\text{O}_2$, b. p. 142—152°/0.15 mm., characterised as its *oxime*, b. p. 180—185°/0.25 mm. The AcOH also formed originates in the COMe , since it is not obtained when pyridine is used as a solvent. CrO_3 in AcOH gives a lactonic substance, $\text{C}_{18}\text{H}_{26}\text{O}_2$, m. p. 123—124°. All the available data are readily explained on the basis of the structure previously suggested (*loc. cit.*, p. 737). Certain colour reactions of sclareol are investigated and thus the location of this compound almost exclusively in the flower, reproductive organs, and the seed is demonstrated. Sclareol possesses no physiological or toxic action on rabbits. J. W. BAKER.

2-Iodofuran and magnesium 2-furyl iodide. H. GILMAN, H. E. MALLORY, and G. F. WRIGHT (J. Amer. Chem. Soc., 1932, 54, 733—736).—Na furoate and I in aq. KI at 130—140° (bath) give 20% of 2-iodofuran, b. p. 43—45°/15 mm. (more stable in Et_2O), convertible into Mg 2-furyl iodide (95% yield).

C. J. WEST (b).

Alcohols obtained by the interaction of primary tetrahydro- α -furylamine and nitrous acid. N. V. WILLIAMS (Bull. Acad. Sci. U.S.S.R., 1931, 1117—1122).—This reaction yields (1) primary tetrahydro-2-furfuryl alcohol, b. p. 86.5—87.5/25 mm. (cf. Wienhaus, A., 1920, i, 863), and (2) 2-hydroxytetrahydrofuran, b. p. 93—95.5/25 mm., which gives 8-hydroxyvaleraldehyde-*p*-bromophenylhydrazone, m. p. 70—71°, with *p*-bromophenylhydrazine (cf. Helferich, A., 1919, i, 386). T. H. POPE.

Amino-acids. I. Synthesis of furylalanine. V. DEULOFEU (Z. physiol. Chem., 1932, 204, 214—218).—Furylalanine was synthesised (a) by Flatow's method (A., 1910, ii, 321), but using conc. aq. Ba(OH)₂ for hydrolysis of the benzoylfurylalanine (m. p. 149°; lit. 162°) in place of NaOH, (b) by hydantoin condensation. Furfuraldehyde and hydantoin in presence of NaOAc give *furfurylidenehydantoin*, m. p. 230°, which on reduction with Na-Hg yields *furfurylhydantoin*, m. p. 154°. Hydrolysis of the latter with aq. Ba(OH)₂ affords furylalanine. 2-Thiohydantoin similarly gives *furfurylidene-2-thiohydantoin*, m. p. 250—251° (decomp.), from which CH₂Cl·CO₂H does not eliminate S, and *furfuryl-2-thiohydantoin*, m. p. 143—144°. J. H. BIRKINSHAW.

Comparison of the stability of some anthocyanidins and anthocyanins towards dilute ferric chloride solutions. R. ROBINSON and A. LEÓN (Anal. Fis. Quim., 1932, 30, 31—36).—Solutions of these compounds containing a 3-OH group are rapidly decolorised by dil. FeCl₃ solution, whilst those containing 3-OMe or 3-glucosidoxy-groups or not substituted in the 3-position are stable. Since pelargonin, cyanin, and malvin are stable, they are 3 : 5-diglucosides, the 5-position being already assigned to one glucose residue. The prep. of cyanin chloride (5-glucoside) by partial hydrolysis of cyanin chloride is described. R. K. CALLOW.

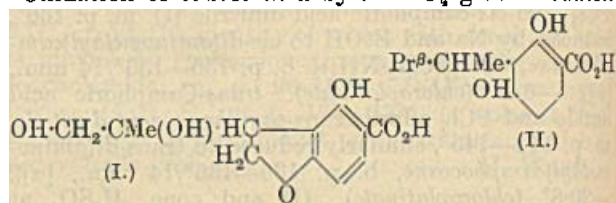
Preparation of dibromofluorescein. M. A. PHILLIPS (J.C.S., 1932, 724—725).—Fluorescein with 2 mols. Br in 80% AcOH at 80° gives an 85—88% yield of (the hydrobromide of) dibromofluorescein, m. p. 285°. H. A. PEGGOTT.

Anthraquinone-2 : 1 : 6 : 5-dioxanthone. O. DISCHENDORFER and E. FRANSEVIC (Monatsh., 1932, 59, 105—112).—1 : 5-Dichloroanthraquinone and *o*-OH·C₆H₄·CHO condense in presence of PhNO₂, K₂CO₃, Cu(OAc)₂, and "Naturkupper C" to give 1 : 5-di-*o*-aldehydophenylantraquinone, m. p. 324° (decomp.) (slight previous sintering) [*dioxime*, m. p. 256° (decomp.) (slight previous sintering)]; *di-phenylhydrazone*, m. p. 136° (decomp.), oxidised by CrO₃ and conc. H₂SO₄ in AcOH to 1 : 5-di-*o*-carbonylphenylantraquinone, m. p. 281° (decomp.) (sinters at 278°) [*Me*₂ ester, m. p. 175° (sinters at 170°)].

Treatment of the acid with PCl₅ in PhNO₂ gives *anthraquinone-2 : 1 : 6 : 5-dioxanthone* (I), darkens from

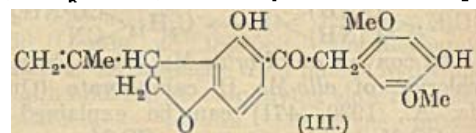
380°, not melted at 400°, which imparts a violet shade (changing to yellow in air) to cotton from an alkaline vat. H. BURTON.

Rotenone, the active constituent of the *Derris* root. VIII. Tubadiolic acid, tetrahydrotubaic acid, derritol, and rotenol. Constitution of rotenone. S. TAKEI, S. MIYAJIMA, and M. ONO (Ber., 1932, 65, [B], 279—289; cf. A., 1931, 847).—Oxidation of tubaia acid by KMnO₄ gives *tubadiolic*

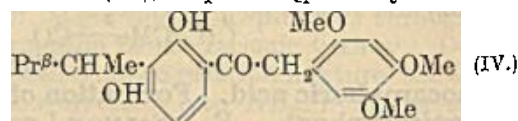


acid (I), m. p. 201° (*Me* ester, m. p. 163°), obtained also from derritol and rotenonic acid. Hydrogenation of tubaia acid in alkaline solution in presence of Pd-BaSO₄ gives *isodihydrotubaic acid*, m. p. 166°, further hydrogenated in AcOEt to *tetrahydrotubaic acid* (II), m. p. 193°, which is oxidised to an acid, C₈H₁₂O₂ (*p*-iodophenacyl ester, m. p. 85°). The 2-*Me*, m. p. 112°, 4-*Me*, m. p. 156°, and 2 : 4-*Me*₂, m. p. 109—110°, ethers of tetrahydrotubaic acid are described.

An improved method for the reduction of rotenone to derritol and rotenol is described. Derritol (III), for which the authors return to the formula C₂₁H₂₂O₆, shows keto-enolic desmotropy owing to the presence of the ·CO·CH₂· group and exists in yellow ketonic and colourless enolic forms, m. p. 158°. *Derritol-oxime*, m. p. 187°, and *dihydroderritol*, m. p. 122°,



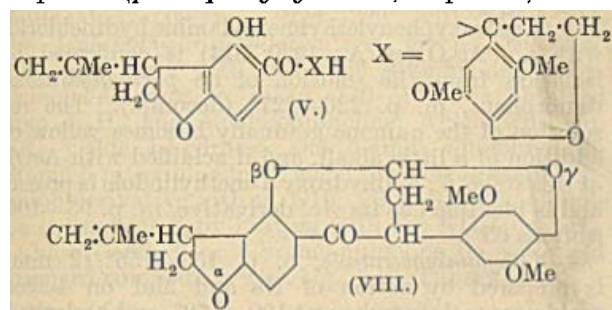
or (+MeOH), m. p. 131°, are described. Derritol is transformed by Me₂SO₄ into *methyl derritol*, C₂₁H₂₂O₆, m. p. 120°, hydrogenated in neutral solution to *methyldihydroderritol*, m. p. 109° (*oxime*, m. p. 171°; *acetylmethyldihydroderritol-oxime*, m. p. 98°), whereas in alkaline solution it affords *methyldihydroisoderritol*, m. p. 145°, further reduced in AcOEt to *methyltetrahydroderritol* (IV), m. p. 160° [probably identical with



the "methyl derritolic acid" of LaForge and Smith (A., 1930, 781)]. The *oxime*, m. p. 189°, *Me* ether, m. p. 98°, and *diacetylmethyltetrahydroderritol-oxime*, m. p. 82°, are described. *isoDerritol*, from *isorotenone* by Zn dust and KOH-EtOH, has m. p. 148°. Oxidation of methyl derritol in COMe₂ by NaOH-H₂O₂ gives 2 : 4 : 5-trimethoxyphenylacetic acid, m. p. 87°, obtained also from methyldihydroderritol or methyltetrahydroderritol. Treatment of the acid with KMnO₄ affords 2 : 4 : 5-trimethoxybenzoic acid, m. p. 143°, obtained also directly from methyl derritol, and oxidised by dil.

HNO_3 to 1-nitro-2:4:5-trimethoxybenzene, m. p. 129° , identical with the product of the action of conc. HNO_3 on 1:3:4-trimethoxybenzene.

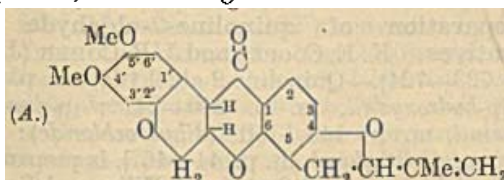
Rotenol (V), m. p. 119° , and rotenoloxime, m. p. 184° , yield a reddish-brown coloration with FeCl_3 , whereas acetylrotenoloxime, m. p. $85-86^\circ$, does not, so that rotenol contains a CO group and an OH in the tubaic acid portion of the mol. Oxidation of rotenol with H_2O_2 affords a little tubaic acid and an acid, $\text{C}_{12}\text{H}_{14}\text{O}_5$ ($\text{X.H.CO}_2\text{H}$), m. p. 90° or $131-132^\circ$ after thorough desiccation, which appears identical with the netoric acid of Smith and LaForge. It contains 1 CO_2H and 2 OMe groups and a non-substitutable O. It is oxidised to a ketone, $\text{C}_{11}\text{H}_{12}\text{O}_4$ (XO), m. p. 121° (p-nitrophenylhydrazone, m. p. 223°).



The modified constitution (VIII) is ascribed to rotenone in explanation of its action towards reducing agents.

H. WREN.

Rotenone. XIX. Alkali-soluble hydrogenation products of rotenone and its derivatives and their bearing on the structure of rotenone. F. B. LAForge and H. L. HALLER (J. Amer. Chem. Soc., 1932, 54, 810-818; cf. this vol., 165).—Catalytic reduction of derrisic acid in AcOEt under pressure (50 lb.) gives dihydro- and tetrahydro-derrisic acid (I), m. p. $204-206^\circ$ (the Et ester, m. p. 180° , gives a coloration with FeCl_3 and is sol. in cold dil. alkali), separable owing to the insolubility of (I) in CHCl_3 . Catalytic reduction of Et derrisate at atm. pressure and subsequent hydrolysis gives (I), also formed by the action of Zn dust and aq. EtOH-KOH on dehydrodihydroderrisic acid (II). (I) and Me_2SO_4 in 5% KOH afford the Me ester, m. p. $111-112^\circ$ (6-Ac derivative, m. p. 111°), of 4-methyltetrahydroderrisic acid (III), m. p. 164° , which gives a colour with FeCl_3 and is oxidised by alkaline H_2O_2 to derrisic acid. Acetylation of (I) or (II) affords 4-acetyldehydrodihydroderrisic acid, m. p. 202° , whilst methylation (Me_2SO_4) of (II) gives 4-methyldehydrodihydroderrisic acid, m. p. 169° , converted by Zn dust and 15% KOH in EtOH into (III). isoDerrisic acid and amyl nitrite in AcOH-HCl give a 1:2-diketone, $\text{C}_{23}\text{H}_{22}\text{O}_9$, m. p. 195° , which also gives a coloration with FeCl_3 .



The reactions of rotenone (and its derivatives) are explicable by the structure (A). (I) and (II) are

phenols which can be methylated in the 4-position; (I) is a dihydric phenol and its ester can be acetylated in position 6. Rotenol is a mono- and derritol a di-hydric phenol. All rotenone derivatives containing a OH group in position 6 are alkali-insol., but they give colorations with FeCl_3 . The lactone group is not present in rotenone or its derivatives; the alkali-sol. hydrogenation products previously designated acids are phenols.

C. J. WEST (b).

Behaviour of the pyridine group on electrolytic oxidation. I. Pyridine. M. YOKOYAMA and K. YAMAMOTO (Bull. Chem. Soc. Japan, 1932, 7, 28-34).—Electrolysis with a Pb anode of $\text{C}_5\text{H}_5\text{N}$ dissolved in dil. H_2SO_4 yields HCO_2H , CO , CO_2 , NH_3 , HNO_3 , and NH_4Me with some NHMe_2 and/or NMe_3 . The amines arise through condensation with NH_3 of the CH_2O first formed.

C. W. DAVIES.

5-Amino- α -picoline and its derivatives. R. GRAF (J. pr. Chem., 1932, [ii], 133, 19-35).—The preps. of aldehydecollidine and 6-methylnicotinic acid are modified. The latter [Me ester, m. p. 32° ; Et ester, b. p. about $130^\circ/15$ mm., $222-224^\circ$ (slight decomp.)/760 mm. (by Emich's method); amide, m. p. 194°] with $\text{Cu}(\text{OAc})_2$ gives the salt, $\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2\text{Cu}(\text{OAc})_2$ (cf. A., 1924, i, 873). The hydrazide, m. p. $133-135^\circ$ [benzylidene, o-chlorobenzylidene, and vanillylidene derivatives, m. p. $184-185^\circ$, $183-184^\circ$, and $245-246^\circ$ (decomp.), respectively], with HNO_3 in cold $N\text{-HCl}$ yields the azide (I), m. p. $44-45^\circ$, and secondary hydrazide, m. p. $247-250^\circ$. (I) with NH_2Ph in dry Et_2O gives the anilide, m. p. $134-137^\circ$, with 5-amino- α -picoline the condensation product, $\text{C}_{13}\text{H}_{13}\text{ON}_3$, m. p. $275-277^\circ$ (decomp.), with EtOH the urethane, m. p. $132-133^\circ$, and with boiling H_2O the s-carbamide derivative, m. p. $285-288^\circ$ (decomp.). 5-Amino- α -picoline, m. p. $95-96^\circ$ [dihydrochloride, m. p. $215-218^\circ$ (decomp.)]; Ac and Bz derivatives, m. p. $122-123^\circ$ and $110-111^\circ$, respectively], was obtained by boiling (I) with dil. AcOH (1:1), by decomp. of the urethane with hot 40% KOH , and by Hofmann degradation of the amide. It led to 5-chloro- α -picoline [oxidised by KMnO_4 to 5-chloro- α -picolinic acid, $+\text{H}_2\text{O}$, m. p. $169-170^\circ$ (acid chloride, m. p. 94°); Me and Ph esters, m. p. $85-87^\circ$ and 92° , respectively; amide, m. p. $200-201^\circ$], 5-bromo- α -picoline, m. p. 32° , o-bromo- α -picolinic acid, m. p. 175° , 4-iodo- α -picoline, m. p. $48-49^\circ$ (hydriodide, m. p. $235-238^\circ$), 5-iodo- α -picolinic acid, m. p. $188-190^\circ$, and 5-hydroxy- α -picolinic acid, m. p. $165-167^\circ$. The structure of comenamic acid (A., 1883, 792) is thus proved.

R. S. CAHN.

4:6-Dichloro- and 4:5:6-trichloro- α -picolinic acid. R. GRAF (J. pr. Chem., 1932, [ii], 133, 36-50).— α -Picolinic acid hydrochloride heated with SOCl_2 (1.75 parts; 10 days) gives ?-chloro-, 4:6-dichloro- (I), and 4:5:6-trichloro- (II) α -picolinic acid, (I) and (II) being separated by distillation of the acid chlorides and subsequent crystallisation of the Me esters. s-Di-(4:6-dichloropicolinoyl)hydrazine melts above 300° . The hydrazide, m. p. 154° (benzylidene derivative, m. p. 165°), of (II) with boiling aq. AcOH (1:2) yields 4:6-dichloro-2-aminopyridine, m. p. 105° (Ac derivative, m. p. $218-219^\circ$), which with

boiling HI gives 4-chloro-6-iodo-2-aminopyridine, m. p. 137°, with HNO_3 in conc. HCl gives 2:4:6-trichloropyridine, and with HNO_3 in dil. acid gives 4:6-dichloro-2-hydroxypyridine, m. p. 151°. The azide, m. p. 74°, of (I) with boiling, abs. EtOH yields the *Et* ester of (I), m. p. 75°. (I) and boiling 80% H_2SO_4 afford 4-chloro-2-hydroxy- α -picolinic acid. The *Me* ester, m. p. 125°, of (II) (m. p. 123° after sintering at 108°), HI, and red P at 150° give 5-chloro- α -picolinic acid, thus proving the structure of (II), but when boiled, give 5-chloro 4-iodo- α -picolinic acid, m. p. 159° (decomp.), transformed by boiling SOCl_2 into the 4:5-dichloro-acid. The amide of (II) has m. p. 169°, the *Ph* ester m. p. 138°, and the acid chloride m. p. 70°. The *Me* ester of (II) with boiling 80% H_2SO_4 yields 4:5-dichloro-6-hydroxy- α -picolinic acid. 3-Amino- α -picolinic acid affords 3-chloro- α -picolinic acid (amide, m. p. 140°; *Me* ester, an oil), which decomposes at the m. p. (121°) into CO_2 and 3-chloropyridine.

R. S. CAHN.

Anhydride of *s*-pyridinetetracarboxylic acid and its condensation products. G. MACHEK (Monatsh., 1932, 59, 175—183).—*s*-Pyridinetetracarboxylic acid (I) (+2 H_2O), best purified by decomp. of the Ag salt with a 10% excess of dil. HCl, is obtained anhyd. when heated from 80° to 100° during 20—30 min. The anhyd. acid is converted by short heating with Ac_2O into pyridine-3:5-dicarboxylic acid and 25% of the dianhydride (II), decomp. 277—278° (darkens at about 220°), of (I), (II), C_6H_6 , and AlCl_3 at 94—95° give a mixture, decomp. 135° (softens at 105°), of dibenzoylpyridinedicarboxylic acids, which could not be cyclised, convertible by SOCl_2 into a mixture, decomp. 115° (softens at about 90°), of chlorides, which with C_6H_6 and AlCl_3 affords 2:3:5:6-tetrabenzoylpyridine, decomp. 165—170° (darkens at about 140°).

H. BURTON.

Binuclear isomerism of diphenyl type. I. (Miss) A. J. CHALMERS, F. LIONS, and A. O. ROBSON (J. Proc. Roy. Soc. New South Wales, 1930, 64, 320—336).—The methosulphate of 2-(*o*-carboxyphenyl)-3-carboxypyridine, m. p. 238—239° (decomp.), could not be resolved through the dibrucine, +7 H_2O , m. p. 235° (decomp.), $[\alpha] -26.8^\circ$, or the distychnine salt, $[\alpha] -23.4^\circ$ and -25.1° .

F. R. SHAW.

Nitroindoles. H. BAUER and E. STRAUSS (Ber., 1932, 65, [B], 308—315).—The following nitrophenylhydrazones are prepared in good yield by the addition of the aldehyde or ketone to a very dil. solution of the requisite nitrophenylhydrazine in HCl or AcOH: propaldehyde-*o*-, m. p. 72°; -*m*-, m. p. 83°; -*p*-, m. p. 125°; *Me Et* ketone *o*-, m. p. 73°; -*m*-, m. p. 99.5°; -*p*-, m. p. 124°; *Et* acetoacetate *p*-nitrophenylhydrazone, m. p. 118°, converted by conc. H_2SO_4 into a nitro-pyrazolone, $\text{C}_{10}\text{H}_9\text{O}_3\text{N}_3$, m. p. 218°; *Et* levulate *p*-nitrophenylhydrazone, m. p. 156°. Treatment of the propaldehydephenylhydrazones with boiling HCl (*d* 1.19) affords 3:3'-dimethyl-2:2'-propylidene-7:7'-dinitrodi-indole, m. p. 205°, -6:6'(4:4')-dinitrodi-indole, m. p. 258°, and -5:5'-dinitrodi-indole, m. p. 268°. Similarly derived from COMeEt are 7-nitro-, m. p. 164°, 6(4)-nitro-, m. p. 120°, and 5-nitro-, m. p. 180°, -2:3-dimethylindole. 5-Amino-, m. p. 178°, and *o*-acetamido-, m. p. 173° (decomp.), -2:3-dimethylindole

are described. Bromination in AcOH gives bromo-7-nitro-, m. p. 172° (decomp.), and bromo-5-nitro-, not molten below 300° after becoming discoloured at 176°, -2:3-dimethylindole. Treatment of 2:3-dimethylindole with conc. H_2SO_4 and KNO_3 at 0° affords the 5- NO_2 -compound. It is therefore probable that in the nitration of proteins the NO_2 group enters the tryptophan preponderatingly in the 5 position.

H. WREN.

Oxidation of 3:3':4-dihydroxyphenylethylmethylamine with silver oxide. Isolation of 5:6-dihydroxy-1-methylindole and synthesis of 5:6-dimethoxy-1-methylindole. H. BURTON (J.C.S., 1932, 546—549).—The formation of 1-methyl-2:3-dihydroindole-5:6-quinone by oxidation of 3:3':4-dihydroxyphenylethylmethylamine hydrochloride with aq. Ag_2O (cf. A., 1930, 814) is confirmed by isolation from the solution of its phenylhydrazone, dimorphous, m. p. 226—227° (decomp.). The red solution of the quinone gradually becomes yellow on addition of a little alkali, and if acidified with AcOH at this stage, 5:6-dihydroxy-1-methylindole is present and is identified as its Ac_2 derivative, m. p. 95—100° (softens 65°).

4-Methylaminoveratrole, b. p. 153—155°/12 mm., is prepared by action of Na and MeI on 4-acetamidoveratrole in xylene at 100—150°, and hydrolysis of the product with conc. KOH in EtOH. It reacts with glyoxal sodium hydrogen sulphite in aq. EtOH to form Na 5:6-dimethoxy-1-methylindolyl 2-sulphite (+1 H_2O), m. p. 187° (decomp.), hydrolysed by aq. HCl to 5:6-dimethoxy-1-methylindole (?), m. p. 120—121°, and reduced by vac. distillation with Zn dust to 5:6-dimethoxy-1-methylindole, m. p. 138—139°, identical with that prepared by Duliere and Raper's method (*loc. cit.*).

H. A. PIGGOTT.

Action of sulphurous acid and its salts on quinoline derivatives. II. N. N. VOROSHCHEV and J. M. KOCHAN (Ber., 1932, 65, [B], 142—145; cf. A., 1930, 1445).—8-Hydroxyquinoline is converted almost quantitatively by $(\text{NH}_4)_2\text{SO}_3$ and 20% NH_3 at 150° into 8-aminoquinoline, m. p. 65—65.5°. 6-Amino-, m. p. 115°, is obtained similarly from 6-hydroxy-quinoline. 8-Aminoquinoline-5-sulphonic acid (*Na* salt; hydrochloride) is described.

H. WREN.

Quinoline derivatives. L. MONTI and G. VERONA (Gazzetta, 1932, 62, 14—18).—*p*-Methoxyacetoacetanilide, m. p. 116—117° (A., 1931 831), with hot conc. H_2SO_4 gives 2-hydroxy-6-methoxy-4-methylquinoline, m. p. 268° (*picrate*, m. p. 196—198°). *p*-Acetylacetoacetanilide, m. p. 108—110°, from *p*-aminacetophenone and *Et* acetoacetate, does not undergo ring-closure in presence of H_2SO_4 or Ac_2O , but is hydrolysed.

E. E. J. MAILER.

Preparation of quinoline-2-aldehyde and derivatives. K. E. COOPER and J. B. COHEN (J.C.S., 1932, 723—724).—Quinoline-2-aldehyde, m. p. 67—69° [*p*-hydroxyanil, m. p. 240—241°; *p*-dimethylaminoanil, m. p. 148—150° (*dihydrochloride*); *p*-dimethylaminomethylanil, m. p. 44—46°], is prepared in >50% yield by a modification of Miller and Spady's method (cf. A., 1886, 265). It condenses with 6-acetamidoquinoline methochloride in EtOH in

presence of piperidine to form 6-acetamido-2-(2'-quinolylstyryl)quinoline methochloride, m. p. 278° (decomp.), hydrolysis of which with HCl at its b. p. gives the free NH_2 -compound, m. p. 262° (decomp.).

H. A. IGGOTT.

Quinoline derivatives. W. BRYDOWNA (Roez. Chem., 1932, 12, 89—99).—*Cinchonic acid azide*, m. p. 69—70°, yields on boiling with EtOH 4-quinolylurethane, m. p. 206—207°, which on hydrolysis gives 4-aminoquinoline. *Cinchonic acid benzylidenehydrazide*, m. p. 220—221°, is prepared by the action of PhCHO on the corresponding hydrazide. 4-Iodoquinoline methiodide, m. p. 234—237° (decomp.), obtained by the action of Mel on 4-chloroquinoline, reacts with NH_2Ph to yield the corresponding 4-quinolino-derivative, m. p. 220—222°, with $NHPhNH_2$ the 4-phenylhydrazino-derivative, m. p. 204—205° (decomp.), and with NH_3 the 4-amino-derivative. Quinolyl-4-hydrazine, m. p. 140—142°, is obtained from N_2H_4 and 4-chloroquinoline, which with aq. NH_3 yields 4-hydroxy- and 4-amino-quinoline. 6-Bromo-5-nitroquinoline yields the corresponding 6-amino-derivative with aq. NH_3 . 3- or 6-Bromoquinoline is unaffected by heating with aq. KOH or NH_3 . 4-Chloro- and 3- or 6-bromo-quinoline do not yield Grignard compounds with Mg. R. TRUSZKOWSKI.

Dimorphism of 2-phenylquinoline-4-carboxylic acid. L. KOFLER and W. DERNBACH (Arch. Pharm., 1932, 270, 153—155).—By micro-sublimation 2-phenylquinoline-4-carboxylic acid is prepared in an unstable, triclinic (m. p. 196—197°) and a stable, rhombic (m. p. 211—213°) form, the former tending to pass into the latter above 160°. R. S. CAHN.

Quinoline derivatives. XXXIV. Derivatives of 2-phenylquinoline-4'-carboxylic acid and 4'-amino-2-phenylquinoline. H. JOHN [with H. OTTAWA] (J. pr. Chem., 1932, [ii], 133, 13—18; cf. A., 1931, 1429).—2-Phenylquinoline-4-carboxylic acid and $SOCl_2$ give the acid chloride, whence the following derivatives were prepared: *Et* (m. p. 87°), β -chloroethyl (m. p. 98°), *Pr*^a (m. p. 72°), and *Pr*^b (m. p. 75°) esters; *amide*,* m. p. 234°; *diethylamide*,* m. p. 112°; β -hydroxyethylamide, m. p. 182°; *carbamide* derivative,* m. p. 233°; *hydrazide*, m. p. above 300° (*benzylidene* derivative, m. p. above 300°). The *amide* and NaOBr at 80—90° give 4'-amino-2-phenylquinoline.* The hydrochloride, sulphate, nitrate, mercurichloride, and picrate of the substances marked * are described.

R. S. CAHN.

Quinoline derivatives. XXXV. 2-(4-Hydroxy-5-methyl-2-isopropylphenyl)quinolines. H. JOHN and E. ANDRASCHKO (J. pr. Chem., 1932, [ii], 133, 114—119).—Isatin and 4-hydroxy-5-methyl-2-isopropylacetophenone (I) in 33% KOH give 2-(4-hydroxy-5-methyl-2-isopropylphenyl)quinoline-4-carboxylic acid, m. p. 279° (*Me* ester, m. p. 192°), converted by distillation into 2-(4-hydroxy-5-methyl-2-isopropylphenyl)quinoline, m. p. 125°. 6-Bromo-2-(4-hydroxy-5-methyl-2-isopropylphenyl)quinoline-4-carboxylic acid, m. p. 295°, is prepared similarly from 5-bromoisatin. *o*-Aminoacetophenone and (I) give 2-(4-hydroxy-5-methyl-2-isopropylphenyl)-4-methylquinoline, m. p. 81°. Various salts of these compounds are described.

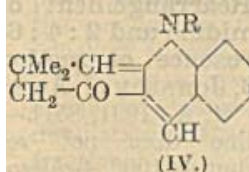
H. BURTON.

Carbylamines. XVIII. Reaction of phenylcarbylamine with nitrosobenzene. T. BONCIANI and M. PASSERINI (Gazzetta, 1931, 61, 959—963).—Phenylcarbylamine when heated with PhNO gives diphenylcarbamide and a compound $C_{21}H_{15}N_3$ (I), m. p. 212—213°, probably 3:4-quinolinequinone-dianil, giving on hydrolysis NH_2Ph , a compound $C_{15}H_{10}ON_2$, m. p. 215—217°, probably a 3:4-quinolinequinonemonoanil, and a compound $C_6H_5O_2N$, m. p. 182—185°, probably 3:4-quinolinequinone, which changes spontaneously to a compound, m. p. above 285°.

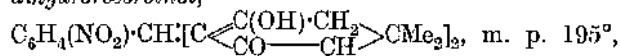
E. E. J. MARLER.

Reactivity of 5:5-dimethyldihydroresorcinol.

II. Behaviour towards *o*-nitro- and *o*-amino-benzaldehyde. B. H. IYER and G. C. CHAKRAVARTI (J. Indian Inst. Sci., 1932, 14, A, 157—171; cf. this vol. 279).—Unlike other substituted benzaldehydes, 1 mol of *o*-aminobenzaldehyde (I) (modified prep.) condenses under all conditions tried with only 1 mol. of dimethyldihydroresorcinol (II), yielding 4-keto-2:2-dimethyl-1:2:3:4-tetrahydroacridine (III), m. p. 117° (*picrate*, m. p. 197—198° after sintering at 184°; *chloroplatinate*; *methiodide*, m. p. 224—225°), yielding quinoline-2:3-dicarboxylic acid on oxidation by HNO_3 and with NH_2NHPh the phenylhydrazones of (I) and (II). (II) and the Ac derivative of (I) in hot EtOH give 2'-acetamido-2:6-diketo-4:4-dimethyl-1:2:3:4:5:6-hexahydrobenzhydrol, $+H_2O$, m. p. 153—154° (slowly giving at 105—110° *o*-acetamidobenzylidenedimethyldihydroresorcinol, m. p. 197—199°), but in presence of $ZnCl_2$ form the substance (IVa); $R=Ac$, $+H_2O$, m. p. 203—204° (also obtained from the two previous products), which with KOH in hot EtOH affords the substance (IVb; $R=H$), m. p. 245—250° (decomp.), isomerised to (III) by acids; (III) is



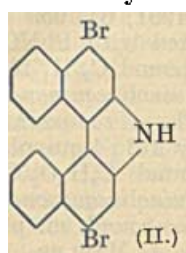
formed directly from (IVa) if aq.-alcoholic KOH is used. 5-Nitro-2-acetamidobenzaldehyde, (II), and KOH in EtOH yield 6-nitro-4-keto-2:2-dimethyl-1:2:3:4-tetrahydroacridine, m. p. 82—83°, whilst in presence of $ZnCl_2$ the 6- NO_2 -derivative, m. p. 171°, of (IVa) is formed. *o*-Nitrobenzaldehyde, (II), and KOH in aq. EtOH give *o*-nitrobenzylidenedimethyldihydroresorcinol,



and a small amount of 4:5-diketo-2:2:7:7-tetra-methyl-9-(2'-nitrophenyl)octahydroxanthene, m. p. 253—254° [produced quantitatively from the previous compound by H_2SO_4 , and reduced, best by Zn dust, AcOH, and HCl, to a mixture containing (III) and a phototropic substance, m. p. 246—249°]. R. S. CAHN.

$\beta\beta$ -Dinaphthacarbazole. A. CORBELLINI and L. MARCONI (Gazzetta, 1932, 62, 39—50).— $\beta\beta$ -Dinaphthacarbazole (I) (*K* derivative; *Bz* derivative, m. p. 269—272°), obtained during the prep. of 2:2'-diamino-1:1'-dinaphthyl by reduction of $\beta\beta$ -azo-naphthol (A., 1929, 1172) with $NaNO_2$ in AcOH, gives *N*-nitroso- $\beta\beta$ -dinaphthacarbazole, m. p. 142—145°, which on reduction with Zn and AcOH regenerates (I), and a small amount of 2-nitro- $\beta\beta$ -dinaphthacarbazole, m. p. 267—268°, which is also obtained by treating

(I) with 1 mol. of HNO_3 (*d* 1.4) in AcOH , and is reduced by SnCl_2 to 2-amino- β -dinaphthacarbazole



[hydrochloride; *Ac* derivative, m. p. 311° (corr.)]. Bromination of (I) in AcOH gives only 2:11-dibromo- β -dinaphthacarbazole (II), m. p. 197°. Nitration of (I) with 2 mols. of HNO_3 (*d* 1.4) gives 2:11-dinitro- β -dinaphthacarbazole, m. p. 324°, reduced by SnCl_2 to 2:11-diamino- β -dinaphthacarbazole (*Ac* derivative, m. p. above 360°).

(I) and (II) are oxidised by chromic acid to phthalic anhydride. E. E. J. MARLER.

Polymorphism of isopropylallylbarbituric acid. R. FISCHER (Arch. Pharm., 1932, 270, 149—152).—By sublimation or crystallisation from aq. EtOH isopropylallylbarbituric acid is obtained in a stable (m. p. 138.5—140.5°) and an unstable (m. p. 133.5—134.5°) form. The latter passes into the former rapidly at 136—137° and slowly at room temp. A third form, m. p. 140.5°, possibly exists.

R. S. CAHN.

Spontaneous oxidation of dialuric acid. III. Oxidation of amino-acids by dialuric acid. E. S. HILL (J. Biol. Chem., 1932, 95, 197—201).—Alloxan, formed by the autooxidation of dialuric acid, reacts with NH_2 -acids (glycine, alanine, glutamic acid, and phenylalanine) giving dialuric acid, CO_2 , NH_3 , and the next lower aldehyde.

F. R. SHAW.

Pyrimidines. CXXIII. Rearrangement of 4-chloro-2:6-dimethoxypyrimidine and 2:4:6-trimethoxypyrimidine in presence of methyl iodide. H. J. FISHER and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 727—732; cf. A., 1931, 851).—4-Chloro-2:6-dimethoxypyrimidine does not rearrange in presence of cold MeI , but at 100°, 4-chloro-1:3-dimethyluracil, m. p. 111°, is formed. 2:4:6-Trimethoxypyrimidine rearranges even in cold MeI to give 2-keto-4:6-dimethoxy-3-methylpyrimidine, m. p. 95.5—97°, and 4-methoxy-1:3-dimethyluracil, m. p. 164—166°. The mechanism of these changes is discussed. 2-Amino-4:6-dimethoxypyrimidine, m. p. 95°, results from the 4:6-dichloro-2-amino-derivative and NaOMe .

C. J. WEST (b).

Pyrimidine azo-derivatives. M. T. BOGERT and D. DAVIDSON (J. Amer. Chem. Soc., 1932, 54, 831).—The authors are working in the same field as Johnson, Baudisch, and Hoffmann (this vol., 66).

C. J. WEST (b).

Derivatives of piperazine. M. GODCHOT and M. MOUSSERON (Compt. rend., 1932, 194, 616—617).—2-Chlorocyclohexanone reacts with piperazine hydrate at 140° to give N-2-ketocyclohexyl-, m. p. 4° [separated as its dithiocarbamate, m. p. 165° (decomp.)], and NN'-bis-(2-ketocyclohexyl)-, m. p. 113—114°, -piperazine, reduced by Na and EtOH , respectively, to the corresponding 2-hydroxy-, m. p. 67—68° [*picrate*, m. p. 220° (decomp.)]; dithiocarbamate, m. p. 205° (decomp.), and bis-2-hydroxy-, m. p. 205—206° [*picrate*, m. p. 215°], derivatives; reduction with Pt and H_2 in AcOH gives the respective stereoisomeric forms, m. p. 105—106° [*picrate*, m. p. 150°; dithiocarbamate,

m. p. 155°], and m. p. 160—161° [*picrate*, m. p. 180°], of these sec.-alcohols. J. W. BAKER.

Course of the reaction in a new type of rearrangement of ketoximes. III. P. W. NEBER and A. BURGARD (Annalen, 1932, 493, 281—294).—The mechanism of the rearrangement previously described (A., 1926, 1247; 1929, 188) is studied. 2:4-Dinitrobenzyl *Me* ketoxime (*Bz* derivative, m. p. 140°), which could not be made to undergo the Beckmann rearrangement, is converted by $p\text{-C}_6\text{H}_4\text{MeSO}_2\text{Cl}$ or PhSO_2Cl in pyridine at 0° into the hydrochloride (I), $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CH}_2\text{N}:\text{CMe}_2\text{HCl}$ ($+ \text{C}_6\text{H}_5\text{N} + \text{H}_2\text{O}$), m. p.

161° [corresponding sulphate ($+ \text{C}_6\text{H}_5\text{N}$), m. p. 141.5° (decomp.), and *picrate* ($+ \text{C}_6\text{H}_5\text{N}$), m. p. 142.5° (decomp.)]. The free base (II), m. p. 79°, from (I) and aq. Na_2CO_3 , gives 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$ when oxidised with KMnO_4 in moist COMe_3 , is converted by conc. HCl into a substance, $\text{C}_6\text{H}_4\text{O}_2\text{N}_2\text{Cl}$, m. p. 136° (decomp.), by 2*N*- NaOH in EtOH into a compound, m. p. 205° (decomp.), by Ac_2O at 0° into α -acetamido- β -keto- α -2:4-dinitrophenylpropane, m. p. 164.5° (oxime, m. p. 168°), and by successive treatment with 36% H_2SO_4 at room temp. and aq. NaOAc at 0° into 3:6-di-(2:4-dinitrophenyl)-2:5-dimethyl-3:6-dihydro-1:4-diazine (III) m. p. 213° (decomp.). (II) and $p\text{-C}_6\text{H}_4\text{MeSO}_3\text{H}$ in hot EtOH give the *p*-toluenesulphonate, m. p. 158°, of α -amino- β -diethoxy- α -2:4-dinitrophenylpropane, m. p. 90°. This acetal is hydrolysed by conc. HCl to α -amino- β -keto- α -2:4-dinitrophenylpropane hydrochloride, m. p. 168° (decomp.), converted by aq. NaOAc into (III). These results show that, contrary to the previous assumption (*loc. cit.*), the reaction does not begin by a Beckmann rearrangement, but through the formation of the *p*-toluenesulphonate of the cyclic ketimine [as (II)].

Bromination of 2:4-dinitrobenzyl *Me* ketone in AcOH gives two *Br*-derivatives, m. p. 98° and 117.5°, both of which are oxidised to 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$; the latter is brominated further to $\alpha\gamma$ -dibromo- β -keto- α -2:4-dinitrophenylpropane, m. p. 108°. 2:4-Dinitrobenzyl iodide, m. p. 78°, is prepared from the chloride and KI in EtOH .

H. BURTON.

New reaction of certain diazosulphonates derived from β -naphthol-1-sulphonic acid. IX. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from 5-nitro-*o*-toluidine. F. M. ROWE and F. J. STIDDLE (J.C.S., 1932, 473—483; cf. A., 1931, 835).—Na 1-(4'-nitro-2'-methylbenzeneazo)-2-keto-1:2-dihydronaphthalene-1-sulphonate is slowly converted by cold NaOH into Na *H* 3-(4'-nitro-2'-methylphenyl)-1:3-dihydrophthalazine-1-sulphonate-4-acetate, which with dil. HCl (conc. acid liberates the sulphonic acid which is difficult to hydrolyse further) affords 1-hydroxy-3-(4'-nitro-2'-methylphenyl)-1:3-dihydrophthalazine-4-acetic acid (I), m. p. 238° (*Me*, m. p. 186°, *Et*, m. p. 165°, esters; *Ac* derivative, m. p. 228°; anilide, m. p. 211—212°). Reduction of (I) with $\text{Na}_2\text{S}_2\text{O}_4$ or boiling acid SnCl_2 affords 1-hydroxy-3-(4'-amino-2'-methylphenyl)tetrahydrophthalazine-4-acetic acid (II), m. p. 217° (*Ac* derivative, m. p. 265°), which with boiling H_2SO_4 or long boiling with conc. HCl yields 4'-amino-3-phenyl-2'-methylphthalaz-1-one, m. p. 255

($+\frac{1}{2}\text{H}_2\text{O}$, m. p. 130°; Ac derivative, m. p. 300—302°). This phthalazone is reduced to 1-keto-3-(4'-amino-2'-methylphenyl)tetrahydrophthalazine, m. p. 203—205° (Ac derivative, m. p. 212—214°), by $\text{Na}_2\text{S}_2\text{O}_4$ and by Zn and HCl to 4'-amino-N-phenyl-2'-methylphthalimidine, m. p. 176—177° (Ac derivative, m. p. 185°), from which 4'-hydroxy-N-phenyl-2'-methylphthalimidine, m. p. 227°, is prepared. Boiling mineral acids or PhNO_2 partly reconvert the phthalazine into the phthalazone. (I) with boiling aq. H_2SO_4 gives 4'-nitro-3-phenyl-2'-methylphthalaz-1-one, m. p. 279° (sulphate, m. p. 244—246°; hydrochloride, m. p. 195—199°, both resolubilizing and melting at 279°; picrate, m. p. 208—210°), which, with Me_2SO_4 and crystallisation from MeOH affords a compound, m. p. 149—150° (from EtOH, the compound has m. p. 93°), both decomposed on drying. When gradually heated to 140°, either is converted into 4-keto-1-methoxy-3-(4'-nitro-2'-methylphenyl)-3:4-dihydrophthalazine, m. p. 184—185°, which, with HBr, affords 1:4-diketo-3-(4'-nitro-2'-methylphenyl)-tetrahydrophthalazine, m. p. 267°. 4'-Nitro-3-phenyl-2'-methylphthalaz-1-one gives with COMe_2 , 1-hydroxy-4-acetonyl-3-(4'-nitro-2'-methylphenyl)-3:4-dihydrophthalazine, m. p. 186—187°, which, unlike berberine-acetone, is unaltered by boiling its EtOH solution with CHCl_3 (cf. A., 1890, 1011). No other nitro-3-phenylphthalaz-1-one shows a reaction with COMe_2 . Reduction of the phthalaz-1-one with Na_2S and Zn and HCl affords 4'-amino-3-phenyl-2'-methylphthalaz-1-one and 4'-amino-N-phenyl-2'-methylphthalimidine. (I) reacts with conc. H_2SO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$ to give 4'-nitro-3-phenyl-2':4-dimethylphthalaz-1-one (II), m. p. 209—210° (picrate, m. p. 229—230°), which with Me_2SO_4 affords 4'-nitro-1-methoxy-3-phenyl-2'-methyl-4-methylene-3:4-dihydrophthalazine, m. p. 118°. (II) and $\text{Na}_2\text{Cr}_2\text{O}_7$ afford 4'-amino-3-phenyl-2':4-dimethylphthalaz-1-one, m. p. 287—288° (Ac derivative, m. p. 304—305°), also obtained by hydrolysing (II) with Na_2CO_3 , NaOH, or best with EtOH-KOH or by reducing (III) with Na.S. On reduction with $\text{Na}_2\text{S}_2\text{O}_4$, the phenyldimethylphthalazone gives 1-keto-3-(4'-aminophenyl)-2':4-dimethyltetrahydrophthalazine, m. p. 204—205°; reduction with Zn and HCl affords 4'-amino-N-phenyl-2':3-dimethylphthalimidine, m. p. 183° (Ac derivative, m. p. 231°). Phthalaldehydic acid and 5-nitro-o-tolylhydrazine in boiling EtOH give the lactone of o-carboxybenzaldehyde-5-nitro-o-tolylhydrazine, m. p. 225—226°, which with warm conc. H_2SO_4 or amylalcoholic HCl affords 4'-nitro-3-phenyl-2'-methylphthalaz-1-one, m. p. 187—188°. Unlike the isomeric phthalaz-1-one, it does not react with mineral acids, picric acid, or Me_2SO_4 . J. L. D'SILVA.

Anthraquinonylguanidines. M. BATTEGAY and H. SILBERMANN (Compt. rend., 1932, 194, 380—382).—1-Aminoanthraquinone, cyanamide dihydrochloride, and an indifferent diluent (PhNO_2 or m-cresol) give with dry HCl at 70—150° a guanidine (cf. A., 1913, i, 1394) which suffers ring closure to give C-amino-1:9-pyrimidineanthrone, m. p. 290—295° [hydrochloride $+\frac{1}{2}\text{H}_2\text{O}$, m. p. 275—280° (decomp.); benzoate, m. p. 205—209° after softening at 135°]. Oxidation of the hydrochloride with HNO_3 affords

pyrimidoneanthrone. 2-Anthraquinonylguanidine, m. p. 244—246° (decomp.), is prepared as above [hydrochloride $+\text{H}_2\text{O}$, m. p. 285—290° (decomp.); dibenzoate, m. p. 274°]. J. L. D'SILVA.

Colorimetric determination of allantoin. K. Ro (J. Biochem. Japan, 1932, 14, 391—403).—The method of Fosse and Bossuyt (A., 1929, 196) is investigated and modified. F. O. HOWITT.

Mercaptotetrazoles. R. STOLLÉ [with A. STRITTMATTER] (J. pr. Chem., 1932, [ii], 133, 60—64).—The Hg salt of 5-thiol-1-methyltetrazole decomposes at about 240° after previous sintering. The following 5-thiol-1-alkyl(or aryl)-tetrazoles were prepared by boiling the appropriate thiocyanato and NaN_3 in EtOH: allyl-, m. p. 69°; Ph-, m. p. 152° [K (decomp. about 240°), Na (m. p. 96°, decomp. about 145°), NH_4 (decomp. about 176°), and Pb (decomp. about 224°) salts]; m-xylyl-, decomp. 141°; β -naphthyl-, m. p. 164° (decomp.). The NH_4 salt of the o-tolyl derivative has m. p. 157°. R. S. CAHN.

Chemistry of the thiazole group. R. F. HUNTER (Proc. Muslim Assoc. Adv. Sci., 1931, 1, 1—47).—A review.

Alkaloids of Anabasis aphylla. II. Constitution of anabesine. III. Bases of high b. p. A. OREKHOV and G. MENSCHIKOV (Ber., 1932, 65, [B], 232—234, 234—241; cf. A., 1931, 498).—II. 2:3'-Dipyridyl, b. p. 294—295° (monoplicate, m. p. 153—154°; diplicate, m. p. 165—168°), prepared from phenanthroline (improved method) is identical with the product of the dehydrogenation of anabesine, which is therefore 2-piperidyl-3-pyridine.

III. The mixture of bases of high b. p. (loc. cit.) cannot be separated into its components by fractional distillation. Dissolution in 2N-HCl followed by fractional pptn. with 2N-NaOH yields aphyllidine, $\text{C}_{15}\text{H}_{22}\text{ON}_2$, m. p. 100—103°, $[\alpha]_D^{25} + 27.5^\circ$ in MeOH (picrolonate, m. p. 235—236°; methiodide, m. p. 217—220°), aphylline, $\text{C}_{15}\text{H}_{24}\text{ON}_2$, m. p. 52—53° becoming transparent at 57°, $[\alpha]_D^{25} + 10.3^\circ$ in MeOH [hydrochloride, $[\alpha]_D^{25} + 13.6^\circ$ in H_2O ; picrolonate, m. p. 230—231° (decomp.); methiodide, m. p. 212—213° (decomp.)], and base V, $\text{C}_{16}\text{H}_{26}\text{O}_2\text{N}_2$ or $\text{C}_{15}\text{H}_{24}\text{O}_2\text{N}_2$, m. p. 137° (decomp.). Aphylline and aphyllidine, like matrine and lupanine, are monacid bases. They are indifferent towards benzoylating agents and do not evolve CH_4 with MgMeI . They are not affected by KOH-EtOH. Attempts to hydrogenate aphyllidine to aphylline were unsuccessful. Aphylline methiodide is readily converted through the NH_4 base or by boiling KOH-MeOH into de-N-methyl-aphylline, $\text{C}_{15}\text{H}_{26}\text{ON}_2$, m. p. 113—115° (yield 82%), the methiodide of which, m. p. 223—226° [or $+\frac{1}{2}\text{H}_2\text{O}$, m. p. (indef.) 159—164°], is transformed by Ag_2O and subsequent distillation into de-N-dimethylaphylline, $\text{C}_{17}\text{H}_{28}\text{ON}_2$, b. p. about 230°/6 mm. The methiodide, m. p. 167—172°, of the last-named compound is converted into NMe_3 and hemiaphyllylene, $\text{C}_{15}\text{H}_{20}\text{ON}$, b. p. 217—220°/7 mm., which has only very feebly basic properties. Since the Hofmann degradation must be thrice applied to cause evolution of NMe_3 , the basic N atom of aphylline, like that of lupanine and sparteine, must be in dicyclic union. Aphyllidine

methiodide is very readily transformed into *de-N-methylaphyllidine*, $C_{16}H_{24}ON_2$, m. p. 121—122°, converted through the *methiodide*, m. p. 115° and m. p. 225° after re-solidification, into *de-N-dimethylaphyllidine*, $C_{17}H_{26}ON_2$, b. p. 230—245°/6 mm. The non-cryst. *methiodide* of the last-named compound passes into NMe_3 and a strongly basic liquid, b. p. 235—255°/11 mm. Normal evolution of NMe_3 appears to occur in part only, but it seems justifiable to assume that the basic N atom of aphyllidine is in dicyclic union.

H. WREN.

Alkaloid extracted from the root of *Stemona tuberosa*, Loureiro (a drug from Annam). E. LOBSTEIN and J. GRUMBACH (Compt. rend., 1932, 194, 386—389).—*Stemonine*, $C_{22}H_{33}O_4N$, m. p. 160°, $[\alpha]_D +76.5^\circ$, extracted from the root by the Stas-Otto method, is slightly basic, contains a pyrrole nucleus, but exhibits no phenolic, aldehydic, or ketonic reactions, neither does it contain OMe or OEt groups. Its physiological effects are described.

J. L. D'SILVA.

New alkaloid from *Holarrhena antidysenterica* seeds. R. D. HAWORTH (J.C.S., 1932, 631—634).—*Norconessine*, $C_{23}H_{35}N_2$, b. p. 238—240°/0.7 mm. [*dihydrogen dioxalate*, m. p. 225—227° (decomp.); *dihydrochloride*, m. p. 340° (decomp.)], is isolated, and separated from conessine by virtue of the greater solubility of its H oxalate in H_2O . It is oxidised by aq. HIO_3 to *dihydroxynorconessine*, basic, m. p. 264—266°, the decomp. of which by heating above its m. p. gives vapours that give the pyrrole reaction. *Norconessine dimethiodide*, m. p. 310—312° (decomp.), when treated with Ag_2O in aq. solution gives NMe_3 and *aponorconessine*, $C_{23}H_{33}N$, b. p. 190—192°/0.2 mm. [*picrate*, m. p. 244—245°; *methiodide*, m. p. 274—276° (not further degraded by aq. Ag_2O)], the *methochloride* of which (from *methiodide* and $AgCl$) is reduced by $Na-Hg$ and H_2O to *dihydroaponorconessine*, b. p. 190°/0.3 mm. [*picrate*, m. p. 260° (decomp.)].

H. A. PIGGOTT.

Alkaloids of the bark of *Holarrhena antidysenterica* (Kurchi bark). II. S. GHOSH and I. B. BOSE (Arch. Pharm., 1932, 270, 100—108; cf. A., 1928, 1265).—*Kurchine*, $C_{23}H_{35}N_2$ [*H oxalate*, +0.25 H_2O , m. p. 221°; *dihydrochloride*, + H_2O , decomp. 220°; *dihydrobromide*; *dihydriodide*, m. p. 275° (decomp.); *sulphate*, decomp. 270°; *chloroplatinate*, decomp. from 240°; *chloroaurate*, m. p. 160—166° after sintering at 120°], has m. p. 75° after sintering at 73°, $[\alpha]_D -7.5^\circ$ in $CHCl_3$, +6.4° in $EtOH$. *Kurchichine*, $C_{20}H_{26}ON_2$ [*dihydrochloride*, m. p. above 260°; *dihydrobromide*, m. p. 260° (decomp.); (*di*)-*hydriodide*, m. p. 259—260°; *sulphate*, +2 H_2O , and *oxalate*, m. p. above 270°; *chloroplatinate*, decomp. from 210°; *chloroaurate*, decomp. from 195°], has m. p. 175° and $[\alpha]_D -11.44^\circ$ in $CHCl_3$, -8.45° in $EtOH$. Colour and pptn. reactions of the bases are recorded.

R. S. CAHN.

Synthesis of quinine. K. KINDLER (Chem.-Ztg., 1932, 56, 165).—A review (cf. A., 1931, 1433; this vol., 289).

R. K. CALLOW.

New reactions of quinine salts, and a new volumetric method of determining the alkaloid.

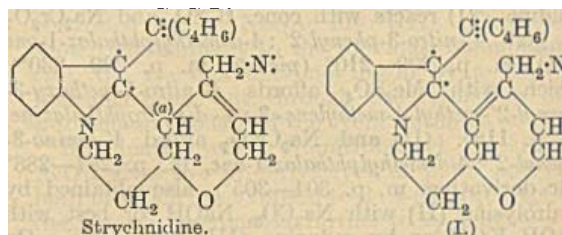
M. J. PAPAVASSILIOU (J. Pharm. Chim., 1932, [viii], 15, 167—177).— $PdCl_2$ gives an amorphous ppt. with quinine, which becomes cryst. if the pptn. is carried out in the presence of Cl_2 water. If CrO_3 is also present, quinine gives a yellow, amorphous ppt., and strychnine a cryst. ppt. Quinine reduces $K_2Cr_2O_7$ or $KMnO_4$ in presence of H_2SO_4 , and may be determined by adding excess of $KMnO_4$ to a hot H_2SO_4 solution, then excess of $H_2C_2O_4$, and titrating the excess with $KMnO_4$.

A. J. MEE.

Quantitative separation of pilocarpine from quinine by means of gallotannin. M. NIERENSTEIN (Analyst, 1932, 57, 94—95; cf. B., 1929, 615).—Quinine gallotannate adsorbs from 15 to 18% of alkaloidal pilocarpine, although the quinine is completely pptd.

T. McLACHLAN.

Strychnine and brucine. XV. *neo*Strychnidine and derivatives. O. ACHMATOWICZ (the late) W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1932, 486—500).—"Methyl- ψ -strychnidine" (A., 1927, 888) is formed from "methyl- ψ -strychnidine methiodide," which is identical with methyl*neo*strychnidinium iodide, by loss of MeI , and is also obtained by heating the similarly prepared benzyl- and ethyl-*neo*strychnidinium chlorides; it is an isomeride of strychnidine, and the name *neo*strychnidine (I) is proposed (cf. also A., 1927, 1208). It differs from strychnidine merely in the position of a double linking and the following formulæ are suggested [a C atom of the C_4H_8 group may possibly be interpolated at (a)]:



Benzylstrychnidinium hydroxide, m. p. 306—307° (+1 H_2O), prepared by action of aq. Ag_2O on the chloride (prep. improved) gives (I) on thermal decomp. Strychnidine benzylochloride (A) when distilled with 10% KOH in MeOH until the temp. reaches 140° gives (I) and *methoxybenzylidihydroneostrychnidine* (II), b. p. 268—271°/1 mm. This on electrolytic reduction (cf. A., 1924, i, 1337) gives *methoxybenzyltetrahydrostrychnidine*, m. p. 106—107°; it does not react with MeI , but in its presence in $COMe_3$ gives a mixture of isomeric oxyderivatives, $C_{29}H_{34}O_3N_2$ (A), m. p. 249°, (B), m. p. 269°, neither of which could be acetylated or converted into an oxime or a semicarbazone. Decomp. of (II) with 20% H_2SO_4 at its b. p. gives (I) and (after addition of NaI) *benzylneostrychnidinium iodide*, m. p. 238—240° (decomp.) (+1 $MeOH$, m. p. 186—188°) [*chloride* ($AgCl$), m. p. 230—232° (decomp.)]; if derived from insufficiently purified (II) the iodide on decomp. gives also *oryneostrychnidine*, $C_{21}H_{24}O_2N_2$, m. p. 239—240°. Similarly, from *strychnidine ethiodide*, m. p. 335° (*chloride*, m. p. 300—302°), *methoxyethylidihydroneostrychnidine* (III), m. p. 102—103° (*methiodide*, m. p. 258—260°), *methoxyethyltetrahydrostrychnidine*, m. p. 175—176°, *ethylneostrychnidinium*

iodide, m. p. 285—286° (decomp.), and chloride, m. p. 285—286° (decomp.) [reconverted into (III) by 20% KOH-MeOH], and (I) are prepared. The use of NaOBu^t in BuOH in place of KOH-MeOH with the benzyl-, ethyl-, and methyl-strychninium salts gives the corresponding butoxyalkyldihydrostrychnidines [and (I)], which were not isolated cryst., but were converted into (I) and derivatives as above. CH₂PhCl and MeI convert (I) into its quaternary salts, but only the more sparingly sol. forms were obtained.

Reduction of (I) electrolytically at 100° or with H₂ and Pd-charcoal gives dihydrostrychnidine (A), m. p. 215—216°. Oxidation of methoxymethyldihydrostrychnidine (IV) with KMnO₄ in COMe₂ gives a substance, C₂₃H₃₀O₃N₂.COMe₂, m. p. 167—168°, converted by MeI at 100° into oxy- (IV) [(B) form of A., 1927, 888 (?), C₂₃H₃₀O₃N₂, m. p. 305—306°, which does not react with Ac₂O, NH₄OH, or (CO-NH₂)₂NH, and is demethylated by 20% H₂SO₄ at its b. p. to the oxymethylnestrychnidinium salt (iodide, m. p. 238—240°; chloride, glassy, on thermal decomp. gives a gum). The iodide, m. p. 238—240°, is also obtained by a similar demethylation of oxymethoxydihydrostrychnidine (A) (*loc. cit.*). A second substance, C₂₂H₂₈O₄N₂, m. p. 186—188°, is produced in small amount by the oxidation.

Tetrahydrostrychnine methosulphate, m. p. 266—268° (decomp.), *methiodide*, m. p. 312—314° (decomp.), *methochloride*, m. p. 270—272°, and *benzylchloride*, m. p. 202—204°, are described. The methosulphate and methochloride are converted by MeOH-KOH at 100° into a mixture in which (IV), methoxymethylhexahydrostrychnine, and (probably) (I) and tetrahydrostrychnine were detected by electrolytic reduction; the crude mixture with boiling 20% H₂SO₄ gives methylnestrychnidinium iodide, and tetrahydrostrychnine (?) and its metho-salt [*methiodide*, m. p. 242—243°; *methochloride*, m. p. 265—267°, converted into (I) by thermal decomp.]. *Tetrahydrostrychnine benzyl iodide*, m. p. 205—207° [*chloride*, amorphous, ready decomp. to (I)], is similarly prepared. The action of KOH-MeOH at 110° on CH₂Ph-NMe₂Cl or CH₂Ph-NPhMe₂Cl gives CH₂Ph-OMe; NaOBu^t in Bu^tOH similarly gives MeOBu^t and NPhMe₂ with NPhMe₂I. H. A. PREGOTT.

Strychnos alkaloids. LXIII. Bromination of tetrahydrostrychnine and its oxidation to strychnine-*p*-carboxylic acid. H. LEUCHS and H. BEYER (Ber., 1932, 65, [B], 201—207).—Bromination of the alkaloid C₂₁H₂₆O₂N₂ in H₂O yields *dibromotetrahydrostrychnine*, C₂₁H₂₄O₂N₂Br₂, m. p. 264—266° (slight decomp.), [α]_D²⁵ -174.9°/d in CHCl₃ [*hydrobromide*; *methiodide*, m. p. (vac.) 285° (decomp.); O-Ac derivative C₂₃H₂₆O₃N₂Br₂, m. p. 260—261°, [α]_D²⁵ -163.2°/d in CHCl₃ and its *methiodide*, m. p. 280° (decomp.); the O-Ac compound is identical with that formulated C₂₁H₂₄O₂N₂Br₂]. Hexahydrostrychnine, similarly brominated, yields *dibromohexahydrostrychnine*, C₂₁H₂₆O₂N₂Br₂, m. p. about 210° or (+MeOH) m. p. 135—138° (decomp.), [α]_D²⁵ -92.2°/d in CHCl₃, also obtained by hydrogenation of the tetrahydro-base in presence of AcOH and PtO₂. The *methiodide*, m. p. 262° (decomp.), and Ac derivative, C₂₃H₂₈O₃N₂Br₂, m. p. 184—186° (obtained also by

hydrogenating the acetylated base, C₂₃H₂₈O₃N₂Br₂), are described. The compound C₂₃H₂₈O₃N₂Br₂.MeI has m. p. 258—259° (decomp.). Tetrahydrostrychnine is converted by HCl or HBr in AcOH into the O-Ac derivative, m. p. 166—168°, [α]_D²⁵ -78.6°/d in 0.1N-HCl. *Diacetyltetrahydrostrychnine methiodide*, m. p. 165—168° (decomp.) from COMe₂ or decomp. 90—95° from MeOH, and *acetyltetrahydrostrychnine methiodide*, m. p. 310° (decomp.) after becoming discoloured at 290°, are described. Revision of the oxidation of tetrahydrostrychnine with CrO₃ shows that the amino-acid, C₂₁H₂₂O₄N₂, is *strychnine-*p*-carboxylic acid*, C₂₂H₂₂O₄N₂; this conclusion is confirmed by analyses of the sulphate, hydrochloride, hydrobromide, Et ester hydrochloride, and Et ester methiodide. Dihydrostrychnine-*p*-carboxylic acid, C₂₂H₂₄O₄N₂, its *perchlorate* and *hydrochloride*, [α]_D²⁵ +32.9°/d, are described. H. WREN.

Strychnos alkaloids. LXIV. Oxidations with permanganate in the brucine series and reduction of the acids formed by degradation. H. LEUCHS and F. KROHNKE (Ber., 1932, 65, [B], 218—226).—Brucinic acid is converted by MeOH-HCl and subsequently by MeI in MeOH at 100° into the Me ester and the Me₂ ester, C₂₆H₃₂O₃N₂, m. p. 151° after softening at 147°, hydrolysed to the substance C₂₄H₂₈O₃N₂, m. p. 207—211° (decomp.). Similar esterification of brucinic acid affords Me₂ N-methylbrucinolate hydrate, the so-called "methiodide" of which is decomposed by 2N-KHCO₃ and CHCl₃ to a non-cryst. resin which yields the hydriodide, C₂₆H₃₄O₃N₂.HI, m. p. 140—144°. The so-called "methiodide" of the Me₂ ester of N-methylbrucinonic acid oxime hydrate (A., 1923, i, 941) is transformed by N-KHCO₃ and CHCl₃ into the ester C₂₆H₃₃O₃N₂, m. p. 80° after softening at 75° and m. p. 110° (decomp.) or 110—119° (decomp.) (from H₂O or AcOEt) after re-solidification. The *hydrochloride*, *hydrobromide*, *hydriodide*, m. p. 184° after softening, and *perchlorate* are described. The *oxime hydrate* of N-methylbrucinonic acid (also *pentahydrate*) and the *oxime* of Me brucinonate *hydroperchlorate* have been prepared.

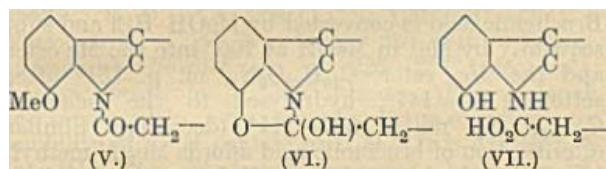
Catalytic reduction (PtO₂) of brucinic acid in 50% AcOH gives brucinolic acid in 75% yield. Electrolytic reduction in presence of 50% H₂SO₄ affords *dihydrobrucinonic acid*, decomp. about 500°, [α]_D²⁵ +64.9°/d in 0.1N-NaOH [Ac derivative, m. p. 275° (decomp.)], and *brucinolic acid*, C₂₃H₂₈O₇N₂, decomp. above 270°, [α]_D²⁵ +42.2°/d in 0.1N-NaOH; the last-named acid is also produced by electrolytic reduction of brucinolic acid, which is not reduced catalytically by H₂. Dihydrobrucinonic acid gives *dihydrobrucinonic acid*, [α]_D²⁵ +69.4°/d in N-NaOH, when electrolytically reduced.

[With H. SCHULTE-OVERBERG.] 2-Ketonucidine-3-acetic acid is oxidised by KMnO₄ to the substance C₁₉H₂₄O₄N₂, m. p. 248—250° (decomp.), [α]_D²⁵ +46.1°/d.

Carboxyapocucine is catalytically hydrogenated to two stereoisomeric acids C₁₆H₂₂O₄N₂, one of which, m. p. 292—294°, [α]_D²⁵ -6.3°/d, yields a *perchlorate*, [α]_D²⁵ -11.8°/d, whereas the other gives a *perchlorate*, [α]_D²⁵ -21.6°/d. H. WREN.

Methylation of vomisinic acid. Derivatives of vomicine. H. WIELAND and F. CALVET (Anal. Fís.

Quim., 1932, 30, 59—70).—The course of methylation of vomivicinic acid by MeI in MeOH-KOH is more complex than that of strychnine, and differs from the previous description (A., 1929, 708). Initially, the NH-group is attacked, giving *N*-methylvomivicinic acid (I), $C_{22}H_{38}O_5N_2$ (+5H₂O), m. p. 255° (decomp.), $[\alpha]_D^{25} +20.7^\circ$, and its *Me* ester (II), m. p. 262—266° (decomp.), $[\alpha]_D^{25} +38.6^\circ$ in EtOH (also prepared from the acid and CH₃N₃). Then ON-di-methylvomivicinic acid (III) (formerly described as the betaine), m. p. 242—244° (loses 2H₂O at 170°), $[\alpha]_D^{25} +48^\circ$ [hydriodide, m. p. 185—200° (loss of H₂O)], and its *Me* ester (IV), m. p. 214—216°, $[\alpha]_D^{25} +61.7^\circ$ in EtOH, are formed. Methylvomicine (V), m. p. 286—290°, $[\alpha]_D^{25} +16.4^\circ$ in EtOH, was once isolated; it gives vomicine with HCl (III) and CH₃N₃ yield (IV); (IV) is hydrolysed to (III). (IV) gives a methiodide, m. p. 210° (decomp.), yielding with Ag₂O a betaine (+4H₂O), m. p. 195—198°, $[\alpha]_D^{25} +14.2^\circ$ in EtOH [methiodide, m. p. 245—250° (decomp.)]. The structures (VI) and (VII) are suggested for vomicine and vomivicinic acid.



Hydrogenation of (IV) yields the dihydro-compound, m. p. 183—185°. Methylation of bisdehydrovomivicinic acid gives an ester (hydrochloride, $C_{48}H_{56}O_{10}N_4 \cdot 2HCl$, m. p. above 320°), hydrolysed to an acid, $C_{48}H_{52}O_{10}N_4$, decomp. 290°.

Benzylidenemomicine, m. p. 280° (decomp.), is formed by condensing vomicine with PhCHO in EtOH. "Benzoylvomicine hydrochloride" (A., 1929, 708) is an additive compound of vomicine and BzCl. An analogous additive compound, m. p. 185°, is formed by dihydrovomicine. Vomivicinic acid nitrosoamine has m. p. 190° (decomp.). R. K. CALLOW.

Deoxycodine. III. Constitution of the so-called α -dihydrodeoxycodine. Bisdihydrodeoxycodine. E. MOSETTIG, F. L. COHEN, and L. F. SMALL. IV. Tetrahydrodeoxycodine. L. F. SMALL and F. L. COHEN (J. Amer. Chem. Soc., 1932, 54, 793—801, 802—809; cf. A., 1931, 1077).—III. The contradiction presented in the supposed existence of the isomeric non-phenolic bases dihydrodeoxycodine-D (I) and α -dihydrodeoxycodine is removed with the discovery that the latter is bimol.; it is renamed bisdihydrodeoxycodine (II). α -Chlorocodide is reduced catalytically (Pd-BaSO₄) to mainly (I), according to the amount of catalyst used; with Pd-CaCO₃ or PtO₂, (II) results. Bromo- and iodo-codides behave like α -chlorocodide, whilst β -chlorocodide gives (I) and tetrahydrodeoxycodine irrespective of the catalyst. (II), obtained as a glassy solid, has $[\alpha]_D^{25} -113.3^\circ$ in EtOH, and gives a methiodide, m. p. 246—250° (decomp.), $[\alpha]_D^{25} -8.6^\circ$ in EtOH, and an amorphous dimethiodide, m. p. 230—250° (gradual decomp.), $[\alpha]_D^{25} -71.5^\circ$ in CH₂Ph-OH. (II) could not be reduced electrolytically in H₂SO₄. Partial reduction of α -chlorocodide gives a glassy

solid, not distillable at 200°/1 mm., whilst β -chlorocodide affords a little tetrahydrodeoxycodine and much unchanged material.

IV. Tetrahydrodeoxycodine (III), always obtained from ordinary solvents as the hemihydrate (IV), m. p. 141—147°, $[\alpha]_D^{25} -32.4^\circ$ in 95% EtOH, $[\alpha]_D^{25} -66.0^\circ$ in C₆H₆, is obtained anhyd. with m. p. 123—124°, $[\alpha]_D^{25} -72.3^\circ$ in C₆H₆, by vac. sublimation of (IV), changing after several months into a second anhyd. form, m. p. 157—158°, $[\alpha]_D^{25} -70.2^\circ$ in C₆H₆, $[\alpha]_D^{25} -33.6^\circ$ in 95% EtOH. (III) and MeI in MeOH-NaOMe give the methiodide, m. p. 256—257°, $[\alpha]_D^{25} -3.54^\circ$ in EtOH, of tetrahydrodeoxycodine *Me* ether, an oil [methochloride, m. p. 255—256° (decomp.), $[\alpha]_D^{25} -9.5^\circ$ in H₂O, prepared from the methiodide and AgCl, and converted by distillation at 0.4 mm. into the ether; hydriodide, m. p. 217—218° (sinters at 97—100°), $[\alpha]_D^{25} -21.8^\circ$ in EtOH]. The methiodide of (III) is decomposed by boiling 50% KOH to *dc*-N-methyltetrahydrodeoxycodine (V), m. p. 152—154°, $[\alpha]_D^{25} +66.2^\circ$ in MeOH, reduced catalytically to a dihydro-derivative (VI), m. p. 148—150°, $[\alpha]_D^{25} -14.5^\circ$ in 95% EtOH (hydrochloride, m. p. 251—252°, $[\alpha]_D^{25} -82.1^\circ$ in 95% EtOH). Dihydrodeoxycodine-A methiodide and 20 or 50% KOH give, according to the length of treatment, unchanged methiodide, the methohydroxide, or crude (V); hydrogenation of the tarry reaction mixture affords (VI). The identity of (III) with dehydroxytetrahydrocodeine and with dihydrothebacodine is discussed. C. J. WEST (b).

Nomenclature of alkaloids similar to berberine. W. AWE (Arch. Pharm., 1932, 270, 156—162).—It is proposed that tetrahydroprotoberberine be called "berbine" and that the names of related alkaloids be derived from this. R. S. CAHN.

Trypanocidal action and chemical constitution. XII. Arylthioarsenites derived from κ -thiolundecic acid. A. COHEN (J.C.S., 1932, 593—598; cf. this vol., 70, 180).— κ -Disulphidoundecic acid (I), m. p. 92°, is prepared by interaction of Na₂S₂ and κ -bromoundecic acid in presence of NaHCO₃, and on reduction with Zn and HCl in aq. AcOH gives κ -thiolundecic acid (II), m. p. 47° [Hg mercaptide, m. p. 185—187° (decomp.)], which is readily oxidised to κ -sulphoundecic acid, m. p. 63—65° [Na₂S salt (+1H₂O)], by HNO₃ (d 1.4 or 1.2). κ -Xanthatundecic acid (III), m. p. 49°, is prepared as described by Bauer and Stockhausen (A., 1931, 824) and is converted into (II) by NH₃ in aq. EtOH, which then gives (I) with H₂O₂ as described by these authors; considerable differences occur, however, in their description of the m. p. and properties of (I), (II), and (III). Di-(κ -carboxydecyl)-benzamide-, m. p. 270° (decomp.: previous sintering), and -acetamide-*p*-thioarsenite, m. p. 117—118°, are prepared by interaction of κ -thiolundecic acid with benzamide- and acetamide-*p*-arsenoxides in aq. NaHCO₃. Both are toxic to *T. equiperdum*. H. A. PIGGOTT.

***p*-Xylylarsinic acid.** A. COHEN and H. KING (J.C.S., 1932, 501—503).—*p*-Xylylarsinic acid, prepared both according to Michaelis (A., 1902, i. 411) or by the Bart-Schmidt reaction (this vol., 180), has m. p. 192°, and gives with HNO₃ (d 1.5) at -5°, or, better, with HNO₃-H₂SO₄ at -10°, the 6-NO-

derivative, m. p. 242° (decomp.). This is reduced by Fe(OH)₃ to an azoxy-compound and 6-amino-*p*-xylyl-2-arsinic acid, m. p. about 255° (decomp.) (Ac derivative, dimorphic, decomp. 238—258°, and above 300°), the orientation of which follows from its conversion by H₂O at 135° into *p*-xylylidine. Neither the NH₂- nor the NHAc-derivative has trypanocidal activity.

H. A. PIGGOTT.

Isomeric nitro- and amino-naphthylarsinic acids. C. R. SAUNDERS and C. S. HAMILTON (J. Amer. Chem. Soc., 1932, 54, 636—641).—Improved methods of separation of the isomeric NO₂-derivatives formed by nitrating α - and β -C₁₀H₇-NH₂ are given. 2-, m. p. 202° (decomp.), and 4-, not melted at 250°, -nitro-1-naphthylarsinic acids, prepared by the usual method, are reduced to 2-, decomp. about 216°, and 4-amino-1-naphthylarsinic acids, m. p. 210° [Ac, m. p. 271° (decomp.); N-carbethoxy-, m. p. 250°, and N- β -hydroxyethyl, m. p. 250°, derivatives]. 1-Nitro-, m. p. 192° (decomp.), 8-nitro-, m. p. above 265°, 1-amino-, m. p. 177° (decomp.) [Ac, m. p. 240—245° (decomp.)], and N-carbethoxy-, m. p. 191° (decomp.), derivatives], and 8-amino-2-naphthylarsinic acids are also prepared. 4-Benzeneazo-1-naphthylarsinic acid is obtained in 8% yield from 4-benzeneazo- α -naphthylamine.

C. J. WEST (b).

[Path to optically active germanium compounds.] E. KRAUSE (Ber., 1932, 65, [B], 374; cf. A., 1931, 1435; this vol., 181).—A reply to Schwarz (this vol., 291).

H. WREN.

Isolation of mercury from its organic derivatives. G. A. RAZUBAYEV and M. M. KOTON (J. Gen. Chem. Russ., 1931, 1, 864—874).—The production of metallic Hg by heating different types of compounds with H₂ under pressure in the presence of various solvents has been examined. No Hg is formed in 24 hr. from HgCl and HgPhCl in C₆H₆ below 325° or from *p*-C₆H₄Me·HgCl below 300° in EtOH. HgCl₂ gives 75% of Hg at 200° and the Ph and *p*-C₆H₄Me compounds up to 95%, and some aldehyde is also formed. In control experiments without H₂ no Hg was liberated, whilst a somewhat greater decomp. of HgCl₂ was observed in aq. solution; it is concluded that the reaction is favoured by ionisation.

Hg(CH₂Ph)₂ decomposes equally readily in C₆H₆ or EtOH, although EtOH is more effective at lower temp.; the presence of H₂ has no effect and the reaction is thus a simple pyrogenic decomp. into Hg and dibenzyl. The decomp. of HgPh₂ is, however, greatly assisted by H₂, and the products are Hg and C₆H₅, not diphenyl, so that H₂ actually takes part in the reaction; this is interpreted as a dissociation of the compound into Hg and the Ph radical which is then reduced to C₆H₅. Support for this view is found in the observation that in EtOH solution the presence of H₂ is no longer essential, the reduction of the free radical taking place at the expense of the solvent with the production of aldehyde; similarly, in Pr^oOH and PrⁿOH, EtCHO and COMe₂ are produced and other oxidisable compounds have the same effect. A quant. study of the decomp. of HgPh₂ shows that the reaction is not a simple one. It is independent of the concn.; the addition of free

Hg has no effect, but aldehyde greatly accelerates the reaction, whilst C₆H₆ and methylcyclohexane have the reverse effect.

G. A. R. KON.

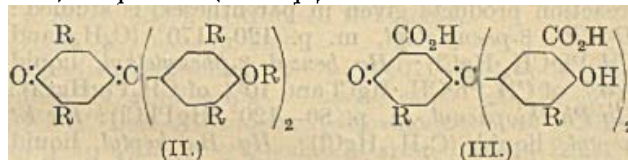
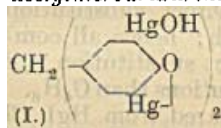
Decomposition of unsymmetrical mercuri-organic compounds: method of establishing the relative degree of electronegativity of organic radicals. II. M. S. KHARASCH and A. L. FLENNER (J. Amer. Chem. Soc., 1932, 54, 674—692; cf. A., 1925, i, 1107).—The effects of lengthening the C chain on the electronegativity of an aliphatic radical and of the introduction of various *o*-, *m*-, and *p*-substituents on the electronegativity of the Ph radical are studied. The validity of the method used (A., 1927, 165) for determining the relative electronegativity of org. radicals is discussed. A table of the order of electronegativity of numerous org. radicals is given and used to study (a) the existence of free radicals, (b) the relative electronegativity of aliphatic radicals, and (c) substitution in the C₆H₅ ring. Increase in the C chain causes a decrease in the electronegativity of straight-chain aliphatic radicals; alternation is not observed. *iso*-Radicals are less electronegative than the *n*-, but more so than *tert*.-groups. The introduction of Ph on C₃ of the Et radical causes a marked decrease in electronegativity. Direct substitution reduces the electronegativity of Ph; hence all compounds formed from C₆H₅ by direct substitution will be less reactive towards new substitutions than C₆H₅.

The following HgR'R'' are prepared from HgR'Cl and MgR''Br and the action of HgCl₂ (whereby Hg R'Cl and HgR''Cl are produced) and EtOH·HCl (reaction products given in parentheses) is studied: Hg Ph β -phenylethyl, m. p. 120—170° (C₆H₅ and CH₂Ph·CH₂·HgCl); Hg benzyl β -phenylethyl, liquid (90% of CH₂Ph·CH₂·HgCl and 10% of CH₂Ph·HgCl); Hg Ph thiophenyl, m. p. 80—120° (HgPhCl); Hg Et heptyl, liquid (C₇H₁₅·HgCl); Hg Bu heptyl, liquid (70% of C₇H₁₅·HgCl and 30% of HgBuCl); Hg Buⁿ Buⁿ, liquid (mainly HgBuⁿCl and a little HgBuⁿCl); Hg Et cyanide, m. p. 180° (decomp.) (HgEtCl); Hg *o*-anisyl cyanide, m. p. 175° (decomp.) (*o*-OMe·C₆H₄·HgCl); Hg Pr^o Prⁿ, liquid (85% of HgPr^oCl and 15% of HgPrⁿCl); Hg Ph *p*-chlorophenyl, prepared from *p*-C₆H₄Cl·MgCl, m. p. 190—210° (decomp.) (80% of *p*-C₆H₄Cl·HgCl and 20% of HgPhCl), prepared from MgPhCl, m. p. 190—210° (70% of *p*-C₆H₄Cl·HgCl); Hg Ph *o*-chlorophenyl, m. p. 90° (decomp.) (90—95% of *o*-C₆H₄Cl·HgCl and 5—10% of HgPhCl); Hg Ph *m*-chlorophenyl, m. p. 68° (decomp.) (*m*-C₆H₄Cl·HgCl); Hg *o*-chlorophenyl *m*-chlorophenyl, m. p. 165—200° (decomp.) (70% of *o*-C₆H₄Cl·HgCl); Hg Ph *o*-tolyl, m. p. 65° (decomp.) (HgPhCl); Hg *o*-tolyl *p*-tolyl, prepared from *o*- and *p*-Me·C₆H₄·MgCl, m. p. 195—200° and 200—210°, respectively (80% of *p*- and 20% of *o*-Me·C₆H₄·HgCl); Hg *o*-tolyl *p*-chlorophenyl, m. p. 210—230° (95% of *p*-C₆H₄Cl·HgCl); Hg Ph *p*-tolyl, m. p. 120—155° (decomp.) (90% of HgPhCl and 10% of *p*-Me·C₆H₄·HgCl); Hg Ph *m*-tolyl, m. p. 65—70° (decomp.) (80% of HgPhCl and 20% of *m*-Me·C₆H₄·HgCl); Hg *m*-tolyl *p*-tolyl, m. p. 180—205° (decomp.) (90% of *m*- and 10% of *p*-Me·C₆H₄·HgCl); Hg *o*-chlorophenyl *m*-chlorophenyl, m. p. 95—100° (decomp.) (80% of *m*- and 20% of *o*-C₆H₄Cl·HgCl); Hg *m*-tolyl *p*-chlorophenyl, m. p.

165—220° (decomp.) (90% p - $C_6H_4Cl \cdot HgCl$ and 10% m - $Me \cdot C_6H_4 \cdot HgCl$); Hg *o*-tolyl *o*-anisyl, liquid (o - $Me \cdot C_6H_4 \cdot HgCl$); Hg *m*-chlorophenyl *Me*, liquid ($HgMeCl$); Hg *o*-anisyl *p*-anisyl, m. p. 102° (decomp.) (o - $OMe \cdot C_6H_4 \cdot HgCl$); Hg *p*-anisyl α -naphthyl, m. p. 130—150° (decomp.) (α - $C_{10}H_7 \cdot HgCl$); Hg *o*-anisyl α -naphthyl, m. p. 200—202° (decomp.) (α - $C_{10}H_7 \cdot HgCl$).

C. J. WEST (b).

Mercury derivatives of certain phenols and polycyclic phenolic acids. M. DOMINIKIEWICZ (Rocz. Chem., 1932, 12, 79—88).—2 : 2'-Dioxyacetylmercuri-3 : 3' : 5 : 5'-tetra-acetylmercuridiphenyl and 2 : 2'-dihydroxy-3 : 3' : 5 : 5'-diacetylmercuridiphenyl are formed from 2 : 2'-diphenol and $Hg(OAc)_2$ in AcOH solution; in aq. solution the product is 2 : 2'-dihydroxy-3 : 3' : 5 : 5'-*o*'-tetra-acetylmercuridiphenyl. 4 : 4'-Diphenol yields 4 : 4'-dihydroxy-3 : 3'-diacetylmercuri- and -3 : 3' : 5 : 5'-*o*'-tetra-acetylmercuridiphenyl. The following further substances have been prepared and described: 4 : 4'-dihydroxy-3 : 3' : 5 : 5'-tetrahydroxymercuridiphenylmethane anhydride (I), dihydroxyacetylmercuri-hexa-acetylmercuriaurin (II, $R = Hg \cdot OAc$), hexa-acetylmercuriaurin, 4 : 4'-dihydroxy-3 : 3'-diacetylmercuridiphenylmethane-5 : 5'-dicarboxylic acid, triacetylmercuriaurintricarboxylic acid (III), 3- and 1-acetylmercuri-1- and -4-hydroxy- β -naphthoic acids (anhydrides), the triacetylmercuri-derivatives of naphthochromic-blue, 3-iodo-1-hydroxy- β -naphthoic acid, m. p. 190° (decomp.), and 1-iodo-4-hydroxy- β -naphthoic acid, m. p. 223° (decomp.).



R. TRUSZKOWSKI.

Rearrangement reactions of magnesium benzyl chloride. H. GILMAN and J. E. KIRBY (J. Amer. Chem. Soc., 1932, 54, 345—355).— $CH_2Ph \cdot MgCl$ (I) undergoes rearrangement reactions with various compounds. The rearrangement may be exclusively *ortho* or *para*, or of both types (in varying proportions depending on the reactants and experimental conditions). Some reagents (e.g., CO_2) behave normally. The rearrangements of (I) and related compounds containing the group $\cdot C \cdot Cl \cdot C \cdot MgX$, can be correlated with the allylic or three-carbon system rearrangements. (I) and Br give 63% of CH_2PhBr ; $PhCN$ affords 53.4% of $Ph \cdot CO \cdot CH_2Ph$; phenacyl chloride furnishes a product yielding only $BzOH$ on oxidation; diphenylcarbonyl chloride furnishes (after hydrolysis) $CH_2Ph \cdot CO_2H$ but no toluic acids; $AcCl$ gives o - $Me \cdot C_6H_4 \cdot Ac$ and related products; ethylene oxide affords an oil, b. p. 113—115°/10 mm., oxidised to $BzOH$ and terephthalic acid; the product from $CH_2Cl \cdot OEt$ indicates that approx. 53% of the reaction is normal, whilst 16% of *ortho* and 31% of *para* rearrangement occurs; with $ClCO_2Et$ approx. 20% of *ortho* rearrangement occurs; HCO_2Et gives both types of rearrangement (*para* comparatively small); CH_2PhCl gives 64.8% of $(CH_2Ph)_2$. Mg cyclohexyl-

methyl bromide and CH_2O afford 46% of β -cyclohexylethyl alcohol. C. J. WEST (b).

Sulphur addition with the aid of thiophosphoryl chloride and the catalysis of triaryl thiophosphate formation. H. B. GOTTLEB (J. Amer. Chem. Soc., 1932, 54, 748—750).— $P(OPh)_3$, b. p. 209—210°/1 mm., m. p. 17—22°, and $PSCl_2$ give 65% of Ph_3 thiophosphate, b. p. 230—240°/1 mm., m. p. 48°; tri-*o*-tolyl thiophosphate, b. p. 260—265°/1 mm., m. p. 45°, is similarly prepared. $PCl(OPh)_2$, b. p. 165—174°/1 mm., and $PSCl_3$ give Ph_2 chlorothiophosphate, b. p. 180—183°/1 mm., m. p. 64°, whilst $PPhCl_2$ affords phosphenyl thiocloride, $PPhSCl_2$, b. p. 150°/26 mm. Small quantities of PCl_3 catalyse the formation of triaryl thiophosphates from phenols and $PSCl_3$. C. J. WEST (b).

Non-identity of "pure" and "isoelectric" gelatins. R. J. WILLIAMS, L. FRIEDMAN, and D. M. WOODS (Science, 1932, 75, 199).—Migration to the anode occurs when electrodialysed, non-ionogenic, "pure" gelatin is electrolysed, indicating that "pure" and isoelectric gelatins are different.

L. S. THEOBALD.

Colours produced by the interaction of alloxan with amino-acids and proteins. F. LIEBEN and E. EDEL (Biochem. Z., 1932, 244, 403—412).—Arranged according to the intensity of the transient pink colour which they give by interaction with alloxan, the following NH_2 -acids form the descending series: cysteine and histidine (equal), glycine, glutamic acid, tryptophan, phenylalanine, arginine, asparagine, tyrosine, leucine, serine, valine, lysine. Proline gives no colour and cystine a colour peculiar to itself. The presence of a free NH_2 -group (but not of a free CO_2H group) is a necessary condition for the production of the colour. Some aromatic NH_2 -derivatives give no colour. The depths of the colours given by NH_4HS and varying amounts of alloxan attain maxima and a table showing the amount of alloxan corresponding with each max. can be used in determining the latter substance. The NH_4HS -alloxan colour is deepened by addition of $(NH_4)_2CO_3$. With proteins and animal organs the alloxan colour reaction runs parallel with the nitroprusside reaction and seems to depend on the presence of free SH groups (in addition to free NH_2 -groups).

W. MCCARTNEY.

Simplified micro-combustion method for determination of carbon and hydrogen. C. KURODA and M. WADA (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 143—159).—A method requiring about 0.01 g. of the material for analysis is outlined.

R. CUTHILL.

Semi-micro-determination of carbon, hydrogen, and nitrogen. H. BERGER (J. pr. Chem., 1932, [ii], 133, 1—12).—Details of apparatus etc. are given, which improve but do not perfect the determination of C, H, and N with 25—35 mg. of substance.

R. S. CAHN.

Determination of chlorine in organic substances by a wet method. B. SJOLLEMA and J. W. DIENSKE (Biochem. Z., 1932, 245, 76—79).—The Cl of org. substances is determined by oxidation

with alkaline KMnO_4 and titration of the Cl^- by Volhard's method. P. W. CLUTTERBUCK.

Distillation apparatus for the Parnas and Wagner micro-Kjeldahl method. F. A. HOPPE-SYLER (*Mikrochem.*, 1932, 10, 446—449).—The apparatus, described in detail, is of simplified construction and reduces condensation of H_2O to a min.; it also reduces the time required for distillation.

H. F. GILLBE.

Methods for determining formaldehyde. J. BÜCHI (*Pharm. Acta Helv.*, 1931, 6, 1—54; *Chem. Zentr.*, 1931, ii, 1172).—The H_2O_2 , Na_2SO_3 , Hg, and I methods give concordant results, but the NH_4Cl method gives vals. approx. 0.1% low. MeCHO and COMe_2 falsify all results, especially those of the I methods; EtOH influences only these. Directions for determining CH_2O in pure solutions with Na_2SO_3 , thymolphthalein, and $N\text{-HCl}$ are given.

L. S. THEOBALD.

Determination and separation of saligenin, salicylic acid, and salicylaldehyde. R. BERG, W. GRIMMER, and A. MÜLLER (*Chem.-Ztg.*, 1931, 55, 975).—The Et_2O solution of the three compounds is extracted with 0.05*N*- NaHCO_3 , which removes salicylic acid and some aldehyde. The solution is titrated with 0.05*N*- H_2SO_4 until colourless, an excess is added, and the solution boiled to expel CO_2 , cooled, and titrated with 0.05*N*- NaOH until yellow; the difference corresponds with salicylic acid. The Et_2O is removed from the ethereal layer and the aldehyde

converted into salicylaldehyde. The solution is extracted with Et_2O , the extract shaken with $N\text{-NaOH}$, and the alkaline solution neutralised with AcOH and treated with 3% CuSO_4 solution to remove the aldehyde. After filtration the saligenin is extracted from the filtrate with Et_2O and weighed after removing the solvent. A. R. POWELL.

Iodometric determination of caffeine. G. WALLRABE (*Apoth.-Ztg.*, 1931, 341—343; *Chem. Zentr.*, 1931, ii, 1170—1171).—The caffeine compound is acidified with dil. H_2SO_4 and a given vol. of 0.1*N*-I solution added. The pptd. $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HI}_4$ is collected and the filtrate titrated with $\text{Na}_2\text{S}_2\text{O}_3$; 1 c.c. of 0.1*N*-I solution = 4.85 mg. of caffeine.

L. S. THEOBALD.

2:4-Dinitrophenylhydrazine in determination of carbonyl compounds. O. FERNÁNDEZ, L. SOCIAS, and C. TORRES (*Anal. Fis. Quím.*, 1932, 30, 37—49).—Under definite conditions in aq.-alcoholic H_2SO_4 solution, the 2:4-dinitrophenylhydrazones of camphor, menthone, pulegone, citral, and furfuraldehyde are pptd. in 98—99% yield, and accurate quant. determinations are claimed by this method.

R. K. CALLOW.

Detection of quinotoxine in presence of quinine. M. BACHSTEZ. **Detection of strychnine.** A. W. NUNN.—See this vol., 301.

Modification of Van Slyke nitrogen distribution method. J. W. CAVETT.—See this vol., 438.

Biochemistry.

Calorimetry of blood and blood constituents from healthy and diseased men and animals. A. GIGON, M. NOVERRAZ, and E. HOFFMANN (*Biochem. Z.*, 1932, 245, 440—451).—The calorific val. of blood (man, cow, bull, calf, horse, pig, rabbit) and of its constituents (corpuscles, serum, plasma) varies with age, species, and state of health. In some cases the serum has a higher calorific val. than has the plasma, in others the reverse is true. Disease in man has often great effects on the val.; pernicious anaemia and Schüller-Christian disease lead to particularly pronounced variations. There are sometimes unexpectedly pronounced variations in the amount of C and N in dried blood. W. MCCARTNEY.

Chamber for measuring oxygen consumption of animals. A. E. KOEHLER (*J. Biol. Chem.*, 1932, 95, 67—72).—A simple type of chamber for animals such as dogs is described. F. O. HOWITT.

Measurements of oxygen consumption of small animals. J. E. DAVIS and H. B. VAN DYKE (*J. Biol. Chem.*, 1932, 95, 73—78).—The apparatus of Koehler (cf. preceding abstract) is modified for use with animals such as mice and rats.

F. O. HOWITT.

Determination of carbon dioxide tension in small amounts of blood. J. K. W. FERGUSON (*J. Biol. Chem.*, 1932, 95, 301—310).—A micro-method of determining the CO_2 tension in blood by measuring the reduction in the vol., after addition of 3% aq.

NaOH , of a bubble of air equilibrated with the blood in a capillary tube, is described. The experimental error is <2 mm. Hg. The effect of glycolysis may be overcome by a preliminary washing of the capillary tube with aq. NaF .

A. LAWSON.

Dog blood. D. B. DELL, H. T. EDWARDS, M. FLORKIN, and R. W. CAMPBELL (*J. Biol. Chem.*, 1932, 95, 143—152).—The physico-chemical properties of oxygenated dog's blood were determined and compared with those of human blood. The buffer val. of the serum is less than (approx. 16%), and that of the whole blood equal to, those of the corresponding fluids of man. No appreciable differences exist in the distribution of Cl^- and HCO_3^- between cells and plasma, in the O_2 dissociation curve or in the CO_2 tension of the arterial blood. Dog's blood has a Cl^- content 4—8% greater than that of human blood and the ratio Na^+/K^+ of the corpuscles is very high. F. O. HOWITT.

Animal species and dissociation curve of blood. H. KONO (*Japan. J. Med. Sci.*, 111, Biophys., 1931, 2, 35—45).—Individual and species differences are due mainly to quant. differences in the alkali reserve of the blood. CHEMICAL ABSTRACTS.

Influence of salts on the dissociation curve of haemoglobin. H. KONO (*Japan. J. Med. Sci.*, 111, Biophys., 1931, 2, 1—24).—The effect is attributed to the physical action of the ions; there is no difference between ions in depressing the dissociation curve.

The action is slight compared with that of acid and alkali.

CHEMICAL ABSTRACTS.

Copper as a supplement to iron in hæmoglobin formation in the pig. C. A. ELVERJEM and E. B. HART (J. Biol. Chem., 1932, 95, 363—370).—When pure Fe is added to the whole-milk diet of anæmic pigs, a small increase in the hæmoglobin content of the blood takes place, but complete recovery is obtained only after addition of Cu. A. LAWSON.

Spectrum and catalytic effects of iminazole-hæmin. W. LANGENBECK (Naturwiss., 1932, 20, 124).—When an aq. NH_3 or Na_2HPO_4 solution of hæmin is brought in contact with iminazole or 4(5)-methyliminazole (I) the colour changes from brown to reddish-brown. The absorption spectrum of an aq. NH_3 solution containing 0.1% of (I) and 0.005% of hæmin consists of three bands very similar to the spectrum obtained from an alkaline solution of methæmoglobin.

The catalytic and peroxidase effects of hæmin are influenced by the presence of methyliminazole and the p_{H} optimum is 7. The catalytic effect of hæmin with different bases and the p_{H} optima are discussed.

W. R. ANGUS.

Micro-determination of blood-peroxidase. H. MASAMUNE and K. KODAMA (J. Biochem. Japan, 1932, 14, 475—479).—The method of Willstatter and Stoll (A., 1918, i, 555) is modified for use with 0.01 c.c. of blood.

F. O. HOWITT.

Catalase of leucocytes. K. G. STERN (Z. physiol. Chem., 1932, 204, 259—282).—The catalase content of leucocytes of different origin was compared. The enzyme solutions were obtained from plasmolysates and extracts from dried preps. The activity is of the same order as that of similarly treated erythrocytes. For the polymorphonuclear exudate leucocytes of the rabbit, the optimum p_{H} is 7, the temp. coeff. Q_{10} is 1.3 for 0—18°. At 37° the activity is depressed, at 52° inactivation is complete. The enzyme is specifically inhibited by Fe^{2+} , HCN, and CO, but not by 2:2'-dipyridyl, tripyridylferrous sulphate, and H_2 . Inhibition by CO_2 and O_2 is due to change of p_{H} . The catalysed reaction is usually unimol.; the catalase of leucocytes agrees in general with that of liver and erythrocytes.

J. H. BIRKINSILAW.

Blood-chlorine during asphyxiation. II. T. SASO (J. Biochem. Japan, 1932, 14, 419—438).—Oral administration of H_3PO_4 , AcOH , and other acids to rabbits induces hyperchloraemia. The plasma-Cl increases and then falls to normal or subnormal levels, according to whether lethal or sub-lethal doses are administered. Such phenomena are characteristic of asphyxiation, the relation of which to acidosis is discussed (cf. A., 1931, 375).

F. O. HOWITT.

Blood analysis. Determination of chlorine, sodium, potassium, lecithin, cholesterol, cholesterol ester, and neutral fat in blood-serum. L. WACKER (Biochem. Z., 1932, 245, 149—158).—Modifications of known methods are described.

P. W. CLUTTERBUCK.

Determination of small amounts of bromide in blood and urine. K. O. MØLLER (Biochem. Z., 1932,

245, 282—289).—By means of a method based on that of Toxopéus (A., 1930, 639) the bromide content of biological fluids (blood, urine) can be determined in 1 c.c.

W. MCCARTNEY.

Spectrographic examination of human body-fluids. L. KARCZAG and M. HANÁK (Biochem. Z., 1932, 245, 166—173).—The selective absorption curve of normal human blood-serum is a combination of the individual curves of the albumin and globulin fractions. Differences in age, blood group, or type of illness had no influence on the selective absorption of blood-sera. Treatment with CH_2O , heat-inactivation, and irradiation with X-rays influence the selective absorption of sera from different sources in the same way. The absorption curve of cerebrospinal fluid is the interference curve of the individual selectively absorptive components (proteins, uric acid, etc.). Treatment of the fluid with CH_2O caused a change in absorption. The ultra-filtrate of the serum gave in no case a pure uric acid curve, and of cerebrospinal fluid showed a flatter curve than did the fluid itself.

P. W. CLUTTERBUCK.

Urobilinogen in blood-serum. L. F. LOEB (Biochem. Z., 1932, 244, 426—430).—Urobilinogen is probably not produced in the kidneys. By a modification of Niemann's method (A., 1925, i, 1206) it can be determined in urine and in blood-serum in concns. of < 3 mg. per 100 c.c. In various diseases the urobilinogen content of the urine increases, sometimes considerably, and in icterus catarrhalis and cirrhosis of the liver there is also a great increase in the amount in the blood-serum.

W. MCCARTNEY.

Refractometric investigation of serum-protein. VIII. Determination of the protein fractions in horse-serum. D. VON DESEO (Biochem. Z., 1932, 244, 382—389; cf. A., 1931, 1319).—Provided that 50% aq. $(\text{NH}_4)_2\text{SO}_4$ is used for the pptn., the refractometric method of determination yields results in good agreement with those obtained by the gravimetric method after twelve-fold dilution.

W. MCCARTNEY.

Fractional precipitation of serum-globulin at different hydrogen-ion activities. H. K. REINER and L. REINER (J. Biol. Chem., 1932, 95, 345—361).—Globulin is pptd. from normal and anti-pneumococcus horse serum at p_{H} 5.0—7.0. Repeated pptn. at p_{H} 5.1 and 6.8, respectively, gives from both sera two fractions, the p_{H} pptn. curves, N content, and acid- and base-binding capacities of which are different. The N val. for the ppt. from a mixture of the two fractions compared with that of the single fractions pptd. under the same conditions supports the view that combination takes place in the mixed solutions either by interionic forces or by virtue of the tendency which amphions have of association near their isoelectric points.

A. LAWSON.

Critical temperature of serum. Ionic equilibrium of serum as a function of its temperature. V. P. L. DU NOÛY (Ann. Inst. Pasteur, 1932, 48, 187—207).—When horse serum is heated at 58° for 10 min. and then diluted with distilled H_2O , the globulin which is pptd. separates in a dispersed form which tends to remain in suspension,

whereas if the serum is unheated or heated for 10 min. at $<57^{\circ}$, the pptd. globulin tends to fall rapidly out of suspension. The crit. temp. is remarkably sharply defined within the limits of about 1° and is lower for longer periods of heating, being 58° for 5 min. and 53° for 2 hr. A similar phenomenon is observed with the sera of other animals, the crit. temp. varying according to the animal from 55° to 59° for a period of heating of 10 min. The relation of this phenomenon to the state of the globulin and the modification induced in the latter by heat is discussed.

W. O. KERMAK.

Calcium and calcaemia in man. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1932, 14, 85—196).—A lecture.

Phosphorus partition of the blood of animals and chemical diagnosis of aphosphorosis. A. I. MALAN (J. S. African Chem. Inst., 1932, 15, 4—9).—In aphosphorosis the inorg. P of the blood of cattle and sheep is lower than in normal healthy animals, and indications of the disease can be obtained in the early stages when clinical symptoms are insufficient to render a diagnosis possible. Addition of bone meal or Na_2HPO_4 to the basic diet raises the blood-inorg. P to normal levels and improves the condition of the animals.

P. G. MARSHALL.

Bound sugar of blood. A. M. DE VRIES (Biochem. Z., 1932, 245, 473—479).—The amount of bound sugar (hydrolysable substance) in the blood of rabbits exhibits considerable individual variations, but is only slightly affected by the taking of samples of the blood or by injection of physiological NaCl solutions. Injection of liver extracts, of insulin, or of the materials separated from crude insulin during purification has no effect on the amount of bound sugar in the blood.

W. MCCARTNEY.

Behaviour of the so-called bound sugar (hydrolysable reducing substance) in human blood-plasma. A. M. DE VRIES (Biochem. Z., 1932, 245, 480—487; cf. preceding abstract).—Neither in healthy nor in diseased persons can any relation between the amounts of free and bound sugar of the blood-plasma be found. The blood in cancer and tuberculosis more often contains a high proportion of bound sugar than does that of healthy persons or persons suffering from other diseases.

W. MCCARTNEY.

Distribution of sugar between blood-cells and plasma. M. JACOBY and H. FRIEDEL (Biochem. Z., 1932, 244, 357—365; A., 1931, 858).—Of the sugar content of the blood the cells usually contain considerably less than 30% and this amount is rarely exceeded. When the content is high the proportion in the cells is less than normal, since their capability to take up sugar is limited. The concn. of sugar in the cells is lower at acid reaction than at neutral because the cell vol. is greater in the former case than in the latter. The increase in vol. results from absorption of H_2O .

W. MCCARTNEY.

Modifications of glucose and water in the blood resulting from administration of glucose and water. A. GALAMINI and E. SERIANI (Atti R. Accad. Lincei, 1931, [vi], 14, 378—381).—Administra-

tion (to man) of glucose (60 g.) in H_2O (200 c.c.) in a no. of doses increases the blood-sugar more than when the glucose is given in one dose. With further increase in the no. of doses, the blood-sugar increases less or may even decrease without preliminary increase. In general, the H_2O content of the blood diminishes slightly as the sugar increases and *vice versa*.

T. H. POPE.

Blood-sugar in man following rectal administration of glucose. E. L. SCOTT and J. F. B. ZWEIGHART (Arch. Int. Med., 1932, 49, 221—226).—Rectal administration of glucose to fasting subjects produced no rise in the blood-sugar curve from the fasting level. The slight fall observed may be due to increased pancreatic activity following the absorption of a small quantity of glucose.

H. DAVSON.

Glycolysis. A. P. BARER (J. Clin. Invest., 1931, 10, 507—520).—Glycolysis is not correlated with age or sex. The optimal temp. is 37° ; citrates and oxalates retard, whilst fluorides arrest, it. Glycolysis is not dependent on the initial glucose concn. of the blood, and it is not affected by insulin *in vitro*.

CHEMICAL ABSTRACTS.

Determination of glutathione. M. DELAVILLE and L. KOWARSKI (Compt. rend. Soc. Biol., 1931, 106, 1220—1224; Chem. Zentr., 1931, ii, 2362).—The direct iodometric titration of glutathione in hepatic and arterial blood yields much smaller vals. than does the indirect method of oxidising the SH-compounds with excess of I, in which the time allowed for oxidation has an effect. A method for determining total glutathione is advanced. In the blood of horses this content varies with the individual, the mean val. being approx. 50 mg. per 100 c.c.

L. S. THEOBALD.

Antiprotease and globulins. A. FISCHER (Biochem. Z., 1932, 244, 464—485; cf. A., 1931, 1441; this vol., 73).—There is an abs. correspondence between the antiprotease action and the globulin content of blood-serum. With serum-albumin antiprotease forms complexes which, physico-chemically, closely resemble natural globulins. It is concluded that the latter are produced by the action of heparin alone, which very rapidly converts serum-albumin into globulin, on a sp. protein of blood.

W. MCCARTNEY.

Nature of Bordet's "colloïde de bœuf" and of "conglutinin." I. GYÖRFFY (Biochem. Z., 1932, 244, 435—439).—The flocculated material obtained by Bordet and Streng and supposed to consist of erythrocytes actually consists of protein (derived from residual fibrinogen) which is pptd. by some complementary substance from the guinea-pig's blood. Consequently it is superfluous to assume the existence of a special "colloïde de bœuf" (or conglutinin).

W. MCCARTNEY.

Kinetics of hæmolysis in amboceptor-complement systems. E. PONDER (Proc. Roy. Soc., 1932, B, 110, 18—45).—Hæmolysis in a system containing amboceptor, sheep's red blood-cells, and guinea-pig complement when components are added in this order proceeds according to the equation previously found (A., 1930, 1306) for hæmolysis by a simple agent such as saponin, provided that comple-

uent be regarded as the essential hæmolytic component. Only a part, however, of the complement is fixed on or near the cells and is active. This fraction increases with increase of amboceptor and is zero when no amboceptor is present. Exactly the same degree of hæmolysis may be obtained with high concns. of complement and a small quantity of amboceptor as with small concns. of complement and large quantities of amboceptor provided these quantities are such that the amount of complement taken up by the cells is the same in both cases. The fraction of amboceptor taken up by the cells is approx. const. and equal to 75% of the amount of that added over a considerable range of concns. W. O. KERMACK.

Hæmolytic action of compounds of the filicic acid group. A. JODLBAUER (Arch. exp. Path. Pharm., 1932, 164, 457—463).—Aq. extracts of an intimate mixture of MgO and *Extractum filicis* have a hæmolytic action on red blood-corpuscles, max. at p_H 8.2. Previous heating of the solution at 90° for 1½ hr. markedly increases the hæmolytic action at 20°, but longer heating gradually destroys it. The solutions are sensitive to light particularly in presence of sensitizers such as eosin. The anthelmintic and hæmolytic actions of various extracts run parallel.

W. O. KERMACK.

Antigenic property of serum-lipin. O. ISHIKAWA (Sei-i-kwai Med. J., 1931, 49, No. 8, 130—146).—Lipin isolated from the sera of man, horse, cattle, dog, pig, goat, fowl, and duck and giving no biuret, xanthoproteic, or ninhydrin tests, when injected into the rabbit, produced antibodies only when an accelerating substance (cattle-serum lipin) was present. There was no definite specificity among the serum-lipins of these animals. The antibody of the serum-lipin does not combine with the serum or the lipin-free serum-proteins, nor does the antibody of a serum or of its lipin-free serum-protein combine with the serum-lipin. The antibody of the serum-lipin seems to be sp.

CHEMICAL ABSTRACTS.

Masking of haptenes by lipins. H. RUDY (Biochem. Z., 1932, 245, 431—439).—Native serum does not mask the antigenic property of brain-extract in complement-fixation, although the isolated serum-lipins display this effect.

H. W. DUDLEY.

Antigenic properties of yeast invertase. K. MATSUOKA (Japan. J. Exp. Med., 1930, 8, 615—626).—Anti-invertase serum, decreasing the optical rotation produced by the action of invertase on sucrose, can be prepared by the injection of yeast autolysate. Heating destroys the antigenic property of invertase, but addition of serum to the heated autolysate reactivates it. Invertase is not completely destroyed by incubation with anti-invertase serum. No antibodies were produced by injection of sucrose, but a weak anti-invertase serum was prepared by injecting sucrose together with normal serum.

CHEMICAL ABSTRACTS.

Cold hæmotoxin in heated serum. II. Cold, non-complementary hæmolysis by the heated normal serum. III. Chemical nature and the influence of inhibitors. K. TOSHIMA (J. Biochem. Japan, 1931, 13, 441—464).—II. The activity of the cold, non-complementary hæmolytic factor in heated

normal serum varies in the order: rabbit > chicken, pig > man, goose, etc. The greatest effect is exhibited with sera heated at 90° and occurs below 5° (usually at 0°); cold hæmolysis occurs in serum free from amboceptor, and in isotonic solutions of KCl, KNO₃, and KBr, but not of sulphates or in an isotonic sucrose solution. The factor is present in the albumin fraction and is weakened by exposure of heated (but not unheated) serum to light. Treatment with Et₂O or CHCl₃ diminishes the effect: 0.1N-HCl or -NaOH is inactive.

III. The factor is not salted out by (NH₄)₂SO₄ or extracted with EtOH, COMe₂, Et₂O, or CHCl₃. It is non-dialysable, but is not related to glyco-gen. Cold hæmolysis is markedly inhibited by fresh, unheated sera, by serum-albumin or cholesterol (but not by lecithin), by egg-yolk but not egg-white, by peptone, caseinogen, and trypsin, but not by ovalbumin or pepsin.

CHEMICAL ABSTRACTS.

Relationship between heated immunised serum viscosity and its antibody. T. TAKAYAMA (Sei-i-kwai Med. J., 1930, 49, No. 12, 1—70).—The viscosity of the serum was parallel with the degree of destruction of the antibodies. The main viscosity changes are due to those of the globulin fractions. Normal serum-albumin and -globulin undergo approx. the same changes in viscosity when heated.

CHEMICAL ABSTRACTS.

Normal immune bodies of the new-born. T. TAKAYAMA (Sei-i-kwai Med. J., 1930, 49, No. 7, 86—103).—The serum of the new-born contains hæmolytic amboceptor and complement, but the hæmolytic power is much weaker than that of the mother. The order of ease of hæmolysis is: rabbit, pig, horse, cattle, guinea-pig, goat. That of the mother is: pig, goat, rabbit, guinea-pig, horse, cattle. The new-born has normal agglutinin, but less than the mother. The serum of the new-born agglutinates corpuscles in the order: rabbit, pig, horse, cattle, guinea-pig, goat; that of the mother: rabbit, pig, horse, guinea-pig, goat, cattle. The agglutinin of the new-born resists heating at 62.5—65° for 30 min. and is destroyed at 65—67.5°; that of the mother resists heating at 65—67.5° and is destroyed at 67.5—70°.

CHEMICAL ABSTRACTS.

Occurrence of an anticoagulant in the extract of the testes and eggs of the lamprey (*Petrom. planeri*). C. JUCCI (Boll. Soc. Ital. Biol. sperim., 1930, 5, 4 pp.; Chem. Zentr., 1931, ii, 1715).—The extract retards or inhibits the coagulation of the blood of a selachian (*Scyllium*); experiments with human blood gave an indefinite result.

A. A. ELDRIDGE.

Physiological-chemical analysis of the depressor action of organ extracts. K. FELIX and A. VON PUTZER-REYBEGG (Arch. exp. Path. Pharm., 1932, 164, 402—416).—In extracts of organs (placenta, kidney, stomach, and mesentery) having a depressor action, the following substances have been isolated by a modification of the method of Kossel and Kutscher: choline, acetylcholine, histamine, adenylic acid, and adenosine. Another substance of unknown composition and very high activity has also been isolated (not pure), which is of relatively low mol.

wt., is not inactivated by treatment with boiling mineral acid, is more unstable to alkalis, readily sol. in EtOH, MeOH, and H₂O, but not in Et₂O. It appears in the guanidine fraction.

W. O. KERMAK.

Depressor action of certain organ extracts. F. LANGE (Arch. exp. Path. Pharm., 1932, 164, 417—440).—From all vascular organs of warm- and cold-blooded animals a substance may be extracted which has a very strong depressor action and is different from any of the known vaso-dilator compounds.

W. O. KERMAK.

Contents of glycogen and galactogen (animal sinistrin) in *Helix pomatia*. F. MAY (Z. Biol., 1932, 92, 319—324; cf. A., 1931, 642).—Polysaccharides were isolated from the body of the snail by hydrolysis with KOH followed by repeated pptn. with EtOH. The product has $[\alpha]_D^{25} +158.3^\circ$ and yields 17.9% of galactose on acid hydrolysis. The sp. rotation when considered as that of a mixture of glycogen and galactogen indicates a content of 17.45% of the latter, thus confirming that galactogen is a polymeride of galactose.

F. O. HOWITT.

Galactogen content of eggs of *Helix pomatia*. F. MAY (Z. Biol., 1932, 92, 325—330).—The eggs on hydrolysis with KOH and treatment with EtOH (cf. preceding abstract) yield a polysaccharide, $[\alpha]_D^{25} -22.73^\circ$, free from glycogen and consisting of pure galactogen, which forms about 38% of the org. matter of the egg.

F. O. HOWITT.

Glycogen content of human kidney. K. LANG (Arch. exp. Path. Pharm., 1932, 164, 449—456).—In various diseases of man the glycogen content of the kidney varied from 12 to 142 mg. per 100 g. with a mean val. of 20—30 mg. In diabetes the figure is sometimes but not always relatively high. The result of the histological test for glycogen does not always correspond with the quantity present as determined chemically.

W. O. KERMAK.

Cephalin from human brain. III. Fatty acids of oxidised cephalin. M. BULOW and I. H. PAGE (Z. physiol. Chem., 1932, 205, 25—37; cf. A., 1931, 380).—The fall in the I, C, H, N, and P vals. of cephalin on keeping is not due to liberation of fatty acids by hydrolysis, or to an oxidative elimination of acids of low mol. wt., since only about 1% of the total acids are H₂O-sol., of which $\frac{1}{2}$ is volatile in steam. On the other hand, considerable amounts of OH-acids are present (about 5% of the total acids); these can be acetylated (Ac val. 0.5—1.5%). The fraction insol. in light petroleum amounts to 3—4%. The liquid acids show a small N content not removable by washing.

J. H. BIRKINSHAW.

Importance of lipins for permeability. M. MAXSHEIM (Biochem. Z., 1932, 244, 268—277).—The findings of Nierenstein (Pflüger's Archiv, 1920, 179, 233) and of Krebs and Nachmansohn (A., 1927, 895) concerning the parallelism between the ability of basic dyes to colour vital tissue, to dissolve in lipins, and to be adsorbed by kaolin are confirmed. All factors (e.g., alkaline reaction and addition of oleic or nucleic acid for basic dyes, acid reaction for acid dyes) which lead to deposition of dyes inhibit their

diffusion into gelatin gels. The diffusion is not influenced by the presence of neutral fat. It follows that the diffusion of both basic and acid dyes in gelatin proceeds most easily through the pores, i.e., in H₂O, and that solubility in lipins is significant for deposition: the same holds for the diffusion of easily diffusible dyes in living animal and vegetable cells. In gelatin membranes the diffusion through the pores cannot be prevented by the presence of narcotics, nor is the diffusion of dyes salts, glucose, or sucrose affected by the presence of solutions of homologous alcohols or esters of appropriate concn.

W. MCCARTNEY.

Plasma-protein of striated muscle. K. YANAGI (J. Biochem. Japan, 1931, 14, 305—323).—Myosin, myogen, and myogen-fibrin were isolated from muscle-plasma by fractional heat-coagulation (A., 1896, ii, 48). Myosin in aq. solution at room temp. is slowly converted into myogen, which in turn changes to sol. myogen-fibrin, these changes being dependent on the salt concn. and [H⁺] of the solution. Hence the three fractions represent phases of a single protein and are probably produced during the treatment for separation.

F. O. HOWITT.

Method for studying the scale structure of medullated and pigmented animal fibres. J. I. HARDY (J. Text. Inst., 1932, 23, 1—5T).—Impressions of the scale structure are obtained by mounting the fibres on a microscope slide and embedding them in a solution of celluloid in COMe₂, and the casts so obtained are examined microscopically.

B. P. RIDGE.

Method for revealing the scale structure of wool and hair. J. MANBY (J. Text. Inst., 1932, 23, 4—13T).—The hairs are arranged on a microscope slide and mounted without a coverglass so that the medium used covers approx. the lower half of the fibre only. For wool fibres and hairs with pronounced scales 5% xylene balsam is a suitable mountant, but when the scales are very fine the following are preferred: 1% celluloid in amyl acetate, 25% glycerol in H₂O, or 3% glycerol jelly.

B. P. RIDGE.

Relation between the colloid content of the thyroid and its bromine and iodine content. F. TANINO (Klin. Woch., 1931, 10, 1406; Chem. Zentr., 1931, ii, 1872).—The total I. is slightly lower in thyroids rich in colloids than in those of low colloid content, but the degree of dependence is small. In glands low in colloids Br: I = 8; the higher Br content of glands high in colloids increases the ratio to 16. For the glands of individuals treated with I the quotient is about 1.

A. A. ELDRIDGE.

Alleged iodide elimination from di-iodotyrosine in tryptic digestion. G. BARKAN and G. KINGSEPP (Z. physiol. Chem., 1932, 204, 219—232).—Electrometric titration shows that iodide is very slowly eliminated at slightly alkaline reaction from di-iodotyrosine. The process is slightly accelerated by active trypsin, but to a much smaller extent than Ostwald's experiments indicate (A., 1909, i, 860). AgNO₃ appears to produce a ppt. other than iodide (possibly an adsorption effect or formation of an insol. complex of di-iodotyrosine).

J. H. BIRKINSHAW.

Fluorescent substances in hens' egg-shells. H. BERRY and B. GOUZON (Compt. rend., 1932, 194, 653—655).—The fluorescence spectrum, produced by ultra-violet light, of the porphyrin extracted from the brown egg-shell of a hen shows a red band between 618 and 650 mμ, and on further exposure a wide green band. The corresponding spectrum for the white egg-shell shows a narrower red band at 622—645 mμ, and a less intense green band on further exposure. The latter spectrum resembles that of haematoporphyrin. A. LAWSON.

Calcium content of rats. H. AIDA (Biochem. Z., 1932, 244, 303—307).—No increase in the Ca content of rats results from the subcutaneous administration of small amounts (0.025% of the Ca content of the diet) of CaCl_2 , CaBr_2 , and CaI_2 , whether the animals rest or exercise vigorously. W. MCCARTNEY.

Application of optical spectroscopy to the determination of heavy elements in tissue. W. MANKIN (Chem. Eng. Min. Rev., 1932, 24, 142—144).—Zn, Al, Li, Mn, and Cu have been detected in the arc spectrum of cancer material, and Li, Zn, Ba, Al, Pb, As, and Cu in that of egg contents. The technique of the method is described. N. H. HARTSHORNE.

Solvent action of gastric juice on calcium phosphate. A. M. MONTEFREDINE (Arch. Farm. speriment., 1932, 53, 192—200).—The solvent action of gastric juice on $\text{Ca}_3(\text{PO}_4)_2$ is greater than that calc. from its acidity. Repptn. occurs in the filtrate. The formation of an unstable Ca-protein complex is assumed. R. K. CALLOW.

Vitamin-A, -B (B_1) and -G (B_2), contents of milk throughout the year. F. L. MACLEOD, J. B. BRODIE, and E. R. MACLOON (J. Dairy Sci., 1932, 15, 14—22).—Seasonal changes were small. A. G. POLLARD.

Vitamin-A content of the milk of Holstein, Ayrshire, Jersey, and Guernsey cows. H. P. DAVIS and I. L. HATHAWAY (Nebraska Agric. Exp. Sta. Res. Bull., 1931, No. 54, 14 pp.).—No significant differences were observed. A. G. POLLARD.

Lactose and chloride concentrations of milk produced during irregular intervals between milkings. C. L. ROADHOUSE and J. L. HENDERSON (J. Dairy Sci., 1932, 15, 1—5).—Milking at irregular intervals did not affect the lactose and Cl⁻ concn. A. G. POLLARD.

Existence of several sugars in the serum of human milk. M. POLONOVSKI and A. LESPAGNOL (Compt. rend. Soc. Biol., 1930, 104, 555—557; Chem. Zentr., 1931, ii, 1712).—The mother-liquors from the MeOH crystallisation of gynolactose afford a very slightly dextrorotatory sugar; it is hygroscopic, of reducing power similar to that of lactose, fairly stable towards AcOH , and on hydrolysis with strong acids affords galactose as one of the products. A. A. ELDRIDGE.

Isolation of [a new] sugar from human milk. M. POLONOVSKI and A. LESPAGNOL (Compt. rend. Soc. Biol., 1930, 104, 557—558; Chem. Zentr., 1931, ii, 1712—1713).—The fresh milk is treated with 8 vols. of EtOH and kept for several hr.; it is evaporated to half its original vol. under reduced pressure,

extracted with Et_2O and light petroleum, and evaporated to dryness. The residue is extracted with boiling MeOH until it contains pure lactose; on evaporation the extract deposits first lactose, then chiefly gynolactose, which is recrystallised from MeOH and EtOH. The MeOH solution, free from gynolactose, is treated with abs. EtOH, when a slightly dextrorotatory sugar is pptd. It is purified by further treatment with MeOH and abs. EtOH. A. A. ELDRIDGE.

Glucosuria and maltosuria. E. HERZFELD (Biochem. Z., 1932, 245, 71—75).—Sugar-free urines gave negative Nylander and osazone tests. Frequently, especially in cases previously showing glycosuria, the Nylander test was negative, but the osazone test positive, both glucose and conjugated glycuronic acid being present. In some cases the Nylander test was faintly positive, but the sugar val. by polarimeter and osazone tests was negative, the presence of conjugated glycuronic acid being then readily detectable. In more than 50 of 800 urines (chiefly from diabetes) the simultaneous presence of maltose as well as of glucose was shown by the osazone test. P. W. CLUTTERBUCK.

Carbohydrate content of normal urine and its relationship to nutrition. B. LUSTIG and L. LANDAU (Biochem. Z., 1932, 245, 174—181).—The carbohydrate content of the normal 24-hr. urine is 1.38—2.53 g. and the amount of dextrans 34—133 mg. Administration of glucose, sucrose, dextrin, or potato starch did not affect the amount of total or EtOH-precipitable carbohydrate of the subsequent 4-hr. urine and the protein-sugar content was also unchanged. After administration of flesh, only a small increase of total and a considerable increase of EtOH-precipitable carbohydrates were obtained. By administration of liver, considerable increase in total and EtOH-precipitable carbohydrate was obtained. After 24 hr. fasting, the total carbohydrate excretion is halved, but the EtOH-precipitable fraction is unchanged. P. W. CLUTTERBUCK.

Determination of oxyproteic acid in urine. S. HORIGUCHI (J. Biochem. Japan, 1931, 14, 257—263).—Urine (250 c.c.) is freed from inorg. SO_4^{2-} , PO_4^{3-} , etc. by addition of $\text{Ba}(\text{OH})_2$ conc., and treated with 20 vols. of abs. EtOH. The EtOH-insol. Ba salts are dissolved in H_2O , and Ba is removed by excess of H_2SO_4 . Free SO_4^{2-} is determined in the filtrate by the benzidine method and total S by oxidation with $\text{Cu}(\text{NO}_3)_2$ followed by a second SO_4^{2-} determination. The difference gives oxyproteic acid-S, the human excretion of which averages 150 mg. per day. F. O. HOWITT.

Excretion of neutral sulphur and oxyproteic acid in urine. S. HORIGUCHI (J. Biochem. Japan, 1931, 14, 265—278).—The amounts of neutral- and oxyproteic acid-S in urine which normally show only a small variation are increased in hyperthyroidism, by ingestion of large amounts of protein, and by strenuous exercise. F. O. HOWITT.

Allantoin content of urines of pregnancy and the new-born and of amniotic fluid. K. RO (J. Biochem. Japan, 1932, 14, 413—417).—In no instance could allantoin be detected. F. O. HOWITT.

Determination of uric acid in urine. J. RENAUDIN (J. Pharm. Chim., 1932, [viii], 15, 109-112).—The method is a modification of that of Ronchese.

A. LAWSON.

Determination of uric acid in human urine. A. A. CHRISTMAN and S. RAVWITCH (J. Biol. Chem., 1932, 95, 115-126).—The method of Benedict and Franke (A., 1922, ii, 669) frequently leads to erroneous results depending on the vol. of urine used. One source of such errors is the presence of NH_4 -acids, the effect of which is minimised by replacement of the 5% NaCN solution by one of 5% NaCN, 10% Na_2CO_3 , and 15% urea. A preliminary pptn. of the uric acid by the ammoniacal Ag-Mg reagent (A., 1915, ii, 602) prior to its colorimetric determination is recommended when greater accuracy is desired.

F. O. HOWITT.

Antigenic properties and group specificity of human urine. Y. TOKUNOYAMA (Tohoku J. Exp. Med., 1931, 17, 293-305).—The EtOH-sol. fraction of human urine is antigenic for rabbits if mixed with a foreign protein (pig serum) before injection. It contains Forsmann antigen, a species-sp. and a group-sp. lipid antigen.

CHEMICAL ABSTRACTS.

Chicken urine. E. J. COULSON and J. S. HUGHES (Poultry Sci., 1930, 10, 53-58).—The N distribution is tabulated.

CHEMICAL ABSTRACTS.

Micro-determination of carbon by Nicloux' method. B. BRAIER (Rev. Centr. Estud. Farm. Bioquim., 1931, 20, 149-161; Chem. Zentr., 1931, ii, 1171).—Nicloux' method is suitable for determining C in urine.

L. S. THEOBALD.

Detection of porphyrin in urine. H. T. SCHREUS and C. CARRIÉ (Klin. Woch., 1931, 10, 1017-1019; Chem. Zentr., 1931, ii, 2362-2363).—Schumm's method for the detection of coproporphyrin in urine is rejected.

L. S. THEOBALD.

Pigment present in the sweat and urine of certain sheep. Isolation, properties, and relationship to bilirubin and the metabolism of haemoglobin. C. RIMINGTON and A. M. STEWART (Proc. Roy. Soc., 1932, B, 110, 75-91).—From the wool of sheep exhibiting a golden colour a pigment *lanaurin*, $\text{C}_{33}\text{H}_{36}\text{O}_{10}\text{N}_4$, has been isolated from the H₂O-sol. suint after removal of the Et₂O-sol. material. This compound resembles bilirubin and is presumably derived from haemoglobin. It has also been isolated from the urine of a sheep showing golden coloration of the wool, together with two other pigments, one sol. in CHCl_3 and the other insol. in CHCl_3 and sol. in EtOH, both of which resemble bilirubin more closely than does lanaurin. The excretion of yellow pigment by the sudoriferous gland of sheep has considerable resemblance to familial acholuric jaundice in man.

W. O. KERMACK.

Effect of uni- and bi-lateral adrenalectomy on blood constituents of rabbits. M. OHGURI (Tohoku J. Exp. Med., 1931, 17, 378-389).—Bilateral adrenalectomy did not affect the blood-total N, -protein-N, -creatinine (preformed or total), -uric acid, -inorg. P, -sugar, -haemoglobin, or -Cl.

CHEMICAL ABSTRACTS.

Effect of removal of adrenals and accessory cortical tissues together on blood constituents of

rabbits. M. OHGURI (Tohoku J. Exp. Med., 1931, 17, 390-411).—Complete removal of the cortico-adrenal system increases the preformed and total, non-protein-, urea-, and uric acid-N of the blood. The Cl is decreased and the serum-inorg. P increased.

CHEMICAL ABSTRACTS.

Allergic skin-test substance. F. S. SMYTH and K. BAIN (J. Allergy, 1931, 2, 177-180).—On treatment of the serum with saturated $(\text{NH}_4)_2\text{SO}_4$ the essential antibody fraction is pptd. with the globulins and is associated with the pseudoglobulin. Non-essential lipid substances may be eliminated by prolonged storage of the serum before treatment with $(\text{NH}_4)_2\text{SO}_4$.

CHEMICAL ABSTRACTS.

Alveolar carbon dioxide tension, alveolar carbon dioxide index in voluntary apnoea, and vital capacity in pulmonary emphysema and bronchial asthma. S. MANCA (Arch. Farm. sperim., 1931, 53, 141-165).—The alveolar CO_2 tension is normal in both conditions. The alveolar CO_2 index is elevated in pulmonary emphysema proportionally to the extent of the lesions and is of diagnostic val. Vital capacity is reduced considerably in emphysema and slightly in bronchial asthma.

R. K. CALLOW.

Decomposition of the lecithins of rice and its connexion with beriberi. S. BELFANTI (Arch. Ital. Biol., 1931, 85, 190-207; Chem. Zentr., 1931, ii, 2029).—Feeding with polished rice is associated with lack of enzymes, which is considered to be important in connexion with the onset of avitaminosis. Particularly noteworthy is the lack of phosphatase, which decomposes toxic lysocithins.

A. A. ELDRIDGE.

Calculus of the tonsil. J. CHABAUD and R. LECOQ (J. Pharm. Chim., 1932, [viii], 15, 228-230).—The occurrence of a calculus (0.585 g.) composed of Ca phosphate is described.

H. W. DUDLEY.

Colloidal phenomena in gall-stones. H. B. WETSER and G. R. GRAY (J. Physical Chem., 1932, 36, 286-299).—Rhythmic rings of Ca-bile pigment and of Ag_2CrO_4 were obtained in a mass of cholesterol crystals pptd. in the presence of a small amount of a hydrophilic colloid such as gelatin, albumin, or fibrin. The concentric rings in gall-stones are a manifestation of the Liesegang phenomenon. Concentric bands are not formed in either natural or synthetic cholesterol stones in the absence of hydrophilic colloids.

F. SAUNDERS (c).

Recent biochemical research in cancer with special reference to the metabolism of the normal and malignant cell. E. C. DODDS (Amer. J. Cancer, 1931, 15, 2765-2779).—Derangement of metabolism of malignant tissues is shown by high glycolysis and defect in respiration; the latter is possibly more sp. than the former. The defect lies almost entirely in the carbohydrate metabolism; probably the breaking up of the triose is at fault. Definite growth-promoting substances similar to those obtained from the anterior pituitary lobe are often present in the urine in cancer.

CHEMICAL ABSTRACTS.

Intracellular hydrogen-ion concentration studies. V. Colorimetric p_H of malignant cells in tissue culture. R. CHAMBERS and R. J. LUD-

FORD (Proc. Roy. Soc., 1932, B, 110, 120—124).—The cytoplasm of various tumour cells grown in tissue culture has p_H 6.4—7.0, whilst the nucleus has p_H >7.2. Injury of the cell accompanied by cytolysis results in the cytoplasm becoming more acid and developing a p_H <5.6, whilst the nucleus retains a p_H >7.2.

W. O. KERJACK.

Lipin content of human serum in cancerous and cancer-free subjects. G. DE VOSS (Z. physiol. Chem., 1932, 205, 20—24).—The phospholipin, total cholesterol, and cholesteryl ester showed average vals. of 150.5, 152.2, and 75.7 mg., respectively, per 100 c.c. for cancerous and 178.7, 169.3, and 92.1 mg. for cancer-free subjects. Only 5 of the latter were healthy; these showed higher lipin vals. than the diseased cancer-free subjects. In cases of cancer of liver and pancreas higher vals. for phospholipin and total cholesterol were observed.

J. H. BIRKINSHAW.

Fermentation-accelerating action of tumour extracts and its relationship with Rosenthal's activator. G. BOSTROM (Biochem. Z., 1932, 245, 85—101).—Rat's tumour extracts increase the anaerobic lactic acid fermentation of the liver of fed rats by 400% (827—124%). In starving rats the action is small. Perfusion with physiological saline for 30—60 min. before the experiment decreases the fermenting power by 35%, a fermentation activator being probably removed by washing. 48 hr. after subcutaneous injection of tumour extract, the liver respiration is greatly decreased and the anaerobic and aerobic lactic acid acid fermentation increased.

P. W. CLUTTERBUCK.

Micro-determination of nitrogen. Its application in the diagnosis of cancer. H. J. FUCHS and M. VON FALKENHAUSEN (Biochem. Z., 1932, 245, 304—313).—An apparatus and colorimetric method for the micro-determination of N are described.

W. MCCARTNEY.

Content and activation of urinary diastase in cancer and other diseases. E. FRANKEL, P. GERKE, and R. SMKE (Biochem. Z., 1932, 245, 44—51).—Although there are no characteristic differences in the diastase of the urine in these diseases, it was found that the latter frequently contained a substance which activated diastase. The activator is inactivated above 45°, is active between p_H 4.0 and 7.5, is adsorbed by kaolin, but is not eluted therefrom by phosphate.

P. W. CLUTTERBUCK.

Enzymes of chicken sarcoma. E. SOMEKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 23—36).—An aq. extract of Rous sarcoma showed slightly greater and more varied enzyme activity than did a musculo extract.

A. COHEN.

Proteins of human serum. Distribution of protein in normal and pathological sera. Diagnosis of tuberculosis and cancer. A. SCHMITZ and F. WULKOV (Biochem. Z., 1932, 245, 408—417).—For the separation of globulins from albumins in serum-proteins pptn. with $(NH_4)_2SO_4$ may be used, but for further fractionation other methods must be applied. The procedure of Goldschmidt and Kahn (A., 1929, 951) gives unsatisfactory results. If dil. solutions of serum (1 c.c.) are added to series of

$(NH_4)_2SO_4$ solutions (saturation ranging from 5 to 100%) and the degrees of turbidity produced (measured with a step photometer) are plotted against the concn. of $(NH_4)_2SO_4$ which causes them, curves termed "protein spectra" are obtained. In these curves one portion represents the globulins and another the albumins. Sera from healthy persons always gives the same type of curve and hence always contains the same type of protein mol. and neither consumption of large amounts of fat nor addition of Na glycocholate to the serum has any effect on the "spectra." In pathological sera of all kinds variations, from which no conclusions can be reached, appear in the globulin portions of the curves. The albumin portions, however, are always similar except in tuberculosis and cancer (and also, to some extent, in cirrhosis of the liver). This finding applied to the diagnosis of the two first-named diseases yielded correct results in 96% of the cases examined.

W. MCCARTNEY.

Catabolism of fats directly introduced into the animal body. Basal metabolism of pancreas-diabetic animals following the infusion of fat. T. BABA (Tohoku J. Exp. Med., 1931, 17, 274—292).—Intravenous injection of a fat emulsion into diabetic dogs causes the R.Q. to fall below 0.707. With animals in which the pancreas had been incompletely resected the R.Q. fell to a val. above 0.707.

CHEMICAL ABSTRACTS.

Distribution of phosphorus compounds and calcium in the blood of children. M. SOKOLOVITCH (Arch. Dis. Childhood, 1931, 6, 183—208).—The blood-P of children tends to be higher and to show greater variation than that of adults. Changes in the partition of P are found in nephritis, diabetes mellitus, and infantile tetany, but the total P content is not increased. The serum-Ca of children is normal in diabetes and slightly increased in nephritis.

CHEMICAL ABSTRACTS.

Clinical calorimetry. XLVIII. Nitrogen equilibrium with a low-protein diet. W. S. McLELLAN and R. R. HANNON (J. Biol. Chem., 1932, 95, 327—333).—A patient with diabetes mellitus was fed on a diet containing 20 g. of protein per day, and having an energy val. of 50% above the basal heat output. N equilibrium was established during the last month of the period of observation (106 days), and wt. equilibrium during the whole period without any ill effects from the low protein level of the diet. A decrease in the carbohydrate content of the diet produced excretion of ketonic substances, but no increase in body-protein metabolism. A low record of 1.78 g. of N per day excreted in the urine was reached.

A. LAWSON.

Toxic fraction in certain eczema sera. F. S. SMYTH (J. Allergy, 1931, 2, 173—176).—Toxicity is not due to allergens or to alteration of the colloidal properties by heat or cold; the effect resembles that of the "histamine-like" substance described by Lewis and Harmer.

CHEMICAL ABSTRACTS.

Essential fatty acids and goitre-producing substances. F. E. CHIDESTER (Science, 1932, 75, 106).—A discussion in which the importance of the I-fat balance is emphasised.

L. S. THEOBALD.

Iodine question in Lettland in relation to goitre. J. KUPZIS (Z. Hyg., 1932, 113, 551—573).—The I content of inland soils is largely dependent on the ease of leaching and on the fertilisers (notably animal manures) used. The prevalence of goitre is in no way associated with the amounts of Ca, Mg, Fe, or org. matter present in drinking-H₂O.

A. G. POLLARD.

Range of effective iodine dosage in exophthalmic goitre. IV. Effect on basal metabolism of daily dose of about 0.75 mg. W. O. THOMPSON, P. K. THOMPSON, and A. C. COHEN (Arch. Int. Med., 1932, 49, 199—214).—The percentage approach of basal metabolism to the normal in cases of exophthalmic goitre is proportional to the dose of I and to the amount of I in the thyroid available for the storage of colloid, between the limits of dosage 0.75—6 mg. A certain min. daily dose of I produces a max. effect.

H. DAVSON.

Thiocyanate therapy in hypertension. I. Its toxic effects. W. GOLDRING and H. CHASIS (Arch. Int. Med., 1932, 49, 321—329).—Toxic manifestations occur independently of the amount of drug administered, there being, in some cases, no margin of safety between the toxic and therapeutic doses.

H. DAVSON.

Effect of insulin therapy on pancreatic enzymes in malnutrition. C. W. LUEDERS and M. E. WATSON (Arch. Int. Med., 1932, 49, 330—342).—Analysis of the pancreatic secretions and the bile salts, together with studies of the stool, before and after doses of 40 units of insulin showed an increase in pancreatic enzymes, improvement in the function of the biliary tract, and a more complete digestion and assimilation of food following the dose.

H. DAVSON.

Calcium and phosphorus metabolism in nephritis. F. J. FORD (Arch. Dis. Childhood, 1931, 6, 209—230).—Retention of Ca and P is approx. normal; excretion tends to be diverted from the urine to the faeces.

CHEMICAL ABSTRACTS.

Plasma-proteins and oedema in children presenting nephrotic syndrome. J. K. CALVIN and A. H. GOLDBERG (Amer. J. Dis. Children, 1931, 42, 314—327).—A marked decrease in serum-albumin is usually associated with the oedema of the nephrotic syndrome. The globulin content is only slightly decreased, or may be increased sufficiently to reverse the albumin : globulin ratio.

CHEMICAL ABSTRACTS.

Iron-deficiency hypothesis in pellagra. S. BLISS (Science, 1932, 75, 266).—Critical (cf. Halliday, *ibid.*, 1931, 74, 1931).

L. S. THEOBALD.

Relationship between calcium and potassium balance and rheumatism agents. I. Relationship between uric acid content and calcium and potassium in serum by the use of narcotics. K. IN (Folia Pharmacol. Japon., 1931, 12, No. 3, 406—416).—Hypnotics, but not morphine, disturb the ionic balance in rheumatic tissue; the serum-Ca is decreased (often increased by morphine) and the -K increased.

CHEMICAL ABSTRACTS.

Experimental scurvy. XI. Glutathione content of tissues of guinea-pigs fed on vitamin-C-

free diet. R. SATO and S. OHATO (J. Biochem. Japan, 1931, 14, 325—329).—Slight increases occur in the suprarenals and skeletal muscle, but no change is detectable in the liver, kidneys, lungs, heart, spleen, and testicles.

F. O. HOWITT.

Scurvy and the potassium and sodium content of the urine and the blood. L. RANDOIN and A. MICHAUX (Compt. rend., 1932, 194, 565—567).—During the course of scurvy in guinea-pigs fed on a diet containing 1% NaCl, the vol. of urine diminishes very greatly, the Na and K content decreasing proportionately. The Na content of the blood-serum and total blood increases slightly. The K content of the serum diminishes, but, unlike that of the controls, is greater than that of the total blood, this being due to a decrease in the no. of red blood-cells caused by the scurvy.

A. LAWSON.

Sodium and potassium content of muscles during the development of scurvy. L. RANDOIN and A. MICHAUX (Compt. rend., 1932, 194, 647—650).—In guinea-pigs on a diet containing no vitamin-C, the content of Na in the muscles increases whilst that of K decreases as scurvy develops. From previous work on the retention of Cl⁻ (A., 1931, 383), it is concluded that the Na is retained as NaCl.

A. LAWSON.

Compound of taurocholic acid with guaiacol. D. GANASSINI (Arch. Ist. Biochim. Ital., 1932, 4, 3—8).—*Guaiacol taurocholate*, OMe·C₆H₄·C₂₆H₄₄O₇NS, m. p. 110°, is tolerated by the human organism, has no irritant effect on the stomach or kidneys, and appears to be of val. in treating chronic tubercular empyema of the lungs.

T. H. POPE.

Embryonic metabolism. VI. The amino-acids of the yolk, white, embryo, and shell membranes during development of the hen's egg. H. O. CALVERY (J. Biol. Chem., 1932, 95, 297—300).—In the developing egg, tyrosine decreases, whilst tryptophan and cystine increase in the embryo, but all three remain const. in the white, yolk, and shell membrane. Arginine and lysine remain const., whilst histidine decreases in all fractions except the shell membrane, which is unaffected by the development of the embryo.

A. LAWSON.

Survival of embryonic tissues of the hen in Ringer's solution at low temperatures. L. BUCCIANTE (Atti R. Accad. Lincei, 1931, [vi], 14, 356—361).—The survival at 5—10° varies with the different tissues. There is a progressive removal of trophic substances, which diffuse from the cells into the liquid. The addition of embryo juice is almost indispensable for the culture of the washed tissues in Ringer's solution; in a culture medium resulting from plasma alone, the tissues grow either not at all or only to a slight extent.

T. H. POPE.

True metabolic rate of the chick embryo and the respiration of its membranes. J. NEEDHAM (Proc. Roy. Soc., 1932, B, 110, 46—74).—The yolk-sac of the hen's egg steadily absorbs 320 cu. mm. O₂ per g. per hr. from the 3rd to the 15th day of development and then the rate of respiration decreases, reaching about 60% of the above val. at the time of hatching. The respiration rate of the allantois rises from 100

cu. mm. O_2 per g. per hr. on the 6th day to a max. of 390 cu. mm. on the 13th day, and then falls to about 250 at the time of hatching. The respiratory rate of the embryo as calculated by subtracting the O_2 consumption of the extra-embryonic membranes from that of the intact egg falls from 1200 cu. mm. O_2 per g. per hr. on the 6th day to 800 cu. mm. on the 19th, the max. rate occurring before the 6th and probably on the 5th day.

W. O. KERMAK.

Influence of chemical composition on tissue respiration. T. DOXIADIS (Biochem. Z., 1932, 245, 52—60).—The O_2 utilisation, CO_2 production, R.Q., and the protein, fat, and carbohydrate contents of slices of rat's liver are determined. The O_2 consumption increases with increasing protein and decreasing fat content of the tissues.

P. W. CLUTTERBUCK.

Effect of amino-acids on respiration of tissues. IV. Serine, valine, sarcosine, isoleucine, and phenylglycine. B. KIRSCH (Biochem. Z., 1932, 244, 451—458; cf. this vol., 82).—With regard to their effect on the respiration of the liver and kidney tissue, serine, valine, sarcosine, and phenylglycine resemble the NH_2 -acids previously examined and isoleucine resembles leucine, but is somewhat less active. The effect of the acids is greater on old than on fresh tissue; the difference between the two kinds of tissue is slight. The $[H^+]$ of the nutrient medium has the same effect as with the acids first examined.

W. MCCARTNEY.

Effect of amino-acids on respiration of retinal tissue. B. KIRSCH (Biochem. Z., 1932, 244, 459—463).—The respiration of fresh retina (pig, ox, dog, and other species) is increased, in some cases very greatly, by glycine, phenylglycine, valine, leucine, serine, sarcosine, alanine, and phenylalanine and in the case of the old tissue the increase is greater. Retinal tissue differs from kidney tissue in that with the former the effects of alanine and phenylalanine are less, those of serine, valine, and sarcosine more, pronounced than with the latter.

W. MCCARTNEY.

Salinity of the medium and its effect on respiration in the sea anemone. C. S. SHoup (Ecology, 1932, 13, 81—85).—Variations in the salt concn. of the medium on either side of the normal concn. of seawater decrease respiration in *Metridium marginatum*. In single-salt media, Na, Ca, and K salts have a pronounced effect.

A. G. POLLARD.

Emission of oxygen by the pelvic filaments of the male *Lepidosiren* with some experiments on *Symbranchus marmoratus*. J. T. CUNNINGHAM and D. M. REID (Proc. Roy. Soc., 1932, B, 110, 234—248).—When *Lepidosiren* is placed in H_2O with a very low content of dissolved O_2 , the dissolved O_2 (determined by Winkler's method) decreases if the specimen is a female or a male with undeveloped pelvic filaments, but definitely increases in the case of a male with well-developed filaments. The decrease is probably due in part at least to the mucus introduced with the fish. The results indicate that the developed pelvic filaments of the male *Lepidosiren* excrete O_2 into the H_2O probably to oxygenate the fertilised eggs.

W. O. KERMAK.

Nature of metabolic regulation of body temperature and its relation to temperature sensations. J. M. O'CONNOR (Proc. Roy. Irish Acad., 1932, 40B, 175—193).—In non-shivering rabbits under urethane anaesthesia O_2 consumption is correlated with rectal temp. Statistical analysis of data shows that the extra O_2 consumption during shivering is independent of head temp. but is max. at a skin temp. of 28° , falling to zero at 35° and at 23° . Cold sensation in the human forearm is abolished at about 21° . Hence chemical temp. regulation is probably a reflex response to cold stimuli from the skin.

J. B. BATEMAN.

Metabolism of cold-blooded animals. D. GOULSTON (J. Proc. Roy. Soc. New South Wales, 1931, 65, 51—58).—Measurements on the O_2 absorption and CO_2 expiration of a resting frog show that its metabolic rate falls continuously during starvation.

N. H. HARTSHORNE.

Basal metabolism of Australian merino sheep. E. W. LINES and A. W. PEIRCE (Bull. Coun. Sci. Ind. Res. Austral., 1931, No. 55, 34 pp.).—The effects of different diets and the duration of fasting on the R.Q. and basal metabolism of ewes are studied. The conditions for standard basal metabolism determinations are defined. A relation between body-wt. and skin-area is obtained.

H. DAVSON.

Fasting metabolism of cattle. E. B. FORBES, W. W. BRAMAN, M. KRISS, and R. W. SWIFT (J. Agric. Res., 1931, 43, 1003—1014).—Conditions for the determination of standard basal metabolism are defined. No const. val. is obtained with two steers fasting for 6 days.

H. DAVSON.

Basal metabolism. I. Error of basal metabolism determination and normal range of basal metabolism. II. Basal pulse complex. R. L. JENKINS (Arch. Int. Med., 1932, 49, 181—187, 188—198).

Carbon dioxide dissociation curve of living mammalian muscle. L. IRVING, H. C. FOSTER, and J. K. W. FERGUSON (J. Biol. Chem., 1932, 95, 99—113).—The CO_2 content and tension (the latter assumed equal to the CO_2 tension of the venous blood leaving the muscle) of the gastrocnemius muscles of the dog were determined for normal and over-ventilation and for ventilation with a CO_2 -rich mixture after removal of the first muscle. The CO_2 dissociation curve is expressed by the equation CO_2 (c.c. per 100 g.) = $3.4\sqrt{pCO_2}$, where pCO_2 is the tension in mm. of Hg. This curve is used for the construction of a combining-power curve, the solubility coeff. being assumed to be 0.41. Also, accepting the pK' val. as equal to that of serum, i.e., 6.07 (A., 1928, 150), and applying the Henderson-Hasselbalch equation, the reaction of the resting muscle is pH 6.9—7.0 for CO_2 tensions of 50—60 mm., whilst the buffering power is determined and resolved into its components.

F. O. HOWITT.

The coupled nature of lactic acid glycogen synthesis in muscle. D. BURK (J. Physical Chem., 1932, 36, 268—272).—The theory (cf. Bancroft and Bancroft, A., 1931, 513) that glycogen may be synthesised in muscle from lactic acid according to a freely reversible shift in the equilibrium point (caused

by adsorption of glycogen on protein) is quantitatively inconsistent. C. T. SNELL (b).

Amount of lactic and other ether-soluble acids in blood and organs at rest, after muscular work, and when supplied with reduced amounts of oxygen. S. L. ØRSKOV (Biochem. Z., 1932, 245, 239—251; cf. A., 1930, 801).—The method for the determination of lactic and other Et_2O -sol. acids in blood can also be applied to tissues (liver, kidney, muscle). The lactic acid content of organs increases during extirpation. The blood, liver, and kidneys of cats and rabbits contain approx. equal amounts of lactic acid, but there is much more of it in the muscles, possibly because production takes place during extirpation. Muscular work results in increase, in organs and in blood, of both lactic and the other acids. The latter disappear from the blood sometimes more, sometimes less, quickly than does lactic acid. In frog muscle also muscular work leads to increase in the amount of the other acids, although this increase is not so great as it is with rabbits. Increase in the amount of the other acids also results from lack of O_2 and in dead organs to which O_2 is not supplied considerable increase takes place. The nature of the acids resulting from muscular work and O_2 lack is not known but they contain neither P nor N. W. MCCARTNEY.

Nervous control of carbohydrate metabolism. I. Position of the centre. II. Chemical changes set up in the body during decerebration hyperglycaemia. III. Nature of the mechanism of the nerve control. C. DONHOFFER and J. J. R. MACLEOD (Proc. Roy. Soc., 1932, B, 110, 125—141, 141—157, 158—171).—I. Decerebration of well-fed rabbits during the short period of anaesthesia induced by the intravenous injection of "amytal" almost always causes marked hyperglycaemia within 2 hr., provided that decerebration is effected in the neighbourhood of the pons. It follows that the centre regulating carbohydrate metabolism is situated in or near the pons. While the animals are under "luminal" or "amytal" anaesthesia, puncture of the floor of the fourth ventricle does not affect the blood-sugar level, nor does mechanical asphyxia or Et_2O , whilst injection of adrenaline causes hyperglycaemia.

II. Decerebration in the neighbourhood of the pons besides causing hyperglycaemia increases the blood-lactic acid, decreases the glycogen in the liver if this is initially above about 0.7%, but otherwise usually increases it, and decreases the percentage of glycogen in the leg muscles. Decerebration not at the level of the pons produces only insignificant changes in these factors, except that decerebration at the medulla oblongata usually brings about an increase in muscle-glycogen. The degree of hyperglycaemia is not correlated with the initial concn. of glycogen in the liver and muscles. When the latter is low, the amount of glucose which must be injected into a normal rabbit to raise its blood-sugar to an extent equal to that observed after decerebration through the pons much exceeds that which can be accounted for by the changes in the liver- and muscle-glycogen. When the liver- and muscle-glycogen is initially high most of the increase in the blood-glucose may be accounted for by changes in these. The blood-non-protein-N, the O_2

consumption, and the R.Q. are not definitely altered after decerebration through the pons, although in one experiment a pronounced increase in O_2 consumption took place. Injection of glucose into rabbits decerebrated at the pons does not prevent the disappearance of muscle-glycogen, but may retard the fall in liver-glycogen or bring about an increase.

III. In rabbits containing relatively little liver- and muscle-glycogen, hyperglycaemia following decerebration through the pons is prevented by double adrenalectomy, atropine and section of both vagi, ergotamine and section of both vagi, or amytal. In well-fed animals containing more liver- and muscle-glycogen, hyperglycaemia does occur under these conditions, but it is usually not so pronounced as with simple decerebration. With little glycogen in the liver, hyperglycaemia following decerebration is probably due to stimulation of gluconeogenesis in the liver through the parasympathetic nerves.

W. O. KERMAK.

Utilisation of lactose in the rat and the pig. E. A. FISHER (New Zealand J. Sci. Tech., 1931, 13, 96—103).—The scouring effect of whey is due mainly to the lactic acid. An inverse relationship exists between the live wt. increase of rats and the amount of lactic acid in the diet in excess of that supplying approx. 25% of the calories. With rats, as with pigs, this is accompanied by considerable excretion of reducing sugar in the urine. W. G. EGGLETON.

Effect of yeast on liver-glycogen with various diets. H. AIDA (Biochem. Z., 1932, 244, 431—434; cf. A., 1931, 1184).—In rats administration of yeast results in increase in the amount of glycogen in the liver only if a certain min. of sugar is added to the basal diet. W. MCCARTNEY.

Influence of yeast on protein metabolism in normal and depancreatized dogs. E. S. NASSER, H. B. PIERCE, and J. R. MURLIN (J. Lab. Clin. Med., 1931, 16, 1151—1168).—N-retention is increased when yeast is included in the diet. Ingestion of yeast tends to reduce the D : N ratio of depancreatized dogs. CHEMICAL ABSTRACTS.

Supplementary feeding of carbohydrates to suckling calves in relation to the utilisation of milk-protein. N. REMER (Biol. Zentr., 1932, B, 3, 463—506).—Calves from a few days old were reared satisfactorily on whole milk supplemented with dried potatoes and distillery malt. The proportion of milk was decreased with increasing age. The % utilisation of milk-protein was slightly reduced by potato feeding. A. G. POLLARD.

Growth and reproduction on milk diets. J. WADDELL, H. STEENBOCK, E. B. HART, and E. VAN DONK (J. Nutrition, 1931, 4, 53—65).—On a diet of whole milk and Cu chronic anaemia, due to low Fe intake, occurred. Growth and reproduction were subnormal. On a diet of whole milk, Cu, and Fe no anaemia was observed, but growth and reproduction were still subnormal, possibly owing to low calorific val. Small quantities of Mn and/or I improve the ovulation rhythm in rats on milk, Cu, and Fe diets. CHEMICAL ABSTRACTS.

Replacement of food protein by ammonium hydrogen carbonate in the feeding of cows. P.

EHRENBERG, E. UNGERER, and H. KLOSE (Biochem. Z., 1932, 245, 113—145).—In experiments of short duration with cows, the food protein can be replaced considerably or totally by acid slices of beet which have been soaked in NH_4HCO_3 . It appears probable that the $\text{NH}_4\text{-N}$ is utilised in milk formation.

P. W. CLUTTERBUCK.

Intermediate protein metabolism. III. Experiments on dogs with liver injuries and Eck's fistula. F. SILBERSTEIN, L. TUCHMAN, and A. GLASER (Biochem. Z., 1932, 245, 102—117).—The effect of various liver injuries (poisoning with P, tolylenediamine, CCl_4 , ligation of the bile duct, and Eck's fistula) on the metabolism of dogs receiving peptone is investigated. In P and tolylenediamine poisoning, the abs. and relative amounts of urea formed are never less and usually greater than in normal animals. With CCl_4 the urea formation is not decreased but the curves are complicated, due to injury of the kidneys. Ligation of the bile duct and Eck's fistula do not affect urea formation.

P. W. CLUTTERBUCK.

Factors which determine renal weight. IX. Endogenous protein metabolism. E. M. MACKAY and J. R. COCKRILL. **X. Effect of feeding desiccated thyroid.** E. M. MACKAY and L. L. MACKAY (J. Nutrition, 1931, 4, 25—32, 33—37).—IX. The kidney wts. of male albino rats which received a diet devoid of protein were almost directly proportional to the endogenous protein metabolism as measured by urinary N excretion.

X. Administration of a diet containing 0.4% of desiccated thyroid causes an increase in kidney wt. greater than could be accounted for by the increase in protein intake incidental to the increased food consumption.

CHEMICAL ABSTRACTS.

Cysteine and taurine as substituents for cystine in nutrition. H. H. MITCHELL (J. Nutrition, 1931, 4, 95—104).—Cysteine, but not taurine, when added to a rat diet deficient in cystine, improved the growth-promoting val. Conversion of cysteine into cystine probably occurs within the body rather than in the intestinal tract where reducing conditions are present.

CHEMICAL ABSTRACTS.

Physiology of creatinine and creatine. Excretion of creatinine and creatine. I. At the minimum nitrogen level of metabolism and during fasting. II. During the course of benzoic acid, phloridzin, and phosphorus poisoning. E. F. TERROINE, R. BONNET, P. DANMANVILLE, and G. MONROT. **III. During exogenous nitrogen metabolism.** E. F. TERROINE and P. DANMANVILLE (Bull. Soc. Chim. biol., 1932, 14, 12—46, 47—67, 68—84).—I. In young pigs, brought to the min. N level of endogenous metabolism by a carbohydrate diet, the weekly excretion of creatinine remains const., whilst that of creatine varies considerably, becoming less as the min. N level is maintained. The ratio creatine-N/total N for the urine varies for different animals of the same species, but is always greater than that for muscle. The substitution of fasting for the carbohydrate diet causes a large increase in creatine excretion corresponding with the increase in total N excreted.

II. Administration of BzOH and phloridzin to young pigs brought to the min. N level of metabolism results in considerable increase of creatine excretion, the creatinine excretion remaining const. Rabbits under similar conditions give parallel results on administration of P. Creatine, therefore, appears to be formed independently of the creatinine-creatine balance.

III. Young pigs fed on various complete diets excrete quantities of creatine which vary inversely with the amount of retained N of the diet. The excretion of creatinine remains nearly const.

A. LAWSON.

Origin of creatine. Treatment of progressive muscular atrophy with glycine. K. THOMAS, A. T. MILHORAT, and F. TEICHNER (Z. physiol. Chem., 1932, 205, 93—98).—Administration of glycine increases the excretion of creatine in creatinuric patients. In some cases after continued administration the creatine in the urine decreases, and creatinine appears, accompanied by an improvement in the patients' condition. Glycine produced no effect in muscular atrophy.

J. H. BIRKINSHAW.

Effect of muscular work on the creatine and creatinine content of normal human blood. K. KAGL (Biochem. Z., 1932, 245, 452—458).—In man muscular exercise leads to great increases in the total creatinine and creatine content of the blood and to very slight increase in the content of preformed creatinine. The contents revert to normal (occasionally to slightly below normal) after 3 hrs.' rest; after 1 hr. they are still somewhat above normal. The increases are not proportional to the extent of the exercise taken. In athletic persons the effect of the exercise is less than it is in others.

W. MCCARTNEY.

Urea formation in the animal body. IV. A. 2. Urea formation in surviving organs and in their press-juice. S. SALASKIN, L. SOLOVIEV, and D. TUKOV (Z. physiol. Chem., 1932, 205, 1—10; cf. A., 1931, 869).—In autolysis of placenta the urea increases, the optimum p_{H} for its production being 5.64—6.20. Addition of physiological saline and of an AcOH mixture increases urea formation, but autolysis probably does not increase the uric acid. Urea, NH_2 -acids, and residual N increase independently. The total urea in placental as in liver autolysis is due to the arginine-arginase system. The arginine content of the protein of fresh placenta is about 7%, about 20% of which is converted into urea on autolysis. Arginase added towards the end of autolysis increases the urea somewhat, but less than the addition of arginine.

J. H. BIRKINSHAW.

Purine metabolism. P. RONDONI (Arch. Ital. Biol., 1931, 85, 101—108; Chem. Zentr., 1931, ii, 1877).—Determinations of uric acid and allantoin in rat's urine indicate that the purine metabolism of the rat is exceptionally analogous to that of man.

A. A. ELDRIDGE.

Post-mortal formation of ammonia in muscle. J. K. PARNAS (Biochem. Z., 1932, 245, 159—165).—The post-mortal formation of NH_3 in frog's muscle kept in physiological fluids at 11—13° amounts only

to 1/10—1/15 of the val. assigned by Embdon (A., 1931, 1449). P. W. CLUTTERBUCK.

Plasma-lipins in lactating and non-lactating animals. P. J. SCHABBLE (J. Biol. Chem., 1932, 95, 79—88).—The plasma contents of fatty acids, lipin-P, and neutral fat are higher in lactating than in non-lactating cows or in steers. In both lactating and non-lactating animals the fatty acids of the plasma-lipin are less unsaturated than those of the cholesteryl esters, whilst the fatty acids of the neutral fat are intermediate. Hence the cholesteryl esters may play a part in fat transportation. The increase in lipin level during the onset of lactation is not accompanied either by a change in character of the fatty acids or by a difference in distribution.

F. O. HOWITT.

Influence of the spleen on cholesterol metabolism. E. LIVERANI (Arch. Farm. speriment., 1932, 53, 166—177).—Stimulation of the spleen provokes a rise in blood-cholesterol in the splenic vein. The spleen regulates the blood-cholesterol level.

R. K. CALLOW.

Composition of the contents of the small intestine in normal dogs after a fatty meal. H. WENDT (Biochem. Z., 1932, 245, 80—84).—The neutral fat, free fatty acid, and soap content of the upper $\frac{2}{3}$ and lower $\frac{1}{3}$ of the small intestine in dogs 3, 4, 5, and 7 hr. after a fatty meal (100 g. of olive oil) is investigated. Only a small portion (26—34%) of the total fat is in the hydrolysed condition.

P. W. CLUTTERBUCK.

Metabolism of tricaprins. M. POWELL (J. Biol. Chem., 1932, 95, 43—45).—Tricaprin fed to rats as the sole source of fat in the diet results in decanoic acid forming 15% of the fatty acids of the fat depots. This confirms the view that, whilst C or lower fatty acids tend to disappear or form longer chains, C₁₀ or higher acids are deposited in the fat depots unchanged (cf. A., 1929, 596, 1484; 1931, 760).

F. O. HOWITT.

Consumption of foodstuffs and the vitamin requirement of cattle from birth to the age of 2½ years. H. ISAACHSEN (Bied. Zentr., 1932, B, 3, 540—548).—Evidence is presented that in ruminants vitamin-B is formed in the digestive tract with the aid of bacteria. 3—4 kg. of roots per day supply sufficient vitamin-C for the winter feeding of cattle.

A. G. POLLARD.

Metabolisable energy and net energy values of maize meal. E. B. FORBES, W. W. BRAMAN, M. KRISS, and R. W. SWIFT (J. Agric. Res., 1931, 43, 1015—1026).—The net energy val. of maize meal is greater when fed in combination with lucerne hay than when it is fed exclusively.

H. DAVSON.

Nutritive value of cereals. V. FAMIANI (Atti R. Accad. Lincei, 1931, [vi], 14, 306—309).—Growing albino rats, fed with maize and barley, grow more rapidly on small-grained seed than on large-grained, but in other respects no substantial differences are observed.

T. H. POPE.

Physiological effect of rations restricted principally or solely to the lucerne plant. III. Influence of various mineral supplements on the calcium, phosphorus, and nitrogen metabolism

of dairy cattle. J. R. HAAG, I. R. JONES, and P. M. BRANDT (J. Dairy Sci., 1932, 15, 23—28; cf. this vol., 299).—Use of Na₂HPO₄ as a supplement to lucerne hay resulted in a small positive P balance, and of bone meal in positive Ca and P balances. CaCO₃ did not affect the storage of Ca or P. N balances were variable.

A. G. POLLARD.

Coefficients of digestibility of the constituents of milk, and the balance of calcium and phosphorus in calves on a milk diet. J. S. HUGHES and H. W. CAVE (J. Nutrition, 1931, 4, 163—169).—Digestion of food including roughage is not impaired by restriction to a milk diet.

CHEMICAL ABSTRACTS.

Utilisation by normal adult subjects of the calcium and phosphorus in raw milk and in ice-cream. M. M. KRAMER, M. T. POTTER, and I. GILLUM (J. Nutrition, 1931, 4, 105—114).—Seven of 10 subjects showed more favourable Ca balances when ice-cream was the chief source of Ca. Normal subjects on an acid-forming diet utilised the Ca in ice-cream made from condensed milk at least as well as that derived from raw milk. In general, P balances followed the trend of the Ca balances.

CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism. XI. W. T. SALTER, C. FULTON, and F. ANGIER (J. Nutrition, 1931, 4, 1—13).—Calculation of the potential acidity and alkalinity of diets is discussed.

CHEMICAL ABSTRACTS.

Absorption of calcium soaps and relation of dietary fat to calcium utilisation in the white rat. O. F. BOYD, C. L. CRUM, and J. F. LYMAN (J. Biol. Chem., 1932, 95, 29—41).—Ca palmitate, stearate, oleate, and their mixtures together with a fat-free diet were fed to rats and the faeces examined for Ca and fatty acids. The Ca utilisation is greatest with the oleate and least with the stearate. Addition of fat to a diet in which Ca is supplied as CaCl₂ results in an increased acidity of the faeces, an increased absorption of Ca and P, and decreased faecal CO₂ and soaps. Replacement of CaCl₂ by Ca lactate results in a disappearance of this effect.

F. O. HOWITT.

Effect of iodine on individuals with normal metabolism. A. LEMORT (Compt. rend. Soc. Biol., 1931, 106, 1283—1284; Chem. Zentr., 1931, ii, 1877).—Administration of Lugol's solution nearly always lowers the basal metabolism.

A. A. ELDRIDGE.

Effect of [administration of] small amounts of iodine on the metabolism of the dog. C. SALVADORI (Biochem. Z., 1932, 245, 314—344).—Administration of daily doses of 2 or 4 mg. of I to the dog (3 years old) results, always after some days, in a 20% increase in the metabolic rate. When 6 mg. are given daily for 50 days the rate alternately rises and falls, the max. increase being about 25%. Toxic effects sometimes appear when the dose is 6 mg., but not when it is 2 or 4 mg. The last-named dose has a much less pronounced and less lasting effect in the young dog. In the full-grown dog daily doses of 2 and 4 mg. of I result in retention of N.

W. MCCARTNEY.

Fluorescence intra-vital microscopy and photo-chemotherapy. G. KOEGL (Mikrochem., 1932, 10, 450—451). H. F. GILLBE.

Local anæsthetics. K. MIESCHER (Helv. Chim. Acta, 1932, 25, 163—190).—The prep. and properties of "percaïn" are described. The essential feature of a local anæsthetic is the presence of a basic or O-containing substituent bound to high aliphatic or hydroaromatic radicals or certain negative groups including CCl_3 , alkyl groups, aromatic and unsaturated heterocyclic rings. The CO group in ketonic or ester form and the $\alpha\text{-NH}_2$ group are particularly favourable. Local anæsthetic effect is strengthened by introducing higher alkyl groups in the form of side-chains, by increasing the no. of aromatic or heterocyclic rings, and by introducing alkoxy-groups or basic substituents. Published work on the relation between anæsthetic effect and surface tension and on the variation of the effect with the amount of anæsthetic administered is reviewed.

E. S. HEDGES.

Micro-detection of soporifics. R. FISCHER (Mikrochem., 1932, 10, 409—429).—A sample of urine, blood, or serum is extracted with Et_2O , and barbituric acid derivatives are separated by treating the extract with aq. NaOH. The acidified solution is then extracted with Et_2O , and the soporific is isolated by evaporation of the solution and micro-sublimation of the residue. Identification is effected by observation of the sublimation temp., m. p., and appearance of the sublimate, and by measurements with the polarising microscope. Tables for identification and chemical tests are given for 21 soporifics, together with the results of applying the method to subjects who had taken veronal, noctal, and phanodorm. Veronal has been isolated from 2 c.c. of serum from a patient to whom 4—5 g. had been administered.

H. F. GILLBE.

Chronaxie. W. D. BANCROFT and G. H. RICHTER (J. Physical Chem., 1932, 36, 215—228).—A narcotic causes the excitability of an isolated tissue to increase to a max., and then to decrease below normal. Coagulating agents (e.g., salts of heavy metals) produce a similar effect. Min. excitability occurs at the isoelectric point of the protein or proteins present in the tissue.

C. T. SNELL (b).

Oxygen consumption and production of ammonia in brain tissue in presence of narcotics. M. BÜLOW and E. G. HOLMES (Biochem. Z., 1932, 245, 459—465; cf. Loebel, A., 1926, 84).—Narcotics (mixtures of O_2 with C_2H_4 , C_2H_2 , $\text{CHMe}:\text{CH}_2$, N_2O under pressure, and also ethylurethane and Et_2O), even in concns. often much greater than those required to produce narcosis, have no effect on the O_2 absorption of tissue from rabbit-brain, although still greater concn. may have some effect. Moreover, the narcosis induced does not affect the power of the tissue to produce NH_3 . In addition to free NH_3 , the lipin- and protein-free filtrate from the tissue contains a substance from which NH_3 is liberated by the action of conc. alkali.

W. MCCARTNEY.

Distribution of chloroform between erythrocytes and blood-serum. N. V. LAZAREV and E.

NUSSELMANN (Biochem. Z., 1932, 244, 417—425; cf. Winterstein and Hirschberg, A., 1927, 893).—*In vitro* in solutions of CHCl_3 in blood (pig, dog, ox, wether) the erythrocytes always contain more of the substance than does the serum. In pig's and (to a smaller extent) in dog's and ox blood, the coeff. of distribution (between erythrocytes and serum) decreases as the concn. increases. Wether's blood gives indefinite vals. Equations showing the relation between the concn. in erythrocytes and that in serum are given for pig's and ox blood. As regards the abs. magnitudes of the coeffs. (at low concn.) the bloods form the descending series: pig, dog, ox. The significance of the results for theories of narcosis is discussed.

W. MCCARTNEY.

Influence of the vegetative nerve poisons on the intermediate protein metabolism. B. ITO (Folia Pharmacol. Japon., 1931, 12, No. 2, 273—303).—As observed by determination of urinary constituents, serum HIO_3 val., and blood-residual N, adrenaline, nicotine, and pilocarpine depress, choline and eserine delay, whilst atropine temporarily increases, the intermediate protein exchange. Muscarine has no action.

CHEMICAL ABSTRACTS.

Pharmacological actions of alkyl derivatives of harmol. I. Ethylharmol. J. A. GUNN and R. ST. A. HEATHCOTE (Quart. J. Pharm., 1931, 4, 549—565).—Ethylharmol, injected subcutaneously, has a min. lethal dose of 0.15 g. per kg. for the frog and 0.2 g. per kg. for the guinea-pig. Of the various pharmacological actions described, the powerful dilatatory action on the coronary vessels is noteworthy.

F. O. HOWITT.

Pilocarpine hyperglycæmia. T. INOUE (J. Biochem. Japan, 1931, 14, 215—255).—Pilocarpine hyperglycæmia is due to sympathetic stimulation of the adrenals.

F. O. HOWITT.

Effect of ergotamine on alimentary hyperglycæmia during disease of the liver produced by phosphorus poisoning. Z. ERNST and S. KARADY (Biochem. Z., 1932, 245, 299—303).—Since administration of ergotamine to rabbits results in increase in the alimentary blood-sugar even during severe poisoning with P, it follows that, in the healthy organism, the prevention of hyperglycæmia by the drug is due to an increase in the power of the liver to assimilate sugar.

W. MCCARTNEY.

Hypoglycæmic action of bile acids. K. TANAKA (J. Biochem. Japan, 1932, 14, 463—473).—*apo*-, *D*hydro-, and dehydrodeoxy-cholic acids have the same hypoglycæmic activity as cholic or deoxycholic acid, whilst cholanic and cholatrienic acids are inactive. Hence the power to lower the blood-sugar appears to depend on the $:\text{CH}:\text{OH}$ or $:\text{CO}$ group in the bile acids.

F. O. HOWITT.

Hydrocyanic acid. VII. Hydrocyanic acid hyperglycæmia. F. KUDO (J. Biochem. Japan, 1932, 14, 447—461).—The hyperglycæmia due to HCN poisoning in rabbits is considerably reduced by removal of the medulla of the suprarenals, whilst the poisoning is accompanied by an increase of adrenaline in the blood. Hence the increased blood-sugar is largely due to abnormal liberation of adrenaline.

F. O. HOWITT.

Influence of trypan on formation of glycogen. Insulin and glycogen. R. MESSINA (Arch. Farm. speriment., 1932, 53, 178—191).—Less glycogen is found in the liver, muscle, and myocardium of rats after injection of trypan. Comparison of the effect of glucose, adrenaline, and insulin on trypanised and normal rats shows that trypan retards tissue-glycogen formation. Insulin stimulates tissue metabolism and provokes combustion of available sugar, and glycogenolysis. R. K. CALLOW.

Sulphonium compounds and the autonomic nervous system. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1932, 44, 63—79).—These show an action similar to though less marked than that of the N-containing compounds. As with the latter, substitution of one or more Me groups by CH_2Ph reduces both the "muscarine" and "nicotine" activities in anaesthetised or pithed cats. P. G. MARSHALL.

General properties and toxicity of propylene glycol. M. A. SEIDENFELD and P. J. HANZLIK (J. Pharm. Exp. Ther., 1932, 44, 109—121).—This compound exerts a local burning sensation on the tongue without injury to the oral mucosa; it has a more acid taste than glycerol or ethylene glycol, and leaves no after-effects. It is less toxic than ethylene glycol, being lethal only in 40% of rats injected intravenously with 15 c.c. per kg. body-wt. Continued drinking of even a 10% solution has no effect on growth and body-wt., and no pathological changes are observed. P. G. MARSHALL.

Toxicity of thiophen. F. FLURY and F. ZERNIK (Chem. Ztg., 1932, 56, 149).—Thiophen is slightly more toxic than C_6H_6 . E. S. HEDGES.

Effect of caffeine and theophylline on the solubility of uric acid and sodium urate. A. JUNG and W. ZORKENDORFER (Schweiz. med. Woch., 1930, 60, 503; Chem. Zentr., 1931, ii, 2332).—Caffeine (2%) increases the solubility of uric acid in H_2O seven-fold. Na urate and uric acid also show increased solubility in phosphate-buffered solution after addition of caffeine; for uric acid the solubility decreases with a rise in p_{H} and for the urate it decreases linearly with an increase in the $[\text{Na}^+]$ of the Na phosphate. Theophylline has an effect similar to but smaller than that of caffeine. L. S. THEOBALD.

Diuretic action of salicylates on uric acid, and solubility of uric acid. I. YAMAGUCHI (Folia Pharmacol. Japon., 1931, 12, No. 3, 397—405).—Alkali (stomach tube) increases whilst acid diminishes the uric acid excretion of rabbits and the diuretic action of salicylates. The solubility of uric acid is increased by salicylates in the (descending) order: Ca, Mg, Li, Na, K; the diuretic action on urinary uric acid was also influenced in this order.

Reversible coagulation in living tissue. X. W. D. BANCROFT, R. S. GUTSELL, and J. E. RUTZLER, jun. (Proc. Nat. Acad. Sci., 1932, 18, 8—15).—A morphine addict was successfully treated by the administration of large doses of NaCNS while morphine was gradually withdrawn. The CNS probably acts by peptising rapidly the protein colloids agglom-

erated by morphine and also by displacing the morphine adsorbed in the tissues and thus causing more rapid elimination. W. O. KERMACK.

Coagulation of proteins in marine borers. W. D. BANCROFT (J. Physical Chem., 1932, 36, 546—548; cf. A., 1931, 657).

Amount of adrenaline secreted from the suprarenal glands of dogs in hæmorrhage and poisoning. Y. SATAKÉ (Tohoku J. Exp. Med., 1931, 17, 333—344).—Hæmorrhage or poisoning by guanidine, peptone, or camphor causes a sudden increase in the adrenaline output of dogs; caffeine and tetrahydro- β -naphthylamine have a slight effect, whilst urethane and strychnine cause a slow increase.

CHEMICAL ABSTRACTS.

Influence of piqûre on the adrenaline discharge, blood-sugar, and blood-pressure. T. YEN, T. KAIWA, and M. WADA (Tohoku J. Exp. Med., 1931, 17, 345—377).—Piqûre of the floor of the fourth ventricle of dogs caused a 50% elevation in blood-sugar within 30 min.; the blood-adrenaline increased from 0.00001—0.00002 to 0.00001—0.00005 mg. per min. per kg. Et_2O anaesthesia obscured the changes.

CHEMICAL ABSTRACTS.

Relationship between chemical constitution and taste. A. L. FOX (Proc. Nat. Acad. Sci., 1932, 18, 115—120).—The bitter taste of many derivatives of phenylthiocarbamide, *s*- and *as*-diphenylthiocarbamide, and certain other derivatives of thiocarbamide, such as *s*-dibenzylthiocarbamide, is felt only by certain individuals; to others they are tasteless. This failure in taste perception, which it is proposed to call "taste blindness," is apparently not correlated with age, sex, or race. The failure of taste in these individuals may be due to the insolubility of the compounds in their saliva.

W. O. KERMACK.

Genetics of sensory thresholds for phenylthiocarbamide. A. F. BLAKESLEE (Proc. Nat. Acad. Sci., 1932, 18, 120—130).—The threshold concns. of aq. solutions of phenylthiocarbamide at which the bitter taste is distinguishable is different for different individuals and in certain instances is so high that a conc. aq. solution of the substance or the dried powder applied to the tongue does not evoke the taste. These taste differences appear to be innate and to be inherited by the offspring. The thresholds for other tastes also differ according to the individual and, further, certain individuals are unable to distinguish between certain tastes such as bitter and acid. W. O. KERMACK.

Liposelection of cations. A new method in experimental hydrology. M. LOEPER and A. MOUGEOT (Compt. rend., 1932, 194, 575—576).—It is suggested that the property of fatty acids of destroying the prophylactic power of mineral waters by pptn. of the cations might be used to determine the effective ions in toxiphylactic or zymosthenic material. A. LAWSON.

Physiological effect of trihydrol in water. T. C. BARNES (Proc. Nat. Acad. Sci., 1932, 18, 136—139).—The growth of *Spirogyra* is increased by the presence of trihydrol, $(\text{H}_2\text{O})_3$, in the culture medium.

A similar effect of trihydrol is probably of wide importance in biological processes.

W. O. KERMACK.

Calcium gluconate solutions for hypodermic use and control of their titre. G. C. GUALDONI (Boll. chim.-farm., 1932, 71, 45—47).—Discussion of de Carli's results (this vol., 16, 22, 44).

T. H. POPE.

Sorption of intestinal gases by "adsorgan," "silargel," "argocarbon," and preparations 779 f and 1112. K. H. BAUER and K. RAUSCHER (Pharm. Zentr., 1932, 73, 129—133).—The sorption of CO_2 , CH_4 , H_2S , CO , air, and H_2 by the above adsorbents in presence of H_2O has been measured. The prep. 1112 (a highly active Ca silicate) has an extraordinarily high sorption capacity for CO_2 . Adsorgan and silargel adsorb intestinal gases strongly.

E. S. HEDGES.

Loss of calcium from blood in oxalate and fluoride poisoning. Transport of calcium in the organism. A. JODLRAUER (Arch. exp. Path. Pharm., 1932, 164, 464—468).—In rabbits on a Ca-poor diet subcutaneous administration of large doses of $\text{Na}_2\text{C}_2\text{O}_4$ or NaF causes a fall in blood-Ca which, although not fatal, may nevertheless be greater than the smaller fall brought about by the administration of a series of small doses of these compounds sufficient to cause the death of the animal. The development of tetanic symptoms does not run parallel with the level of the blood-Ca. In the nucleated red blood-corpuses of the fowl the fall in Ca concn. following administration of $\text{Na}_2\text{C}_2\text{O}_4$ is much greater than in the plasma.

W. O. KERMACK.

[Physiological] action of calcium. V. Autonomously equilibrium in the ox in relation to the composition of the blood-serum in experimental and pathological hypocalcæmia. Toxic action of intravenous injections of oxalates and citrates. L. SEERLES, B. SJOLLEMA, and F. C. VAN DER KAAJ (Biochem. Z., 1932, 244, 253—267).—In cattle the decrease in the Ca content of the blood-serum following intravenous injection of $\text{Na}_2\text{C}_2\text{O}_4$ reaches its max. in a few min. The extent of the decrease and the severity of the accompanying toxic symptoms are relatively greater in cows than in young calves. Injection of even a large excess of oxalate does not ppt. all the serum-Ca: 30—40% of it is present in non-ionised form and is only incompletely and with difficulty pptd. by oxalate. If only a small part of this fraction is pptd. by a large excess of oxalate, death ensues. As a rule the injections cause decreases of about 10—15% in the inorg. P and Mg content of the serum. No decrease in the Ca content of the serum follows intravenous injection of Na citrate.

W. McCARTNEY.

Distribution of chlorides and iodides in the skin and muscles of the rabbit after administration of potassium iodide. H. A. SHOEMAKER and F. P. UNDERHILL (J. Pharm. Exp. Ther., 1932, 44, 23—42).—A single dose of 0.5 g. of KI per kg. body-wt. administered *per os* causes an increase in the I content of tissues which reaches a max. 3 hr. after administration. Multiple doses do not further increase the I content of tissues. The Cl : I ratio is

const. in the same animal and I shows no tendency to displace Cl.

P. G. MARSHALL.

Can iodides replace chlorides in chloride deficiency? H. A. SHOEMAKER and F. P. UNDERHILL (J. Pharm. Exp. Ther., 1932, 44, 43—46).—When there is a demand for Cl^- , as in the case of superficial burns, this cannot be replaced by I^- .

P. G. MARSHALL.

Parenteral resorption of colloids. IV. M. MURATA (Biochem. Z., 1932, 245, 67—70).—With sufficiently large doses of NaI, after oral and intraperitoneal administration, I appears in the serum. After administration of lipoiodine orally, I slowly appears in the serum and remains detectable for a long time. After subcutaneous administration, I appears in the serum very late and transiently and after intraperitoneal administration it does not appear in the serum, although detectable in the urine for a long time. With iodised caseinogen I never appeared in the serum, but was present in the urine.

P. W. CLUTTERBUCK.

Effect of feeding titanium oxide to sheep. H. O. ASKEW (New Zealand J. Sci. Tech., 1931, 13, 76—77).—Daily ingestion by sheep of large quantities (2—3 g.) of TiO_2 produces no ill-effects after 3 months. The complete elimination of the TiO_2 in the excreta suggests its suitability for use as a reference substance for digestibility trials.

W. G. EGGLETON.

Oxygen-transporting enzyme of respiration. O. WARBURG (Angew. Chem., 1932, 45, 1—6).—A lecture.

Histochemical detection of peroxidases. L. LISON (Compt. rend. Soc. Biol., 1931, 106, 1266—1268; Chem. Zentr., 1931, ii, 222).—A reagent prepared from acid-violet or -fuchsin (1.5 g.), Zn dust (5 g.), AcOH (2 c.c.), and H_2O (100 c.c.), a further 2 c.c. of AcOH being added after cooling, remains colourless for days; before use, 10 c.c. of the filtered solution are treated with 1 c.c. of H_2O_2 and the tissue is immersed in it for 10 min. "Leucozine" is particularly suitable for the detection of hæmoglobin.

A. A. ELDRIDGE.

Action of peroxidases. I. Determination of activity by means of benzidine. K. L. ZIRM, F. REUTER, and H. WALLSTAEDT (Biochem. Z., 1932, 245, 290—298).—The coloured solution obtained by the action of peroxidase on benzidine in AcOH in the presence of H_2O_2 yields with excess of NaOH a dye sol. in EtOH and capable of being used for colorimetry. This dye (termed purpurobenzidine) can be obtained in the same way by the action of KMnO_4 on benzidine in AcOH. The peroxidase of hæmin and of horse-radish can be determined colorimetrically with the help of solutions of the dye, units similar to those given by Willstätter and Pollinger (A., 1923, i, 262) being used to express the activity.

W. McCARTNEY.

Action of carbon monoxide on peroxidase. K. A. C. ELLIOTT and H. SUTTER (Z. physiol. Chem., 1932, 205, 47—54).—The apparent inhibition of peroxidase by CO (A., 1931, 1455) is an unsp. effect due to agitation by the gas stream and is also given by N_2 , air, and H_2 . If a saturated solution of CO is used in place of a stream of gas, no inhibition is observed,

even with a $\text{CO}/\text{H}_2\text{O}_2$ quotient of 14, using the malachite-green method (A., 1926, 1275).

J. H. BIRKINSHAW.

Lipin-oxidase in the soya bean. E. ANDRÉ and K. HOU (Compt. rend., 1932, 194, 645—647).—Exposure to air of the unboiled residue from the prep. of soya-bean "milk" causes an increase in d and Ac val. and a decrease in I val. of the Et_2O extract as compared with the corresponding vals. for the boiled material. This is believed to indicate the presence of a lipin-oxidase.

A. LAWSON.

o-Quinones as enzyme models. II. Experiments with various substrates. B. KISCH (Biochem. Z., 1932, 244, 440—450; cf. this vol., 90).—Of the pyrocatechol derivatives investigated for oxidative deamination of NH_2 -acids, the most active, between p_{H} 6.9 and 8.0, are, for glycine and phenylglycine, adrenaline; for glycine Et ester, glycylglycine, serine, and leucine, hydroxyquinol. The $[\text{H}^+]$ has a great effect on the activity. Isatin and alloxan do not effect deamination under the conditions chosen. α -Leucine differs from leucine and resembles valine and α -aminobutyric acid in not being appreciably deaminated by any of the catalysts. From the notable specificity of the latter it is concluded that within the mol. of org. substances groups apparently exactly similarly constituted differ as a result of the influences of other parts of the mol.

W. MCCARTNEY.

Influence of chlorine ions on salivary amylase. T. OMORI (J. Biochem. Japan, 1931, 14, 339—342).—Electrodialysis of saliva yields a liquid which exhibits no amylolytic activity except when NaCl is added. This activity is proportional to the amount of Cl^- bound by the constituents of the solution. PO_4^{3-} and SO_4^{2-} , which do not activate the enzyme, do not reduce the total conductivity of the system. Hence neutral salts such as NaCl and to a smaller extent NaNO_3 , which activate amylase, combine chemically with the enzyme.

F. O. HOWITT.

Activation of amylase. R. H. CLARK, F. L. FOWLER, and P. T. BLACK (Trans. Roy. Soc. Canada, 1931, [iii], 25, 111, 99—105).—The rate of hydrolysis of dil. starch solutions (0.1—5%) at 25° by "malt diastase, U.S.P." is increased by "activators" such as ethylene chlorohydrin, KCNS, and thiourea. The increase in enzyme activity is approx. proportional to the concn. of the "activator" for low concns. There is an optimum concn. for each "activator" which gives the max. rate of hydrolysis. The course of the reaction was followed by (a) using 0.005N-I solution to detect the presence of starch, (b) determining the reducing substances in the sample. The activation of the enzyme cannot be attributed to small changes in p_{H} .

J. L. D'SILVA.

Effect of reaction on the destruction of ptyalin. R. EGE (Biochem. Z., 1932, 244, 243—257).—The ptyalin of different individuals varies very greatly in its power to resist destruction. p_{H} 6.5 is the reaction optimum for the enzyme; at 5.9 and 7.5 the resistance falls to about half and beyond these vals. further loss of power to resist occurs. For equal changes in $[\text{H}^+]$ the change in the resistance is the greater the further the $[\text{H}^+]$ is removed from the

optimum.

optimum. It follows that ptyalin cannot be regarded as an ampholyte with isoelectric point at p_{H} 6.5 and having a stable undissociated mol. but very labile ions. The destruction of ptyalin at p_{H} < about 3.2 is not a unimol. process, but is very nearly so at other reactions.

W. MCCARTNEY.

Hydrolytic and synthetic action of preparations from the pancreas of pigs receiving different diets. E. BACH and L. LOVAS (Biochem. Z., 1932, 245, 345—349).—As regards their power to hydrolyse and synthesise esters, pancreas preps. from fat pigs are two or three times as effective as are those from thin animals. Inactivated pancreas powder from fat pigs contains material which promotes enzymic esterification.

W. MCCARTNEY.

Enzymic fission of dehydrogenated peptides. Discovery of a dipeptidase. M. BERGMANN and H. SCHLEICH (Z. physiol. Chem., 1932, 205, 65—75).—Glycyldehydrophenylalanine (I) with $\text{CH}_2\text{Cl}-\text{COCl}$ yields chloroacetyl-glycyldehydrophenylalanine, m. p. 212° (corr.), which in aq. NH_3 gives diglycyldehydrophenylalanine (II), becomes brown at 214°, decomp. 226°. Extracts of pig's and sheep's kidney hydrolyse (I). The enzyme responsible, dehydrodipeptidase, is stable in glycerol extracts and is very sensitive to HCN. The optimum p_{H} is 7.5. The enzyme does not hydrolyse the tripeptides glycyldehydrophenylalanyl-glycine and glycyldehydrophenylalanyl-d-glutamic acid (in which the dehydro-amino-acid has no free CO_2H), but mixed with other enzymes it does attack (II), yielding 2 mols. of glycine and 1 mol. each of NH_3 and phenylpyruvic acid. In the last case the first stage of the hydrolysis is due to the aminopolypeptidase.

J. H. BIRKINSHAW.

Histochemistry of enzymes. II. Distribution of peptidase in roots and sprouts of malt. K. LINDERSTROM-LANG and H. HOLTER (Compt. rend. Lab. Carlsberg, 1932, 19, No. 6, 39 pp.).—Microtome sections of the primordial root and leaf-shoot of sprouting barley are examined for peptidase activity by a micro-method in which alanyl- or leucyl-glycine is used as substrate and the hydrolysis is followed by titration (cf. A., 1931, 1455). The activity varies strongly along the primordial root, being at a max. at a distance of 0.8 mm. from the root-tip, but only slightly along the leaf-shoot. The ratio of the velocities of hydrolysis of the two substrates also varies along the root and has a min. val. at the growth region of the tip.

F. O. HOWITT.

Salicylaldehyde-phosphoric acid and oxidative dephosphorylation. C. MANAKA (J. Biochem. Japan, 1932, 14, 481—487).—Salicylaldehyde-phosphoric acid is hydrolysed by taka- or kidney-phosphatase, the p_{H} optima being 3 and 10, respectively. In presence of oxidising agents such as H_2O_2 the aldehyde forms the corresponding acid, which spontaneously undergoes dephosphorylation. The p_{H} optima of these reactions are 10 and 5.6, respectively, that of the complete process being 7.

F. O. HOWITT.

Influence of bile acids on glycerophosphatase. II. H. TAKATA (J. Biochem. Japan, 1932, 14, 439—445).—The *in vitro* synthesis of glycerophosphoric acid

in liver- and, to a greater extent, in kidney-tissue is increased by addition of Na cholate.

F. O. HOWITT.

Influence of thiol compounds on phosphatase. E. WALDSCHMIDT-LEITZ and A. SCHAFFNER (*Naturwiss.*, 1932, 20, 122).—Catheptic enzymes are activated by SH-compounds (this vol., 85). The hydrolysis of org. esters of H_3PO_4 is also influenced by SH-compounds. The rate of hydrolysis of glycerophosphate by kidney-phosphatase is diminished considerably by cysteine, whilst its synthesis is only slightly affected by this substance. W. R. ANGUS.

Allantoinase. K. Ro (*J. Biochem. Japan*, 1932, 14, 405—411).—An aq. extract of soya bean is pptd. with $COMe_2$, the ppt. extracted with 70% aq. EtOH followed by 90% aq. EtOH and finally Et_2O , yielding a powder containing allantoinase. This prep. hydrolyses allantoin quantitatively to allantoic acid, the reaction being unimol. with p_H and temp. optima of 7.3 and 50—60°, respectively. F. O. HOWITT.

Isolated liver-cells. I. Vitality of the cells and their enzymes. II. Effect of dyes. S. KODAJIMA (*J. Biochem. Japan*, 1931, 14, 279—289, 291—304).—I. The peptidase, lipase, and, to a greater extent, the amylase of liver-cells in physiological saline retain their activities for some days. The nucleus-staining capacity is lost after 14 days. No enzyme capable of hydrolysing NH_2 -acids could be detected.

II. The vitality of the cells is reduced more by acidic than by basic dyes. Amylase is the least affected of the cell-enzymes, whilst neutral-red has a marked action on the lipase activity. F. O. HOWITT.

Uricase. K. Ro (*J. Biochem. Japan*, 1931, 14, 361—390).—Uricase is prepared from ox-kidney by $COMe_2$ -pptn. of an aq. extract, the ppt. being washed with aq. EtOH followed by Et_2O and finally dried. Such a prep. contains proteins closely associated with the enzyme, which is readily extracted by solutions at p_H 9.4, the optimum reaction. The temp. optimum is 45°, the activity being destroyed by heating to 70° and by the presence of 12% EtOH or Et_2O . During its action on uric acid oxidation-reduction potentials indicate the presence of an intermediary of high oxidation potential between the substrate and the allantoin produced. The enzyme is inhibited by KCN or by absence of O_2 and is accelerated by small concns. of $CuSO_4$. Injection into rabbits results in the formation of an anti-enzyme in the serum.

F. O. HOWITT.

Kinetics of carboxylase action and its significance in controlling the biological decomposition of carbohydrates. K. WETZEL (*Planta [Z. wiss. Biol.]*, 1932, 15, 697—738).—The action on org. acids of carboxylase from yeast and from seeds is largely restricted to the decomp. of α -keto-acids. Oxalacetic and pyruvic acids are readily decomposed. Mesoxalic acid is not attacked and tends to inhibit the action of the enzyme on pyruvic acid. Carboxylase action is depressed by aldehydes which may be adsorptively combined with the enzyme. The reactive group of carboxylase is probably an NH_2 -group. Regulation of carbohydrate decomp. and acid production in plants is probably related to the inhibitory action of

certain products (e.g., MeCHO and methylglyoxal) on carboxylase. The production of lactic acid rather than EtOH from methylglyoxal by yeast and the action of "ketone-aldehyde mutase" are similarly explained. Relationships between carboxylase activity and the temp. and reaction of the substrate are examined. The autolytic decomp. of carboxylase at const. temp. and p_H is of the nature of an irreversible unimol. reaction.

A. G. POLLARD.

Oxygen consumption and carbon dioxide production during the growth of yeast. O. W. RICHARDS and F. W. HAYNES (*Plant Physiol.*, 1932, 7, 139—144).—The O_2 consumption of yeast cultures reached a max. during the equilibrium interval between the first and second cycles of growth. The utilisation of O_2 for the oxidation of metabolic products in the culture medium is suggested. CO_2 production declines as the sugar remaining in the medium decreases.

A. G. POLLARD.

Nature of zymase fermentation. W. A. BELTZER and E. N. GORKIN (*Biochem. Z.*, 1932, 245, 146—148).—The prep. of an active yeast juice from powdered dried yeast without maceration is described. The view that the fermentation of yeast juice is due to the activity of ultramicroscopic micro-organisms which are not removed by centrifuging is discredited, since the unpowdered yeast always gave an inactive extract.

P. W. CLUTTERBUCK.

Fermentation of trehalose. A. J. KLUYVER and F. L. W. VAN ROOSMALEN (*Biochem. Z.*, 1932, 245, 13—24).—The fermentation velocities of glucose, fructose, maltose, and trehalose with dried yeast under comparable conditions and the effect of phosphate are investigated. It is probable that the formation of trehalosemonophosphate in the fermentation of fructose and glucose by dried yeast is due at least partly to the phosphorylation of trehalose pre-existing in the yeast, but the results leave open the possibility of formation of the ester by synthetic processes.

P. W. CLUTTERBUCK.

Action of iodine on yeast. II. K. SCHARER and W. SCHWARTZ (*Biochem. Z.*, 1932, 245, 218—233).— I^- and IO_3^- under determined conditions increase the growth and the germinating power of yeast. Mol. I is more toxic than I^- . "Uroscleetan" and "yatren" show the stimulatory action and "alivan" gives an increased growth, but only in very low concn. (10⁻⁸%). Iodoethylthiosinamine gives a small increase in growth at concns. of 5×10^{-5} to 5×10^{-4} , larger amounts being toxic and causing rapid diminution of yield. (Cf. A., 1927, 903.) P. W. CLUTTERBUCK.

Nomenclature of catalysts involved in alcoholic fermentation. A. J. KLUYVER and A. A. STREEMAN (*Biochem. Z.*, 1932, 244, 366—369).—Since the simultaneous action of several activators, of which Euler's co-enzyme is merely one, is necessary in the fermentation of hexoses by yeast, the nomenclature suggested by Neuberg and Euler (A., 1931, 1333) is inapplicable. The names holozymase and apozymase may logically be retained for the present, but the term cozymase should be abandoned. W. MCCARTNEY.

Biological gas reactions. II. Formation of acetic acid in the biological conversion of carbon

mon- and di-oxide into methane. F. FISCHER, R. LIESKE, and K. WINZER (Biochem. Z., 1932, 245, 2—12).—The biological conversion is described of $\text{CO} + \text{H}_2\text{O}$ in presence of a colloidal substance into $\text{CO}_2 + \text{H}_2$ and of $\text{CO}_2 + \text{H}_2$ into AcOH , which in presence of colloidal substance is further converted into $\text{CO}_2 + \text{CH}_4$. The formation of AcOH from $\text{H}_2\text{CO}_3 + \text{H}_2$ is an essential stage in the biological formation of CH_4 . P. W. CLUTTERBUCK.

Conversion of lactic into pyruvic acid by means of *Bacterium Delbrücki*. E. SIMON (Biochem. Z., 1932, 245, 488—493).—When *B. Delbrücki* is cultivated in a suitable medium containing pure Ca lactate pyruvic acid is produced and consequently the view of Kostytshev and others (A., 1930, 960) that this acid is an intermediate stage in the conversion of methylglyoxal into lactic acid is disproved. Also, there is no production, in the circumstances mentioned, of acetoin, diacetyl, or β -butylene glycol. *B. Delbrücki* lives and grows for at least 12 days in the medium, eventually destroying the pyruvic acid. W. MCCARTNEY.

Bacteria producing trimethylene glycol. C. H. WERKMAN and G. F. GILLEN (J. Bact., 1922, 23, 167—182).—Trimethylene glycol is produced from glycerol by many organisms. A. G. POLLARD.

Fermentation of glyceraldehyde. A. I. VIRTANEN and J. VON HAUSEN (Z. physiol. Chem., 1932, 204, 235—246).—*B. coli* I ferments only the *l*-form of *dl*-glyceraldehyde. No acclimatisation of the organism to glyceraldehyde was observed. Glyceraldehyde had a definitely toxic action on the bacteria. In broth containing glyceraldehyde no growth was observed although the bacteria grew in broth alone. As with dihydroxyacetone the main portion is probably converted by a Cannizzaro reaction into glycerol and glyceric acid (which is further fermented to AcOH , HCO_2H , CO_2 , and H_2), whilst a parallel reaction gives lactic acid (25%) by way of methylglyoxal. J. H. BIRKINSHAW.

Aerobic pectin fermentation. A. I. MAKRIKOV (Zentr. Bakt. Par., 1932, II, 85, 339—348).—Anaerobic fermentation of pectin substances by *Granulobacter pectinovorum* yields butyric acid and AcOH with small amounts of CO_2 and H_2 . With aerobic organisms (*Pectinobacter amylophilum*) 75% of the pectin is converted into CO_2 and H_2 with smaller proportions of HCO_2H and AcOH . During the retting of flax by the latter organism pigment and extractive matter are destroyed and retting can be completed in one operation. A. G. POLLARD.

Decomposition of pentosans by soil bacteria. J. ZIEMIECKA (Rocz. Nauk Roln. Les., 1931, 25, 313—332; Chem. Zentr., 1931, ii, 2470).—*B. xylanophagus*, which decomposes xylan in non-acid medium, but not cellulose, was isolated from soil, straw, and stable manure. A. A. ELDRIDGE.

Metabolism of bile acids. IV. Influence of bacteria and of ultra-violet and X-rays on bile acids. H. MIKAMI (J. Biochem. Japan, 1932, 14, 489—500).—Bile acids in sterile aq. solution experience gradual decomp. on keeping at room temp., a decomp. which is slightly greater following inoculation

with *B. coli*. EtOH solutions are more stable. Ultra-violet but not X-irradiation of aq. solutions accelerates the decomp. F. O. HOWITT.

Secretion and thermostability of bacterial proteases. A. I. VIRTANEN and J. TARNANEN (Z. physiol. Chem., 1932, 204, 247—258).—Young proliferating cells of *B. fluorescens liquefaciens* and *B. subtilis* excrete practically all their proteinase into the medium, since after filtration the bacterial mass shows only 0.4—0.6% of the activity of the filtrate. The bacterial mass contains polypeptidase and dipeptidase, which are liberated only after autolysis. The proteinase is stable at 100° for several min. in cultures containing protein and is not immediately inactivated at 110°. In protein-free cultures, the enzyme is inactivated at 60° in 30 min. The apparent thermostability at 100° is due to protective action of protein and may be imitated by addition of caseinogen, with which the protection is minimal at 60°, but marked above 70°. J. H. BIRKINSHAW.

Mechanism of the reduction of nitrates [by bacteria]. IV. M. P. KORSKOVA (Bull. Acad. Sci. U.S.S.R., 1931, 833—846; cf. A., 1930, 251; 1931, 265).—*B. turanicum* grows well at first in solutions in which the source of N is solely inorg., but gradually loses the ability to do so. When this organism is grown in yeast water-glucose solutions containing KNO_3 it activates the system org. compound-nitrate to an oxidation-reduction process, during which CO_2 is evolved and KNO_3 is apparently reduced to $\text{H}_2\text{N}_2\text{O}_2$ or HNO . T. H. POPE.

New autotrophic bacterium which oxidises ammonia directly to nitrate and decomposes petroleum. C. B. LIPMAN and L. GREENBERG (Nature, 1931, 129, 204—205).—An organism, which grows under autotrophic conditions in an inorg. salt medium with $(\text{NH}_4)_2\text{SO}_4$ or KNO_3 as the source of N, oxidises NH_3 directly to NO_3 and more quickly than do the nitrifying bacteria. It also decomposes petroleum completely without forming gases other than CO_2 . Cellulose is not decomposed. L. S. THEOBALD.

Intake of dissolved substances by bacteria. I. H. HABS (Z. Hyg., 1932, 113, 239—272).—Under uniform conditions the I-absorbing capacity of an individual species of bacteria is const. Variations among different strains of the same species are small, but between different species differences in I fixation are significant. The intake of I probably results from physical adsorption followed by chemical combination. The I absorption of bacterial cultures increases with age and is not entirely accounted for by the additional amount of bacterial substance formed. Killing bacteria by heat does not destroy their I-fixing power provided the bacterial substance is not destroyed. Products of bacterial metabolism affect the I intake, especially if they tend to change the $[\text{H}^+]$ of the suspension. The proportion of "loosely combined" I is not related to the nature of the organism nor to the total surface exposed, but definite amounts of "chemically combined" I can be associated with particular species of organisms. A. G. POLLARD.

Bacterial fluorescence in various media. II. Production of fluorescence in peptone media. F. R. GEORGIA and C. F. POE (J. Bact., 1932, 23, 135—145; cf. this vol., 198).—Peptones vary considerably in their ability to cause pigmentation in bacterial cultures. The production of fluorescence was not facilitated by the use of media containing high concn. of peptone, nor by the presence of purines, meat bases, or asparagine. A. G. POLLARD.

Agglutination. E. FREUND and R. KATZ (Biochem. Z., 1932, 245, 35—43).—The behaviour of normal serum and serum in various cases of sepsis against bacteria is investigated, and tables summarise the amount of agglutination with various organisms in different pathological conditions. The agglutination obtained with normal is not obtained with septic serum. P. W. CLUTTERBUCK.

Bacterial agglutination and its relation to colloidal theory. S. MUDD, R. L. NUGENT, and L. T. BULLOCK (J. Physical Chem., 1932, 36, 229—258).—The addition of electrolyte to a suspension of bacteria reduces the electrokinetic potential, ζ , but does not necessarily cause pptn., since the stability of the suspension depends also on the degree of hydration of the bacterial surface, which is different for different bacteria. The stability of a bacterial or other suspension depends on the relation between the repulsive forces, principally ζ , and the work of cohesion, W , which is the product of the interfacial tension, γ , between particle and medium, and the area of contact. Hydration reduces W by reducing γ . Agglutination by antibodies may be due to changes either in W or in ζ . Non-sp. agglutination by tannin produces a high negative charge on the particles, but also a relatively hydrophobic surface with a high W . K. V. THIMMANN (c).

Bacterial substances isolated from *B. typhosus* and *B. paratyphosus*. K. NAGASE (Japan J. Exp. Med., 1930, 8, 365—369).—Nucleoproteins and residue antigens were prepared. The latter gave only ninhydrin and Molisch reactions; they showed no antigenic activity *in vivo*, but gave sp. precipitin reactions with homologous antibacterial sera. The nucleoproteins were antigenic *in vivo*, but gave only group precipitin reactions. CHEMICAL ABSTRACTS.

Bacterial substances isolated from dysentery bacilli. K. NAGASE (Japan J. Exp. Med., 1930, 8, 371—378).—The nucleoprotein and residue antigen prepared from *B. dysenteriae* are analogous to those from *B. typhosus*. CHEMICAL ABSTRACTS.

Unitarian hypothesis of antibodies. I. II. Quantitative relationship among antibodies of serum and different serum-protein fractions. T. TAKAYAMA (Sei-i-kwai Med. J., 1930, 49, No. 7, 21—57, 58—85).—All the antibodies in the serum immunised against cholera vibrio and goat corpuscles are in the serum-globulin fractions, the greater amount being sometimes found in the pseudo-globulin. The concns. of the antibodies in the serum are the same as the sum of those in serum-globulin fractions. When immune cholera serum and serum immune against goat corpuscle are heated, all the antibodies decrease as the temp. rises, those in the pseudo-

globulin being more resistant than those in the euglobulin. Probably all the antibodies are the same substance. CHEMICAL ABSTRACTS.

Antigens and antibodies of the staphylococcus. O. GENGOV (Ann. Inst. Pasteur, 1932, 48, 135—143).—Neither washed suspensions of pyogenic staphylococci killed with CH_2O nor cultures of staphylococci which have been lysed by bacteriophage contain demonstrable toxin and neither of these preps. when injected into rabbits produces antibodies to the toxins of the staphylococci. These antitoxins can be produced only by the injection of free toxin or of anatoxin. W. O. KERMACK.

Hæmolysis of blood-cells by staphylo toxin. O. GENGOV (Ann. Inst. Pasteur, 1932, 48, 19—26).—Hæmolysis of blood-cells caused by staphylo toxin does not destroy the ability of the leucocytes to transform cholera vibrios into granules, or their power to immunise rabbit serum against *B. anthracis*, or to prevent the participation of the blood-platelets in the coagulation of the blood. A. LAWSON.

Hæmotoxin of bacteria. K. NAGASE (Japan J. Exp. Med., 1930, 8, 379—389).—Purified hæmotoxins, giving negative protein and positive Molisch reactions, produced sp. antihæmotoxins *in vivo*, but gave negative precipitin and anaphylactic reactions. They were destroyed by taka-diastase, but not by proteolytic enzymes. CHEMICAL ABSTRACTS.

Detoxication of bacterial toxins and their antigenic properties. Y. NISHIURA (Sei-i-kwai Med. J., 1930, 49, No. 11, 10—34).—Toxoid formation from vibrio toxin differs from that of tetanus and diphtheria toxins. Many aldehydes and the salts of aromatic acids can detoxicate vibrio toxin without destroying its power to produce immunity; these reagents are detoxicants to the others without (except for CH_2O and furfuraldehyde) producing toxoids. The differences are attributed to different chemical structures of the toxins. CHEMICAL ABSTRACTS.

Precipitation between tetanus toxin and tetanus antitoxin. T. INOUE (Arb. med. Univ. Okayama, 1931, 2, 369—395).—There are indications that the pptn. of tetanus toxin by antitoxin is not sp. Serum and bacterial precipitins show the same phenomena. There is no parallelism between the pptn. reaction and the toxicity of toxins prepared in different ways and subjected to different treatments (e.g., CH_2O). CHEMICAL ABSTRACTS.

Relation of copper and iron to the production of toxin and enzyme action. A. LOCKE and E. R. MAIN (J. Infect. Dis., 1931, 48, 419—435).—The production of diphtheria toxin in proteose medium is inhibited by substances [cysteine, $\text{K}_2\text{Fe}(\text{CN})_6$] which diminish the available Cu content of the medium or augment its available Fe content. Addition of Fe and Mn to cysteine-treated broth is followed by an abnormally great depression of toxin production. Broth treated with H_2S behaves similarly to cysteine-treated broth. The production of neurotoxin by the tetanus bacillus is partly inhibited by cysteine. The hæmotoxin of *B. welchii* is unaffected by cysteine, CN' , or $\text{Fe}(\text{CN})_6'''$, inhibited by $\text{Fe}(\text{CN})_6'$.

and stimulated by Fe^{++} . The neurotoxins appear to be dispersions of bacterial protoplasm containing fragments of a cationic respiratory substance having Cu as the predominant catalyst. The hæmotoxins appear to contain fragments of an anionic respiratory substance having Fe^{II} as the predominant catalyst.

CHEMICAL ABSTRACTS.

Cultivation of anaerobic bacteria with the help of leucocytic and bacterial products. H. GOLDIE (Ann. Inst. Pasteur, 1932, 48, 179—186).—By the addition of leucocytes to anaerobic growths of bacteria (*B. botulinus*) very rapid growth is induced which may continue even under aerobic conditions. A small quantity of the actively growing culture is in turn able to stimulate other cultures so that a type of transmissible activation is obtained. The activating substance is stable to heat, but is destroyed by Et_2O . Old cultures of *B. botulinus* contain substances, one thermolabile, stable to acids, and enzyme-like in nature, which when added to cultures of anaerobes allows them to be grown aerobically and is probably catalase, and a thermostable substance readily destroyed by acid, which is growth-inhibiting.

W. O. KERMAK.

Effect of iron oxides on the growth of bacteria. O. BAUDISCH (Biochem. Z., 1932, 245, 265—277).—Since the catalytic and biocatalytic properties of the Fe oxides vary greatly according to degree of purity and physical state, various samples of the oxides prepared from Fe carbonyl, Fe nitrate, and spectroscopically pure Fe have been examined. All of these samples except one, prepared in an electric arc, behave either like catalase or like peroxidase or in both ways. The experiments of Webster and Baudisch (J. Exp. Med., 1925, 42, 473) have been repeated using *B. hæmoglobinophilus* and *B. influenzae*.

W. MCCARTNEY.

Catalase action of iron compounds in culture media. O. BAUDISCH and R. DUBOS (Biochem. Z., 1932, 245, 278—281; cf. preceding abstract).—The life of pneumococci in culture media can be prolonged by addition of Fe oxides or certain Fe compounds: these destroy the peroxides which kill the organisms.

W. MCCARTNEY.

Virus problems. G. PYL (Naturwiss., 1932, 20, 131—134).—The chemical and physico-chemical methods of purifying and concentrating virus preps. are discussed with some reference to a lymph infected with foot-and-mouth disease. Such a virus is most effectively preserved by glycerol, whilst purification up to $\times 1000$ is achieved by adsorption methods when consideration is given to the $[\text{H}^+]$ of the medium. The ultra-filtration and the electrophoretic separation of an activating agent are briefly discussed.

F. O. HOWITT.

Tubercle ultra-virus. I. G. SANARELLI and A. ALESSANDRINI (Ann. Inst. Pasteur, 1932, 48, 144—178).—Ultrafiltrates through collodion of cultures of tubercle bacilli when injected intraperitoneally into guinea-pigs give rise to a definite but a typical tuberculous pathological condition, leading ultimately to the death of the animal and due apparently to the existence in the ultrafiltrate of tubercle ultra-virus. The disease may be transmitted to

other guinea-pigs and although tubercle bacilli do not appear in the first guinea-pig these usually may be observed, at first in an attenuated form, after a no. of passages.

W. O. KERMAK.

Acceleration of the dehydrogenation of mercaptans by metals. Oligodynamic action of metals. T. BERSIN (Biochem. Z., 1932, 245, 466—472; cf. Tammann and Rienacker, A., 1928, 675).—In presence of O_2 and in an alkaline medium the conversion of the SH group of thioglycollanilide into the $\cdot\text{S}\cdot\text{S}\cdot$ group is accelerated by metals in the order $\text{As} > \text{Cu} > \text{Sb} > \text{Zn} > \text{Cd} > \text{Ag} > \text{Fe} > \text{Ni}$; this series agrees well with that showing extent of oligodynamic activity. The results of Harrison (A., 1928, 44) and of Labes and Freisburger (A., 1931, 120) concerning the effect on the conversion of the disulphide itself and of alloxan are confirmed and a method for the alkalimetric titration of aliphatic mercaptans is given.

W. MCCARTNEY.

Effects of salts on disinfection by alkalis. O. E. LOWMAN, J. H. BUCHANAN, and M. LEVINE (Iowa State Coll. J. Sci., 1931, 5, 251—268).—Experiments were performed at 60° with an organism resembling *B. subtilis* and 0.25N-NaOH alone or with 0.342N-NaCl, -NaBr, -NaI, or -NaF (p_{H} 12.92—12.83). The solution containing NaI was the most effective germicidal agent.

CHEMICAL ABSTRACTS.

Bactericidal action of mixtures of different monochloro-derivatives of homologues of phenol. R. ETINGER-TULCZYNSKA and W. ULRICH (Z. Hyg., 1932, 113, 437—444).—Various mixtures of chlorocresols, -xylenols, and -thymols have greater bactericidal power than either constituent used alone.

A. G. POLLARD.

Effect of $[\text{H}^+]$ on the toxicity of several preservatives to micro-organisms. W. V. CRUICK, P. H. RICHERT, and J. H. IRISH (Hilgardia, 1931, 6, No. 10, 295—314).—The min. concn. of solutions of NaOBz, Na salicylate, Na_2SO_3 , and KOAc necessary to prevent the growth of micro-organisms was greater at p_{H} 5.0—9.0 than at p_{H} 2.0—4.5. The influence of these solutions on rates of fermentation was similarly affected by p_{H} but to a smaller extent. The retarding effect of NaOBz on the reproductivity of yeast was less at neutrality than at p_{H} 3.0—2.9. The action of solutions of NaCl and of CH_2O on *Saccharomyces ellipsoideus* was affected only to a small extent by $[\text{H}^+]$. The effective concn. of NaOBz solutions in food preservatives was in some cases 200 times as great at p_{H} 7.0 as at p_{H} 3.0.

A. G. POLLARD.

Is the hyperinsulinæmia following injection of adrenaline of pancreatic origin? E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1931, 106, 1241—1244; Chem. Zentr., 1931, ii, 1873).—Experiments on dogs indicate that adrenaline, or a substance mobilised by it, stimulates the insulin production of the pancreas.

A. A. ELDRIDGE.

Mechanism of insulin and synthalin action. K. OCHIAI (Nagoya J. Med. Sci., 1931, 5, 110—124).—The liver-glycogen of the normal rat decreases gradually after injection of insulin and disappears in hypoglycæmic convulsions; the muscle-tissue

glycogen is increased. After starvation for 24 hr. the liver and skeletal muscle of rats contained no appreciable quantity of glycogen. On administration of insulin with glucose little glycogen is deposited in the liver and much in the muscle of rats and guinea-pigs. In rabbits the reverse holds. Synthalin gives similar results. Histological changes in the liver and kidney after administration of synthalin are identical with those occurring in cases of severe poisoning, e.g., by P, As, CHCl_3 , HgCl_2 , or EtOH .

CHEMICAL ABSTRACTS.

Form of the insulin particle. K. FREUDENBERG (Z. physiol. Chem., 1932, 204, 233—234; cf. this vol., 96).—A corrected calculation of the dimensions of the insulin particle. The smallest mol. aggregate appears to consist of a double mol.

J. H. BIRKINSHAW.

Induced oxidation of glucose in presence of insulin acting as an inductor. H. L. DUBE and N. R. DHAR.—See this vol., 346.

Variations of the secretion of insulin in intra- and extra-pancreatic hyperglycæmia. J. LA BARRE (Compt. rend. Soc. Biol., 1931, 106, 1244—1246, 1247—1248; Chem. Zentr., 1931, ii, 1873).

"Heart hormones." P. B. REHBERG (Dansk Tidsskr. Farm., 1932, 6, 41—54).—A lecture.

H. F. HARWOOD.

Nature of the so-called circulatory hormone preparations. T. BRUGSCH, H. HORSTERS, and H. ROTHMANN (Med. Klinik, 1931, 27, 1378—1379; Chem. Zentr., 1931, ii, 2340).—Co-enzyme characteristics were detected in Eutonin, Auriculin, Padutin, Lacarnol, and muscle-adenylic acid. The so-called hormone preps. should therefore be regarded as co-enzyme preps.

L. S. THEOBALD.

Effect of cortico-adrenal extract on energy output. E. EAGLE and S. W. BRITTON (Science, 1932, 75, 221—222).—Intraperitoneal injection of cortico-adrenal extract increases the working capacity of a dog; a similar effect is observed with man.

L. S. THEOBALD.

Determination of thyroxine in the thyroid. J. P. LELAND and G. L. FOSTER (J. Biol. Chem., 1932, 95, 165—179).—The gland is hydrolysed for 18 hr. with boiling 2N-NaOH. Thyroxine is then separated from other I compounds in the hydrolysate by extraction with BuOH, I being determined in the BuOH extract. The alkaline hydrolysis is accompanied by a destruction of thyroxine not exceeding 15% of the total amount. Comparison with the method of Harington and Randall (A., 1930, 504) indicates that the latter method gives results exceeding the true vals. by approx. 100%. The average thyroxine content of 52 human thyroids was 25.2% of the total I when no correction was applied for destruction during hydrolysis.

F. O. HOWITT.

Thyroid action and tissue catabolites. I. ABELIN and R. SATO (Sei-i-kwai Med. J., 1930, 49, No. 8, 1—16).—Small quantities of thyroid fed continuously to dogs and sheep slightly decrease the blood viscosity; the serum-albumin decreases slightly, then rises, and again decreases. CHEMICAL ABSTRACTS.

Hormone of the anterior lobe of the pituitary and the magnesium, calcium, and phosphorus contents of blood. L. CANNAYO (Biochem. Z., 1932, 245, 234—237).—The influence of prolactin on the Ca, P, and Mg contents of blood-serum in man, dog, and rabbit is investigated. In man, the Ca and P concn. and the acid-base equilibrium remained unchanged. In dogs and rabbits, the Mg content was considerably, the P content slightly, increased and the Ca content remained unchanged.

P. W. CLUTTERBUCK.

Influence of anterior pituitary substances on the total iodine content of the thyroid gland in the young duck. J. A. SCHOCKAERT and G. L. FOSTER (J. Biol. Chem., 1932, 95, 89—94).—Injection of fresh saline emulsions of anterior lobes of ox-pituitary glands into young male ducks induces a rapid decrease in the total I of the thyroid gland. This decrease ceases after a few days, but the percentage of I continues to fall for some weeks owing to hypertrophy of the gland. A similar action is brought about by the growth-promoting hormone of the anterior lobe of the pituitary gland (A., 1931, 268).

F. O. HOWITT.

Pituitary hormone. Intermedin, a hormone of the pars intermedia. B. ZONDEK and H. KROHN (Naturwiss., 1932, 20, 134—136).—The anterior pituitary hormone of warm-blooded animals is not identical with that of cold-blooded. The formation of the "mating cloak" in fish is not influenced by female or male sexual hormone, whilst pituitary extracts will cause its formation. Vasopressin and to a smaller extent oxytocin produce increase in melanophore area in frogs; it is concluded, however, that the dark coloration in frogs due to expansion of melanophores is not sp. for one hormone. The formation of erythrophores in the fish *Phoxinus phoxinus* is sp. for a definite pituitary hormone, negative responses being given by corpus luteum extracts, male and female sexual hormones, insulin, thyroxine, yohimbine, etc. A certain standard increase in erythrophore area in this fish is defined as a "Phoxinus unit." This sp. hormone is prepared from the pituitary by extraction of the powdered, COMe_2 -dried gland with 0.25% AcOH at the b. p. It is present also in the tuber cinereum and the thalamus, but seldom in the fluid of the third ventricle. From ox-pituitary glands were obtained 2857 units per g. from the anterior lobe, 80,000 from the pars intermedia, and 11,904 from the posterior lobe. This hormone of the pars intermedia is designated "intermedin." Human pituitary glands contain 4000—7000 units per gland. Intermedin is prepared as a solution, free from proteins, vasopressin, and oxytocin, which has no action on the heart, vessels, blood-pressure, or smooth musculature, but produces a rise in O₂ consumption of warm-blooded animals. Intra-vital microscopy of the thyroid gland in rats following injection of the hormone reveals a marked attenuation of the colloid matter.

F. O. HOWITT.

Action of hypophysin and its fractions on water and salt metabolism. F. ROBERT (Arch. exp. Path. Pharm., 1932, 164, 367—382).—In a young male subjected to H_2O diuresis, the antidiuretic action and the effect on the NaCl metabolism of "tonephin"

and "orasthin," fractions separated from hypophysis, are qualitatively the same as those of the latter, but the first is possibly more and the second considerably less active. The diuretic action of these substances appears to be primarily on the kidney.

W. O. KERMACK.

Pituitary hormones. IV. Relation between the hypophysis and vitamin-C. V. Influence on the germination of *Lupinus albus*. L. R. T. AGNOLI (J. Pharm. Exp. Ther., 1932, 44, 47-53, 55-62).—IV. Hormones of the anterior lobe cannot be substituted for vitamin-C in a C-deficient diet, although a slightly greater initial increase in wt. occurs in guinea-pigs than with other pituitary hormones.

V. Only lipoidal pituitary hormone affects growth of *L. albus*, producing a slight increase.

P. G. MARSHALL.

Sex hormone in butterflies. S. LOEWE, W. RAUDENBUSCH, H. E. VOSS, and J. W. C. VAN HEURN (Biochem. Z., 1932, 244, 347-356).—The fresh sex organs of freshly hatched sexually mature female butterflies (*Attacus atlas*) contain 90-130 mouse units of oestrin per kg.

W. MCCARTNEY.

Production of mucification of the vaginal epithelium of rodents by the oestrous hormone. R. K. MEYER and W. M. ALLEN (Science, 1932, 75, 111-112).—Theelin produces mucification in guinea-pigs, rats, and mice. This indicates that previous mucifications produced by corpus luteum extracts are due to the oestrin present and not to other sp. hormones such as progesterin and relaxin. Mucification in mice has also been produced by oestrin extracted from male urine with C_6H_6 .

L. S. THEOBALD.

New crystalline sexual hormone from the urine of pregnant mares. A. GIRARD, G. SANDULESCO, A. FRIDENSON, and I. J. J. RUTGERS (Compt. rend., 1932, 194, 909-911).—From the middle fractions of theelin cryst. from EtOH ($[\alpha]_D^{25} > +250^\circ$) a new hormone is extracted by Et_2O and purified by fractionation from EtOAc. From 7 tons of urine 100 mg. of hormone, m. p. 238-240°, $[\alpha]_D^{25} +308^\circ$ (1% in dioxan), were obtained, closely resembling theelin in chemical properties. The name "equilin" is proposed. The following const. are reported for theelin: m. p. 259-260°, $[\alpha]_D^{25} +163^\circ$ (semicarbazone, m. p. 266-267°; oxime, m. p. 241-242°; benzoate, m. p. 218-219°, $[\alpha]_D^{25} +128^\circ$; Me ether, m. p. 173-174°).

A. COHEN.

New plant source of vitamin-A activity. D. H. COOK and J. AXTMAYER (Science, 1932, 75, 85-86).—Extraction of the crude red annatto powder from *Bixa orellana* with cold 80-90% EtOH gives a reddish-brown solution which yields a dark-coloured, resinous material. Administration of this fraction, which is practically free from bixin, to rats fed on a vitamin-A-free diet results in increased growth. The seeds contain approx. 2% of active material, the nature of which is not yet definitely ascertained.

L. S. THEOBALD.

Vitamin-A content of ghee. A. L. BACHARACH (Brit. Med. J., 1930, II, 141-142).—Low vals. were obtained.

CHEMICAL ABSTRACTS.

Variations in vitamin-A and chemical composition of maize. G. S. FRAPS (Texas Agric. Exp.

Sta. Bull., 1931, No. 422, 46 pp.).—Yellow maize was rich and white maize poor in vitamin-A. Different varieties of maize showed no significant variation in protein, fat, N-free extract, ash, Ca, Mg, or $PO_4^{'''}$ contents. Maize grown in different localities varied in Ca, $PO_4^{'''}$, and notably in protein content. A significant correlation between protein content and rainfall is indicated.

A. G. POLLARD.

Carotenoids and vitamin-A in the blood-serum and organs of higher animals. H. VON EULER and E. VIRGIN (Biochem. Z., 1932, 245, 252-264).—Results of determinations of carotenoids (xanthophyll etc.) and vitamin-A in the serum of cattle, rats, and guinea-pigs, in the livers of cattle, rats, hens, fresh- and salt-water fish, and in the kidneys of guinea-pigs are recorded. In rats the vitamin-A content of the liver decreases with age, and feeding with hæmin results in a great reduction in the amount of the carotenoids in the liver. To obtain the best yield of vitamin-A from the livers of marine fish fresh organs should be used.

W. MCCARTNEY.

Effect of ultra-violet light on the vitamin-A of butter. C. L. SHREWSBURY and H. R. KRAYBILL (Science, 1932, 75, 86).—Butter-fat exposed to the light of a quartz-Hg arc in air loses its colour and vitamin-A potency; exposure in N_2 results in no loss of colour, but in some loss of growth-promoting power. Loss of potency does not appear to be a direct effect of ultra-violet light. Oxidation produced indirectly may destroy the vitamin-A, and irradiation in air and, to some extent, in N_2 appears to produce a substance which retards the growth of rats.

L. S. THEOBALD.

Vitamin-A and -D studies with growing chicks. H. S. GUTTERIDGE (Sci. Agric., 1932, 12, 327-337).—Pitchard oil had a similar antirachitic efficiency to cod-liver oil, but in the proportion of 1% of the ration did not provide sufficient vitamin-A. Vitamin-D in the oil was reduced by purification.

A. G. POLLARD.

Reserves of vitamins-A and -D of some elasmobranchs. E. ANDRÉ and R. LECOQ (Compt. rend., 1932, 194, 912-914).—The relative vals. of the liver oils of *Scymnus Lichia*, *Centrina vulpecula*, and *Rana batis* are 90, 40, and 30 for vitamin-A, and 40, 35, and 25 for vitamin-D, as determined by rat tests. The elasmobranchs can therefore store these vitamins without affecting the nature of the skeleton.

A. COHEN.

Antineuritic vitamin. V. Empirical formula of the antineuritic vitamin. VI. Properties of the antineuritic vitamin of rice-bran. A. G. VAN VEEN (Rec. trav. chim., 1932, 51, 265-272, 279-283).—V. Numerous analyses of the vitamin hydrochloride (and chloroaurate), obtained essentially by the method previously described (A., 1931, 880), indicate the probable formula $C_6H_{10}O_2N_2.HCl$.

VI. A dil. (1 in 10,000) aq. solution of the vitamin hydrochloride gives a definite ppt. with tungstic acid or $AuCl_3$. The biuret reaction is negative, and NH_2 , CO_2H , NH , NMe , OH , OMe , and CO groups are absent. The activity is destroyed by conc. H_2SO_4 at 0° but not by warm dil. H_2SO_4 or dil. HCl . Reduction

with Zn, Sn, Mg, or Fe in acid gives inactive oily or resinous products; at least 1 mol. of H_2 is absorbed during catalytic (PtO_2) reduction, but the resulting product is freed from Pt only with difficulty. The hydrochloride is oxidised readily by $KMnO_4$, $NaOBr$, and H_2O_2 at room temp., and slowly by CrO_3 in $AcOH$. The pure vitamin, unlike the crude product, is largely destroyed by HNO_2 at 30–40°. Adsorption on protein occurs readily. H. BURTON.

Concentration of vitamins- B_1 and - B_2 . P. A. LEVENE (J. Biol. Chem., 1932, 95, 317–326).—Large variations in the growth from month to month of rats fed on a normal diet are recorded. The effect on the growth of the administration of progressively increased amounts of dried yeast, $EtOH$ extract of yeast, and the $COMc_2$ ppt. from yeast press-juice is studied, the two last-named materials being the most potent. Adsorption from the $EtOH$ extract and the press-juice with SiO_2 gel gave preps. more active in promoting normal growth, but less active in producing growth above normal. Further concn. of the adsorbed material by pptn. with 70% aq. KI in $EtOH$ caused decrease in activity, but by combination of this prep. with the $EtOH$ crude extract heated to 140°, the SiO_2 adsorption was shown to have produced a highly active prep. of the (heat-labile) factor. Pptn. of the solution remaining after the SiO_2 adsorption with $COMc_2$ and treatment of the aq. solution of this ppt. with aq. KI and $EtOH$ gave a ppt. (B_2 factor) inactive alone, but highly active with the above B_1 concentrate. A. LAWSON.

Vitamin- B_1 and - B_2 requirements of lactation. D. L. HUSSEMAN and R. A. HETLER (J. Nutrition, 1931, 4, 127–140).—Lactation in the rat depends on vitamins- B_1 and - B_2 , between which a quant. relationship may exist. The latter is probably the more important. CHEMICAL ABSTRACTS.

Vitamin- B_2 and the growth factor in tomato juice. R. G. DAGGS and A. G. EATON (Science, 1932, 75, 222–223).—Experiments on rats showing the absence of vitamin- B_2 from tomato juice are recorded, and evidence for the differentiation of this vitamin and a purely growth-promoting factor is advanced.

L. S. THEOBALD.

Effect of heat on vitamin- B_2 in protein-free milk at varying hydrogen-ion concentrations. N. HALLIDAY (J. Biol. Chem., 1932, 95, 371–385).—Protein-free milk prepared from skim-milk powder by pptn. of the caseinogen with 1% HCl has p_H 4.3, and contains the total vitamin- B_2 content of the milk powder. Heating the protein-free milk at p_H 4.3, 7, and 10 for 1 hr. causes 10, 30, and 40% loss in B_2 activity, respectively, and for 4 hr., 30, 50, and 75% loss; keeping for 1 week at p_H 4.3 and 7 causes no loss but at p_H 10, 75% of the vitamin is destroyed. Evidence is shown of the presence of some growth factor in the milk powder which is destroyed in the prep. of the protein-free milk. Results for vitamin content based on the cure of dermatitis in rats were different from the above results, which were obtained from a study of the growth. A. LAWSON.

Nitrogenous metabolism during unbalanced nutrition. III. Nitrogenous metabolism of

pigeons during the development of polyneuritic avitaminosis. B. A. LAVROV and N. JARUSOVA (Biochem. Z., 1932, 244, 390–402; A., 1928, 1161).—Experimental avitaminosis in pigeons produces a negative N balance, although there is no connexion between the loss of N, which increases regularly as the disease develops, and the under-nourishment involved. In normal pigeons the N content of the body is greater at the end of the experiment than at the beginning, whilst in the diseased birds the reverse is the case. It follows that the avitaminosis leads to increased degradation of the N compounds in the body.

W. MCCARTNEY.

Antiscorbutic vitamin in home-canned carrots. A. SPOHN and A. HUNTER (J. Agric. Res., 1931, 43, 1101–1108).—A daily dose of 15–20 g. of raw carrot protects guinea-pigs (350 g.) from scurvy. Canned carrots, heated at 100° for 90 min. with a little vinegar, or under 10 lb. pressure for 40 min., with or without acid, were fed to guinea-pigs in daily doses of up to 50 g. All the animals developed scurvy and died within the test period. Carrots canned with and without added acid gave similar results.

A. COHEN.

Antiscorbutic vitamin in the juice of home-canned tomatoes. A. SPOHN (J. Agric. Res., 1931, 43, 1109–1113).—The protective daily dose of raw tomato juice for guinea-pigs (300–400 g.) is 3.5 c.c. After heating at 100° for 20 min., 4 c.c. of juice daily does not prevent scurvy.

A. COHEN.

Action of irradiated ergosterol and its relationship to parathyroid function. I, II. H. B. TAYLOR, C. B. WELD, H. D. BRANION, and H. D. KAY (Canad. Med. Assoc. J., 1931, 24, 763–777; 25, 20–34).—Similarity is revealed. The study has been extended to rats, mice, rabbits, and fowl.

CHEMICAL ABSTRACTS.

Prevention of convulsions. E. J. SHEEHY (Science, 1932, 75, 81).—Convulsions appeared in pigs fed on a non-vitamin- D diet and confined to a compartment lighted through glass. Animals receiving vitamin- D did not develop convulsions.

L. S. THEOBALD.

Growth-promoting vitamin (M). L. P. ROSENOV (Biochem. Z., 1932, 244, 413–416).—Hay contains a vitamin (vitamin- M) which, in addition to those already known, is necessary for normal growth. A vitamin present in yeast is similar or identical. The growth produced by the new vitamin proceeds according to the law of mass action.

W. MCCARTNEY.

Growth-promoting vitamin (M). A. SCHEUNERT (Biochem. Z., 1932, 245, 494–495).—Rosenov's experiments (preceding abstract) provide no evidence for the existence of a vitamin- M .

W. MCCARTNEY.

Vitamin- E in iron-treated dry rations. J. WADDELL, H. STEENBOCK, and E. VAN DONK (J. Nutrition, 1931, 4, 79–93).—The Fe-treated stock ration produces male and female sterility; treatment with Fe produces an anti-vitamin- E . Fe is also apparently pro-oxygenic. CHEMICAL ABSTRACTS.

Reproduction and lactation on simplified diets. M. W. TAYLOR (Iowa State Coll. J. Sci., 1931, 5,

No. 4, 355—356).—Cod-liver oil contains vitamin-*B*. Mineral oil prevents reproduction even when wheat-germ oil is included in the diet. Crude cane molasses, beet molasses, and sorghum contain vitamin-*E*. Vitamins-*A* and -*E* are destroyed by FeCl_2 . Vitamin-*B* is the limiting factor in lactation on these diets.

CHEMICAL ABSTRACTS.

Male sterility on milk diets. J. WADDELL and E. VAN DONK (J. Nutrition, 1931, 4, 67—77).—Sterility, not due to lack of vitamin-*E*, was observed in rats fed on whole cow's milk, Fe, and Cu.

CHEMICAL ABSTRACTS.

Influence of temperature on the rate of accumulation of chlorophyll in etiolated seedlings. V. N. LUBIMENKO and E. R. HUBBENET (New Phytologist, 1932, 31, 26—57).—The greening of etiolated wheat seedlings takes place between 2° and 48° with a max. rate at 26—30°. The effect of temp. on the process depends on its influence on the synthesis of leucophyll and its transformation into chlorophyll. Diminution in the rate of chlorophyll production above 30° is associated with the formation of a colourless substance instead of chlorophyll from leucophyll. Technique for the spectrophotometric determination of chlorophyll is appended.

A. G. POLLARD.

Action of carbon monoxide on fresh plants. Absorption spectra of chlorophyll-*a* and -*b* in presence of carbon monoxide, nitrogen, oxygen, and carbon dioxide. M. PADOA and N. VITA (Biochem. Z., 1932, 244, 296—302).—Spectroscopic examination of C_6H_6 solutions of chlorophyll-*a* and -*b* treated with N_2 , O_2 , CO_2 , and CO shows that these gases (N_2 excepted) form labile compounds with the pigments, that with CO being the most stable. The result is in agreement with findings concerning the suppression by CO of assimilation in green plants.

W. MCCARTNEY.

Black raspberry. I. Expressed tissue fluids. II. Rates of water movement through excised parts of fruiting canes and current season shoots. III. Growth and yield as influenced by fertilisers. R. E. MARSHALL (Michigan Agric. Exp. Sta. Tech. Bull., 1931, No. 111, 3—9, 9—17, 18—32).—I. The f.-p. depression of the tissue fluids of leaves and shoots increased with the advancing season, changes being greater in leaves than in shoots.

II. The rate of movement of H_2O under 0.5 atm. pressure through sections of old and fruiting canes decreased and in stems and new shoots increased as the season advanced.

III. Early applications of $(\text{NH}_4)_2\text{SO}_4$ increased yields during the first part of the picking season, but max. yields followed autumn or spring dressings of the fertiliser. Increased yields were associated with the production of smaller berries. Rainfall largely influenced both yield and berry size. Early applications of $(\text{NH}_4)_2\text{SO}_4$ resulted in an increased no. of shoots per plant, but smaller elongation per shoot. Superphosphate produced an increased shoot elongation after harvesting. Fertilisers did not affect the no. of canes per crown nor the diameter of the canes.

A. G. POLLARD.

Changes accompanying fruit development in the garden pea. C. S. BISSEY and H. A. JONES

(Plant Physiol., 1932, 7, 91—105).—The abs. wts. of N, total sugars, starch, and ash contents of the pods reached a max. early in development (20—24 days) and subsequently declined with advancing maturity. Acid-hydrolysable polysaccharides (other than starch) and crude fibre increased steadily throughout. In the peas the abs. wt. of N, starch, crude fibre, and ash increased throughout growth. The max. abs. wt. of sucrose was reached about the 32nd day and subsequently declined rapidly, whereas that of acid-hydrolysable polysaccharides was attained towards the end of the development period (40 days). Peas were of harvesting size when the total sucrose content was a max., but the highest % of the sucrose was attained at an earlier date. A. G. POLLARD.

Ripening [of fruit]. L. MOREAU and E. VINET (Compt. rend. Acad. Agric. France, 1932, 18, 197—202).—The sugars which accumulate rapidly in grapes during ripening are derived not only from material synthesised in the leaves, but also from reserves translocated from stems and trunk. A. G. POLLARD.

Biochemistry of the ripening of fruits of the Japanese medlar (*Eriobotrya japonica*). A. L. KURSSANOV (Planta [Z. wiss. Biol.], 1932, 15, 752—766).—Ripening of the fruit is characterised by an accumulation in the pericarp of fructose, sucrose, and malic acid and the almost complete disappearance of maltose, tartaric acid, and amygdalin. The glucose content increases slightly and that of citric acid increases in the early stages of the development of the pericarp and subsequently declines as full ripeness approaches: the proportions of dextrin, starch, hemicellulose, cellulose, proteins, and non-protein-N compounds decrease as ripening advances. In the seed, ripening is accompanied by an increase of amygdalin, starch, hemicellulose, and cellulose and the elimination of maltose. There is a characteristic periodic inversion and synthesis of sucrose and a decrease in I val. The dextrin content remains practically const. and N matter declines. A. G. POLLARD.

Early and late ripening and the acids of fruit. R. NUCCORINI (Annali Chim. Appl., 1932, 22, 10—16).—A study of the variation in the amount of tartaric, citric, and malic acids obtained at three stages of ripening in early and late varieties of cherries, peaches, and plums confirms previous observations (A., 1930, 1482). O. F. LUBATTI.

Variation in fruiting ability of oil palms. H. W. JACK and R. B. JAGOE (Malay. Agric. J., 1932, 20, 14—19).—Comparison of crops from naturally- and artificially-pollinated young palms, grown under average conditions, show a coeff. of variability of 47 for the yield. E. LEWKOWITZ.

Movement of organic materials in plants. F. C. STEWARD and J. H. PRIESTLEY (Plant Physiol., 1932, 7, 165—171).—A criticism of Crafts (A., 1931, 774). A. G. POLLARD.

Variation of the oxygen content of culture solutions. W. A. CANNON (Science, 1932, 75, 108—109).—When certain plants, e.g., willow, sunflower, and cotton, are exposed to sunlight, a movement of O_2 takes place from shoot to root when the latter is in a culture solution, particularly in pure H_2O . O_2

liberated during photosynthesis thus appears to move downward to supply, wholly or partly, the O_2 requirements of the root. L. S. THEOBALD.

Life-history and composition of the soya-bean plant. H. L. BORST and L. E. THATCHER (Ohio Agric. Exp. Sta. Bull., 1931, No. 494, 88 pp.).—The % of N in soya-bean leaves was much greater than in the stems. As maturity approached the N content of leaves, stems, and pods decreased considerably and that of seeds to a smaller extent. The % of N in the whole tops decreased during the period of active growth and increased towards maturity. At maturity more than one half of the total N was stored in the seed. The P content of leaves and stems decreased as the plants matured. The % of P in mature seeds was approx. four times that of leaves, stems, and pods. The storage of K in the leaves reached a max. in the early stage of pod formation and decreased later. In stems, leaves, and pods there was a decline in K content as the plants matured. The % of K in ripened seeds was greater than that of any other part of the plant. The proportion of Ca and Mg in the whole tops decreased towards maturity. The % of Ca in the various plant organs was in the order leaves > pods > stems > roots > seeds. In leaves and pods the total and % of Mg were much lower than those of Ca. A. G. POLLARD.

Utilisation of atmospheric nitrogen by germinating (lupin) seeds. N. VITA (Biochem. Z., 1932, 245, 210—217).—The absorption of N by lupin seeds which were germinated in an atm. containing CO was investigated. The absorption of N is related to the development of the seeds and not to bacterial activity. The influence of the concns. of CO_2 , O_2 , and CO on the absorption is tested. The absorption is not obtained with the seed-meal.

P. W. CLUTTERBUCK.

Physiological significance of hydrocyanic acid glucosides in plant metabolism. N. J. STEKELENBURG (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1179—1189).—HCN or the corresponding cyanohydrin arises in the leaves, not as the first assimilation product of N, but as a secondary product of protein metabolism. It has no essential significance in the N cycle. No appreciable transport of HCN occurs and the HCN glucosides can act as carbohydrate and N reserve. J. W. SMITH.

Seasonal changes in the composition of the non-protein-nitrogen in the current year's shoots of Bartlett pears. A. S. MULAY (Plant Physiol., 1932, 7, 107—118; cf. A., 1931, 990, 1197).—The distribution of amide-, humin-, basic, NH_2 -, and residual N in pear shoots is recorded. Commencement of new growth is associated with high amide- and NH_2 -N contents in both wood and bark. These subsequently decline, reaching a min. in autumn and winter, and rising again as the growing season approaches. During growth amide-N is > NH_2 -N in the wood. Basic N is at a min. in June, rising to a max. some time before growth starts and then falling rapidly. Hydrolysis of the humin-N of the bark and the residual N in wood results in an increase of the amide-, NH_2 -, and basic N fractions. A. G. POLLARD.

Local variation in nitrogen content of vine leaves. H. LEGATU, L. MAUME, and L. CROS (Compt. rend., 1932, 194, 679—681).—Heavy phosphate manuring inhibits the initial absorption of N by growing leaves. The variation in N content of the base leaves is the same for different stocks in the same environment, a finding which justifies the usual method of sampling. P. G. MARSHALL.

Natural regulation of protein metabolism in plants. K. MÖRRES (Naturwiss., 1932, 20, 102—103).—A substance, rich in NH_2 -acids, which regulates protein metabolism occurs in the onion. Synthesis of protein induced by this medium is favoured by the presence of O_2 . Protein-fission and -synthesis is inhibited by narcosis, but such an inhibition is less in an atm. of H_2 . Extraction by $COMe_2$ yields a substance which when in the reduced state activates and when oxidised inhibits proteases. Towards the proteolysis of autolysates Cu^{++} and Fe^{+++} exhibit an inhibition which is supported by the reduced but not by the oxidised form. The reduced form gives a positive nitroprusside reaction for -SH and hence its similarity to or identity with glutathione is indicated. F. O. HOWITT.

Biology of tobacco alkaloids. J. CHAZE (Compt. rend. Acad. Agric. France, 1932, 18, 239—240).—Nicotine in the tobacco plant occurs in the actively dividing cells. In mature plants there is a translocation towards the periphery of the leaves. The nicotine content decreases in etiolated leaves and in the plant generally after fertilisation of the flowers. Nicotine appears in the aleuronic grains of germinating seeds. A proportion of nicotine is exuded from the leaf surface and is considered as a metabolic by-product. A. G. POLLARD.

Distribution and variation of the æsculin content of *Aesculus hippocastanum*. L. G. KLEIN and H. LINSE (Planta [Z. wiss. Biol.], 1932, 15, 767—816).—Æsculin occurs mainly in the bark, bud scales, and in the pith. The amount in the wood is small and decreases with age. Leaves and leaf-stems contain but little. Roots have a considerable proportion but less than the trunk. The total æsculin content reaches a max. in summer, declining before leaf-fall, and rising to a second max. in early spring. With advancing age the proportion increases. Æsculin is regarded as a reserve material. A. G. POLLARD.

Glucosides of oleander leaves. G. TANRET (Compt. rend., 1932, 194, 914—916).—Neriin ($[\alpha]_D^{20}$ -32.5°) and oleandrin ($[\alpha]_D^{20}$ -5°) have been isolated and separated. Neriin differs from strophanthin ($[\alpha]_D^{20}$ +30°) in its colour reactions and in yielding glucose as one of its hydrolytic degradation products. Its designation as *l*-strophanthin is unjustified. A. COHEN.

Celluloses of two water plants, *Ottelia ovalifolia* and *Eichornia crassipes*. J. C. EARL and T. M. REYNOLDS (J. Proc. Roy. Soc. New South Wales, 1931, 65, 75—79; cf. A., 1930, 1415).—The celluloses are probably identical with cotton cellulose. N. H. HARTSHORNE.

***l*-Fucose in *Pelvetia canaliculata*, Dec. and Thur.** H. COLIN and P. RICARD (Compt. rend., 1932,

194, 643—645).—After preliminary washing with EtOH, H₂O, and dil. aq. alkali, the dried material is hydrolysed with 2% H₂SO₄ for 1 hr. at 120°. The solution is neutralised with BaCO₃, conc., and taken up in EtOH, the *l*-fucose being isolated as the phenylhydrazone. Besides *l*-fucose, a dextrorotatory carbohydrate (osazone, m. p. 225°) is produced by the hydrolysis. A. LAWSON.

Determination of glucose and fructose in maize tissues. V. H. MORRIS and E. F. WEST (Plant Physiol., 1932, 7, 47—62).—Comparison is made of the I oxidation method for determining glucose and Nyn's method for fructose with the combined reduction-polarimetric method for mixed sugars in expressed maize juices and EtOH extracts. With pure sugar solutions there is good agreement, but in saps etc. the latter method gave consistently higher results (8%). The separate determination of glucose and fructose as above yielded vals. corresponding with total reducing sugars indicated by Fehling's method. A. G. POLLARD.

Intake of sugar from hypotonic solutions by *Elodea*. T. WARNER (Planta [Z. wiss. Biol.], 1932, 15, 739—751).—Shoots of *Elodea*, under uniform conditions of temp., light intensity, and nutrition, contain practically const. amounts of mono- and di-saccharides. Immersion in hypotonic (5%) solutions of glucose or sucrose results in a rapid intake of sugar. After 6 hr. the proportional distribution of mono- and di-saccharides in the tissues becomes normal irrespective of the nature of the sugar taken up. Exclusion of light does not affect the sugar distribution, although the total intake is reduced. A. G. POLLARD.

Productivity and sugar content of the sugar beet, and the reactive power of its plasma. G. HAFKOST (Z. Ver. deut. Zucker-Ind., 1931, 81, 813—824).—Increase of osmotic pressure in a liquid with which living and growing plant cells are in contact causes a corresponding increase inside the cells and contraction of the protoplasm. The highest osmotic pressure of the external liquid at which the contracted plasma is still able to function normally and effect growth is termed the max. osmotic power of the plant, and is a measure of capacity for growth and resistance to drought and cold. It is the same for all living cells in a given plant, and the same for a seed as for the plant grown therefrom. It is transmitted in greater measure to the earliest blooms of a plant than to later ones, and is therefore probably not a Mendelian character. In sugar beets it determines not only capacity for growth and resistance, but also the max. sugar content which the plasma can produce in the cell juice. In beet strains having a high max. osmotic power, high sugar content is possible with high wt. of roots, but in those of low max. osmotic power there is less ability to absorb moisture from the soil, and high sugar contents are the result of restricted root growth. A knowledge of the max. osmotic power is therefore of val. in the selection of seeds. J. H. LANE.

Ergosterol contents of several edible mushrooms. M. SUMI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 120—123).—Ergosterol contents of

0.1—0.4% of the dry wt. have been found. The amount of ergosterol in *Cortinellus shiitake* increases during growth. R. CUTHILL.

Carotene and dihydroergosterol in green tea. M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 13—21).—From a light petroleum extract, α - and β -carotenes and a sterol, probably dihydroergosterol, were isolated. A. COHEN.

Isolation of carotene. H. N. HOLMES and H. M. LEICESTER (J. Amer. Chem. Soc., 1932, 54, 716—720).—The following carotene contents are reported (mg. per 100 g.): lucerne (cured) 2.3; dehydrated spinach 1.5; fresh spinach 4.8; canned spinach (drained) 15.6; yellow maize gluten 0.3; canned carrots (drained) 6.5. Carotene (+xanthophyll) can be obtained free from chlorophyll by treating (during 3 hr.) green leaves with sufficient 3*N*-NaOH to form a thick paste; the mixture is diluted with an equal vol. of H₂O and extracted with CHCl₃. This method is not quant. and the subsequent separation of the two pigments is troublesome. A modification of the usual method of isolation of carotene from (canned) carrots is given, the yield being 0.037 g. per kg. of carrots. C. J. WEST (b).

Are leaf-lipins responsive to solar radiation? W. E. TOTTINGHAM (Science, 1932, 75, 223—224).—Irradiation of the tomato under "Vitaglass" appears to increase the carotenoid and sterol contents of the leaf tissue, which suggests a causal relation between lipins and increased vegetative development. L. S. THEOBALD.

Biochemical examination of fertile soil. VII. Soil bacteria and plant germination. A. J. J. VANDE VELDE and A. VERBELEN (Natuurwetensch. Tijds., 1932, 14, 11—16).—During the germination of carrots and lettuce, the [H'] of the soil falls; with parsley it rises. There is no definite relationship between the [H'] of the soil and that of the plant sap, and none was observed between soil acidity and no. of microbes. S. I. LEVY.

Microbiology of the soil. V. S. VINOGRADSKI (Ann. Inst. Pasteur, 1932, 48, 89—134).—The technique of a method of studying the bacterial content of soil is described. The method consists essentially in the examination of the cultures of single species of bacteria obtained by the use of media infected with all the species in the soil, but containing only one substrate of a type on which that species exercises its natural function. The cultures are made on discs of SiO₂ gel impregnated with mineral salts and the chosen substrate. If a source of N is required, NH₄Cl or NH₄NO₃ is included. To study the fixation of N, no combined N is introduced, and in the case of the nitrifying bacteria, NH₄Cl or NH₄NO₃ is used as substrate. The media thus prepared are treated with definite quantities of soil, varying according to the bacterial content, and incubated for definite periods, after which a morphological and, if necessary, chemical examination is carried out. A. LAWSON.

Fixation of protein by the soil. A. DEMOLON and J. BRIGANDO (Compt. rend., 1932, 194, 311—313).—Colloidal solutions of humus and clay suspensions adsorb considerable quantities of protein.

Nitrification of protein incorporated in soil proceeds at the same rate when the protein is free as when it has been adsorbed on humic acid, whilst humic acid alone or in combination with protein does not undergo nitrification. W. O. KERMAK.

Alleged permeability of *Fontinalis* cells to alkaloid cations. R. COLLANDER and K. SOMMER (Protoplasma, 1931, 14, 1—10; cf. Borech, A., 1920, i, 800).—Addition of HCl reduced the toxic action of quinine hydrochloride on leaf cells of *Fontinalis*. The emulsifying action of the salt on the fat of the leaf cells increases regularly with the proportion of undissociated mols. in the solution. Alkaloids enter the cell principally in the form of undissociated mols. of the free base. A. G. POLLARD.

Abstraction of ions from salt solutions by higher plants. K. PIRSCHLE and H. MENGDEHL (Jahrb. wiss. Bot., 1931, 74, 297—363; Chem. Zentr., 1931, ii, 256).—In salt or nutrient salt solutions the abstraction of cations and anions by pea seedlings is not equiv. The change in p_H of the solution, calc. on equiv. H^+ or OH^- , does not accord with that corresponding with the excess of one or other ion; hence ion exchange must have taken place at most on a small scale. A. A. ELDRIDGE.

Toxic action of aqueous sodium chlorate on *Nitella*. H. R. OFFORD and R. P. D'URBAL (J. Agric. Res., 1931, 43, 791—810).—The toxicity of $NaClO_3$ is due to the anion and is decreasingly effective to *Nitella* at p_H vals. ranging from 4.8 to 8.2. A mixture of $CaCl_2$ reduces toxicity. NH_4Cl and $NaClO_3$ are together more toxic than $NaClO_3$ alone. Neither $NaClO_3$ nor ClO_3^- accumulates in the cytoplasm of *Nitella*; penetration is slow, and still slower in reduced light intensity. Injury of *Nitella* cells by solutions of $NaClO_3$ is manifested by the outward diffusion of Cl^- from the vacuolar sap, loss of turgidity, and appearance of opalescence in the immersion solution. W. G. EGGLETON.

Potash manuring and susceptibility [of plants]. ARELAND (Ernähr. Pflanze, 1931, 27, 470—474).—The sensitiveness of plants to fungal infection is associated with the no. of active stomata per unit leaf area and with transpiration rates. K fertilisers, while increasing crop yields, decrease transpiration whether expressed per g. of tissue or per unit of leaf area. The actual H_2O content of the tissues is but little affected. A. G. POLLARD.

***Penicillium* injury to maize.** H. JOHANN, J. R. HOLBERT, and J. G. DICKSON (J. Agric. Res., 1931, 43, 757—790).—*P. oxalicum* is essentially a saprophyte. H_2CO_3 , the production of which by *P. oxalicum* depends on the amount and availability of nutrient substances, kills or injures the host cells. Low relative humidity, rather than high temp. alone, may accelerate blighting by increasing the transpiration rate of the host. W. G. EGGLETON.

Nutritional disorders in maize grown in sand cultures. N. A. PETTINGER, R. G. HENDERSON, and S. A. WINGARD (Phytopath., 1932, 22, 33—51).—Three types of chlorosis are distinguished: A, due

to Mg deficiency, causes chlorotic streaks from leaf base to tip with irregular margins; B, due to excess of Na, similar streaks with smooth margins, and C, due to Mn deficiency, discontinuous streaks. Absence of B produces sterility in flowers. Addition of Mn, Zn, Cu, B, and As to nutrients increase the frost-resistance of young plants. A. G. POLLARD.

Plant cancer and potassium. M. VIALA (Compt. rend. Acad. Agric. France, 1932, 18, 63—67).—Deficiency of K favours the development of plant cancer caused by *B. tumefaciens* in geranium plants. A. G. POLLARD.

Mosaic disease in *Solanum tuberosum*. R. C. MALHOTRA (J. Biochem. Japan, 1931, 13, 473—487).—The effect of a potato mosaic disease on the wt., org. constituents, ash, and calorific val. of its host was investigated. F. O. HOWITT.

X-Ray analysis of the structure of the wall of *Valonia ventricosa*. I. W. T. ASTBURY, T. C. MARWICK, and J. D. BERNAL (Proc. Roy. Soc., 1932, B, 109, 443—450).—X-Ray analysis indicates the presence in the cell wall of *V. ventricosa* of two main sets of cellulose chains crossing at an angle $>60^\circ$ and usually about 80° . The fine crossed striae on the surface of the wall are parallel to the directions of the chains. W. O. KERMAK.

Fluorometric determination of hydrogen-ion concentration. H. LINSE (Biochem. Z., 1932, 244, 157—164).—A method is described for determination of the p_H of solutions in terms of the intensity of fluorescence of various substances (asculin, fluorescein, umbelliferone) at a known p_H . The accuracy is 0.05 p_H . P. W. CLUTTERBUCK.

Volumetric determination of small quantities of phosphorus. M. ODIN (Acta Pæd., 1930, 9, 392—404; Chem. Zentr., 1931, ii, 602).—The total, acid-sol., and lipin-P of the blood or cerebrospinal fluid is pptd. as NH_4 phosphomolybdate, which is determined titrimetrically. The suspension of the ppt. in ice-cold H_2O is filtered through a hardened filter secured to the end of a tube 6—8 mm. in diameter. 0.015—0.5 mg. of P can be accurately determined. A. A. ELDRIDGE.

Determination of residual nitrogen by direct Nesslerisation. R. STOHR (Z. physiol. Chem., 1931, 203, 154—156; cf. A., 1931, 1437).—Lublin's method is very similar to a modification (A., 1924, ii, 871) of Folin's method. "Perhydrol" often contains N, for which tests should be made. J. H. BIRKINSHAW.

Modification of the Van Slyke nitrogen distribution method. J. W. CAVETT (J. Biol. Chem., 1932, 95, 335—343).—A modification of the method requiring only 0.5 g. of protein and less than half the time of the previous method is described. Micro-Kjeldahl determinations are used, cystine is determined by a slight modification of the method of Folin and Marenzi (A., 1929, 1093), and histidine directly by that of Koessler and Hanke (A., 1920, ii, 67). A. LAWSON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1932.

General, Physical, and Inorganic Chemistry.

Perturbed series in line spectra. A. G. SHENSTONE and H. N. RUSSELL (Physical Rev., 1932, [ii], 39, 415—434).—Mathematical. The series in the spectra of Ca I, Ba I, Hg I, Cu I, and Al II are discussed.
N. M. BLIGH.

High-intensity discharges in gases. Z. BAY (Math. Nat. Anz. Ungar. Akad. Wiss., 1930, 47, 569—585; Chem. Zentr., 1931, ii, 3308).—The spectra of discharges in H₂, N₂, Ne, and Ne-Hg mixtures were studied.
A. A. ELDRIDGE.

Fine structure of the 4686 He⁺ line in parallel electric and magnetic fields. D. P. RAY-CHAUDHURI (Z. Physik, 1932, 74, 711—713).

A. B. D. CASSIE.

Absorption and resonance of the helium infra-red lines. M. R. WEHR (Physical Rev., 1932, [ii], 39, 796—801).—The absorption and variation of absorption with source tube conditions of He excited at low voltages for its own lines 10,830 and 20,582 Å. were determined. The 10,830 Å. line shows strong resonance directly proportional to the % absorption; the 20,582 Å. line shows very small absorption and no detectable resonance.
N. M. BLIGH.

Mean free path, excitation probability, and excitation function in sodium vapour. L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1259—1263).—The excitation probability in Na vapour is calc. from a comparison of the intensities of the Hg line 5461 Å. and the Na D line. The mean free path is calc. from the diminution of intensity with distance from the grid.
E. S. HEDGES.

Influence of inert gases on Na resonance radiation. L. VON HAMOS (Z. Physik, 1932, 74, 379—387).—An unsuccessful attempt to obtain emission from excited atoms enhanced by collision is described. Inert gases do not extinguish Na resonance radiation, but merely broaden the lines.

A. B. D. CASSIE.

***g(I)*-Factors for the nuclei of chlorine, phosphorus, and aluminium.** S. TOLANSKY (Z. Physik, 1932, 74, 336—343).—Line spectra of Cl II, P II, Al I, and Al II indicate exceptionally small *g(I)*-factors for the nuclei 27, 31, 35, and 37, suggesting that the magnetic nuclear moment is not determined by proton spin alone.
A. B. D. CASSIE.

Hyperfine structure of resonance lines of gallium. D. A. JACKSON (Z. Physik, 1932, 74, 291—294).—The nuclear spins of the two isotopes of Ga are either both 3/2 or 0 and an undetermined quantity

(cf. Campbell and Bacher, Physical Rev., 1931, [ii], 38, 1906).
A. B. D. CASSIE.

Fine structure of the visible absorption bands of bromine. W. G. BROWN (Physical Rev., 1932, [ii], 39, 777—787; cf. A., 1931, 1344).—Analyses of the group of bands in the main absorption band system of Br₂^{79,81}, vibrational isotope shift of band origins, and vibrational and rotational consts. are given.
N. M. BLIGH.

Spectrum of strontium hydride. W. W. WATSON and W. R. FREDRICKSON (Physical Rev., 1932, [ii], 39, 765—776).—Full data for the three groups of SrH bands in the near infra-red with main heads at 7020, 7347, and 7508 Å. are recorded.

N. M. BLIGH.

Mean life of cadmium atom in states ³P₁ and ¹P₁. P. SOLEILLET (Compt. rend., 1934, 194, 783—784; cf. A., 1928, 930).—The calc. mean life of the Cd atom in the states ²³P₁ and ²¹P₁ (2 × 10⁻⁶ sec. and approx. 10⁻⁸ sec.) is confirmed experimentally.

C. A. SILBERRAD.

Mean lives of atomic states. H. D. KOENIG and A. ELLETT (Physical Rev., 1932, [ii], 39, 576—584).—Direct measurements are made by means of the thermal motion of excited atoms in two forms of resonance lamps. The val. 2.5 × 10⁻⁶ sec. was found for the ²³P₁ state of Cd.
N. M. BLIGH.

New resonance series in diatomic tellurium vapour. J. PIÉCARD (Bull. Acad. roy. Belg., 1932, [v], 18, 180—185; cf. A., 1931, 1204).—From the two series previously investigated the vibration levels of Te₂ are deduced. Term vals. and separations for the 4058 Å. series are tabulated, and for a new series excited by the 5005 Å. line of N. It was not possible to separate the 4245 and 4387 Å. series.

N. M. BLIGH.

First spark spectrum of caesium (Cs II). O. LAPORTE, G. R. MILLER, and R. A. SAWYER (Physical Rev., 1932, [ii], 39, 458—466; cf. A., 1931, 1204).—The ultra-violet spectrum was photographed; wavelengths, classifications, and intensities are tabulated for 87 lines. The ionisation potential of Cs II is 23.4 volts.
N. M. BLIGH.

Spectrum of barium hydride. W. R. FREDRICKSON and W. W. WATSON (Physical Rev., 1932, [ii], 39, 753—764).—Full data for the BaH band system in the region 6925—6380 Å. are recorded.

N. M. BLIGH.

Spectrum of doubly-ionised cerium. A. S. KING and R. B. KING (*Astrophys. J.*, 1932, 75, 40—45).—208 lines from 2167 to 3544 Å. have been measured. These lines probably belong mainly to doubly-ionised Ce. L. S. THEOBALD.

Temperature classification of the spectra of ytterbium and lutecium. A. S. KING (*Astrophys. J.*, 1931, 74, 328—341).—Details of the electric furnace, arc, and spark spectra between 2950 and 6800 Å. are given for Yb and Lu. L. S. THEOBALD.

First spark spectrum of mercury. R. RICARD (*Compt. rend.*, 1932, 194, 781—783).—49 hitherto unclassified lines of Hg II are tabulated and 18 other lines are classified by the aid of three new terms.

C. A. SILBERRAD.

Metastable atoms in mercury fluorescence. (LORD) RAYLEIGH (*Nature*, 1932, 129, 344).—Experiments which prove that both kinds of metastable Hg atoms, 2^3P_0 and 2^3P_2 , are present in the stream of fluorescent vapour excited by the resonance line 2537 Å. are described. L. S. THEOBALD.

Hyperfine structure of the mercury resonance line 2537 Å. II. S. MROZOWSKI (*Bull. Acad. Polonaise*, 1931, A, 489—521).—An examination of the hyperfine structure of the Hg resonance line, 2537 Å., showed that the lower 1^1S_0 level of the Hg atom is not split up. By adding inert gases it was found that three of the components arise from one kind of isotope, whilst the other two components arise from another isotope. W. R. ANGUS.

Wave-length shifts of certain spectral lines of Hg II. A. IMAZATO (*Sci. Rep. Tokyo Bunrika Daigaku*, 1932, A, 1, 179—192).—The wave-length shifts of lines in the Hg II spectrum at fairly high pressures were studied. A. J. MEE.

Hyperfine structure of the mercury line 5461 Å. L. SIBAIYA (*Nature*, 1932, 129, 472).—A new satellite of the line is recorded.

L. S. THEOBALD.

Hyperfine structures and nuclear moments of mercury. II. H. SCHÜLER and E. G. JONES (*Z. Physik*, 1932, 74, 631—646; cf. this vol., 2).—The hyperfine structures of a further 8 Hg II lines suggest a nuclear moment of $1/2$ for the isotope 199 and $3/2$ for 201. A. B. D. CASSIE.

Effect of nuclear spin on the radiation excited by electron impact. W. G. PENNEY (*Proc. Nat. Acad. Sci.*, 1932, 18, 231—237).—A theory of the polarisation of radiation excited by electron impact must take into account nuclear spin. Exact expressions are deduced for a few special cases and applied to the particular case of Hg. The anomalous behaviour of the Hg 2537 Å. line is due to the exaggerated importance which electron exchange has in exciting the 2^3P_1 level. J. W. SMITH.

Intensity measurements in the arc spectrum of thallium. S. E. WILLIAMS and J. HERLIHY (*Physical Rev.*, 1932, [ii], 39, 802—805).

N. M. BLIGH.

Spectrum of bismuth hydride. E. HULTHÉN and A. HEIMER (*Nature*, 1932, 129, 399).—Further details of the band spectrum previously reported (A.,

1931, 664) are recorded and discussed. The band system shows indications of a hyperfine structure due to the high nuclear spin in the Bi atom (cf. this vol., 104).

L. S. THEOBALD.

Wave-length determinations in the higher spark spectra of lead and bismuth in the farthest ultra-violet. G. ARVIDSSON (*Ann. Physik*, 1932, [v], 12, 787—819).—The determination of the wave-lengths of the spectral lines of Pb and Bi in the region 1400—200 Å. was carried out by means of a vac. spectrograph and a concave grating, using grazing incidence. A. J. MEE.

Central intensity in the Fraunhofer lines. A. PANNEKOEK (*Proc. K. Akad. Wetensch. Amsterdam*, 1931, 34, 1352—1364).—Mathematical.

J. W. SMITH.

Arc, spark, and glow : a note on nomenclature. J. THOMSON (*Phil. Mag.*, 1932, [vii], 13, 824—834).—Suggestions for rationalisation. H. J. EMELEUS.

Electrodeless discharges. J. S. TOWNSEND (*Phil. Mag.*, 1932, [vii], 13, 745—759).—Theoretical.

H. J. EMELEUS.

Mechanism of the positive column in monatomic gases. I. R. SEELIGER (*Physikal. Z.*, 1932, 33, 273—294).—A summary of theoretical and practical investigations on this subject.

J. W. SMITH.

Simple method of estimating the intensity relationships of two neighbouring spectral lines. H. STUCKLEN (*Ann. Physik*, 1932, [v], 12, 701—729).

W. R. ANGUS.

Nuclear spin and hyperfine structure in band spectra. S. MROZOWSKI (*Nature*, 1932, 129, 399—400).—A discussion (cf. this vol., 104).

L. S. THEOBALD.

Intensities in singlet-triplet bands of diatomic molecules. R. SCHLAPP (*Physical Rev.*, 1932, [ii], 39, 806—815).—Theoretical. N. M. BLIGH.

Zeeman effect of quadrupole lines according to Dirac's theory. B. MILLANCUK (*Z. Physik*, 1932, 74, 810—824).

A. B. D. CASSIE.

Transition effects in quadrupole lines. B. MILLANCUK (*Z. Physik*, 1932, 74, 825—845).

A. B. D. CASSIE.

Dispersion of light in the region of quadrupole lines. J. BLATON (*Z. Physik*, 1932, 74, 418—428).

A. B. D. CASSIE.

Dynamical systems of continuous spectra. B. O. KOOPMAN and J. VON NEUMANN (*Proc. Nat. Acad. Sci.*, 1932, 18, 255—263).—Mathematical.

Theory of widening of spectral lines according to wave-mechanics. B. MROWKA (*Ann. Physik*, 1932, [v], 12, 753—786).

Spectrum of cosmic radiation. I. Measurements of autumn 1928. E. REGENER (*Z. Physik*, 1932, 74, 433—454).—Measurements of ionisation due to cosmic radiation at depths down to 230 m. in Lake Constance show a homogeneous radiation after absorption by 80 m. of H_2O ; the absorption coeff. for this radiation is 1.9×10^{-4} per cm. H_2O , and probably corresponds with the radiation of the mass of a He nucleus. A. B. D. CASSIE.

Spectrographic observations of infra-red lines in the auroral spectrum. L. VEGARD (*Nature*, 1932, 129, 468).—A strong and a weak narrow band have been observed at 7883 and 8095 Å., respectively. None of the infra-red O lines can be identified with these two lines. L. S. THEOBALD.

Non-polar auroral light from the night sky in the tropics. K. R. RAMANATHAM and J. V. KARANDIKAR (*Nature*, 1932, 129, 545).

L. S. THEOBALD.

Red radiation from oxygen in the night sky. W. GROTRIAN (*Naturwiss.*, 1932, 20, 182—183).—A criticism of Sommer's work (*ibid.*, 85).

W. R. ANGUS.

Peculiar stellar spectra. III. Occurrence of europium in A-type stars. W. W. MORGAN (*Astrophys. J.*, 1932, 75, 46—59).

L. S. THEOBALD.

Spectrum of the corona. S. A. MITCHELL (*Astrophys. J.*, 1932, 75, 1—33). L. S. THEOBALD.

Origin of the coronal lines. T. L. DE BRUIN (*Nature*, 1932, 129, 468—469).—Unclassified lines are discussed. The green auroral line 5577 Å. and the green coronal line 5303 Å. have their origin in the same metastable level of the neutral oxygen level 1S_0 ; thus "coronium" is neutral oxygen. L. S. THEOBALD.

M- and N-series. E. LINDBERG (*Nova Acta Reg. Soc. Sci. Upsaliensis*, 1931, 7, No. 7, 7—74; *Chem. Zentr.*, 1931, ii, 2833).—M-Emission spectra of U, Th, Bi, Pb, Tl, Au, Pt, Ir, Os, Re, W, Ta, and Hf were studied; the difference in wave-length for a doublet is approx. const. for different elements. M- and N-series lines of Lu, Yb, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce, La, and Ba, and the M-absorption spectra of U, Th, Bi, Pb, Tl, Hg, Au, Pt, and W were also studied. A. A. ELDRIDGE.

Intensity ratio of fluorescent X-ray lines. G. VON HEVESY and E. ALEXANDER (*Nature*, 1932, 129, 315).—The intensity ratio of the Ag $L\beta_2$ and $L\beta_3$ lines varies with the effective wave-length; hence, in chemical analysis, when exciting secondary lines with continuous radiation, the same voltage must be applied as is used in the standardisation.

L. S. THEOBALD.

Complex X-ray characteristic spectra. M. N. SAHA, S. BHARGAVA, and J. B. MUKERJI (*Nature*, 1932, 129, 435).—Attention is directed to a third class of characteristic lines, which are due to double ionisation and double transition. L. S. THEOBALD.

Scattering of X-rays by polyatomic gases. Y. H. WOO (*Physical Rev.*, 1932, [ii], 39, 555—560).—The general expression for the intensity of total scattering is modified by substituting the average for the true at. structure factor. Results are in agreement with the measurements of Wollan (*cf. A.*, 1931, 781).

N. M. BLIGH.

[Scattering of X-rays by polyatomic gases.] G. E. M. JAUNCEY (*Physical Rev.*, 1932, [ii], 39, 561).—A note on Woo's paper (*cf. preceding abstract*).

N. M. BLIGH.

Cross-section for transference of charge and ionisation of argon by argon⁺. F. WOLF (*Z. Physik*, 1932, 74, 575—592).

A. B. D. CASSIE.

Secondary phenomena that influence the primary photo-electric effect of caesium atoms adsorbed on salt layers. J. H. DE BOER and M. C. TEVES (*Z. Physik*, 1932, 74, 604—623).—The sensitivity of photo-electric cathodes can be considerably increased by using thick salt layers with adsorbed Cs, which renders the layer photo-electrically conductive; the red wave-length limit can also be extended from 0.9 μ for thin layers to 1.2 μ for the thick layers.

A. B. D. CASSIE.

Rate of ionisation of the atmosphere. G. R. WAIT and O. W. TERRESO (*Nature*, 1932, 129, 401—402).

L. S. THEOBALD.

Spark potentials in pure gases. Spark potential in pure hydrogen. K. ZUBER (*Ann. Physik*, 1932, [v], 12, 665—700).—The representation of the spark potentials by a half-logarithmic method is discussed and compared with the usual methods of representation. Measurements have been made on very pure H₂.

W. R. ANGUS.

Hydrogen chromosphere. J. WOLTJER, jun. (*Nature*, 1932, 129, 580).—Theoretical considerations lead to a hypothesis of the convection of H atoms by outward-moving Ca⁺ atoms in the solar chromosphere.

L. S. THEOBALD.

Electron isomerism. R. SCHMID (*Magyar Chem. Fol.*, 1931, 37, 157—163; *Chem. Zentr.*, 1931, ii, 2695).—A discussion of the rôle of electron quantum numbers in atoms and mols.; differences between para- and dia-magnetic NO are discussed. The equilibrium const. of the change $p\text{-NO} \rightleftharpoons d\text{-NO} + 343 \text{ g.-cal.}$ is dependent on the temp.

A. A. ELDRIDGE.

Dirac's equation and the spin-spin interactions of two electrons. G. BREIT (*Physical Rev.*, 1932, [ii], 39, 616—624; *cf. A.*, 1930, 1327).—Mathematical.

N. M. BLIGH.

Magnitudes characteristic of the Dirac electron. A. PROCA (*Compt. rend.*, 1932, 194, 836—838).

C. A. SILBERRAD.

Two quantum terms of an electron in a two-centred system. G. C. WICK (*Z. Physik*, 1932, 74, 773—779).

A. B. D. CASSIE.

Wave equations of an electron in real form. D. MESKYN (*Phil. Mag.*, 1932, [vii], 13, 834—844).

Eigenfunctions for calculating electronic vibrational intensities. P. M. DAVIDSON (*Proc. Roy. Soc.*, 1932, A, 135, 459—472).—Mathematical. It is suggested that the Morse formula is valid only under certain conditions, and some new eigenfunctions, useful for the graphical calculation of intensities, are established. Transitions from the fixed vibrational and rotational state of the upper electronic level to states in the lower electronic level differing from each other only in their vibrational quantum no. are considered.

L. L. BIRCUMSHAW.

Polarisation of electrons by double scattering. N. F. MOTT (*Proc. Roy. Soc.*, 1932, A, 135, 429—459).—Mathematical. A continuation of previous work (*A.*, 1929, 861) on the application of Dirac's relativistic theory of the electron to the scattering of electrons by atoms.

L. L. BIRCUMSHAW.

Electrons, protons, and the so-called electron magnetism. A. GUNTHER-SCHULZE (Z. Physik, 1932, 74, 692—706).—Theoretical. Electron-magnetism appears to be an unnecessary fiction.

A. B. D. CASSIE.

Excitation of atomic mercury by electron impact. W. G. PENNEY (Physical Rev., 1932, [ii], 39, 467—473).—Mathematical. N. M. BLIGH.

Precision method for determining the thermal diffusivity of solids. R. H. FRAZIER (Physical Rev., 1932, [ii], 39, 515—524).—Results for Ni are accurate to 0.1%.

N. M. BLIGH.

Multiple excitation of complex atoms by electronic collisions. L. GOLDSTEIN (Compt. rend., 1932, 194, 773—776).—Mathematical.

C. A. SILBERRAD.

Angular distribution of slow electrons scattered by gas molecules. III. C. RAMSAUER and R. KOLLATH (Ann. Physik, 1932, [v], 12, 837—848; cf. A., 1931, 782, 1107, 1206).—The method previously described is applied to Kr and Xe, and to these gases mixed with A, using electrons of velocity < 1 volt. Whilst all the gases behave similarly, there are undoubted differences at the smallest electron velocities.

A. J. MEE.

New determinations of light production by electronic and ionic collisions. W. HANLE [with O. THIEME, G. HAFT, O. FISCHER, and K. LARCHE] (Physikal. Z., 1932, 33, 245—247).—Work on the He, Hg, Na, A, and N₂ spectra is described.

A. J. MEE.

Inelastic and elastic electron scattering in argon. A. L. HUGHES and J. H. McMILLEN (Physical Rev., 1932, [ii], 39, 585—600).

N. M. BLIGH.

Doppler effects in hydrogen canal rays of uniform energies. H. F. BATHO and A. J. DEMPSTER (Astrophys. J., 1932, 75, 34—39)

L. S. THEOBALD.

Spectroscopic detection of a new isotope of lead. H. SCHULER and E. G. JONES (Naturwiss., 1932, 20, 171).—A new isotope of Pb (Pb²⁰⁴) has been detected by an examination of the hyperfine structure of the 7228, 5201, and 5005 Å. lines of Pb I and the 5609 Å. line of Pb II.

W. R. ANGUS.

Isotope investigations of hydrogen and helium by mass spectrograph. H. KALLMANN and W. LASAREV (Naturwiss., 1932, 20, 206).—A spectrograph method indicates the presence in ionised H of ions of mass 1, 2, and 3. By another method traces of an ion of mass 4 were found. The intensity ratio of ions of mass 3 to that of ions of mass 2 was found for very low pressures to be 1:4000. In He an ion of mass 5 was detected in traces.

A. J. MEE.

Choice of basis for at. wts. S. MEYER (Physikal. Z., 1932, 33, 301—302).—The val. 16.00000 for the O¹⁶ isotope is regarded as the best present standard for at. wts.

J. W. SMITH.

At. wts. of selenium and tellurium. H. L. JOHNSTON (J. Amer. Chem. Soc., 1932, 54, 824—825).—Aston's work on the isotopes of Se and Te and their relative percentages is discussed.

C. J. WEST (c).

Highest atomic number. V. V. NARLIKER (Nature, 1932, 129, 402).—Theoretical considerations for the view that the highest possible at. no. is 92 and not 137 are advanced.

L. S. THEOBALD.

Radioactivity and theorising. B. WILLIS (Amer. J. Sci., 1932, [v], 23, 193—226).—A discussion of the views of Holmes, Joly, Chamberlin, Barrel, and Adams.

C. W. GIBBY.

Fine structure of α -rays of thorium-C. S. ROSENBLUM and M. VALADARES (Compt. rend., 1932, 194, 967—970; cf. A., 1931, 280; this vol., 5).—Using an improved method the probable existence in the spectrum of Th-C+C' of the rays (figures in parentheses denote velocities $\times 10^{-9}$) α_1 (2.24₈), α_{II} (2.13₁), α_{III} (2.14)[?], α_4 (1.642), and α_5 (1.621) is confirmed. Two new lines (H₂ 542 and 660) were measured in the β -ray spectrum of Th-B+C+C' (cf. A., 1925, ii, 922).

C. A. SILBERRAD.

Composition of atomic nucleus. W. D. HACKH (J. Amer. Chem. Soc., 1932, 54, 823—824).—Nuclear structure and the explanation of radioactive loss of α -particles are discussed. Isotopes differ only in the no. of neutrons.

C. J. WEST (c).

Long-range α -particles from Th-C'. J. PORT (Z. Physik, 1932, 74, 740—743).—Measurements accurate to 2% were made of the intensity and range of these particles by means of the simple Geiger method (cf. *ibid.*, 1928, 49, 753).

A. B. D. CASSIE.

Measurement of ionic mobility. G. STETTER (Physikal. Z., 1932, 33, 294—296).—The valve electrometer (A., 1929, 737) is applied to the measurement of ionic mobility. α -Particles are fired into an ionisation chamber, one wall of which is connected to a high potential whilst an end-plate and part of one wall are connected to the electrometer. The time is observed between the registration of a deflexion due to the α -particle and of the deflexion due to the discharge of the ions. The results are in good agreement with previous vals., but indicate that the mobilities of similar ions are much more uniform than was previously supposed.

J. W. SMITH.

α -Radiations of radiothorium, radioactinium, and their derivatives; complexity of α -radiation of radioactinium. (MME.) I. CURIE (J. Phys. Radium, 1932, [vii], 3, 57—72).—The rays from Ra-Ac consist of two groups; the relative formation of Ac-X indicates that the latter is formed by the emission of an α -particle from one of these groups. The energy difference, 2.8×10^5 volts/electron, of the groups is that of one of the groups of γ -rays of Ra-Ac, or of the most penetrating γ -rays of Ac-X.

N. M. BLIGH.

Ionisation effects of rays from beryllium due to α -rays from radon. M. DE BROGLIE, F. D. LA TOUR, L. LEPRINCE-RINGUET, and J. THIBAUD (Compt. rend., 1932, 194, 1037—1040; cf. this vol., 443).—The particles produced in an ionisation chamber by the rays resulting from the bombardment of Be with α -rays from Rn are more strongly ionising, although only 1/2 to 1/3 as numerous, when there is no sheet of paraffin at the entrance to the chamber. Their no. and nature seem connected with the vol. of gas therein, but are unaffected by the material of

the walls or by moisture thereon. A screen of ZnO (7.6 g. per sq. cm.) between the Be and the chamber absorbs about 40% of the radiation; KNO_3 and paraffin act similarly. No retrograde emission of protons from paraffin was detected. The no. of particles turned through $0-45^\circ$ in the ionisation chamber is about 5 times, that of those showing double tracks double, the no. mathematically probable.

C. A. SILBERRAD.

β -Rays of radium-D. E. STAHEL (Nature, 1932, 129, 314).—A discussion and a criticism (cf. A., 1931, 1349).

L. S. THEOBALD.

β -Rays of radium-D. N. FEATHER and H. O. W. RICHARDSON (Nature, 1932, 129, 314—315).—A reply to criticism (cf. preceding abstract).

L. S. THEOBALD.

Magnetic spectrum of β -rays of thorium-B. S. SHIH-YUAN (Compt. rend., 1932, 194, 874—876).—By reducing the continuous spectrum by a special arrangement, H_p and intensity for 20 β -rays (6 doublets) of Th-B have been determined, H_p 1398 being taken as standard (cf. A., 1925, ii, 922). The corresponding levels of origin and γ -ray energies are tabulated.

C. A. SILBERRAD.

Upper limit of the continuous β -ray spectrum of Ra-E. K. C. WANG (Z. Physik, 1932, 74, 744—747).—A Geiger-Müller counter gave the upper limit of this spectrum at an H_p val. of 5300.

A. B. D. CASSIE.

Half-value period of uranium-V. O. GRATIAS and C. H. COLLIE (Proc. Roy. Soc., 1932, A, 135, 299—306).—A redetermination of the half-val. period of U-Y leads to the val. 24.0 ± 0.58 hr.

L. L. BIRCUMSHAW.

Passage of neutrons through matter. H. S. W. MASSEY (Nature, 1932, 129, 470).—A theoretical investigation of the interaction of a neutron with an electron.

L. S. THEOBALD.

Possible existence of a neutron. J. CHADWICK (Nature, 1932, 129, 312).—The radiation emitted when Be is bombarded by α -particles of Po ejects particles from H_2 , He, Li, Be, C, air, and A. The particles from H_2 behave like protons with speeds up to approx. 3.2×10^9 cm. per sec., whilst those from the other elements appear to be recoil atoms of the elements. The results are best explained on the assumption that the radiation from Be is not a quantum radiation, but consists of neutrons or particles of mass 1 and charge 0.

L. S. THEOBALD.

Ejection of atoms by very penetrating radiation excited in light atoms. (MME.) I. CURIE and F. JOLIO (Compt. rend., 1932, 194, 876—877).—Several photographs of the tracks of protons and He nuclei referred to previously (cf. this vol., 318) are reproduced, and show that the ejections are not due to the impact of anything that produces an ionising path.

C. A. SILBERRAD.

Ejection of light nuclei by very penetrating radiation. Paths photographed by a Wilson chamber. P. AUGER (Compt. rend., 1932, 194, 877—879; cf. this vol., 210, 318).—The effects produced by the penetrating radiation emitted by Be under the influence of Po have been examined in a

Wilson expansion chamber in a strong magnetic field. With moist air in the chamber electronic tracks arising from the impact of the radiation on the wall were obtained, indicating potentials of up to 6.5×10^6 volts, due possibly to the Compton effect. With a moist mixture of H_2 and A (3 : 1) the tracks originated in the gas and are due to protons of energies from 50,000 to several million electron-volts, projected at all angles $< 90^\circ$, with no apparent relation between their velocity and the direction of projection. It is suggested that the different effects are due to two types of radiation, one, electromagnetic, causing the Compton effect, the other, the neutrons suggested by Chadwick, which project the protons (see above).

C. A. SILBERRAD.

[Ejection of light nuclei by very penetrating radiation.] M. DE BROGLIE (Compt. rend., 1932, 194, 879—880; cf. preceding abstract).—Similar results have been obtained by bombarding Be with α -particles from Ra, the γ -rays being filtered out by a Pb screen. The no. of particles observed by means of an ionisation chamber was trebled when paraffin was placed at the entrance. Similar results were obtained whether the chamber was of Al, Zn, Cu, or Pt.

C. A. SILBERRAD.

Chemical behaviour of ekatantalum. O. GRATIAS and C. H. COLLIE (J.C.S., 1932, 987—988).—The protoactinium from about 1 g. of pitchblende, conc. with Ta oxide and placed in the ionisation chamber of a valve amplifier, was estimated by registering on a counter the no. of particles emitted. The reactions with fused KOH and KHSO_4 and with HF were similarly studied and were in agreement with those of Grosse (cf. A., 1930, 883) using relatively large quantities.

N. M. BLIGH.

Radioactive disintegration and nuclear spin. G. GANOW (Nature, 1932, 129, 470).—The radii of radioactive nuclei have been calc. The spins of such nuclei can also be estimated.

L. S. THEOBALD.

Chart of atomic structure. W. D. HACKH (Chem. News, 1932, 144, 168—171).

Number of free protons in the nucleus. A. J. RUTGERS (Nature, 1932, 129, 361—362).—A discussion of certain difficulties.

L. S. THEOBALD.

Distribution of elements and curve of atomic volumes. J. J. SASLAVSKI (Z. anorg. Chem., 1932, 204, 222—224).—Among the first 28 elements the most widely distributed are those which occur at minima in the curve of at. vols.

F. L. USHER.

Some periodic properties of atomic nuclei. G. I. POKROVSKI (J. Amer. Chem. Soc., 1932, 54, 623—625).

E. J. ROSENBAUM (c).

Possible explanation of the difference in mass of the proton and electron. A. PROCA (J. Phys. Radium, 1932, [vii], 3, 83—101).—By the introduction of a new invariant in the theory of the electromagnetic field it is shown that the "rest mass" of a proton and electron can be expressed as $A + eB$ and $A - eB$, respectively, where A is a coeff. termed the "true mass," which is the same for the proton and electron, and B is a variable term depending

on the electromagnetic field called into action by all measurements of mass. N. M. BLIGH.

Relations between fundamental physical constants. J. E. MILLS (Science, 1932, 75, 243).—A numerical relation between the velocity of light, on the one hand, and e , Planck's const., the mass of the electron, the mass of the proton, or other fundamental const. on the other, has been found.

L. S. THEOBALD.

New determination of e/m from the Zeeman effect. J. S. CAMPBELL and W. V. HOUSTON (Physical Rev., 1932, [ii], 39, 601—615).—The val. $e/m = 1.7579 \pm 0.0025 \times 10^7$ e.m.u. per g. was obtained from the Zeeman separations of the λ 6439 Cd and the λ 6362 Zn lines. N. M. BLIGH.

Ratio of the masses of the proton and the electron. C. H. D. CLARK (Naturwiss., 1932, 20, 182).—The ratio of the masses of the proton and the electron, m_p/m_e , may be written equal to $274 - (-1)$ by accepting the relationships of Perles and Eddington. This gives a val. of 1843.5 which is approx. the arithmetic mean of the spectroscopic and "deflexion" vals. of the ratio. W. R. ANGUS.

Ultra-violet absorption of ammoniacal solutions of inorganic salts. H. FREDHOLM (Svensk Kem. Tidskr., 1932, 44, 44—48).—A 0.5*N* solution of LiCl containing 0.5 equiv. of NH_4Cl and 0.433 equiv. of NH_3 per litre shows absorption in the ultra-violet; MgCl_2 and CaCl_2 show similar effects, which are ascribed to the formation of complexes, but K, Na, Ba, and Sr have no action. ZnCl_2 <0.2*N* has absorption in the far ultra-violet. The addition of increasing amounts of NH_3 to the solution diminishes the absorption. CdCl_2 in aq. NH_3 behaves similarly. The effects with Zn and Cd are probably due to differing absorption of the two complexes of type $\text{M}(\text{NH}_3)_2$ and $\text{M}(\text{NH}_3)_4$; the asymmetric diammine has a strong absorption, whilst the symmetrical tetra-ammine shows less absorption than a solution containing the corresponding quantity of free NH_3 . A similar phenomenon has been observed in the case of the system $\text{CuSO}_4 + n\text{NH}_3$ (cf. A., 1927, 1009). H. F. HARWOOD.

Simple relations between molecular spectra and structures. H. DESLANDRES (Compt. rend., 1932, 194, 1033—1037; cf. this vol., 211).—An amplification of views previously expressed, with further examples. C. A. SILBERRAD.

Relation between ultra-violet absorption spectra and the velocity of reaction of certain types of amines. M. GRUNFELD (Compt. rend., 1932, 194, 1083—1085).—The ultra-violet absorption of *n*-amyl-, -octyl-, -dodecyl-, cyclohexyl-, and 2-methylcyclohexyl-amines in EtOH and in hexane, and of their hydrochlorides in H_2O , has been determined. Those which have the same velocity of reaction with $\text{CH}_2(\text{CO}_2\text{Et})_2$ (this vol., 371) have the same absorption. J. W. BAKER.

Structure of the third positive group of CO bands. G. H. DIEKE and J. W. MAUCHLY (Nature, 1932, 129, 546).—The bands $0 \rightarrow 0$ to $0 \rightarrow 4$ with

heads at 2833, 2977, 3134, 3305, and 3493 Å. have been studied. They are due to a $^3\Sigma \rightarrow ^3\Pi$ transition.

L. S. THEOBALD.

Certain relations between constitution of dyes and their colour intensity. A. R. PETERSON and W. C. HOLMES (J. Physical Chem., 1932, 36, 633—641).—The absorption coeffs. of various dyes were determined in aq. and EtOH solution. The absorptive power of the azo-, CHPh_3 , and quinoneimine dyes is greater in 94% EtOH than in aq. solution. On a mol. basis of comparison, the CHPh_3 and pyronine dyes are the most intensely coloured. In a given group of dyes, substitution which increases the mol. wt. increases the mol. absorption, but usually reduces the sp. absorption. S. LENHER (c).

Infra-red photography. H. WILLENBERG (Z. Physik, 1932, 74, 663—680).—Local changes in thickness of a thin oil film, due to evaporation by the heat of incident infra-red rays, are detected interferometrically. Photography is thus extended to 6.5 μ .

A. B. D. CASSIE.

Infra-red region of the spectrum. V. Absorption spectrum of carbonyl sulphide. C. R. BAILEY and A. B. D. CASSIE (Proc. Roy. Soc., 1932, A, 135, 375—391).—An analysis of the infra-red absorption spectrum of COS shows that this substance is intermediate in structure to CO_2 and CS_2 . The mol. behaves as though its structural formula were O:C:S. Further evidence in favour of this is adduced from thermochemical data. L. L. BIRUMSHAW.

Behaviour of the spectrum of water in the temperature interval 20—220° and in the spectral range 1—3.2 μ . B. STANSFELD (Z. Physik, 1932, 74, 460—465).—Comparison of the spectra of H_2O at 20° and of H_2O vapour at 120° shows that absorption max. for the vapour state occur at lower wave-lengths. This displacement of the absorption max. is also found when the spectra of H_2O at 20° and 97° are compared. The 1.414 μ and 1.881 μ bands of H_2O vapour are not displaced by raising the temp. to 220°, but there is a slight displacement in the 2.62 μ band. Results on Raman spectra of H_2O and its vapour are discussed. The shifts in the absorption max. are probably due to changes in the state of mol. aggregation. W. R. ANGUS.

Comparison of the rotation-vibration spectra of the liquid and gaseous states of certain organic substances (ethyl alcohol, formic acid, acetic acid, ether, nitrobenzene). B. STANSFELD (Z. Physik, 1932, 74, 466—475).—The absorption spectra of EtOH, HCO_2H , AcOH, and Et_2O in the liquid and gaseous states have been measured from 1 to 2.7 μ ; liquid and gaseous PhNO_2 have been investigated from 1 to 3.8 μ . Some of the bands in these substances appear to be influenced by temp., the absorption max. of the liquid occurring at a longer wave-length than the corresponding max. for the vapour. The spectra are compared with each other. The displacements of the max. are discussed and a tentative explanation is put forward.

W. R. ANGUS.

Measurements in the long wave-length infra-red from 20 μ to 135 μ . R. B. BARNES (Physical Rev., 1932, [ii], 39, 562—575).—The technique of

the region and the elimination of shorter wave-lengths are discussed. New data for the transmission of fused and cryst. quartz, S, paraffin, mica, celluloid, black paper, cellophane, soot films, Bi-black, and a lamp-black-water-glass prep. are recorded. S showed 8 absorption bands which are compared with Raman effect data (cf. Krishnamurti, A., 1930, 1237).

N. M. BLIGH.

Near infra-red absorption spectra of the rare earths. R. FREYMAN and S. TAKVORIAN (Compt. rend., 1932, 194, 963—964).—The following max. of absorption bands between 0.82 and 1.16 μ were determined with the author's apparatus (cf. this vol., 6) and solutions of the neutral chlorides of concn. 8N—N/32 (where different the most persistent bands are denoted by an *): Pr 10,182, Nd 8660*, 8755, 8891; Sm 9508, 10,869*; Dy 9090, 11,054; Ho 8930 (weak); Er 9742; Lu (probably) 9400, 9740; none was observed with La, Ce, Eu, Gd, Tb, Y, and Tm.

C. A. SILBERRAD.

Infra-red absorption spectra of nuclear hydrocarbons. P. LAMBERT and J. LECOMTE (Compt. rend., 1932, 194, 960—962).—Absorption spectra between 7 μ and 16 μ of the following have been determined: cyclohexane and 1:3- and 1:4-dimethylcyclohexanes (show some resemblances to, but more essential differences from, the corresponding benzenes); cyclohexene and the three methylcyclohexenes (show no further approach to the corresponding benzenes); C₁₀H₈, 1- and 2-methyl-, 1:6- and 2:6-dimethyl-, tetra- and deca-hydro-naphthalene (all show a characteristic band near 12.8 μ except the last, which differs as cyclohexane from C₆H₆); Ph₂ (distinctly different from C₆H₆ or C₁₀H₈); and CH₂Ph₂ and CHPh₃ (show clearly their relation to PhMe). C. A. SILBERRAD.

Near infra-red absorption spectra of some halogen derivatives of methane. J. G. MOORHEAD (Physical Rev., 1932, [ii], 39, 788—795; cf. this vol., 212; Bennett and Meyer, A., 1929, 239).—The fine structure of 7 bands of MeCl, MeBr, and MeI in the region 1.5—3.0 μ was measured.

N. M. BLIGH.

Molecular rotation of solid sodium nitrate. J. M. BIJVOET and J. A. A. KETELAAR (J. Amer. Chem. Soc., 1932, 54, 625—628).—A structural model for NaNO₃ in agreement with intensities of the lines of the powder diagram is proposed. R. H. LAMBERT (c).

Structure of Rayleigh radiation. E. H. L. MEYER and W. RAMM (Physikal. Z., 1932, 33, 270—272).—The spectra of C₆H₆, PhMe, and CCl₄ have been investigated with an interference spectroscope. Besides the primary lines there are new lines due to splitting. The displacements agree closely with those calc. from a formula due to Gross. The red displacement noticed by Cabannes and others is not found.

A. J. MEE.

Atoms and molecules as Fitzgerald oscillators. R. BÄR (Nature, 1932, 129, 505).—With incident light horizontally polarised, the Raman lines of thiophen show complete depolarisation; the anomalous polarisation reported by Venkateswaran (*ibid.*, 1931, 128, 795) does not exist.

L. S. THEOBALD.

Polarised phosphorescence light. P. FRÖHLICH (Math. Nat. Anz. Ungar. Akad. Wiss., 1930, 47, 79—95; Chem. Zentr., 1931, ii, 3305).

Angular distribution of intensity of Raman lines. D. P. RAY-CHAUDHURI (Z. Physik, 1932, 74, 574; cf. A., 1931, 1353).—A correction; the law of distribution for the 4617 Å. line of C₆H₆ is different from that of the 4215 and 4555 Å. lines.

A. B. D. CASSIE.

Raman effect and dipole moment. A. KASTLER (Compt. rend., 1932, 194, 858—861).—The Raman frequency, $\Delta\nu$, is usually less in the liquid than in the gaseous state, rarely, e.g., in HCN, the reverse. In general $\Delta\nu$ is largest where the mols. have a permanent dipole moment, being due to the influence of the electrostatic fields of neighbouring mols. on the linkings attaching the valency electrons. These being negatively charged and as a rule screening the positive nucleus, the nearer approach of another negative charge weakens the linking and diminishes $\Delta\nu$. Where, as in HCN, there is an unscreened H⁺ the effect is the reverse. This agrees with other relations between the Raman effect and constitution (cf. A., 1924, ii, 372; 1930, 840; this vol., 7).

C. A. SILBERRAD.

Polarisation of Raman scattering. S. BHAGAVANTAM and S. VENKATESWARAN (Nature, 1932, 129, 580).—Improved measurements with many liquids show that no line has a depolarisation >6/7, the limiting val. Certain vibration lines of C₆H₆, HCO₂H, C₄H₄S, and the tetrachlorides of Sn, C, Si, and Ti show this val., which is also reached in all cases of a rotational scattering whether by gases or liquids. The 992 cm.⁻¹ line of C₆H₆ shows 7% depolarisation and the lines 459, 426, 382, and 367 of CCl₄, SiCl₄, TiCl₄, and SnCl₄, respectively, show depolarisations of 4, 11, 12, and 16%. The Rayleigh scattering in these tetrachlorides is accompanied by a rotational Raman scattering and is depolarised to an extent which increases with an increase in the at. no. of the central atom.

L. S. THEOBALD.

Raman effect with inorganic complexes, especially co-ordinated compounds. I. DAMASCHUN (Z. physikal. Chem., 1932, B, 16, 81—101).—A Raman frequency attributable to internal vibration of the complex ion has been observed with aq. solutions of some only of the various amines and complex cyanides examined. The intensity of these lines is great enough to indicate that the binding forces in the complex ions are almost non-polar. The Raman lines of the various tungstic and molybdic acids are sufficiently characteristic to serve as a means of identification. Aq. ZnCl₂ gives a line traceable to ZnCl₆⁴⁻. No line which could be ascribed to the complex Cu(H₂O)₄²⁺ has been found. R. CUTHILL.

Influence of sulphur dioxide on the glow of phosphorus. A. BLAHA and F. SCHACHERL (Coll. Czech. Chem. Comm., 1932, 4, 69—71).—P does not glow in pure SO₂. Curves representing the influence of poisons on the max. pressure limit of the glow of P are always convex towards the concn. axis if the concns. of the poisons are expressed by the ratio of the partial pressures of the poison and O₂.

E. S. HEDGES.

Discoloration and after-glow of carbonate and oxide phosphors. L. WESCH (Ann. Physik, 1932, [v], 12, 730—742).—The experimental arrangement and the prep. of the phosphors are discussed. The

discoloration of carbonate phosphors is not influenced by the phosphorescence of different metals; in the molten state the phosphor is discoloured. The discoloration results from discoloration of the alkali halides. The heavier is the alkali halide the greater is the discoloration. The light emitted by phosphors on irradiation with ultra-violet light or with cathode or high-frequency radiation is considered.

W. R. ANGUS.

Detection of *K*-absorption constants in phosphors and a new sensitive method for the spectral analysis of high-frequency radiation. L. WESCH (Ann. Physik, 1932, [v], 12, 743—752).—Several sulphide phosphors have been examined.

W. R. ANGUS.

Elementary processes of chemiluminescence. H. BEUTLER (Angew. Chem., 1932, 45, 249—254).—A lecture.

E. S. HEDGES.

Energy transformations at surfaces. V. Phosphorescence of adsorbed, fluorescing dyes and its relationship to reversible and irreversible structural changes of gels. H. KAUTSKY and A. HIRSCH (Ber., 1932, 65, [B], 401—406; cf. this vol., 7).—The luminescence of dyes on dry org. adsorbates (paper, cellophane, cotton-wool, artificial silk, ramie, wool, silk, gelatin) does not differ essentially from that on inorg. media (*loc. cit.*) and is best observed on writing paper. The displacement of the bands towards longer wave-length with diminishing temp. is very marked. Dry paper phosphors are not sensitive to O_2 , but become increasingly sensitive with increasing H_2O content. Large amounts of H_2O completely inhibit phosphorescence. The effect of O_2 can therefore be observed only with papers of low H_2O content and is not comparable with its effect on SiO_2 adsorbates. The diminution of intensity and duration of phosphorescence depends on the length of pre-illumination of the phosphor. The bearing of these observations on the structure and ageing of gels is discussed.

H. WREN.

Cold temperature radiation. A. GUNTHER-SCHULZE and H. BETZ (Z. Physik, 1932, 74, 681—691).—A temp. can be ascribed to an energy distribution among electrons in an electrolyte; this temp. determines the intensity of light observed at an Al anode in citric acid, assuming black-body conditions. The temp. and the corresponding intensity of black-body radiation were varied by varying the potential across the cell and verified the assumption of a Maxwell distribution of energy among the electrons.

A. B. D. CASSIE.

Temperature crests in cando-luminescence. E. L. NICHOLS and H. L. HOWES (J. Opt. Soc. Amer., 1932, 22, 170—189; cf. A., 1927, 7, 607).—Further evidence for the existence of maxima, characteristic of the activator, in the brightness-temp. curves of rare earths in the H flame is given; the brightness greatly exceeds that of a black body at like temp. The effects of adding an activator, Gd, Nd, Pr, Sm, were investigated.

N. M. BLIGH.

Micrographic investigations of the "cuprous" rectifier. M. TORRES (Z. Physik, 1932, 74, 770—772).—Photomicrographs indicate that Cu crystal extends throughout the Cu_2O layer.

A. B. D. CASSIE.

Conductivity of silver sulphide. W. JOST (Z. physikal. Chem., 1932, B, 16, 129—142).—The high val. for the sp. conductivity, κ , of α - Ag_2S previously reported (A., 1929, 1369; 1931, 1213) has been verified. In an atm. free from S, and also in presence of S, κ is depressed considerably by the formation of mixed crystals with Cu_2S . This suggests that the mobility of the Cu ions in these mixed crystals is much less than the mobility of the Ag ions in pure Ag_2S , which would account for the fact that the val. of κ deduced from the rate of diffusion of Cu ions into Ag_2S is far smaller than the directly determined val. The possible explanations of high ionic mobilities in solid compounds are examined, none being found quite satisfactory.

R. CUTHILL.

Photo-electric properties of cadmium sulphide. R. AUDUBERT and (MLLE.) C. STORA (Compt. rend., 1932, 194, 1124—1126).—A CdS electrode is prepared by electrolysis an alkali sulphide with Cd as anode (cf. this vol., 126). The photo-electric effect of the cell $Cd|CdS|Na_2S, aq. | Cd$ shows max. for λ 5200 Å., and 3900 (smaller), and a min. for 4100 Å. Photo-electronic effect, if present, is quite secondary.

C. A. SILBERRAD.

Photoconductivity of diamonds. (SIR) R. ROBERTSON, J. J. FOX, and A. E. MARTIN (Nature, 1932, 129, 579).—Four more diamonds (cf. A., 1930, 1237) of the type transparent at 8μ and as far as 2300 Å. in the ultra-violet region are reported. Most of the diamonds of the transparent character produce a current on illumination without applying a voltage across the diamond; the most effective wave-length is approx. 2300 Å.

L. S. THEOBALD.

Peculiar form of activity of matter. G. REBOUL (Compt. rend., 1932, 194, 1122—1124; cf. this vol., 321).—In addition to the relatively intense ionisation in the neighbourhood of a resistance cell there emanates therefrom a gas capable of affecting a photographic plate, of producing relatively feeble ionisation, and of imparting activity to objects it touches. It is suggested that this gas is not in electrical equilibrium and emits radiation in returning slowly thereto (cf. A., 1931, 405).

C. A. SILBERRAD.

Effective radii of combined atoms, and ortho effect in dipole moments. M. MAGAT (Z. physikal. Chem., 1932, B, 16, 1—18).—Since Wohl's data for mol. diameters (A., 1931, 1216) show that space-filling of a mol. is additive, the effective radii of various atoms and groups have been calc. from liquid vols. at 0° abs. and from mol. radii deduced from viscosity data. The results show that in *o*-disubstitution products of C_6H_6 the dimensions of the substituents are not, in general, great enough for steric effects to be responsible for the *ortho* effect in dipole moments. It is probable that the effect is primarily due to the influence of directive valency forces on the angle between the linkings by which the substituents are attached, mutual polarisation of the dipoles also playing a part. In *o*-dinitrobenzene the plane of the NO_2 -groups seems to make an angle, not exceeding 40° , with the plane of the ring.

R. CUTHILL.

Total electric polarisation and the electric moments of certain organic molecules. L. M.

HEIL (Physical Rev., 1932, [ii], 39, 666—674).—The dielectric consts. and densities of PhBr and PhI in dil. solution with C_6H_{14} , and of C_6H_{14} and *o*-, *m*-, and *p*-xylenes as pure liquids, were investigated. The vals. obtained for the electric moments are: *p*-xylene 0; *m*-xylene, 0.34×10^{-18} ; *o*-xylene 0.44×10^{-18} ; PhBr, 1.35×10^{-18} ; PhI, 1.25×10^{-18} ; in each case the Debye law was valid. Results supported a decrease of the electric moment of the mol. with increase of at. wt. of a substituted atom, and indicate that the induced polarisation is a function of the temp., and that this effect may neutralise or diminish the effect of a small dipole. N. M. BLIGH.

Dielectric constants of certain liquids. Crystal-controlled resonance apparatus. H. ULICH and W. NESPITAL (Z. physikal. Chem., 1932, B, 16, 221—233).—The dielectric consts. of various org. liquids have been determined at several temp. by the resonance method, using an apparatus in which the frequency of the generator is controlled by a quartz crystal. By modifications in the resonance circuit the range and precision of the apparatus may be varied. R. CUTHILL.

Inorganic halides and their molecular compounds. IV. Dipole moment measurements with aluminium, boron, and beryllium halides and their molecular compounds. W. NESPITAL (Z. physikal. Chem., 1932, B, 16, 153—179; cf. A., 1931, 1354).—Dielectric const. measurements at 20° with C_6H_6 and CS_2 solutions show that in general the polarisation of the solute increases with the dilution. Since the solutes have a strong tendency to associate, the products of association must have smaller dipole moments than the unimol. complex compounds. The difference between the moment of a mol. compound and that of its org. component is fairly const. among the Al and also among the B compounds. The compounds $AlCl_3 \cdot NH_2Et$, m. p. 63°, $BCl_3 \cdot MeCN$, and $BeBr_2 \cdot 2Et_2O$, m. p. 49°, have been prepared by interaction of their constituents. R. CUTHILL.

Quantum-mechanical calculation of the constants of some polar molecules. J. G. KIRKWOOD (Physikal. Z., 1932, 33, 259—265).—Mathematical. The electrical moments and other properties of some polar mols. are calc., starting from ionic models. There is good agreement between the theoretical and experimental vals. A. J. MEE.

Ionic conductivity of glass. R. L. MÜLLER (Nature, 1932, 129, 507—508).—A discussion for the system $B_2O_3-Na_2O$. L. S. THEOBALD.

Dielectric constant and power factor of rosin oil and ethyl abietate. S. O. MORGAN and A. H. WHITE (J. Franklin Inst., 1932, 213, 313—319).—Data for the range 10 cycles—100 kilocycles indicate essentially the same behaviour in accordance with Debye's theory. N. M. BLIGH.

Influence of X- and γ -radiation on the conductivity of paraffins. G. GUÉZEN (Z. Physik, 1932, 74, 714; cf. Seidl, this vol., 9).—Ceresin showed a change in conductivity consistent with the assumption of formation of ions by γ -radiation; the sum of the ionic mobilities is 18×10^{-7} (cm./sec.)/(volts/cm.). A. B. D. CASSIE.

Dependence of conductivity of rock-salt on field strength. F. QUITNER (Z. Physik, 1932, 74, 344—349).—Polemical against Hochberg (A., 1931, 1112). A. B. D. CASSIE.

Specific volumes of some gaseous refrigerants. J. H. AWBERY and E. GRIFFITHS (Proc. Physical Soc., 1932, 44, 115—120, 126—131).—The sp. vols. of the vapours of SO_2 , $C_2H_2Cl_2$, Et_2O , C_5H_{12} , and C_2HCl_3 have been measured between 0° and 40° by determining the mass of liquid required to saturate a known evacuated vol. a definite no. of times.

C. W. GIBBY.

Refractivity of some compounds with several acetylenic linkings. V. KRESTINSKI and (MLLE.) N. PERSIANZEVA (J. Gen. Chem. Russ., 1931, 1, 880—889).—The refractivities, $[R_L]_a$, $[R_L]_b$, $[R_L]_c$, and $[R_L]_d$, of di(phenylacetylenyl)methylcarbinol (I), tri(phenylacetylenyl)carbinol (II), β -di(phenylacetylenyl)hexane- β -diol (III), and $\alpha\alpha$ -tetra(phenylacetylenyl)butane- α -diol (IV), all of which contain unconjugated triple linkings, have been determined in solution. The solvents used were AcOEt, cyclohexanone, amyl alcohol, MeOH, C_6H_6 , $COMe_2$, and NH_2Ph , all four substances being examined in the first two solvents. The refractivities observed were in all cases higher than those calc., the increments increasing with the no. of $CPh:C$ residues in the mol. The increment ΣR varies considerably with the solvent used (e.g., ΣR_b from 2.25 in NH_2Ph to 4.00 in $COMe_2$); nevertheless average vals. have been calc.: ΣR_a 3.07, ΣR_b 3.29, ΣR_c 3.77, ΣR_d 4.30. Moureu's vals. for $CPh:CH$ (A., 1906, ii, 1) have been recalcd. and fresh determinations have also been made; the increments are of the same order as those given above. Acetylacetone and $CPh \cdot C \cdot MgBr$ give (III) (two stereoisomeric forms, m. p. 105—106° and 92—96°; only the former was used in the refractometric work). Et succinate similarly gives (IV), m. p. 136°. G. A. R. KON.

Measurement of the optical constants of crystals in the ultra-violet. P. SÈVE (Ann. Physique, 1932, [x], 17, 137—197).—Methods of measurement of birefringence and results for gypsum, calamine, and barytes are discussed.

W. R. ANGUS.

Molecular refraction of nitrobenzene. J. N. FRIEND (Nature, 1932, 129, 471—472).—The density-temp. and the mol. refraction-temp. curves of ordinary, "pure" $PhNO_2$ show no discontinuities (cf. A., 1931, 1354). L. S. THEOBALD.

Rotation dispersion and circular dichroism of bornylene nitrosite. S. MITCHELL and S. B. CORMACK (J.C.S., 1932, 415—419).—Bornylene nitrosite, being in the bimol. form, does not give blue solutions in org. solvents at room temp., but with rise of temp. dissociation and development of colour occur. At 63° a $PhMe$ solution is blue, absorption bands with heads at 6800 and 6250 Å. being present, and the solution exhibits circular dichroism. Absorption and ellipticity were measured and the anisotropy factors calc. The influence of the bands on the rotation dispersion and ellipticity was examined. N. M. BLIGH.

Effect of solvents on the optical rotation of menthene, bornylene, and borneol. (Miss) I. M. McALPINE (J.C.S., 1932, 543—546).—The rotations of *d*-bornylene, *l*-borneol, and *d*-menthene in C_6H_6 , EtOH, C_5H_5N , $CHCl_3$, ethylene dibromide, $PhNO_2$, and quinoline, for 6 wave-lengths from λ 6716.3 to 4358.6, decreased proportionately with fall of temp. The solvents had increasing effect on the rotation of the three substances respectively; the increase was greatest in C_5H_5N for borneol and in ethylene dibromide for menthene; quinoline produced the lowest rotation in all cases. The effect of temp. on the rotation dispersion of menthene in the homogeneous state was examined. Calc. dispersion coeffs. were in good agreement. N. M. BLIGH.

Theory of rotatory dispersions. G. ARAKI (Sci. Rep. Tokyo Bunrika Daigaku, 1932, A, 1, 193—201).—Mathematical. A. J. MEE.

Rotatory dispersion of benzene solutions of α - and β -pinenes. J. RABINOVITCH (Compt. rend., 1932, 194, 855—858).—Rotatory dispersion curves for varying mixtures of α -pinene (dextrorotatory, b. p. 150—155°), and of β -pinene (laevorotatory, b. p. 163°) with C_6H_6 , show in the case of α -pinene results in strict proportion to concn.; with β -pinene the presence of a third active constituent is indicated.

C. A. SILBERRAD.

Theory of optical activity. K. SCHERINGA (Chem. Weekblad, 1932, 29, 218—219).—A discussion of the space geometry of asymmetric mols. For optical activity one atom must be present with at least four satisfied valencies, forming two or more planes crossing obliquely. S. I. LEVY.

Magnetic rotatory power of neon. R. DE MALLEMANN, L. GABIANO, and F. SCHNER (Compt. rend., 1932, 194, 861—862).—The sp. magnetic rotation of Ne for λ 5460, determined at 1606 mm. Hg in a field of 935,000 c.g.s. units, is 1.1×10^{-6} , with an error $\pm 20\%$. This gives 2.3 optical electrons for the atom, which agrees with the figure deduced from the dispersion const. (cf. A., 1909, ii, 85, 561).

C. A. SILBERRAD.

Optical properties of thin layers of nitrobenzene subjected to p.d. A. COTTON and H. MOUTON (Compt. rend., 1932, 194, 924—926).— $PhNO_2$ in a cell consisting of two cover glasses 2 cm. sq., and separated 6 mm. apart by thin strips of Sn or Pt on opposite sides, which form electrodes whereby an alternating p.d. is maintained, shows birefringence, gradually increasing to const. val. of about $10'$ for a p.d. of 1000 volts, and $42'$ — $64'$ for 2000—2500 volts.

C. A. SILBERRAD.

Test of the rival theories of active nitrogen. B. D. CHHABRA and H. R. LUTHRA (J. Indian Chem. Soc., 1932, 9, 21—24).—Photographs of the spectrum of the bluish glow which replaces the yellow glow of active N when S vapour is introduced do not show the S line 6300 Å. which is to be expected on Kaplan's theory of active N (A., 1928, 566). D. R. DUNCAN.

Thermomagnetic effects in nickel and iron. S. T'AO and W. BAND (Proc. Physical Soc., 1932, 44, 166—170).—The e.m.f. produced when a magnetic field is applied to a ferromagnetic substance parallel

to a temp. gradient has been measured at various temp. Hysteresis was observed. C. W. GIBBY.

Assumed paramagnetic anomaly of nickel sulphate heptahydrate at low temperatures, and types of deviation from the Curie-Weiss law at low temperatures. C. J. GORTER, W. J. DE HAAS, and J. VAN DEN HANDEL (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1254—1258).—Former measurements (A., 1924, ii, 90) have been repeated and extended and the results fail to show any striking anomalies. Earlier measurements at the temp. of liquid C_2H_4 and N_2 must have been inaccurate. At temp. higher than those of liquid N_2 , $NiSO_4 \cdot 7H_2O$ follows the Curie-Weiss law. The different types of anomalies at low temp. are described.

E. S. HEDGES.

Susceptibilities of cerium chloride and praseodymium sulphate at low temperatures. C. J. GORTER, W. J. DE HAAS, and J. VAN DEN HANDEL (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1249—1253).—The magnetic susceptibilities of $CeCl_3$ and $Pr_2(SO_4)_3$ have been measured between 373° and 14° abs. At higher temp. $CeCl_3$ follows the Curie-Weiss law, with $\chi(T-21.0) = 31.81 \times 10^{-4}$. At lower temp. the $1/\chi'$ — T line is curved towards the T axis. $Pr_2(SO_4)_3$ follows the Curie-Weiss law with $\chi(T-45.0) = 57.43 \times 10^{-14}$. It appears that an even no. of electrons is not the only condition required for an independent relation between susceptibility and temp. The magneton nos. obtained are in good agreement with the predictions of Hund.

E. S. HEDGES.

Even and odd numbers of electrons; susceptibilities of praseodymium and neodymium sulphate octahydrates at low temperatures. C. J. GORTER and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1243—1248).—The magnetic susceptibilities of $Pr_2(SO_4)_3 \cdot 8H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$ have been measured between room temp. and 14° abs. At the lowest temp. the susceptibility of the Pr salt is nearly independent of the temp., whilst that of the Nd salt varied more strongly. It is suggested that the lowest energy level of Pr^{III} is not degenerated, in agreement with the theory that non-degenerated terms can occur only when the no. of electrons is even.

E. S. HEDGES.

Paramagnetic rotatory power of cerium magnesium nitrate and two minerals containing manganese (spessartite and dialogite) at very low temperatures. J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1231—1242).—The paramagnetic rotatory power of $3Mg(NO_3)_2 \cdot 2Ce(NO_3)_3 \cdot 24H_2O$ at 1.5° abs. is very low. The corresponding vals. for spessartite and dialogite indicate magnetic moments of the order of 1 magneton. A moment of 5 magnetons is attributed to Mn^{II} , but the rotatory power observed for spessartite and dialogite at 1.47° abs. is determined by a magnetic moment > 2 magnetons.

E. S. HEDGES.

Magnetic permeability of thin iron wires and of iron compounds in weak high-frequency fields. K. VOLKOVA (Z. Physik, 1932, 74, 388—395).—Measurements of the axial permeability of hard Fe wires and of powdered Fe compounds show a linear

variation of the real and imaginary components of permeability between 90 and 111 m.

A. B. D. CASSIE.

Calculation of the magnetic permeability of wires and the origin of apparent bands in the magnetic spectrum. V. ARKADIEV (Z. Physik, 1932, 74, 396—417).—Theoretical.

A. B. D. CASSIE.

Permeability of ferromagnetic substances at high frequencies. N. N. MALOV (Z. Physik, 1932, 74, 431—432).—Polemical, against Strutt (cf. A., 1931, 790).

A. B. D. CASSIE.

Ferromagnetism and electrical properties. IV. W. GERLACH (Ann. Physik, 1932, [v], 12, 849—864).—The behaviour of Ni is studied. Above the Curie point Ni has a magnetic resistance decrease proportional to the square of the magnetisation. The resistance increase in the ferromagnetic range is connected with rotation processes of magnetisation.

A. J. MEE.

Magnetic saturation. E. CZERLINSKY (Ann. Physik, 1932, [v], 13, 80—100).

Composition of complex metal-cyanide radicals. Complex nickel-cyanide radical. K. MASAKI (Z. physikal. Chem., 1932, 159, 223—226).—Electrometric titration indicates that the ion probably has the composition $\text{Ni}(\text{CN})_4^{1-}$ at all concns., the stability const. being about 1×10^{12} .

R. CUTHILL.

Anomalous diamagnetism of bismuth. S. R. RAO (Nature, 1932, 129, 545—546).—Further experiments with Bi indicate that the fall in magnetic susceptibility with a decrease in particle size is a genuine effect (cf. A., 1931, 1000, 1357).

L. S. THEOBALD.

Oxygen compounds containing fluorine. I. True fluoroxy-compounds. H. SEIFERT (Z. Krist., 1932, 81, 396—468).—In view of the fact that the space requirements of the O and F atoms are approx. equal, the true O-F compounds, i.e., those in which the O and F atoms can be regarded as similarly related to the central atom, have been classified according to the co-ordination no. of that atom, and the periodic system, bringing out numerous chemical and crystallographic relationships. As the form of the resulting tables brings related compounds, e.g., HClO_4 , HSO_3F , HPO_2F_2 , (HSiOF_3) , unknown, and HBF_4 , into a diagonal line, the law is called that of diagonal relationship.

C. A. SILBERRAD.

Early development of stereochemistry and Pasteur's law. B. K. SINGH (J. Indian Chem. Soc., 1932, 9, 1—19).—Presidential address.

Thermal law of homopolar linkings: laws of Curie points and m. p. R. FORRER (Compt. rend., 1932, 194, 868—869; cf. this vol., 325).—The law of efficacious contacts or "homopolar linkings" is extended to explain fusion, allotropic transformations, anomalies, and probably combination, decomposition, and other reactions.

C. A. SILBERRAD.

The triple collision process. W. STEINER (Z. physikal. Chem., 1932, B, 15, 249—273).—A general equation for the frequency of effective triple collisions is derived by resolving the triple collision into two

processes, viz., the formation of an atom pair under the influence of homopolar valency forces, and the stabilisation of the atom pair by transference of energy to the third participant in the collision. This procedure is, however, justifiable only if the latter is an inert gas atom or a saturated mol. If this condition is not fulfilled, as when the participants in the collision are all H atoms, a satisfactory treatment of the collision process would require a full solution of the three-body problem. In calculating the mean life of the atom pair it is necessary to take account of the fact that when under the influence of the forces of homopolar valency the atoms move at a speed much greater than the mean thermal relative velocity. The effective diameter in the energy transfer from a H atom pair to a H_2 mol. is calc. from the velocity coeff. (cf. A., 1931, 1239) to be $6.7\text{--}12.4 \times 10^{-8}$ cm. This figure points to resonance in the transformation of the energy of the atom pair into vibrational and rotational energy of the mol. For the collision of two Br atoms with a H_2 mol. the diameter of energy transfer is 10.3×10^{-8} cm., and here too there is probably a resonance effect.

R. CUTHILL.

Hypothesis of a molecular field. P. WEISS (Ann. Physique, 1932, [x], 17, 97—136).—Different aspects of the question are discussed.

W. R. ANGUS.

[Energy relations of inorganic halides.] E. BERGMANN and L. ENGEL (Z. physikal. Chem., 1932, B, 16, 180—182).—A reply to Huckel (this vol., 217).

R. CUTHILL.

Physical properties of carbonyl sulphide. T. G. PEARSON, P. L. ROBINSON, and J. TROTTER (J.C.S., 1932, 660—661).—The surface tension and density were measured; $d^{20} = 1.073$, and the temp. coeff. of surface tension is 0.1626 dyne per cm. per degree. The calc. val. of the Eotvos-Ramsay-Shields const. is 2.02, indicating that the liquid is not associated, and the parachor 111.1 units. N. M. BLIGH.

Chemical linking. F. HUND (Z. Physik, 1932, 74, 429—430).—A correction of the calculation showing that the triangular mol. has a lower energy val. than the linear model (cf. this vol., 10).

A. B. D. CASSIE.

Parachor and chemical constitution. XVII. Fluorine compounds. E. C. ALLEN and S. SUGDEN (J.C.S., 1932, 760—763).—Measurements of surface tension and density of PhF , $p\text{-C}_6\text{H}_4\text{FCl}$, $p\text{-C}_6\text{H}_4\text{FBr}$, $p\text{-Me-C}_6\text{H}_4\text{F}$, $1\text{-C}_{10}\text{H}_7\text{F}$, and pp' -difluorodiphenyl give a mean at. parachor for F of 25.0. Methoxyboron difluoride shows a large negative anomaly attributed to association into double mols. held together by singlet linkings between F atoms. N. M. BLIGH.

Surface tension and density of nitric oxide. G. H. CHEESMAN (J.C.S., 1932, 889—890).—Measurements were made between -147° and -162.5° ; the parachor deduced therefrom is approx. 52 and rises with the temp.; the val. calc. from the sum of the at. consts. is 32.5. The data do not indicate non-association of the liquid. N. M. BLIGH.

Universal X-ray apparatus for crystal structure investigations. H. BRAEKKEN (Z. Krist., 1932, 81, 309—313).

New method of complete fine structure X-ray investigations of technical materials. F. REGLER (Z. Physik, 1932, 74, 547—564).—A method which obtains photographs on two conical films is described; this gives Laue, "fibre," and grating const. diagrams, and indicates strains in the material.

A. B. D. CASSIE.

Regler's standard method for the accurate determination of lattice dimensions and that of the authors. N. H. KOLKMEIJER and A. L. T. MOESVELD (Physikal. Z., 1932, 33, 265—269).—A comparison of the two methods leads to satisfactory agreement.

A. J. MEE.

Cause of twinning of crystals. W. G. BURGERS (Nature, 1932, 129, 363—364).—A reply to criticism (A., 1928, 817) and a discussion.

L. S. THEOBALD.

Crystallisation velocities. M. E. KRAHL (J. Amer. Chem. Soc., 1932, 54, 1256).—Max. linear velocities of crystallisation are reported for various aromatic compounds. The symmetry of the mol. largely determines the rate of crystallisation.

C. J. WEST (c).

Persistence and development of crystal nuclei above melting temperature. W. T. RICHARDS (J. Amer. Chem. Soc., 1932, 54, 479—495).—Investigations with salol and COPh_2 indicate that the most probable explanation of the effect on the rate of crystallisation of the extent and manner of preheating above the m. p. is that preheating reduces the catalytic activity of the impurities present. Pure salol and COPh_2 have very little tendency to spontaneous crystallisation, and of various activating adsorbents studied charcoal and powdered quartz were the most effective. The crystallisation of piperonal, *p*-toluidine, NaOAc , and $\text{Na}_2\text{S}_2\text{O}_3$ has also been studied. The relation of the above theory to "the law of transformation in stages" is discussed.

R. H. LAMBERT (c).

Vicinal faces on scolecite. G. KALB (Z. Krist., 1932, 81, 243—247).

C. A. SILBERRAD.

Significance of vicinal appearances for crystal measurements. G. KALB (Z. Krist., 1932, 81, 342—351).—Irregular variations in the axial ratios of barytes are due to vicinal faces. Corrected for these $a:b:c=0.8146:1:1.3130$ in good agreement with X-ray results (cf. A., 1925, ii, 18); similarly for scolecite $a:b:c=0.9778:1:0.3437$, $\beta=90^\circ 42' 15''$.

C. A. SILBERRAD.

Vicinal faces and edges. G. KALB (Z. Krist., 1932, 81, 333—341).—Rules regarding these are illustrated by reference to such appearances on natrolite.

C. A. SILBERRAD.

X-Ray examination of crystalline fluids. IV. K. HERRMANN and A. H. KRUMMACHER (Z. Krist., 1932, 81, 317—332).—X-Ray examination of the mesomorphic substances Et azoxybenzoate (I), allvl phenetoleazoxybenzoate (II), Me *p*-ethoxybenzylideneaminocinnamate (III), Et *p*-phenylbenzylideneaminocinnamate (IV), and Et *p*-xylylidenebisaminocinnamate (V), show that (I), (II), and (III) support Friedel's view (cf. A., 1931, 898) that there are only two—nematic and smectic—mesophases, but (IV) and (V), although decomposed, prevented complete

examination, give distinct evidence of at least one additional phase, as reported by Vorländer (*ibid.*). Structures explaining these phases are discussed.

C. A. SILBERRAD.

Dispersion of X-rays in CuSO_4 crystals. J. L. NAGY (Math. Nat. Anz. Ungar. Akad. Wiss., 1930, 47, 70—77; Chem. Zentr., 1931, ii, 3303—3304).

Chemical nature of oxide layers formed by anodic polarisation on aluminium, zirconium, titanium, and tantalum. W. G. BURGERS, A. CLAASSEN, and J. ZERNIKE (Z. Physik, 1932, 74, 593—603).—Chemical and X-ray studies of these oxide layers showed that the film deposited on Al in borax-boric acid solutions was a form of cubic $\gamma\text{-Al}_2\text{O}_3$, on Zr monoclinic ZrO_2 , on Ti tetragonal TiO_2 , and on Ta Ta_2O_5 .

A. B. D. CASSIE.

Crystal structure of β -zirconium. W. G. BURGERS (Z. anorg. Chem., 1932, 205, 81—86).—A detailed account of work already noted (this vol., 325).

Structure of the regular sodium tungsten bronzes. W. F. DE JONG (Z. Krist., 1932, 81, 314—315).—The structure of these bronzes closely resembles that of KIO_3 , with a 3.83 Å. Analysis shows results between $\text{Na}_2(\text{WO}_3)_2$ and $\text{Na}_2(\text{WO}_3)_7$, with part of the Na replaced by H in the red and violet varieties (cf. A., 1927, 327).

C. A. SILBERRAD.

Influence of RO_4 and related ions on the habit of potassium sulphate. H. E. BUCKLEY (Z. Krist., 1932, 81, 157—168; cf. A., 1931, 1358).

C. A. SILBERRAD.

Preparation and crystal structure of normal (meta) silver periodate. L. BIRCKENBACH and F. BUSCHENDORF (Z. physikal. Chem., 1932, B, 16, 102—112).— AgIO_4 , obtained as a yellow solid, d 5.57, by interaction at $40\text{--}50^\circ$ of KIO_4 and Ag_2SO_4 in solution in conc. H_2SO_4 , or reaction of AgClO_4 with KIO_4 in conc. HNO_3 at room temp., has the lattice dimensions a_0 5.368 \pm 0.02 and c_0 12.013 \pm 0.03 Å., the space-group being C_{3h} . The unit cell contains 4 mols.

R. CUTHILL.

Crystal structure of lead chlorofluoride. W. NIEUWENKAMP and J. M. BIJVOET (Z. Krist., 1932, 81, 469—474).— PbFCl has a 4.09, c 7.21 Å., with 2 mols. per unit cell; d 7.05. The crystals consist of alternate layers of Cl and F separated by layers of Pb.

C. A. SILBERRAD.

Symmetry of gismondite with reference to its vicinal faces. G. KALB (Z. Krist., 1932, 81, 248—252).

C. A. SILBERRAD.

Crystal structure of romeite and schneebergite. O. ZEDLITZ (Z. Krist., 1932, 81, 253—263; cf. A., 1916, ii, 630).—Romeite, from St. Marcel (Piedmont), has a 10.26 Å.; schneebergite, from Schneeberg (Tirol), a 10.296 Å., both with 8 mols. in the unit cell, and of space group O_h^2 . They are isomorphous *inter se* and with pyrochlore (cf. A., 1930, 1352; 1931, 289). The ideal formula of both is $\text{CaNaSb}_2\text{O}_6(\text{OH})$, but part of the Ca is usually replaced by Fe and/or Mn, and, in romeite, part of the OH by F. Atopite is identical with romeite.

C. A. SILBERRAD.

X-Ray and crystallographic study of kernite. J. GARRIDO (Anal. Fis. Quím., 1932, 30, 91—98).—Kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, has a 15.65 ± 0.02 , b 9.07 ± 0.02 , c 7.01 ± 0.02 Å.; 4 mols. in the unit cell; space-group probably $P_{2/a}$. The crystals are binary holohedral (lit. orthorhombic). H. F. GILLBE.

Silicate structures of cristobalite type. II. $\text{Na}_2\text{CaSiO}_4$. III. Relationships of high-cristobalite, α -carnegieite, and $\text{Na}_2\text{CaSiO}_4$. T. F. W. BARTH and E. POSNJAK (Z. Krist., 1932, 81, 370—375, 376—385; cf. this vol., 218).—II. $\text{Na}_2\text{CaSiO}_4$ is cubic with a 7.48 Å., space-group $P2_14$.

III. The close similarity of the high-temp. (cubic) forms of cristobalite and α -carnegieite (cf. *loc. cit.*) with $\text{Na}_2\text{CaSiO}_4$ with a 7.17 , 7.37 , and 7.48 Å., respectively, is discussed. The three substances form mixed crystals. C. A. SILBERRAD.

Crystallinity of opals and existence of high-temperature cristobalite at room temperature. I. LEVIN and E. OTT (J. Amer. Chem. Soc., 1932, 54, 828—829).—Since various types of opals yield X-ray diagrams identical with that of high-temp. cristobalite the existence of this compound at room temp. for an indefinite period of time is proved.

C. J. WEST (c).

Orientation of crystals of the epsomite series on mica. L. ROYER (Compt. rend., 1932, 194, 1088—1090).—The orientation of crystals of epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, goslarite, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and morenosite, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, on mica is in accordance with the spacings between the crystal planes in contact.

C. A. SILBERRAD.

Crystalline structure of benzene. E. G. COX (Proc. Roy. Soc., 1932, A, 135, 491—498).—X-Ray reflexion spectra for cryst. C_6H_6 give evidence for a flat-ringed structure, the average distance from centre to centre of C atoms in neighbouring mols. being about 3.8 Å. The balance of evidence is in favour of a flat, rather than a puckered, ring. L. L. BIRCUMSHAW.

Crystal structure of hexabromobutylenes. W. EISSNER and R. BRILL (Z. Krist., 1932, 81, 316; cf. A., 1931, 1219).—The symmetrical isomeride of m. p. 185° must be the *s-trans*-form, and consequently that of m. p. 114° may be either the corresponding *cis*-form, or, as previously stated, the *as*-isomeride.

C. A. SILBERRAD.

Rotation of chain molecules in solid paraffins. A. MÜLLER (Nature, 1932, 129, 436).—X-Ray measurements show that the a and b axes of $\text{C}_{21}\text{H}_{44}$ gradually change ($a > b$) from room temp. to the m. p.; from $\text{C}_{24}\text{H}_{50}$ to $\text{C}_{34}\text{H}_{70}$ there is a sudden transition 5 — 10° below the m. p. The change in lattice dimensions and the increased symmetry which result are discussed. L. S. THEOBALD.

Dimorphism of certain aliphatic compounds. II. J. W. C. PHILLIPS and S. A. MUMFORD (J.C.S., 1932, 898—906; cf. A., 1931, 1003).—Previous data are amplified, and discussed in conjunction with that of Malkin (this vol., 326) for higher aliphatic esters. In the Et ester, and probably in the acetate series, a well-defined alternation of polymorphic type is shown, the odd members exhibiting enantiotropic, and the even members monotropic, dimorphism. The alternation

resembles that of the fatty acid series. Solidification and fusion curves for the Et esters of decoic, lauric, and myristic acids are given. N. M. BRIGHT.

X-Ray analysis of crystals of 1:4-di-iodo-cyclohexane (m. p. 142°) and 1:4-dibromo-cyclohexane (m. p. 111°). E. HALMOY and O. HASSEL (Z. physikal. Chem., 1932, B, 16, 234—248).—1:4- $\text{C}_6\text{H}_{10}\text{Br}_2$ has a 11.92 , b 5.56 , and c 6.02 , and 1:4- $\text{C}_6\text{H}_{10}\text{I}_2$ has a 12.50 , b 5.72 , and c 6.20 Å. Each has the space-group C_{2h}^2 and 2 mols. in the unit cell. The data for $\text{C}_6\text{H}_{10}\text{I}_2$ show that the C atoms do not lie in a flat ring. R. CUTHILL.

Structure of simple glycine polypeptides. F. V. LENEL (Z. Krist., 1932, 81, 224—229).— α -Diglycylglycine, d 1.569 , has a 8.53 , b 4.3 , c 11.4 Å., β $105^\circ 30'$, 2 mols. in unit cell; β -diglycylglycine, d 1.57 , a 14.6 , b 4.79 , c 11.67 Å., β $105^\circ 30'$, 4 mols.; d -alanyl-glycine, d 1.435 , a 5.29 , b 11.67 , c 5.47 Å., β $101^\circ 30'$, 2 mols. From these and other results (cf. A., 1931, 790, 1002) three types of such compounds are recognised, exemplified by α -glycine, β -glycine, and β -glycylglycine. The mols. form long chains arranged in layers, the distance between which is less as the chains are longer. The numerous modifications are perhaps due to different orientations of the NH_2 -acid residues in the mol. C. A. SILBERRAD.

[Crystal structure of] *d-ψ*-cocaine *l*-ephedrine *d*-tartrate (*a*) and *d-ψ*-cocaine *l*-methylephedrine *d*-tartrate (*b*). K. BRUCKL (Z. Krist., 1932, 81, 219—223).—Both salts are domal monoclinic; in (*a*) $a:b:c=1.8939:1:0.9512$, β $107^\circ 21'$; the unit cell has a 18.90 , b 9.92 , c 9.36 Å., and contains 2 mols., space-group C_2^1 or C_2^2 ; d 1.311 . In (*b*) $a:b:c=2.0145:1:0.9446$, β $98^\circ 42'$; the unit cell has a 19.62 , b 9.76 , c 9.61 Å., and contains 2 mols.; d 1.291 . Both show strong dispersion. C. A. SILBERRAD.

[Crystal form of] some tartrates. S. MIALL (Chem. and Ind., 1932, 317—318).

Crystal structure of thiocarbamide. R. W. G. WYCKOFF and R. B. COREY (Z. Krist., 1932, 81, 386—395).—Previous results (cf. A., 1928, 819, 1175) are confirmed. The atoms in the mol. lie in one plane, with interat. distances (C—N 1.35 Å., N—N 2.24 Å.) almost the same as in carbamide (1.33 and 2.18); C—S is 1.64 Å. C. A. SILBERRAD.

Molecular structure of textile fibres. W. T. ASTBURY and H. J. WOODS (J. Text. Inst., 1932, 23, 17—34T).—Recent work on the structure of textile fibres, rubber, chitin, asbestos, etc. is discussed and a general theory of fibre structure based chiefly on X-ray data is put forward. Fibres may consist of fully extended chain mols., e.g., cellulose, natural silk, stretched wool, hair, and rubber, or of folded mols., e.g., unstretched hair and rubber. The extended chain mols. are almost non-elastic, and fibres built from them extend by internal slipping, but folded mols. may unfold and pass into the extended state, thus giving a long-range elasticity to fibres composed of them. In stretching the “fixed” fibres the intercryst. linkings give way before the intracryst. linkings, whilst with “folded” fibres the converse holds. The fibrous material from feathers represents an intermediate stage between the “fixed” and “folded”

fibres. Typical stress-strain diagrams of various fibres, and the supercontraction of fixed fibres, *e.g.*, natural silk, are also discussed. B. P. RIDGE.

Verification of the law of discontinuous distribution of Curie points. R. FORRER (Compt. rend., 1932, 194, 779—781; cf. this vol., 325).—The validity of the relation $\Theta = T_1 \sqrt{N}$ is examined by comparing the val. of N thence deduced with the properties of the lattice as determined by X-ray examination. Agreement is satisfactory for FeS (pyrrhotine) and MnSb ($N=4$). The change from ferro- to para-magnetism is due to rupture of the effective contacts, or external electronic orbits and may be spread over a considerable temp. interval. The relation differs from Heisenberg's results by making $N \propto \Theta^2$ instead of Θ . C. A. SILBERRAD.

Change in resistance and magnetisation at the Curie point. E. ENGLERT (Z. Physik, 1932, 74, 748—756).—Measurements are described of the change in resistance and magnetisation of Ni at the Curie point. A. B. D. CASSIE.

Variation of the Hall effect with intensity of magnetic field. C. BELLIA (Z. Physik, 1932, 74, 655—662).—Theoretical. A. B. D. CASSIE.

Hall effect in solid mercury. J. T. SERDUKE and T. F. FISHER (Physical Rev., 1932, [ii], 39, 831—834).—Investigations were made on strips of various thickness. The Hall effect was independent of field strength, *c.d.*, and thickness. The average val. of the Hall const. was -0.000784 . N. M. BLIGH.

Cohesion. III. The (110) cleavage of rock-salt. H. TERTSCH (Z. Krist., 1932, 81, 264—274; cf. A., 1931, 422, 1360).

The cleavage process in crystals. H. TERTSCH (Z. Krist., 1932, 81, 275—284).

Strength of wetted salt crystals. III. Dependence on orientation of the tensile strength of dry and wet rock-salt crystals. G. F. SPERLING (Z. Physik, 1932, 74, 476—502).—An investigation of the plasticity and tensile strength of dry and wetted rock-salt crystals indicates that only a quant. difference exists between the two, and this difference is similar to that of two dry crystals at different temp. A. B. D. CASSIE.

Surface tension of gold foils. G. TAMMANN and W. BOERME (Ann. Physik, 1932, [v], 12, 820—826).—The surface tension is found by observations of the wrinkling of foils on heating. A. J. MEE.

Stability of certain heteropolar crystals. H. M. EVJEN (Physical Rev., 1932, [ii], 39, 675—687).—An irregular cryst. behaviour is deduced in the region of small vals. of the exponent of the repulsive energy between the ions, and is illustrated and discussed for the calcite family of crystals. N. M. BLIGH.

Development of strain by stretching. A. CAGLIOTTI and G. SACHS (Z. Physik, 1932, 74, 647—654).—A systematic investigation of the development of strain in Cu crystals by means of broadening of X-ray interference lines of higher orders. A. B. D. CASSIE.

Electronic structure and properties of metals. U. DEHLINGER (Z. Elektrochem., 1932, 38, 148—

154).—A discussion of the relation between valency electrons and the properties of metals and their alloys. M. S. BURR

Behaviour of single crystals of bismuth subjected to alternating torsional stresses. H. J. GOUGH and H. L. COX (Inst. Metals, Mar. 1932, 21 pp.).—The slip phenomena associated with fatigue have been examined by subjecting single crystals of Bi to alternating torsional couples. No slip bands were observed, but in the early stages of the test numerous bands parallel to the cleavage planes were produced, and finally cleavage cracking occurred, the nature of the cracks indicating that these bands were twin bands. Signs of recrystallisation were observed especially in the vicinity of the bands. The energy relations during twinning are discussed and it is shown that the process of twinning may be due to the presence of stresses which at first sight appear to be too small to affect the process. A. R. POWELL.

Behaviour of a single crystal of aluminium under alternating torsional stresses while immersed in a slow stream of tap water. H. J. GOUGH and D. G. SORWITH (Proc. Roy. Soc., 1932, A, 135, 392—411).—Failure under corrosion fatigue is due to a corrosive action superimposed on the stress effects applied in ordinary fatigue tests. The two effects are mutually accelerative and failure is most marked in the plastically deformed areas. L. L. BIRCUMSHAW.

Polish on metals. F. KIRCHNER (Nature, 1932, 129, 545).—Results similar to those of French (this vol., 219) have been obtained [by H. RAETHER]. The sharpness of the diffraction rings gives information of the degree of levelling of the surface and not of the real size of the crystals. L. S. THEOBALD.

Polish on metals. C. A. MURISON, N. STUART, and G. P. THOMSON (Nature, 1932, 129, 545).—Pt surfaces sputtered on glass show various electron diffraction patterns which include that of ordinary Pt. When the Pt is sputtered in O_2 at 0.014 mm. pressure and a voltage >1150 , the surface is catalytically active towards mixtures of H_2 and O_2 and shows, at first, diffuse rings similar to those described by French (this vol., 219). When the catalytic activity of the surface is finished, the diffuse change to the sharp rings characteristic of normal Pt. Heating in a vac. produces the same change, which is also accompanied by an improvement in the specular reflexion, suggesting that the surface becomes smoother. It is probable that the diffuse rings are due, not to extreme flatness of the surface (cf. preceding abstract), but to a finely-divided substance with possible inclusions of gas mols. L. S. THEOBALD.

Allotropy of liquid benzene. A. W. C. MENZIES and D. A. LACOSS (Proc. Nat. Acad. Sci., 1932, 18, 144—147).—Various physical properties of C_6H_6 (*e.g.*, sp. vol., refractive index, effect of pressure on m. p., dielectric const., sp. heat, viscosity, *v. p.*) show a more or less abrupt alteration in the neighbourhood of 40° . A. J. MEE.

Physical properties of plastic sulphur. J. J. TRILLAT and H. FORESTIER (Bull. Soc. chim., 1932, [iv], 51, 248—253).—Work previously noted (A., 1931, 548) is described in detail.

[Probable values of the general physical constants.] T. BATUECAS (J. Chim. phys., 1932, 29, 26—29).—A criticism of a publication by Birge (Phys. Rev. Supp., 1929, 1, 1—73). E. S. HEDGES.

Wave mechanics and superconductivity. R. SCHACHENMEIER (Z. Physik, 1932, 74, 503—546).

A. B. D. CASSIE.

Measurements with liquid helium. XIII. Contact resistance between superconductors and non-superconductors. R. HOLM and W. MEISSNER (Z. Physik, 1932, 74, 715—735).—Superconducting metals give superconducting contacts when the metal surfaces are freed from impurities by heating to incandescence in vac. A. B. D. CASSIE.

Thermo-electric forces of lead and tin down to the temperature of liquid helium. G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON, and J. O. LINDE (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1365—1371).—The thermo-electric forces of Pb and Sn against Ag alloy have been measured down to 1.7° and 48° abs., respectively. The thermo-electric force per degree for a couple superconducting Pb—Ag alloy is small and that for superconducting Pb—superconducting Sn is zero. de/dT and hence the Thomson effect change rapidly at the superconducting temp.; it is concluded that the Thomson effect at the crit. temp. falls rapidly from finite vals. to zero.

J. W. SMITH.

Relation of the platinum to the absolute scale of temperature between 0° and 100°. J. M. GAINES (Abs. Theses Mass. Inst. Tech., 1932, 54—56).—The comparison of the scales was made by standardising three Pt resistance thermometers against a const.-vol. gas thermometer filled with He.

A. J. MEE.

M. p. of zirconium dioxide and of hafnium dioxide. P. CLAUSING (Z. anorg. Chem., 1932, 204, 33—39).—Working with very pure materials, the m. p. of ZrO_2 has been found to be $2950 \pm 20^\circ$, and that of HfO_2 $3047 \pm 25^\circ$ abs.

F. L. USHER.

Determination of the b.-p. and the v.-p. curves of normal hydrogen and para-hydrogen. Normal b. p. of normal hydrogen as a basic point in thermometry. W. H. KEESOM, A. BIJL, and (Miss) H. VAN DER HORST (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1223—1230).—The following data have been determined by means of the He thermometer: normal b. p. of normal H_2 -252.754° , normal b. p. of para- H_2 -252.871° . The normal b. p. of normal H_2 (the mixture of ortho- H_2 and para- H_2 which is in equilibrium at room temp.) may be used as a basic point in thermometry with an accuracy of 0.005° , provided that certain precautions are taken. The v. p. of normal H_2 and of para- H_2 have been determined up to 1 atm.

E. S. HEDGES.

Surface energy of molecules and their physico-chemical properties. I. Surface energy and b. p. of homologous organic compounds. S. G. MOKRUSHIN (J. Gen. Chem. Russ., 1931, 1, 856—863).—Plummer's (A., 1916, ii, 550) and Walker's (J.C.S., 1894, 65, 193) empirical equations for the b. p. of members of homologous series are derived on the basis of the author's theory of mol. surface energy

(A., 1924, ii, 820), in the forms $T = kN + m$, and $T = \alpha(M/d)^{2/3} + b$, where T is the b. p., k , m , α , and b are consts. for a given liquid, d is its density at the b. p., M its mol. wt., and N the no. of C atoms. The b. p. for several homologous series calc. from the former equation are in fair, and from the latter equation are in good, agreement with the experimental vals.

R. TRUSZKOWSKI.

Latent heat of some refrigerants. E. GRIFFITHS and J. H. AWBERRY (Proc. Physical Soc., 1932, 44, 121—126).—The latent heat of vaporisation of EtCl is 92.3 g.-cal. per g. at 14.5° and 90.5 at 23.0° , of MeCl 93.3 at 10.8° , of C_5H_{12} 92.2—0.238t between -20° and 30° , $C_3H_7Cl_2$ about 78—80 between 11.2° and 30° , SO_2 95.5—0.34t from -14° to 25° .

C. W. GIBBY.

Complexity of arsenic trioxide. II. A. SMITS and E. BELJAARS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1318—1326; cf. this vol., 326).—The following data have been determined: mol. heat of sublimation (g.-cal.), α - As_2O_3 23,676, β - As_2O_3 29,833, γ - As_2O_3 21,130; mol. heat of vaporisation (g.-cal.), α - As_2O_3 14,734; mol. heat of melting (g.-cal.), α - As_2O_3 8942, β - As_2O_3 15,099, γ - As_2O_3 6396. Equilibrium diagrams are given and explained in terms of Smits' theory of allotropy.

E. S. HEDGES.

Complexity of aluminium chloride. I. A. SMITS, J. L. MEYERING, and M. A. KAMERMANS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1327—1339).—The v. p.-temp. curve of $AlCl_3$ has been constructed and the following data have been determined: mol. heat of sublimation 28,000 g.-cal., mol. heat of vaporisation of liquid 9600 g.-cal., mol. heat of melting 19,200 g.-cal. V.-p. determinations after partial distillation show that cryst. $AlCl_3$ behaves as a mixed-crystal phase. At higher temp. a transformation in the direction of inner equilibrium is observed and above the triple point a rapid establishment of inner equilibrium takes place.

E. S. HEDGES.

Energy content of lead in the vicinity of the change point of superconductivity. K. MENDELSSOHN and F. SIMON (Z. physikal. Chem., 1932, B, 16, 72—76).—Heating curves of Pb between 2° and 10° abs., determined by a new apparatus utilising the Linde principle, were continuous, indicating that there can be no anomalous change in energy content at the change point of superconductivity exceeding 0.01 g.-cal. per mol.

R. CUTHILL.

Specific heats of saturated vapours at b. p., and theory of formation of mist and rain. III. N. DE KOLOSOVSKI and W. UDOVENKO (Z. physikal. Chem., 1932, 159, 161—171).—The relation previously discovered between the sign of the sp. heat of a saturated vapour at the b. p. and the no. of atoms in the mol. (A., 1931, 1362) has been verified by observations on the rapid adiabatic expansion of saturated vapours, mist and rain being formed from those with a negative sp. heat, but not from those having a positive sp. heat.

R. CUTHILL.

Specific heats of certain ammonium salts. J. L. CRENSHAW and I. RITTER (Z. physikal. Chem., 1932, B, 16, 143—152).—The sp. heats of NH_4NO_3 , $(NH_4)_2SO_4$, NH_4CN , $(NH_4)_2C_2O_4$, and a mixed crystal of NH_4Cl and NH_4Br have been measured between

—90° and 10° and the sp. heats of NH_4OBz and NH_4I between —180° and 10°. NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ exhibit anomalies similar to those observed with the NH_4 halides, the change points being —60.4° and —50°, respectively. The change point of the mixed crystal was higher than that of either of the components. The other compounds behave normally.

R. CUTHILL.

Heat of expansion of gases against a variable pressure. J. R. COE (Abs. Theses Mass. Inst. Tech., 1932, 53—54).—An equation is derived for the heat of expansion of gases against a variable pressure, and it is tested with CO_2 and NH_3 with good agreement.

A. J. MEE.

Physical properties of the hydrides of selenium and tellurium. P. L. ROBINSON and W. E. SCOTT (J.C.S., 1932, 972—979).—Data for the surface tensions and densities are recorded. For H_2Te the m. p. is $-51.2^\circ \pm 1^\circ$; the b. p. is -4° or -5° . The calc. parachors are: H_2Te , 115.7 at -28° , 115.2 at -4.6° ; H_2Se , 94.5 at -27° , 94.8 at 0° , giving the vals. 81.5 and 81.0 for Te, and 60.3 and 60.6 for Se, at the respective temp., in good agreement for those of the elements in compounds containing C. The curves of the b. p. and of the surface tensions at the b. p. are of the same form as for groups of compounds of related elements.

N. M. BLIGH.

Vapour pressure of $\beta\beta'$ -dichlorodiethyl sulphide. S. A. MUMFORD, J. W. C. PHILLIPS, and W. C. BALL (J.C.S., 1932, 589—592).—Vals. of the v. p. are given by the equation $\log_{10} p = 8.3937 - 2734.5/T$. Physical consts. were determined as $D_4^t = 1.2960 - 0.001068t$; $n_D^t = 1.5292 - 0.00044(t - 15)$; $\gamma_t = 43.3 - 0.12(t - 15)$ dynes per cm.; $\eta_t = 0.001117/(1/D_t - 0.7589)$ dynes per sq. cm.

N. M. BLIGH.

Vapour tensions, critical point, and triple point of carbon monoxide. C. A. CROMMELIN, W. J. BIJLEVELD, and E. G. BROWN (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1314—1317).—The following data have been obtained for pure CO: (a) v. p. liquid—gas from -141° to -205° ; this can be represented approx. by $\log p_{\text{atm}} = -544.66/T - 10.217 \log T + 24.45338 + 0.02178T$; (b) v. p. solid—gas from -205° to -216° ; (c) b. p. 81.61° abs.; (d) crit. point 132.88° abs.; (e) triple point 68.10° abs.

E. S. HEDGES.

Physical properties of lithium vapour. A. BOGROS (Ann. Physique, 1932, [x], 17, 199—282).—A method of determining very low v. p. by measuring the delivery of an at. jet is applied to Li between 459° and 572° ; the calc. heat of vaporisation is 28 kg.-cal. per g.-atom. The method is extended to the study of optical resonance; the structure of the line 6708 shows two principal components, and a satellite 13 times weaker attributed to the isotope Li^6 .

N. M. BLIGH.

Optical method for the determination of vapour densities. H. A. STUART and M. WEISS (Physikal. Z., 1932, 33, 302—304).—Assuming the mol. refraction of a gas to be independent of the pressure, measurements of the refractive index enable the density of the gas at any pressure to be calc. from the formula $R = (n^2 - 1)M/[(n^2 + 2)\rho]$.

J. W. SMITH.

Equation of state of water vapour. F. NAUMANN (Z. physikal. Chem., 1932, 159, 135—144).—Equations of state of the forms $v = f(p, T)$ and $f(v, T)$, respectively, valid over a wide range of temp. and pressure, have been deduced from empirical equations for sp. heat.

R. CUTHILL.

Entropy, reversible processes, and thermocouples. E. H. KENNARD (Proc. Nat. Acad. Sci., 1932, 18, 237—241).—It is only an isolable reversible process which never changes the entropy of the universe. Reversible thermo-electric cycles and transpiration circuits both lead to an entropy change in the surroundings.

J. W. SMITH.

Entropy, reversible processes, and thermocouples. P. W. BRIDGMAN (Proc. Nat. Acad. Sci., 1932, 18, 242—245; cf. preceding abstract).—Polemical.

J. W. SMITH.

Nernst heat theorem. Calculation of entropy constants. II. J. M. BIJVOET and H. J. VERWEEL (Chem. Weekblad, 1932, 29, 210—218; cf. A., 1931, 307).—Application of the theory to the transition points of Sn and S shows poor agreement with the known vals.; in the case of S, the val. 96.4° , calc. by Nernst in 1905, was based on inadequate measurements, whilst more recent determinations of the sp. heats over a wide temp. range indicate 90 — 140° (authors) or 160 — 190° (Bakhuizen, Diss., Leiden, 1921) as the limits for the transition point. Whilst better agreement is shown between calc. and observed vals. for e.m.f. of various cells, the accuracy of the data available cannot in general be considered sufficient for calc. vals. to afford any useful practical basis.

S. I. LEVY.

Viscosities of phosphoric esters. D. P. EVANS and W. J. JONES (J.C.S., 1932, 985; cf. A., 1930, 1019).—Data are recorded for Me_3 , Et_3 , Pr_3 , Bu_3 , and *o*-tolyl orthophosphates at various temp. The last-named has d_4^{25} 1.17176.

N. M. BLIGH.

Viscous friction. P. E. MERCIER (J. Phys. Radium, 1932, [vii], 3, 73—82; cf. A., 1931, 793).—Mathematical. Expressions for the tangential and normal viscous forces are deduced and their physical significance is discussed.

N. M. BLIGH.

Rate of diffusion of copper into gold. W. JOST (Z. physikal. Chem., 1932, B, 16, 123—128).—The diffusion coeff., D , between 300° and 600° , determined by following the change in the lattice consts. of a film of Au deposited electrolytically on a Cu wire, may be represented by the equation $D = 91e^{-27,400/R}$, where T is the temp.

R. CUTHILL.

Transformation of solid metallic phases. III. Kinetics from the atomic basis. U. DEHLINGER (Z. Physik, 1932, 74, 267—290; cf. A., 1930, 1360; 1931, 673).—The influence of particle size and temp. on phase changes in metallic crystals is discussed, illustrations being drawn from the behaviour of Au—Cu alloy, martensite, and austenite, and the formation of pearlite.

J. W. SMITH.

Production of single crystals of binary inter-metallic compounds. C. ROSSI (Z. Physik, 1932, 74, 707—710).—Cu, Zn, Ag, Sn, Al, Mg, and Au have been used.

A. B. D. CASSIE.

Iron-beryllium system. R. H. HARRINGTON (*Metals and Alloys*, 1932, 3, 43—45).—Photomicrographs of etched alloys support the conclusions of Oosterheld (A., 1917, ii, 89) rather than those of Wever and Muller (A., 1930, 1510).

C. W. GIBBY.

Transformational characteristics of iron-manganese alloys. H. SCOTT (*Amer. Inst. Min. Met. Eng. Tech. Pub.*, 1931, No. 435, 19 pp.).—A dilatometric study has been made of Fe-Mn (5.1—23.7%) alloys of low C content (0.05—0.22%). The Acl change, ferrite \rightarrow austenite, occurs with a decrease in vol., and Ar3 with an increase in vol. A new transformation Ac5 accompanied by an increase in vol., and a corresponding contraction on cooling, Ar5, was noted in certain alloys containing 14% or more of Mn. The intensity diminishes greatly at 20% Mn. A 1% C Mn steel showed irreversible contraction on heating above 500° after rapid cooling from a high temp. An irreversible expansion was found during the heating of alloys showing the Ar3 change at a temp. which was nearly independent of the Mn content. Ar3 can be determined graphically from the composition of the alloys. Ar5 indicates the change from the γ - to the ϵ -phase. X-Ray spectrograms failed to show a strong ϵ -line before or after cooling in liquid air. The permanent contraction in austenitic Hadfield steel at 500° is due to pptn. of carbide; it is followed by a corresponding irreversible expansion above 550° because of redissolution of carbide. Le Chatelier's principle of pressure restraint is applied to the behaviour of the Ar3 transformations as exhibited in the expansion curves.

CHEMICAL ABSTRACTS.

Alloys of iron, manganese, and carbon. I. F. M. WALTERS, jun. II. Thermal analysis of binary alloys. F. M. WALTERS, jun., and C. WELLS. III. X-Ray study of the binary iron-manganese alloys. IV. Dilatometric study of iron-manganese binary alloys. M. GENSAMER, J. F. ECKEL, and F. M. WALTERS, jun. (*Min. Met. Invest. Bull.*, 1931, 101, 1—13, 14—22, 23—31, 32—45).—I. Introductory.

II. The $\alpha \rightarrow \gamma$ transformation in the 13% Mn alloy takes place above 600°. From 26 to 60% Mn no definite thermal disturbance was detected.

III. The work of Schmidt and of Ohman is in general confirmed. The formation of the hexagonal close-packed phase is favoured by stress.

IV. Thermal indications of phase changes were confirmed dilatometrically. The low-temp. transformations on cooling alloys with 13% or more Mn may be ascribed to the ϵ -phase. The rate of heating and cooling makes little difference to the temp. at which the transformation begins, but has a marked effect on the transformation range.

CHEMICAL ABSTRACTS.

Effect of alloy constituents on the polymorphic transformations of iron. F. WEVER (*Mitt. Kaiser Wilh. Inst. Eisenforsch.*, 1931, 13, 183—186; *Chem. Zentr.*, 1931, ii, 3145).—The constituents are classified according to their effect on the polymorphic transformations. Their behaviour is not related to crystallographic properties, but is related to atomic radii.

A. A. ELDRIDGE.

Lanthanum alloys. G. CANNERI (*Met. Ital.*, 1931, 23, 803—823; *Chem. Zentr.*, 1931, ii, 3035—3036).—Alloys of La with Pb, Sn, Ti, Mg, Ag, Cu, and Au have been studied by thermal analysis and microscopically. La and Pb form Pb_2La , m. p. 1090°, PbLa , m. p. 1246°, and PbLa_2 , m. p. 1318°; eutectics at 962°, 1044°, and 776°. La and Sn form Sn_2La , m. p. 1150°, Sn_3La_2 , m. p. 1192°, and SnLa_2 , m. p. 1425°, with eutectics at 219°, 1108°, 1142°, and 716°. La and Ti form Ti_2La , m. p. 1096°, TiLa , m. p. 1182°, and TiLa_2 , m. p. 1260°, with eutectics at 1018°, 942°, and 604°. La and Mg form Mg_2La , Mg_3La , MgLa , and solid solutions. La and Cu form Cu_2La , m. p. 902°, and Cu_3La , m. p. 834°, with eutectics at 851°, 742°, and 468°. La and Ag form Ag_3La , m. p. 955°, Ag_2La , inflexion at 864°, and AgLa , m. p. 886°, with eutectics at 778°, 741°, and 518°. La and Au form Au_3La , m. p. 1204°, Au_2La , m. p. 1214°, AuLa , m. p. 1360°, and AuLa_2 , inflexion at 665°, with eutectics at 798°, 1054°, 1148°, and 561°.

A. A. ELDRIDGE.

Systems Ag-Sb-Zn, Ag-Cd-Sb, and Ag-Cu-Sb. W. GUERTLER and W. ROSENTHAL (*Z. Metallk.*, 1932, 24, 7—10, 30—34).—The ternary diagrams have been constructed by Guertler's "Klarkreuz" method and suitable etching reagents for distinguishing the various constituents are tabulated. In all the systems the homogeneous solid solution range in the Ag corner is bounded by a slightly convex line joining the points on the sides of the triangle corresponding with the composition of the α -phases of the binary Ag systems. There are no ternary compounds. Addition of Zn to Ag_3Sb results in the formation of Ag_2Zn_2 and ZnSb , and addition of Sb to Ag_3Zn_3 in the formation of Ag_3Sb and ZnSb . Ag_3Sb is converted by Cd or CdSb into β or ϵ solid solution and free Sb, and addition of Sb to Ag-Cu alloys results first in the formation of Sb-rich ϵ , then of Cu_2Sb , and finally, when all the Cu is saturated, of Ag_3Sb .

A. R. POWELL.

Effect of a third metal on the constitution of brass alloys. IV. Aluminium. I. O. BAUER and M. HANSEN (*Z. Metallk.*, 1932, 24, 1—6).—Previous work on the ternary system Al-Zn-Cu is critically reviewed.

A. R. POWELL.

Metals and alloys. III. Polyantimonides, polybismuthides, and their transformation into alloys. IV. Lattice structure of NaTi and its relation to structures of the β -brass type. E. ZINTL and W. DULLENKOPF. V. Lattice structure of KBi_2 . E. ZINTL and A. HARDER (*Z. physikal. Chem.*, 1932, B, 16, 183—194, 195—205, 206—212; cf. A., 1931, 695).—III. Substances of the compositions Na_3Sb_7 , $\text{Na}_3\text{Sb}_7 \cdot \text{NH}_3$, and $\text{Na}_3\text{Sb}_7 \cdot 6\text{NH}_3$ were obtained by extraction of a Na-Sb alloy with liquid NH_3 , the last-named two being amorphous. NaBi has a tetragonal body-centred at. lattice with a 3.46 and c 4.80 Å., and the unit cell contains 1 atom of each element. The lattice contains no complexes of Bi atoms, so that the compound is not, e.g., a tribismuthide, $\text{Na}_3[\text{Bi}_3]$, and the same is true of NaSb. When NH_3 is removed from salt-like higher polyantimonides or polybismuthides, such as $\text{Na}_x\text{Sb}_y \cdot x\text{NH}_3$ or $\text{Na}_x\text{Bi}_y \cdot x\text{NH}_3$, the complex anions break up, and

a mixture of metallic phases, Sb with NaSb, or Bi with NaBi, results.

IV. NaTl has a cubic lattice with a 7.473 Å. and 8 atoms of each element in the unit cell. The coordinated lattice consists of two interpenetrating diamond lattices of Na and Tl atoms, with a relative displacement equal to half the cube diagonal of the unit cell. Both atoms have the radius 1.62 Å. The prerequisites for the formation of a lattice of this type are equality in radius of the two at. species and smallness of the asymmetry of the distribution of charge. The relations which have been suggested between lattice structure and average no. of valency electrons per atom (A., 1926, 356; 1929, 987) are not valid for alloys of very base metals.

V. KBi₂ has a similar lattice structure to MgCu₂ (A., 1928, 109, 1175) with a 9.501 ± 0.005 Å.

R. CUTHILL.

Intermetallic compounds formed in mercury.

I. Tin-copper system. II. Zinc-copper system. A. S. RUSSELL, P. V. F. CAZALET, and N. M. IRVIN. III. Zinc-iron system and part of the tin-iron system. A. S. RUSSELL and H. A. M. LYONS (J.C.S., 1932, 841—851, 852—857, 857—866; cf. A., 1930, 177).—I. A new method for detecting the formation of intermetallic compounds in Hg and for determining their composition is described. In the system Sn-Cu-Hg, in addition to SnCu₂ the following compounds are formed: SnCu₃Hg, Sn₂Cu₅Hg₁₁, SnCu₃Hg₁₀, SnCu₄Hg₂, SnCu₄Hg₈. SnCu₃Hg can have its Hg atom substituted by 1 and probably 2.5 Zn atoms, and can also exist with either 4.5 or 9 additional atoms of Hg. SnCu₄Hg₂ can have 2 atoms of Zn in place of the Hg, and can also exist with 6 additional atoms of Hg. All the compounds are insol. in Hg.

II. The existence of compounds ZnCu₃Hg₂, Zn₂Cu₅, and Zn₂Cu₆Hg has been established, and their modes of formation and decomp. at room temp. and at 100° have been studied. Both with Sn and Zn there is a series of compounds of the general formula R(CuHg)_{*n*}, where *n* is a small integer, and R denotes SnCu₂, ZnCu, or Zn₂Cu₅.

III. Zn and Fe react in Hg at room temp. to form compounds Zn₂Fe₅, Zn₂Fe₆Hg, ZnFe₄, Zn₂Fe₁₃Hg, and ZnFe₈Hg; and Sn and Fe the compounds SnFe₂ and SnFe₈Hg. All are insol. in Hg. For all the compounds of the Sn-Cu, Zn-Cu, Sn-Fe, and Zn-Fe systems formed in Hg the total of valency electrons is 6, 9, or 12, or a simple multiple of these. Aq. Fe₂(SO₄)₃ oxidises the Sn in SnFe₂ or SnCu₂ directly to Sn⁺⁺⁺ in conditions such that Sn is oxidised to Sn⁺⁺.

F. L. USHER.

Iron-mercury and nickel-mercury. R. BRILL and W. HAAG (Z. Elektrochem., 1932, 38, 211—212).—By dropping Fe(CO)₅ on Hg at 300° a soft silvery paste is formed. On exposure to air a black skin, consisting chiefly of metallic Fe, appears. The paste may contain up to 10% Fe and this may be raised to 12% by centrifuging. By partial removal of Hg in vac. a hard, but rather unstable mass, with a silvery fracture was obtained. It contained 25.2% Fe, shown by X-ray analysis to be present mainly as cryst. α-Fe. The paste was, therefore, a suspension of Fe in Hg, confirming Palmaer's conclusion (this vol., 330). By dropping Ni(CO)₄ on Hg a hard, brittle,

dull grey mass, containing 8.83% Ni and stable in air, is obtained. X-Ray analysis shows a cubic lattice different from that of Ni, the lattice const. being 3.00 Å. The solid carbonyls, Co(CO)₄ and Mo(CO)₆, also react with Hg to form amalgams. The amalgams react violently with H₂O₂.

M. S. BURR.

System iron-cobalt-tungsten. W. KÖSTER and W. TONN (Arch. Eisenhüttenw., 1931—1932, 5, 431—440).—The system, up to a W content corresponding with the pseudo-binary system Fe₃W₂-CoW, has been investigated by thermal and dilatometric analysis, by micrographic examination, and by pptn.-hardening methods. There are no ternary compounds; Fe₃W₂ and CoW form a continuous series of solid solutions (θ-phase), and the three-phase equilibrium, liquid+W Fe₃W₂, of the Fe-W system is displaced to lower temp. by addition of Co and finally merges into the equilibrium, liquid+W ⇌ CoW of the Co-W system. The peritectic reaction liquid+Fe₃W₂ ⇌ α in the Fe-W system and the reaction liquid+α ⇌ γ in the Fe-Co system merge in the ternary system at 1465° into the four-phase reaction liquid+α ⇌ γ+θ. The equilibrium liquid=γ+θ is eutectic and merges into the equilibrium liquid=γ+CoW of the Co-W system, whereas the equilibrium between α+γ+θ remains stable down to room temp. The composition of the α- and γ-phases of the last-named equilibrium remains const. down to 950°, but below this temp. it is displaced towards the Co side corresponding with the changes which take place in the binary Co-Fe system. Ternary diagrams, space-models, and pseudo-binary sections of the ternary system are included, together with photomicrographs of characteristic structures.

A. R. POWELL.

Optimal conditions for the separation of binary liquid mixtures by distillation. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1932, 12, 161—166).—When the ratio of the partial pressures of the constituents is near to unity, no separation can be effected by distillation. When it differs from unity, but is const. at all temp., the temp. of fractionation is immaterial.

R. TRUSZKOWSKI.

Constant-evaporation systems. E. ROBINSON, W. A. WRIGHT, and G. W. BENNETT (J. Physical Chem., 1932, 35, 658—663).—The shift in azeotropic composition with the temp. of evaporation has been determined for the mixtures: PhMe with MeOH, EtOH, PrⁿOH, PrⁱOH, and BuOH; xylene-BuOH; C₆H₆-MeOH; and CHCl₃-AcOMe. The mol. fraction composition of the azeotropic mixture bears a simple linear or quadratic relation to the temp. of evaporation.

H. F. JOHNSTONE (c).

Surface tensions of binary mixtures of four volatile fatty acids. E. I. FULMER and J. ANDES (J. Physical Chem., 1932, 36, 467—474).—Tables of vals. for all possible binary mixtures of HCO₂H, AcOH, PrCO₂H, and BuⁿCO₂H, the total acidity *a* which is either 0.1*N* or 0.2*N*, are given. For all mixtures at both normalities the relation of the surface tension, *γ*, to the percentage composition, *p*, is log (*γ*—45) = *mp* + *b*, where *m* and *b* are consts. depending on the acids and the total concn.

F. E. BROWN (c).

Solution of oxygen in silver. J. H. SIMONS (J. Physical Chem., 1932, 36, 652—657).—Experiment shows that the O dissolved in Ag is present as Ag_2O . The min. solubility at 400° is explained and the solubility curve of Ag_2O derived.

CHEMICAL ABSTRACTS (c).

Solubility of hydrogen sulphide in water [deduced] from the vapour pressures of the solutions. R. H. WRIGHT and O. MAASS (Canad. J. Res., 1932, 6, 94—101).—The v. p. of solutions of H_2S in H_2O have been measured between 5° and 60° , using a new type of glass diaphragm manometer. The results show that Henry's law is not strictly obeyed. A bibliography of flexible glass manometers is given.

W. J. BOYD.

Solubility of ammonia in aqueous sodium hydroxide. S. J. MILOSLAVSKI (J. Gen. Chem. Russ., 1931, 1, 900—904).—The solubility falls at first linearly with increase of the NaOH concn.; above 35% NaOH the slope of the curve decreases progressively. Unidentified cryst. deposits containing Na and NH_3 were observed, the amount of which increased with the NaOH concn. Freshly-ignited NaOH is capable of absorbing or combining with small quantities of NH_3 .

R. TRUSZKOWSKI.

Solubilities of copper, manganese, and some sparingly soluble metals in mercury. N. M. IRVIN and A. S. RUSSELL (J.C.S., 1932, 891—898).—Solubilities of metals of at. nos. 22—29 and of Mo, W, and U in Hg have been determined by chemical methods. The solubility of Cu is 0.0020 and of Mn 0.0010%, that of the others being below $10^{-4}\%$. The results do not agree well with previous determinations by electrometric methods.

F. L. USHER.

Solubility of calcium carbonate and magnesium carbonate in carbon dioxide-free water. J. LEICK (Z. anal. Chem., 1932, 87, 415—422).—The solubility of CaCO_3 in CO_2 -free H_2O , determined by volumetric methods, depends on the amount of solid phase present and varies between 0.7 and 0.8 milliequiv. per litre at 100° . The solubility rises with the temp., is increased by NaCl or Na_2SO_4 , and decreased by alkalis. The solubility of MgCO_3 is independent of the amount of solid phase and decreases with rising temp. At 100° the solubility is 1.50 milliequiv. per litre, of which 1.0 milliequiv. is dissolved as MgCO_3 , and 0.5 as $\text{Mg}(\text{HCO}_3)_2$. The boiling solution decomposes into $\text{Mg}(\text{OH})_2$ and CO_2 ; the decomp. is accelerated by neutral salts and alkalis.

E. S. HEDGES.

Aqueous solubility of salts at high temperatures. I. Solubility of sodium carbonate from 50° to 348° . W. F. WALDECK, G. LYNN, and A. E. HILL (J. Amer. Chem. Soc., 1932, 54, 928—936).—The transition from $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ to Na_2CO_3 occurs at $112.5 \pm 1^\circ$ under 1.27 atm. pressure. Optical data for anhyd. Na_2CO_3 and the v. p. of saturated solutions of Na_2CO_3 are reported.

H. J. WING (c).

Photometric determination of solubility of silver chloride and of mercurous chloride. W. G. EVERSOLE and R. W. MCLACHLAN (J. Amer. Chem. Soc., 1932, 54, 864—869).—The solubilities of AgCl in H_2O and in 0.0024—0.524N- HNO_3 and of

HgCl in 0.0005—0.2N- HClO_4 and 0.0005—0.1N- HNO_3 have been determined by means of a modified tyndall-meter and a gradation photometer.

H. J. WING (c).

Solubility of silver thiocyanate in aqueous ammonia. F. J. GARRICK and C. L. WILSON (J.C.S., 1932, 835—841).—The solubility of AgCNS in aq. NH_3 of concn. 1—14N has been measured at 25° . The solid phase stable above $[\text{NH}_3] = 3.05\text{N}$ is $\text{AgCNS} \cdot \text{NH}_3$, whilst that stable between $[\text{NH}_3] = 2.28$ and 3.05N is provisionally considered to be $\text{AgCNS} \cdot \frac{1}{2}\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$.

F. L. USHER.

Solubility of thallous chloride in solutions of glycine and glycine salts. C. F. FAILEY (J. Amer. Chem. Soc., 1932, 54, 576—579).—The solubility in H_2O at 25° is 0.01617 ± 0.00002 mol. per 1000 g. The solubility at 25° in solutions of glycine, HNO_3 , NaOH, and glycine with added HNO_3 or NaOH was also determined.

L. KELLEY (c).

Multiply reversed solubility curves. R. MÜLLER (Z. Elektrochem., 1932, 38, 227—232).—The solubility of AlBr_3 in $\text{C}_5\text{H}_5\text{N}$ indicates the existence of compounds of 1 mol. of AlBr_3 with 7.5 mols. of $\text{C}_5\text{H}_5\text{N}$ below 2° , 5.5 at $2-4^\circ$, 6 at $4-7.5^\circ$, 3 at $7.5-40^\circ$, and 10—12 above 40° . The successive sections of the solubility curve have alternately positive and negative temp. coeffs. The solubility in PhCN shows that compounds are formed of 1 mol. of AlBr_3 with 6 mols. of PhCN below -2° , 4.5 at -2° to $+15^\circ$, 4 at $15-30^\circ$, 2 at $30-60^\circ$, and 1 above 60° . The only negative temp. coeff. is between -2° and $+15^\circ$. These results have been confirmed in both cases by e.m.f. measurements, using an Al amalgam electrode and Ag as a reference electrode. The solubility of CeBr_3 in $\text{C}_5\text{H}_5\text{N}$ indicates compounds of 1 mol. of CeBr_3 with 3 mols. of $\text{C}_5\text{H}_5\text{N}$ below 3° , 1.5 at $3-5^\circ$, 2 at $5-18^\circ$, 1 at $18-30^\circ$, and 2/3 above 30° . The second, fourth, and fifth sections have negative temp. coeff.

M. S. BURR.

Theory of coprecipitation; formation and properties of crystalline precipitates. I. M. KOLTHOFF (J. Physical Chem., 1932, 36, 860—881).—Depending on the thermodynamic potential of the ppt. during crystal growth, pptn. of anions or of cations may be expected. Up to a certain limit, copptn. with a slightly sol. substance increases with crystal size. On keeping, a change of the internal structure of the crystal takes place, and the amount of copptd. ions decreases with time of keeping before filtration. An extension of the Paneth-Fajans pptn. rule and some theoretical aspects of copptn. are discussed.

I. J. PATTON (c).

Ionic partition coefficients. II. Solubilities of tetraethylsilane and tetraethylammonium halides in various solvents. N. BJERRUM and E. JÓZEFOWICZ (Z. physikal. Chem., 1932, 159, 194—222).—The partial and total v.-p. isotherms for binary mixtures of SiEt_4 with EtOH, COMe_2 , and C_6H_6 at 20° , 35° , and 50° , the miscibility curve for SiEt_4 and MeOH, the solubility of SiEt_4 in H_2O at 20° , 35° , and 50° , and the solubilities at 20° and 35° of NEt_4Br , NEt_4Cl , and NEt_4I in COMe_2 , EtOH, MeOH, and H_2O have been determined. From the

results the distribution ratios of SiEt_4 between the various solvents and the vapour phases in equilibrium have been calc. The results are used to test certain relations deduced from the theory of ionic partition coeffs. (A., 1927, 828). R. CUTHILL.

Solubility of picric acid in mixed solvents. II. Benzene-alcohol mixtures. J. C. DUFF and E. J. BILLS (J.C.S., 1932, 881—884; cf. A., 1931, 794).—In mixtures of C_6H_6 with MeOH , EtOH , Pr^nOH , Pr^iOH , or BuOH , MeOH has the greatest and BuOH the least effect in increasing the solubility of picric acid. The dissociating action of the alcohols is in the same order. The proportion of alcohol in the mixture exerting the greatest solvent effect is also greatest with MeOH and least with BuOH , and decreases with rise of temp. for all the alcohols. An empirical formula connecting solubility with composition is given. F. L. USHER.

Distribution ratios of some fatty acids and their halogen derivatives between water and olive oil. M. BODANSKY and A. V. MEIGS (J. Physical Chem., 1932, 36, 814—818).—The distribution ratios have been determined at 25° and 37.5° .

H. A. BEATTY (c).

Adsorption of gases by vacuum-fused electrolytic iron. F. DURAU and C. H. TECKENTRUP (Ann. Physik, 1932, [v], 12, 927—960).—The prep. of electrolytic Fe powder, free from gases and having a chemically clean surface for adsorption, is described. At 18° , A , H_2 , N_2 , CO , N_2O , CH_4 , C_2H_6 , C_3H_8 , C_2H_4 , C_2H_2 , and MeCl are adsorbed reversibly, whilst chemisorption is observed with O_2 , CO_2 , C_2N_2 , HCl , NH_3 , SO_2 , and NO . Not only is the chemisorption irreversible, but considerable difficulty is experienced in degassing in high vac., and subsequent chemisorption is relatively small. In no case, even with H_2 , was absorption observed. When the surface of the Fe powder is first contaminated by a small amount of O_2 , the gases CH_4 , C_2H_6 , and C_3H_8 are adsorbed reversibly, but CO_2 and C_2N_2 are taken up by chemisorption. N_2O , CO , C_3H_8 , N_2 , and H_2 are adsorbed reversibly and O_2 irreversibly by Fe powder which has previously been exposed to CO_2 or C_2N_2 . No notable increase was observed in the velocity of sorption of O_2 by Fe powder charged with H_2 . A unimol. adsorption layer is probably formed in each case. The dipole moment of the adsorbed mol. is of little importance, but a double linking in the mol. diminishes the adsorption. The experiments support previous conclusions (cf. A., 1928, 1317) concerning the relation of adsorption to the van der Waals forces, the influence of lattice distortion, and the difficulty of completely outgassing adsorbents.

E. S. HEDGES.

Sorption of gases by zeolites. E. RABINOVITSCH (Z. physikal. Chem., 1932, B, 16, 43—71).—In the sorption of H_2O and other gases by chabasite at -253° to 100° and 1—500 mm., a state of saturation is approached as the temp. is lowered at const. pressure, or the pressure increased at const. temp., the amount of gas sorbed then being approx. proportional to its mol. vol. The val. of the quotient of the square of the heat of sorption for infinitesimal concn. of sorbate by the mol. heat of vaporisation of the sorbate

is almost the same for all the gases except H_2O . The sorption isotherm cannot be represented by Langmuir's equation, but by assuming the heat of sorption and the space-filling of the sorbate to be functions of the concn. of the latter in the solid phase an acceptable equation for the effect of pressure and temp. on the sorption is obtained. The sorbed mols. are probably merely "condensed" in the cavities of the zeolite, without being anchored in any particular positions. Replacement of Ca by Na ions in chabasite lowers the sorptive power. Preliminary data for sorption by other zeolites are reported. R. CUTHILL.

Adsorption of electrolytes by ash-free charcoal charged with nitrogen. J. K. SYRKIN and I. POTAPOV (Kolloid-Z., 1932, 59, 47—49).—Ash-free sugar-charcoal which has been heated at 900 — 1000° in N_2 does not adsorb alkali and adsorbs very little acid. Probably a surface layer of a nitride C_2N is formed. N_2 should not be used as an inert gas in the prep. of adsorbent C. E. S. HEDGES.

Adsorptive power of Philippine wood charcoals. I. Adsorption of acids and bases from solutions. A. C. SANTOS and A. CLEMENTE (Univ. Philippines Nat. Appl. Sci. Bull., 1930, 1, No. 1, 21—40).—In general charcoals with a high adsorptive capacity for acids have a low capacity for bases, and *vice versa*. CHEMICAL ABSTRACTS.

Adsorption of silver nitrate by finely-divided silver. H. V. TARTAR and O. TURINSKY (J. Amer. Chem. Soc., 1932, 54, 580—583).—No adsorption could be detected. The results of Euler and Hedelius (A., 1921, ii, 490) are due to the presence of Zn in their Ag. S. LENHER (c).

Effect of aqueous solutions on colloidal powders. J. L. SHERESHEFSKY (J. Physical Chem., 1932, 36, 696—702).—An apparatus for measuring sorption by colloidal powders is described. The effect of NaCl and MgCl_2 on the rate of sorption by Jackson shale passes through a max. as the concn. increases. The probable mechanism is discussed.

F. URBAN (c).

Adsorption of acetate buffers on "carbo medicinalis Merck." A. SKAPSKI (Rocz. Chem., 1932, 12, 135—160).— NaOAc is not adsorbed by this type of C, and the adsorption of AcOH is not affected by the presence of the salt. Change in p_{H} of acetate buffers consequent on the addition of C is not due to the existence of an isoelectric point of C, but to adsorption of undissociated AcOH . Van Slyke's conception of "buffer effect" cannot be applied to such adsorbents. The "resistivity" and "sensitivity" of buffer to adsorbent are discussed in relation to Freundlich's equation.

R. TRUSZKOWSKI.

Adsorption and reactions at surfaces of zinc oxide. H. S. TAYLOR and D. V. SICKMAN (J. Amer. Chem. Soc., 1932, 54, 602—613).—Adsorbed H_2O plays an important part in the decomp. of alcohols on the surface of ZnO , the adsorption probably being activated. The v. p. of H_2O adsorbed on ZnO prepared from ZnC_2O_4 has been measured at 300 — 400° ; the calc. heat of adsorption is 30 kg.-cal. The rate

of adsorption of H_2 by ZnO at 0—360°, the isotherms for —191° and —78.5°, and the heat effects of the two types of adsorption have been determined. Equations giving the temp. of max. adsorption have been deduced. S. LENHER (c).

Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. A. P. VANSELOW (Soil Sci., 1932, 33, 95—112).—Base-exchanging components of soil and bentonites are very similar, but differ from those of zeolites and artificial permutites. Two, and possibly more, classes of bentonite and soil colloids are indicated. The complex anions in these appear to be monobasic. $Ca^{++}-NH_4^+$ exchange reactions in soil and bentonite are ascribed to the presence of a mixed crystal with replaceable cations. There is a definite hysteresis in the Na^+-K^+ and $Ca^{++}-NH_4^+$ exchanges in all materials recorded. This phenomenon was not obliterated by repeating the $Ca^{++}-NH_4^+$ exchanges several times with bentonite. Exchange of bivalent cations in bentonite exhibited no hysteresis.

A. G. POLLARD.

Electrokinetics and base-exchange capacity of some inorganic colloids. N. H. PARBERRY and S. MATSON (Soil Sci., 1932, 33, 75—94).—The prep. of isoelectric ppts. of "ferric ferrocyanide," "sulphide of Sn," and electronegative "sulphides" of Sb, Bi, and As is described. As_2S_3 is definitely electronegative. As appears unable to exist as a colloidal cation. The isoelectric points of a series of sulphides of Sn occur at lower p_H vals. as the proportion of S increases. With excess of S no isoelectric point exists. All sulphides of Sb are electronegative. The isoelectric point of Sb oxychloride is at a comparatively low p_H . The oxychloride of Bi is electronegative over a wide range of p_H and has no isoelectric point. At p_H ranges in which no decomp. occurs, the base-exchange capacity of Fe^{+++} ferrocyanides increases with increasing proportion of the acidoid to the ampholytoid component. As_2S_3 has a moderate exchange capacity at p_H 7, and that of Bi sulphides is slight.

A. G. POLLARD.

Gibbs' adsorption equation for the case of binary mixtures. R. K. SCHOFIELD and E. K. RIDEAL (Phil. Mag., 1932, [vii], 13, 806—809; cf. A., 1925, ii, 960).—The authors criticise Wynne-Jones' interpretation of their results for the adsorption of EtOH at the surface of EtOH- H_2O mixtures (A., 1931, 1366), and reassert their original view.

H. J. EMELÉUS.

Rate of adsorption from solution. L. E. SWEARINGEN and B. N. DICKINSON (J. Physical Chem., 1932, 36, 534—545).—The rates of adsorption of mono-, di-, and tri-chloroacetic acids from solutions by SiO_2 gel and by blood charcoal were measured by a conductivity method. Initially the rate is proportional to the solute concn., but is greatly influenced by agitation. For the gel the initial rates of absorption decrease in the order mono- > di- > tri-chloroacetic acid; for charcoal the order is reversed.

H. F. JOHNSTONE (c).

Adsorption of binary vapour mixtures on silica gel. B. S. RAO (J. Physical Chem., 1932, 36, 616—625).—Mixtures of C_6H_6 with EtOH and

CCl_4 , and of H_2O with $COMe_2$ and EtOH have been studied. Adsorption from some of these mixtures in the liquid state has also been determined. Selective adsorption of EtOH from C_6H_6 solutions and of C_6H_6 from CCl_4 solutions occurs at all concns. From aq. solutions of EtOH or $COMe_2$ the H_2O is selectively adsorbed at high concns. and the org. component at low concns.

P. H. EMMETT (c).

Heats of adsorption of sulphur dioxide and propane on sodium chloride, and of ethane and propane on decomposed potassium permanganate. F. DURAU and V. SCHRATZ (Z. physikal. Chem., 1932, 159, 115—130).—Since the average vals. of the heats of adsorption on NaCl and $KMnO_4$ decomposed by heating calc. from adsorption measurements at 0—40° are of the same order as the mol. heats of vaporisation of the adsorbates, it is inferred that the adsorption is brought about by van der Waals forces. The data point to the presence of centres of exceptionally high adsorption potential, comparable with active centres in catalysis. Such centres, which on heating disappear owing to recrystallisation, are responsible for chemisorption, which is particularly apparent with the $KMnO_4$ adsorbent.

R. CUTHILL.

Anomalous first heats of adsorption. G. M. SCHWAB and W. BRENNER (Z. physikal. Chem., 1932, B, 16, 19—42).—The experiments leading to the results previously reported (A., 1931, 1228) are described in detail.

R. CUTHILL.

Thermodynamics of the surfaces of solutions. J. A. V. BUTLER (Proc. Roy Soc., 1932, A, 135, 348—375).—Mathematical. The hypothesis that the influence of the discontinuity does not extend beyond a surface layer of mols. the variations of which are subject, when the area of surface remains const., to the condition $A_1 dn_1^s + A_2 dn_2^s + \dots + A_n dn_n^s = 0$ (where n_1^s, n_2^s , etc. are the no. of mols. of the substance S_1, S_2 , etc. in a given area of the surface layer, and A_1, A_2 , etc. their superficial areas), is shown to be in agreement with experimental data.

L. L. BIRCHUMSHAW.

Law of equilibrium between two phases. G. ANTONOFF (Kolloid-Z., 1932, 59, 7—12).—An apparatus and technique are described by which the surface tension of volatile liquids may be determined by the drop method in an atm. saturated with the vapour. The relation $a_{12} = a_1 + a_2$, where a_1 and a_2 are the surface tensions of two liquids saturated with one another and a_{12} is their interfacial tension, is believed to express a general law of equilibrium and has been verified experimentally with the systems H_2O-Bu^iOH , H_2O -isoamyl alcohol, H_2O-NH_2Ph , H_2O-Et_2O , $H_2O-CHCl_3$, $H_2O-C_6H_6$, H_2O-CCl_4 , and $H_2O-PhNO_2$ at 20°.

E. S. HEDGES.

Cæsium films on tungsten. I. LANGMUIR (J. Amer. Chem. Soc., 1932, 54, 1252—1253).—The W surface after considerable heating at 2800° abs. is homogeneous, except for a small fraction which can hold atoms more firmly than the rest. With rising temp. and a filament at 1100—1200° abs., the first atoms are adsorbed on this active surface, which becomes saturated before 0.5% of the remaining

surface is occupied. From the active spots, which are spaces holding 1 atom each, the heat of evaporation is 80 kg.-cal. per g.-atom. With low filament temp. and high pressures, σ reaches a limit $\sigma_1 = 3.563 \times 10^{11}$ atoms per sq. cm. of true surface (34% greater than the apparent surface), corresponding with a monat. film of 1 Cs atom for 4 W atoms. The electron emission at const. temp. reaches a max. at $\theta = \sigma/\sigma_1 = 0.67$. C. J. WEST (c).

Dependence of surface tension of glass on temperature. M. NISHIDA (Z. anorg. Chem., 1932, 204, 60—66; cf. A., 1930, 1530).—Experiments previously described have been amplified by extending the temp. range over which the force of shrinking and the surface tension of a soda-lime glass have been measured. The results show that the latter decreases whilst the former increases with rise of temp. For the particular glass examined, no extension could be observed between 590° and 630° for a considerable range of load. F. L. USHER.

Features of the orientation of molecules and their application to problems of lubrication. P. WOOD (Kolloid-Z., 1932, 59, 1—6).—A summary of the properties of mol. films at liquid surfaces and the significance of orientation of the mols. of lubricating media. E. S. HEDGES.

New method of measuring molecular layers. E. GORTER and W. A. SEEDER (Kolloid-Z., 1932, 58, 257—260).—A method has been developed for measuring mol. surface layers by observing the damping produced in capillary waves set up by an electrically-driven tuning-fork vibrating in the surface. Some preliminary results are given. E. S. HEDGES.

Thin lamellæ and their physical properties. H. DEVAUX (Kolloid-Z., 1932, 58, 260—274; cf. this vol., 333).—A summary and discussion of published work, together with a bibliography. E. S. HEDGES.

Light-sensitive surface layers. I. F. WEIGERT and E. EBERIUS (Kolloid-Z., 1932, 58, 276—282).—Homogeneous AgBr-gelatin emulsions have a surface layer in which the spectral relations are quite different from those in the interior of the film, the surface being particularly sensitive to red light. On development the Ag in the surface is reduced as a bright mirror. This "mirror activity" can be destroyed simply by wiping the film in the wet state, but it is regenerated after a time. The mechanical method of sensitisation thus recorded, possibly acting through surface tension, may have an important bearing on photo-biological and photo-electric problems. E. S. HEDGES.

Influence of interfaces on crystallisation velocity. K. SOLLNER (Kolloid-Z., 1932, 59, 58—60).—The velocity of crystallisation of an undercooled liquid may be greater in the surface than in the interior, because of the oriented layer of mols. at the surface. The probability of formation of nuclei may be increased at a liquid-gas interface. E. S. HEDGES.

Formation of hair-silver and similar structures. K. SOLLNER (Kolloid-Z., 1932, 59, 55—58).—The production of fibrous structures of this type is

related to the mobility of mols. adsorbed at a solid surface. E. S. HEDGES.

A phenomenon of surface chemistry. R. DUBRISAY (Compt. rend., 1932, 194, 1076—1079).—Partial separation of two solutes may be effected by making use of the fact that the solute which produces the greater lowering of the surface tension is present in greater proportion in the surface layer. C. A. SILBERRAD.

Surface relations of potassium ethyl xanthate and pine oil. I. C. C. DE WITT and E. E. ROPER. II. C. C. DE WITT and R. F. MAKENS (J. Amer. Chem. Soc., 1932, 54, 444—455, 455—464).—I. For aq. solutions of K Et xanthate at 25° up to 1.3M $d\gamma/dm$ is negative. For the interfacial tension between dil. aq. xanthate and pine oil at 25°, $d\gamma/dm$ is positive. Hydrolysis cannot account for the changes in p_H of xanthate solutions on keeping.

II. The surface tensions of aq. solutions of xanthate (up to 6.7M) and of aq. solutions of pine oil and various terpenes have been measured at 25°. Pinene, terpinolene, and dipentene depress the surface tension of H₂O slightly. S. LENHER (c).

Influence of particle size on the heat of wetting of technical adsorbents. II. F. KRCZIL (Kolloid-Z., 1932, 59, 44—46; cf. this vol., 333).—The variation of heat of wetting with particle size of the adsorbent has been studied with active C, SiO₂ gel, and Al(OH)₃ gel in abs. EtOH. Although the heat of wetting increases with increasing dispersity, in all cases a limiting val. is reached at a particle size of about 0.5 mm. The phenomenon is probably due to the more complete wetting of the surface of the finely-divided adsorbent during the time of the experiment. E. S. HEDGES.

Electrokinetic potentials. X. Effect of particle size on potential. H. B. BULL and R. A. GORTNER (J. Physical Chem., 1932, 36, 111—119; cf. A., 1931, 795).—The electrokinetic potential for streaming through a diaphragm of quartz particles is a linear function of the pressure only if the particles are uniform in size. The explanation is that the surface potential of the particles increases approx. as the cube root of the diameter, probably because the amount of salt adsorbed per unit area diminishes. M. DOLE (c).

Special cases of osmosis in binary systems. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1282—1291).—Theoretical. E. S. HEDGES.

Intervention of oxidation-reduction equilibria in the permeability of a membrane. P. REISS (Compt. rend., 1932, 194, 970—972).—Two vessels are separated by a collodion membrane with means of determining the oxidation-reduction potential in each. With differently conc. solutions of a reducing agent, e.g., Na₂S₂O₄ or TiCl₃, on the two sides equilibrium is attained within 24 hr. If, however, the membrane is dyed by an oxidation-reduction buffer, e.g., nigrosine, phenosafranine, etc., several days elapse before equilibrium results, although this is rapidly attained if the dye in the membrane is reduced. Permeability is affected only as regards reducing agents; in other respects it is unchanged. There

seems to be in the membrane some substance possessing a reversible oxidation-reduction equilibrium (cf. A., 1919, i, 461). C. A. SILBERRAD.

Blocking phenomena in ultra-filters. F. ERBE (Kolloid-Z., 1932, 59, 32-44).—The permeability of membranes and the influence of mechanical, electrical, and other conditions on the distribution and size of the pores are discussed theoretically. An apparatus is described for determining the permeability of membranes under pressure. Preliminary results are given for membranes of cellophane, "cellafilter," cellulose acetate and nitrate, showing the influence of purity of the liquid, the permeability for different liquids, and the displacement of one liquid in the membrane by another. E. S. HEDGES.

State of hydroxyaldehydes and hydroxyketones in solution. W. HEROLD (Z. physikal. Chem., 1932, B, 16, 213-220).—The absorption band of the CO group in the ultra-violet (cf. A., 1931, 573) is used to measure the proportion of free aldehyde in solutions of γ -hydroxyvaleraldehyde in various solvents. Part of the aldehyde is present as an inner semiacetal, and with hydroxylic solvents semiacetal formation with the solvent also occurs. The change of the absorption curves of solutions of monohydroxyacetone with time indicates that part at least of the ketone is polymerised owing to the CO groups forming semiacetal mols. with the OH groups of other mols. On dissolution, these polymerides are resolved into the simple mols. Bimol. dihydroxyacetone seems to contain neither CO groups nor double linkings. R. CUTHILL.

Viscosity measurements with carbohydrates in liquid ammonia, formamide, and water. L. SCHMID and R. FALKE (Monatsh., 1932, 59, 357-380).—The sp. viscosity (η) of solutions of inulin in liquid NH_3 at -64° , -54° , and -44° is directly proportional to the concn. ($c=0.04-0.41$) and is independent of the pressure, indicating that neither association nor polymerisation occurs. The vals. of η are approx. the same at all the temp. Similar results are obtained with glycogen, glucose, sucrose, raffinose, and NH_4NO_3 , indicating that inulin and glycogen are substances of low mol. wt.

The sp. viscosities of solutions (1-11%) of inulin, glucose, and sucrose in H_2O at 13° are all similar and are again proportional to the concn. The results for inulin in HCO-NH_2 are analogous to those of Staudinger *et al.* (A., 1930, 1414). H. BURTON.

Apparent volumes of salts in solution. III. Saturated solutions of mixed electrolytes. A. F. SCOTT (J. Physical Chem., 1932, 36, 1022-1034; cf. this vol., 335).—A discussion. L. ONSAGER (c).

Quantitative limit law for the internal friction of any simple strong electrolyte. H. FALKENHAGEN and E. L. VERNON (Physikal. Z., 1932, 33, 140).—A general theoretical expression is given for the coeff. of the square root of the concn. term in the viscosity formula for strong electrolytes at infinite dilution. A. B. D. CASSIE.

Verification of the laws of Brownian motion. E. M. BRUMBERG and S. I. VAVILOV (Z. Physik, 1932, 73, 833-843).—From relations which involve the

time mean square of the Brownian displacement and the diffusion coeff. of a spherical particle in a viscous fluid, a formula is deduced giving the mean area that will be illuminated in a finite time in the field of view of a microscope in terms of the viscosity of the supporting medium and known consts. This formula, which eliminates the uncertain particle size, has been verified for gamboge in H_2O , glycol, and glycerol.

A. B. D. CASSIE.

Unusual example of regional sedimentation. H. NICOL (Kolloid-Z., 1932, 58, 302-305).—The production of horizontal periodic layers in a suspension of filter-paper cellulose in dil. H_2SO_4 is described. Unlike those observed in clay suspensions, these layers are not affected by light. The phenomenon is due to small gas bubbles, which adhere to the particles of the suspension and alter the effective sp. wt.

E. S. HEDGES.

Electric conductivity and capacity of disperse systems. H. FRICKE (Physics, 1931, 1, 106-115).—The theory of the passage of a.c. through suspensions is developed and applied to cream, wet sand, blood, and animal tissue. CHEMICAL ABSTRACTS.

Colloidal properties of bentonite suspensions. H. A. AMBROSE and A. G. LOOMIS (Physics, 1931, 1, 129-136).—The curve correlating p_H with % sediment in a definite time has a max. at the isoelectric point with minima on each side corresponding with points of max. adsorption. The viscosity curve is closely related to the rate of settling. Max. swelling occurs approx. at the point of max. viscosity. NaCl and KCl prevent the swelling of bentonites.

CHEMICAL ABSTRACTS.

Preparation and properties of chloride-free ferric oxide hydrosols. C. H. SORUM (Kolloid-Z., 1932, 58, 314-325).— Fe(OH)_3 hydrosols free from Cl^- can be prepared by hydrolysis and dialysis at high temp. Lower flocculation vals. were obtained than with ordinary Fe(OH)_3 sols and the behaviour on dilution was in accordance with the Burton-Bishop rule. The addition of traces of electrolyte caused the sol to behave as ordinary Fe(OH)_3 sols and suggests that the variation of the flocculation val. of a univalent ion with the dilution of the sol is a function of the purity of the sol. Experiments on heating Fe(OH)_3 sols under pressure in an autoclave and on treating with EtOH and COMe_2 indicate that the degree of hydration has an important influence on the stability of the sol. Highly purified Fe(OH)_3 sols with low flocculation val. can be pptd. completely by EtOH or COMe_2 . E. S. HEDGES.

Dielectric behaviour of disperse systems. A. PIEKARA (Kolloid-Z., 1932, 59, 12-25).—Mainly theoretical. The dependence of the dielectric const. of disperse systems on the degree of dispersion cannot be explained in terms of the mutual influence of charged spheres, but is probably due to the following causes: (1) the mols. in the surface of the particle are in a different electric field from those in the interior; (2) asymmetrical mols. are oriented in the surface layer; (3) the surface layer contains other adsorbed substances, which have a strong influence on the dielectric const. E. S. HEDGES.

Role of dielectric constant, polarisation, and dipole moment in colloid systems. IX. Swelling and solubility of cellulose acetate and their relations to dielectric data. WO. OSTWALD and H. ORTLOFF (Kolloid-Z., 1932, 59, 25—32; cf. A., 1928, 705, 835, 1091).—The solubility and swelling of cellulose acetate in 90 org. liquids has been studied qualitatively. The liquids are (a) inactive, (b) "swelling-active," or (c) "dissolution-active." The inactive liquids are mainly those of simple constitution, but include certain halogenated hydrocarbons; the active liquids include esters, ketones, alcohols, amines, and other types. The three groups are sharply differentiated in the case of 35 liquids by the val. of the function μ^2/ϵ , where μ is the dipole moment and ϵ is the dielectric const. This function has the val. 0—0.105 for inactive liquids, 0.115—0.235 for swelling-active liquids, and 0.251—0.528 for dissolution-active liquids. In many cases the vals. of μ and ϵ are not known with sufficient accuracy for the application of the rule. Cellulose acetate dissolves in mixtures of $C_2H_2Cl_4$ — H_2O , $PhNO_2$ — $EtOH$, and diacetone alcohol— H_2O , although not in any of these solvents taken singly. Solutions of cellulose acetate in liquids or mixtures of strong dissolution-activity have a low viscosity and *vice versa*. Max. dissolving power is parallel with max. viscosity.

E. S. HEDGES.

Dielectric solvation of disperse systems. Determination of mol. wt. of colloids by anomalous dielectric dispersion. N. MARINESCO (Kolloid-Z., 1931, 58, 285—294).—The existence of structure-viscosity in hydrophilic colloidal solutions is held to invalidate the calculation of the degree of hydration from viscosity. In some cases the viscosity data may lead to vals. of hydration exceeding the total amount of H_2O present. A method is worked out for calculating the degree of hydration from dielectric data. The results obtained, expressed as g. of H_2O of hydration per g. of substance, are: ovalbumin 1.5, serum-albumin 0.11, metahæmoglobin 2.7, sol. starch 0.48, cholesterol 0.23, lecithin 1.86. The hydration of gelatin varies with the p_H ; it is 0.01 at the isoelectric point (p_H 4.7), 0.13 at p_H 6.6, and 0.57 at p_H 3.5. A method is developed for determining the mol. wt. from dielectric data; the val. obtained is not identical with the wt. of the micelle.

E. S. HEDGES.

Dielectric constant of colloidal solutions. T. NANTY and M. VALET (Compt. rend., 1932, 194, 883—884).—Measurements of the dielectric consts. of aq. solutions of various dyes are recorded.

C. A. SILBERRAD.

Dielectric behaviour of emulsions. A. PIKARA (Kolloid-Z., 1932, 58, 283—285).—Measurements of the dielectric const. of emulsions of paraffin oil in $EtOH$ — H_2O (both liquids having d 0.850) show that any deviations from the Clausius-Mosotti law are small. The dielectric const. increases very slightly with decreasing particle size.

E. S. HEDGES.

Nature of "aluminium oxide" hydrosols. A. W. THOMAS and A. P. TAI (J. Amer. Chem. Soc., 1932, 54, 841—855; cf. A., 1931, 425).—The proper-

ties of Al oxydide hydrosols prepared by the action of amalgamated Al on dil. HI solution have been examined in detail.

F. E. BROWN (c).

Effect of low temperatures on the state of colloidal systems. S. I. DIJATSKOVSKI (J. Gen. Chem. Russ., 1931, 1, 964—971).—In those cases in which frozen metal hydroxide hydrosols coagulate on thawing, the peptisating electrolyte is given up to the perimicellar fluid. Sols can be stabilised against coagulation due to freezing by addition of the requisite concn. of $EtOH$. Hydrosols rapidly frozen by cooling at -182° do not in many cases coagulate on thawing. The behaviour of $Fe(OH)_3$, $Al(OH)_3$, SnO_2 , V_2O_5 , Prussian-blue, Mo-blue, As_2S_3 , Sb_2S_3 , Au, Ag, $AgCl$, and hæmoglobin hydrosols frozen at -5° , -15° , and -21° , and then thawed, has been studied. Those sols which have $p_H < 8.5$ do not freeze homogeneously, ice first forming at the peripheries of the solution, leaving a more conc. sol in the interior, whilst those of $p_H > 8.5$ freeze homogeneously.

R. TRUSZKOWSKI.

Influence of gases on stability of Zsigmondy gold sols. W. H. CONE, H. V. TARTAR, and T. I. TAYLOR (J. Physical Chem., 1932, 36, 735—739).—Various gases were bubbled through Au sols for 2 hr. and the resistance to pptn. by NaCl was then determined. H_2 , air, N_2 , and O_2 were the most effective in stabilising the sols. The effect was much greater with more turbid sols than with clear dil. sols. Since cataphoretic experiments failed to detect any change of the charge on the particles on bubbling H_2 through the sol, whilst this treatment caused the turbid sols to become a brighter red, the effect is attributed to adsorption of gas which causes disintegration of the larger, aggregated particles.

J. W. PERRY (c).

Effect of non-electrolytes on coagulation values of electrolytes. H. LACHS and S. CHWALINSKI (Z. physikal. Chem., 1932, 159, 172—180, and Roczn. Chem., 1932, 12, 103—111).—Capillary-active non-electrolytes either have no influence on the coagulation vals. of electrolytes for As_2S_3 and C sols prepared by the action of H_2SO_4 on sucrose, or depress the coagulation vals. for univalent cations and increase the vals. for multivalent cations. The adsorption of the non-electrolyte may be supposed to influence the charge on the dispersed particles, and therefore the coagulation vals., by reducing both the thickness of the double layer and the dielectric const. With univalent ions the thickness of the multimol. layer is affected only slightly and the reduction in the dielectric const. determines the change in coagulation val., whereas with multivalent ions the variation in thickness of the unimol. layer is the deciding factor. Substances of very high capillary activity may, however, materially influence the thickness of the multimol. layer; strophanthin raises the coagulation vals. even of univalent cations.

R. CUTHILL.

Flocculation of ferric hydroxide sols by various electrolytes and the Schulze-Hardy law. A. BOUTARIC and J. BOUCHARD (J. Chim. phys., 1932, 29, 18—25).—The flocculation vals. of anions for $Fe(OH)_3$ sols, prepared by hydrolysis of $FeCl_3$ and subsequent dialysis, are in the order: Cl^- , I^- , Br^- ,

NO_3' , ClO_3' , ClO_4' , CNS' , MnO_4' , OAc' , $\text{H}_2\text{PO}_4'$, F' , OH' , CN' , $\text{S}_2\text{O}_3''$, $\text{S}_2\text{O}_4''$, CO_3'' , SO_4'' , CrO_4'' , PO_4''' , citrate. The flocculation cannot be considered, therefore, as a chemical reaction between the added electrolyte and the electrolyte normally present in the micelle. Although the anions appear in the order of valency, they do not support the Schulze-Hardy rule, because there is a greater difference among the univalent ions than between the uni- and bi-valent ions, whilst the bi- and ter-valent ions have equal flocculation vals. Among the univalent anions the anomalous members are CNS' , MnO_4' , OAc' , $\text{H}_2\text{PO}_4'$, F' , OH' , and CN' . With progressive dialysis the stability of the $\text{Fe}(\text{OH})_3$ sol decreases, but the effect varies with the different electrolytes.

E. S. HEDGES.

Coagulation of ferric hydroxide sol under the simultaneous influence of two electrolytes. V. KRESTINSKAJA and O. MOLTSCHANOVA (*Kolloid-Z.*, 1932, 59, 68—76, and *J. Gen. Chem. Russ.*, 1931, 1, 792—802).—The coagulating effect of two electrolytes on a $\text{Fe}(\text{OH})_3$ sol is additive when (a) neither electrolyte has any chemical effect on the micelle (BaCl_2 and KCl), (b) the stability of the sol is not altered (NaNO_3 and KCl), (c) both electrolytes have equal effects (MgSO_4 and K_2SO_4). An increase in coagulation is observed when (a) one of the electrolytes can react with the kernel of the micelle, producing a soluble, strongly dissociated salt [$\text{Al}(\text{NO}_3)_3$ and KCl ; HNO_3 and KCl], (b) one of the electrolytes can increase the solubility or stability of the sol by reacting with the outer part of the micelle, (c) one electrolyte produces a highly-adsorbed Fe salt. A decrease in coagulating power is observed when one of the electrolytes reacts with the active part of the micelle to form a slightly sol. or weakly dissociated compound (KOH and KCl ; MgSO_4 and KCl).

E. S. HEDGES.

Particle size and constitution of colloidal ferric oxide. II. **Dialysis and ageing.** J. B. NICHOLS, E. O. KRAEMER, and E. D. BAILEY (*J. Physical Chem.*, 1932, 36, 505—514).—Sols formed by boiling aq. FeCl_3 are unstable, the hydrolysis being reversed at room temp. During ageing, the particle size distribution shifts slightly towards larger sizes. Dialysis of fresh and aged sols leads to hydrolysis of FeCl_3 in the intermicellar liquid and to formation of additional colloidal Fe_2O_3 , but the particle size distribution is not appreciably changed. Changes during ageing and dialysis are also revealed by changes in light adsorption.

F. URBAN (c).

Sensitisation and stabilisation of hydrosols.

I. Hydrophiles. A. DUMANSKI and N. BONDARENKO. **II. Hydrophobes.** A. DUMANSKI and S. E. CHARIN (*J. Gen. Chem. Russ.*, 1931, 1, 933—936, 937—942).—I. The behaviour of 1% gelatin or 0.2% agar hydrosols towards EtOH has been studied in the presence of N electrolytes. Those yielding acid products of hydrolysis (AlCl_3 , ThCl_4) stabilise gelatin hydrosols with respect to EtOH , whilst NaCl , BaCl_2 , and Na_2HPO_4 exert the opposite effect. Gelation is totally inhibited by AlCl_3 and ThCl_4 , and partly by FeCl_3 ; NaCl , BaCl_2 , and Na_2HPO_4 augment gelation. NaCl and Na_2HPO_4 stabilise agar sols to a small

extent, whilst BaCl_2 , AlCl_3 , CeCl_3 , and ThCl_4 sensitise them. Gelation is partly prevented by NaCl and Na_2HPO_4 .

II. The effect of electrolytes (0.02*N*- NaCl , 0.15*N*- Na_2SO_4 , 0.0025*N*- BaCl_2 , 0.0002*N*- CeCl_3 , 0.0003*N*- AlCl_3 , and 0.0002*N*- ThCl_4) on the behaviour of As_2S_3 or $\text{Fe}(\text{OH})_3$ hydrosols towards EtOH has been studied, and the results are expressed on triaxial diagrams, giving areas of coagulation or turbidity. In general the sensitising action of electrolytes diminishes with increase in the valency of the coagulating ion.

R. TRUSZKOWSKI.

Mechanism of mutual flocculation. D. C. BAHL (*Kolloid-Z.*, 1932, 59, 60—68).—Experiments on the mutual flocculation of sols of As_2S_3 , $\text{Fe}(\text{OH})_3$, Au , AgI , water-blue, methylene-blue, Pd , Ag , Fe , Bi , and $\text{Cu}_2\text{Fe}(\text{CN})_6$ indicate that both neutralisation of the electric charges and chemical reaction between the stabilising ions determine the result. Dilution of the oppositely-charged sols causes the zone of max. flocculation to be more sharply defined.

E. S. HEDGES.

Mechanism of mutual coagulation process. II. H. B. WEISER and T. S. CHAPMAN (*J. Physical Chem.*, 1932, 36, 713—721; cf. *A.*, 1931, 563).—Free electrolyte in a mixture of oppositely-charged sols affects considerably the composition of the coagulum. The zone of mutual pptn. is quite narrow if the intermicellar solution in both sols contains little or no free electrolyte or if the electrolyte consists of ions of low pptg. power. Under these conditions the determining factor in the mutual coagulation is electrical neutralisation by mutual adsorption of oppositely-charged particles. The mutual coagulation zone is broad if the positive sol, say, is quite pure and the negative sol contains an anion of high pptg. power. In these circumstances the coagulating action is only supplementary to the coagulation by mutual adsorption of the oppositely-charged particles. Variations of the order of pptg. power of a series of positive sols for different negative sols are presumably connected with the presence of electrolyte impurities.

H. B. WEISER (c).

Isoelectric precipitates and their properties. S. MATTSON (*Kolloid-Z.*, 1932, 58, 305—314).—Three kinds of isoelectric ppts. are recognised: (1) Amphoteric hydroxides, $\text{Al}(\text{OH})_3$, $\text{Th}(\text{OH})_4$, etc., the properties of which are explained by the representation $\text{Al}(\text{OH})_4^- + \text{Na}^+$ and $\text{Al}(\text{OH})_2^+ + \text{Cl}^-$, whilst the isoelectric depends on their sp. nature and the degree of dissociation. (2) The proteins, the isoelectric p_H of which depend on the relative strengths of the acidic and basic groups. (3) Ppts. formed from strong acids and bases (e.g., BaSO_4 and AgCl). Their behaviour depends on the solution pressure of the respective ions and on which is in excess and is generally independent of $[\text{H}^+]$. These three groups are termed "primary ampholytoids." "Derived ampholytoids" result from (a) two primary ampholytoids of different isoelectric point or (b) a primary ampholytoid and an ion with which it forms a non-dissociable compound. In the case of (a) the isoelectric point of the derived ampholytoid lies between those of the constituents; in case (b) the isoelectric point is displaced in one

direction by acid groups and in the other direction by basic groups. The facility for cation exchange increases as the isoelectric p_H is lowered, whilst the reverse holds for anion exchange. Ion exchange is attributed ultimately to residual OH' and H' . The behaviour of ampholytoids is characterised by the isoelectric point, the point of exchange-neutrality, and the end p_H . E. S. HEDGES.

Co-ordination of periodic structures. M. COPISAROW (J. Physical Chem., 1932, 36, 752—759).—Periodic effects have been observed in a variety of changes of state and heterogeneous reactions. Periodicity seems to bear no relation to the complexity and no. of the components. R. H. LAMBERT (c).

Periodic precipitation structures. M. COPISAROW (Nature, 1932, 129, 400—401).—A discussion. Periodic pptns. are not restricted to any sp. state or phase of matter or to any definite no. of components. They present a record of the undulatory movement in a mobile magma which characterises the relationship of matter and energy, and can be expressed in terms of wave mechanics. L. S. THEOBALD.

Periodic precipitation structures. E. S. HEDGES (Nature, 1932, 129, 400).

L. S. THEOBALD.

Periodic precipitation structures. S. C. BLACKTIN (Nature, 1932, 129, 401).—When a drop of oil is placed on a smoked glass and allowed to remain a periodic structure of concentric rings of C develops.

L. S. THEOBALD.

Preparation of upper liquids producing satisfactory boundary condition in cataphoretic measurements, and uncertainties of usual measurements of cataphoretic speed. J. N. MUKHERJEE (J. Physical Chem., 1932, 36, 595—603; cf. A., 1928, 1192; 1929, 143).—The conditions which must be satisfied before the movement of the boundary can be used for measuring the abs. rate of migration are discussed, and the difficulties of the microscopic method of measuring speed of cataphoresis reviewed.

F. E. BROWN (c).

Application of Mudd interfacial technique in the study of protective protein films in oil-in-water emulsions. R. L. NUGENT (J. Physical Chem., 1932, 36, 449—466).—The method used consists in bringing a drop of the emulsion into contact with a drop of oil under the microscope and observing the changes which occur at the interface. The interface moves into the H_2O , and particles with oily surfaces are swallowed up, aq. particles remain stationary or retreat before the interface, and particles wetted by both oil and H_2O remain in the interface. In an olive oil emulsion stabilised with gelatin the hydration of the protecting film of gelatin seems to vary with p_H in the same way as the hydration of the gelatin micelles. The results obtained make it possible to differentiate experimentally between the resistance of protective films to disruption and their hydration.

F. E. BROWN (c).

Pure silicic acid sols. Electrodialysis. A. LOTTERMOSER and H. J. KIEHN (Kolloid-Beih., 1932, 35, 123—164).—A study of the dialysis and electrodialysis of SiO_2 sols (prepared from Na_2SiO_3 and

various acids) by following the change of electric conductivity revealed no agreement among the sols; the course depends on the different degrees of adsorption of the acid anion. Electrodialysis of the SiO_2 sols is most complete using clay and collodion membranes in combination; during the process some Na^+ is replaced by H^+ , but not quantitatively. The $[\text{Cl}']$ of a sol prepared from Na_2SiO_3 and HCl increases during electrodialysis, probably due to desorption. Similar experiments were conducted with SiO_2 sols made by hydrolysis of SiCl_4 or $\text{Si}(\text{OMe})_4$ and by membrane hydrolysis of Na_2SiO_3 . It is inferred that electrolyte-free, purely acidoid SiO_2 sol cannot be prepared; the purest product is obtained by hydrolysing SiCl_4 by leading the vapour into H_2O .

E. S. HEDGES.

Relations between the concentration of silicic acid solutions and the silica gels produced therefrom. G. STOELTZNER (Kolloid-Z., 1932, 59, 60).—When the concn. ratio of $\text{HCl} : \text{Na}_2\text{SiO}_3$ is varied from 1 to 100, the amount of SiO_2 gel produced varies only in the ratio 1 : 2.

E. S. HEDGES.

Silicic acid gels. I. Measurements of surface tension during setting, and effect of temperature on time of setting. C. B. HURD and H. A. LETTERON (J. Physical Chem., 1932, 36, 604—615).—A graph of apparent surface tension against gel age suggests that gelation starts slowly, progresses rather uniformly, and then, as setting becomes imminent, passes rapidly through a period characterised by considerable changes. The time of gelation, t , of several mixtures was determined at 288 — 353° abs. On plotting $\log t$ against $1/\text{temp.}$, a series of parallel straight lines were obtained for the various gel concns. From this graph Q in the Arrhenius equation is calc. to be 16,940 g.-cal. The order of the reaction involved in the polymerisation of silicic acid depends on the p_H .

J. W. PERRY (c).

Activated silica gel; relation of activity to water content and temperature of activation. F. E. BARTELL and E. G. ALMY (J. Physical Chem., 1932, 36, 475—489).—The heat of wetting by H_2O affords a measure of the degree of activation of the gels, but the same relative activities would apparently be obtained with any other liquid which wets SiO_2 . The most active gels can be prepared by heating at 300° for about 2 hr. At temp. up to 500° the activity depends mainly on temp., time of heating becoming an important factor only at about 750° . Activation is attributed to removal of the H_2O present in the microcapillaries. If, however, by continued heating the H_2O mols. forming an integral part of the structure of the fibrils are removed, the porous structure collapses, in part at least, with attendant loss in activity. This may readily happen at temp. as much as 500° below the normal m. p. of the solid.

J. W. PERRY.

Heat of immersion of silica gel in various petroleum substances. R. W. STENZEL (J. Amer. Chem. Soc., 1932, 54, 870—876).—Heats of immersion in g.-cal. per g. are: cyclohexane, 6.5; n -decane, 7.8; n -hexane, 7.9; C_6H_6 , 13.1; H_2O , 25.4; n -butyl mercaptan, 25.9. Heats of immersion are the

best indication of the capillary characteristics of porous and finely-divided solids. F. E. BROWN (c).

Changes in viscosity of sols of cellulose nitrate and acetate. A. Y. DRINBERG (J. Appl. Chem., Russia, 1931, 4, 293—320).—Decrease in viscosity and in the degree of polymerisation of cellulose nitrate sols on ageing is attributed to the influence of electrolytes. CHEMICAL ABSTRACTS.

Dissolution and desolution of cellulose esters by homologous series of carbon compounds. S. E. SHEPPARD and S. S. SWEET (J. Physical Chem., 1932, 36, 819—829).—The pptn. of cellulose acetate from solution in COMe_2 on addition of members of various homologous series has been studied. The pptg. power of the added substance is markedly affected by the presence of OH and CO_2H groups, is lowered by branching of the C chain and, in aromatic compounds, by unsaturation, and for the higher members of a series is proportional to the mol. wt. With addition of H_2O the solvent power of COMe_2 rises to a max. and then falls again, the magnitude of the effect depending on the precipitant.

H. A. BEATTY (c).
Kinetic studies of the dissolution of cellulose acetate. W. OSTWALD and H. ORTLOFF (Kolloid-Z., 1932, 58, 295—297).—The velocity of dissolution of cellulose acetate in cyclohexanone, EtOAc, Me phthalate, and diacetone alcohol follows a normal course, but the curves representing the velocity of dissolution in $\text{CH}_2\text{Ph}\cdot\text{OH}$ and in COMeEt are complex and suggest "autopeptisation" (increased solubility due to the peptising action of the substance already in solution). The solubility varies with the amount of solid phase present. E. S. HEDGES.

Systematology of celluloses based on their viscosity in solution. H. FIKENTSCHER (Cellulosechem., 1932, 13, 71—74; cf. this vol., 335).—A function, which is sensitive to variations in structure, is found to be characteristic of a colloid over a wide concn. range (0.5—15%) when the relative η is not greater than 6000. Figures are given for many celluloses. J. L. D'SILVA.

Physico-chemical degradation of starch. E. HEINIGER (Kolloid-Beih., 1932, 25, 1—48).—Published work on the formation and characterisation of sol. starch is reviewed. Experiments are described on the characterisation of the solution remaining after centrifuging starch paste. The change in the properties of this solution obtained after repeated dispersion and re-setting of the paste has been examined. Differences in the yield of sol. matter and degree of hydration are attributed to differences in the temp. at which the paste is formed. The sp. gr. of the solutions is independent of the no. of settings, the surface tension is const., and the solution contains no reducing substance; viscosity vals. vary with the method of measurement. Centrifuging of starch paste (one setting) showed it to contain 65.2% of suspensoid material having a particle size $>1-1.5\mu$; the remainder includes 4.2% of highly-disperse non-adsorbable matter and 2.7% of ultrafiltrable material. E. S. HEDGES.

Lyophilic colloids. X. Capillary electric charge and hydration as state-variables of hydrophilic gels. II. Adsorption of iodine by agar gel and starch grains. H. G. B. DE JONG and J. C. LANZING (Kolloid-Beih., 1932, 35, 89—122).—The adsorption of I from KI solutions by agar gel is increased by the presence of neutral salts, which have the effect of increasing the val. of k in the adsorption isotherm without altering that of $1/n$. In the case of starch grains, the neutral salts have a definitely capillary-electric influence on the const. k ; this increases with the valency of the cation, whilst that of the anion is relatively unimportant. Lyotropic effects are observed with agar gel at higher concns. of electrolyte, but with starch at low concns. of neutral salt, giving the series $\text{Li} < \text{Na} < \text{K}$ and $\text{Mg} < \text{Sr}, \text{Ca} < \text{Ba}$. Capillary electric charge and hydration are regarded as variables of the gels on which the adsorption const. k depends. E. S. HEDGES.

Concentration of cations in clay sols. R. BRADFIELD (J. Physical Chem., 1932, 36, 340—347).—The concn. of cations at the surface of colloidal clay particles in a purified sol. is higher than in the intermicellar liquid, and the concn. of Ca^{++} and Ba^{++} is of about the same order of magnitude as in solutions of such salts as CaC_2O_4 and BaSO_4 . Addition of 50% $\text{Na}_2\text{C}_2\text{O}_4$ in excess of the amount required for complete pptn. removed 98% of Ca from a Ca-clay, but only 54.6% of Ba from a Ba-clay. Clays can decompose CaC_2O_4 and BaSO_4 , liberating anions in amounts comparable with those supplied in ordinary fertiliser practice. H. M. STARK (c).

Effect of diluting action of sucrose on viscosity of the colloidal suspension skim milk. A. LEIGHTON and A. LEVITON (J. Physical Chem., 1932, 36, 523—528).—The addition of 6% sucrose to skim milk increases the vol. of the liquid phase and lowers the viscosity so that 60—75% of the total lactose may be separated mechanically.

C. T. SNELL (c).
Internal friction of protein sols in relation to the composition of the ash. N. JERMOLENKO (Biochem. Z., 1932, 245, 182—188).—The relation of the viscosity of gelatin sols to the ash content is investigated. A lyotropic series is given in which the cations (with the same anions) are ranged in the order of their power to decrease the viscosity of gelatin sols: Ringer's solution $> \text{Li} > \text{Na} > \text{Ca}$.

P. W. CLUTTERBUCK.
Morphological and kinetic investigation of the protein molecule. II. Electrochemical analysis of the action of alkali on caseinogen. G. ETTISCH and G. V. SCHULZ (Biochem. Z., 1932, 245, 189—209).—A method of electrochemical analysis of protein is described depending on the potentiometric measurement of its affinity for Cu, and the conception of the Cu-titration curve is introduced. Changes with caseinogen on addition of varying amounts of alkali are followed. The Cu-affinity increases discontinuously in stages, the complete series of stages from p_H 9.7 to 12.6 being surveyed. The titration curves suggest the presence of two groups, the affinity of both groups towards Cu increasing with increasing p_H . P. W. CLUTTERBUCK.

Evidence of structure in gelatin gels. A. G. OLSEN (J. Physical Chem., 1932, 36, 529—533).—For gels having approx. the same jelly strength, the time required to melt at 22.5° depends on the previous history; gels solidified and stored at 0° melt more quickly than those solidified at either 0° or 14.5° and then stored at 14.5°. For the latter the time of melting increases with duration of storage. It is concluded that gelation involves both solidification and orientation. At 0° the latter is largely prevented, whilst at 14.5° both occur. Since destruction of structure at temp. above the m. p. proceeds slowly, gels stored at 14.5° melt more slowly than those kept at 0°.

J. W. PERRY (c).

Free and bound water in elastic and non-elastic gels. I. D. JONES and R. A. GORTNER (J. Physical Chem., 1932, 36, 387—436; cf. A., 1916, ii, 230; 1925, ii, 777).—Dilatometric methods show that free H₂O in gelatin gel freezes at about -6°; "bound" H₂O is not frozen at -50.0°. The amount of bound H₂O varies with the concn., 0.70 g. of H₂O per g. of dry gelatin being bound in a 32% gel and 4.675 g. in a 2% gel. The freezing of H₂O both in gelatin gel and in the thick portion of fresh egg-white is completely reversible. The amount of "capillary H₂O" which can be frozen from Fe(OH)₃ gel and from activated SiO₂ gel varies linearly with the temp. Capillary H₂O freezes more rapidly below -30.0° than above.

C. T. SNELL (c).

Peptisation of gels by electrolytes. A. P. BUNTIN (J. Gen. Chem. Russ., 1931, 1, 943—963).—The product of peptisation of Fe(OH)₃ or Al(OH)₃ by various salts and acids may be a mixture of hydrated and peptised sols. Peptisation velocity curves are S-shaped; this is ascribed to difficulty of contact of peptiser with unpeptised gel in the initial stages of the reaction. Peptisation may in some cases be due to formation of salt from the gel with subsequent hydrolysis of the salt to yield hydroxide hydrosol and free acid.

R. TRUSZKOWSKI.

Electrochemical method of following changes in gelatin solutions as a function of time. P. JACQUET (Compt. rend., 1932, 194, 870—872).—Electrolysis of CuSO₄ solutions to which gelatin has been added is said to exhibit contraction effects at the electrodes which are very sensitive to the method of preparing the gelatin solutions (cf. A., 1928, 837).

C. A. SILBERRAD.

Freezing of oxide gels and oxide sols. A. LOTTERMOSER and F. LANGENSCHIEDT (Kolloid-Z., 1932, 58, 336—341).—When gels of Fe₂O₃, Al₂O₃, Cr₂O₃, ThO₂, and SiO₂ are cooled at -20° for 1 hr. the vol. decreases greatly and a flaky deposit forms. The deposit of Al₂O₃ is insol. in acids and can therefore be separated from a small quantity of Fe₂O₃ by treating with HCl. It is suggested that this separation may be useful in the prep. of Fe-free Al₂(SO₄)₃ for the textile and paper industries. Only the Al₂O₃ gel assumes a marked cryst. structure after freezing when examined by the Debye-Scherrer X-ray method. The behaviour of the corresponding sols on freezing is similar in the main, but an increase in the electrolyte content retards or prevents the pptn.

E. S. HEDGES.

A heat-coagulable protein in gelatin. S. E. SHEPPARD, J. H. HUDSON, and R. C. HOUCK (Kolloid-Z., 1932, 58, 348—351).—By hydrolysing gelatin with AcOH at about the isoelectric point for 12 hr. at 80—100° a clear solution and a coagulum of protein are formed. The protein has an isoelectric point between p_H 3.9 and 4.2 and contains about 18% N.

E. S. HEDGES.

Coacervation of gelatin and chondroitin-sulphuric acid. H. R. KRUYT and A. H. A. DE WILLEM (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1271—1281).—The prep. of chondroitin-sulphuric acid is described; the sol contains negatively-charged particles and its viscosity follows Poiseuille's law. The coacervation phenomena of the mixture with gelatin resemble those of the gelatin-gum arabic mixture. Curves relating viscosity to the composition of the mixture show marked min., which are characteristic of the dehydration causing the coacervation. These min. correspond with the max. of turbidity.

E. S. HEDGES.

Hydration or combined water of gelatin. T. MORAN (Proc. Roy. Soc., 1932, A, 135, 411—428).—If pure ice separates on freezing a gelatin gel, the equilibrium concn. of the frozen gel is a function of the temp. and is independent of the concn. of the gel before freezing and of the rate of cooling. Below -20° the concn. is const. and the H₂O content of the gel is 0.5 g. per g. of gelatin (approx.). NaCl, KCl, and NaNO₃ reduce the combined H₂O to its limiting val. of 0.5 g. at all temp. Sucrose also reduces the combined H₂O in the gel, but not to the same extent. From a consideration of the activity of the H₂O in the gelatin gels an attempt is made to calculate the combined H₂O.

L. L. BIRCUMSHAW.

Structure of gelatin. J. J. TRILLAT (Ann. Inst. Pasteur, 1932, 48, 400—412, and J. Chim. phys., 1932, 29, 1—10).—X-Ray study of gelatin films shows that during the process of drying the micelles become oriented in directions parallel to the supporting surface. When the gelatin is stretched to twice the initial length an intense orientation of micelles occurs in the direction of stretching. The mechanical properties change simultaneously. A variation with the p_H of the gelatin was not observed. The results suggest that gelatin is composed of a highly polymerised portion, probably formed of chains of NH₂ acids, arranged in a network resembling that of a sponge and enclosing a less polymerised, amorphous form. The amorphous portion is capable of slight orientation by drying or by stretching, but the orientation of the network caused by stretching gives rise to X-ray diffraction effects similar to those produced by crystals. The swelling produced by immersing gelatin in H₂O influences the X-ray diagram in a way which suggests that the H₂O mixes with the amorphous phase, and widens the net-work of the highly-polymerised portion. The identity period is normally about 9.5 Å.

E. S. HEDGES.

Role of water in gelatin sols and gels. H. BINGER (Kolloid-Z., 1932, 59, 88—93).—Published work on the solvation of gelatin and its dependence on temp. is reviewed. Probably forces other than adsorption are involved.

E. S. HEDGES.

Viscosity of gelatin sols in relation to concentration. H. BINCER (*Kolloid-Z.*, 1932, 59, 82—87).—The viscosity of gelatin solutions increases with concn. more rapidly than is expressed by the Fickenscher-Mark formula (A., 1929, 1379). The increase of sp. viscosity is attributed to increasing association of the gelatin particles at higher concns.; a similar effect is observed with sucrose solutions, in which the mols. are known to associate as the concn. is increased. With rising temp. the association decreases. In general, the sp. viscosity of gelatin increases as the m. p. rises.

E. S. HEDGES.

Combining weight of gelatin as an acid. A. L. FERGUSON and A. W. SCHLUCHTER (*J. Gen. Physiol.*, 1932, 15, 463—475).—Conductivity measurements for three concns. of gelatin indicate that the addition of gelatin to NaOH does not change the concn. of Na⁺ in solution. A given amount of gelatin reacts with the same amount of NaOH independently of the NaOH concn. or the ratio NaOH/gelatin, provided hydrolysis does not take place, and the combining wt. of gelatin as an acid is 1370 g.

A. LAWSON.

Separate diffusion of Liesegang reagents in gelatin. (Mlle.) S. VEIL (*Compt. rend.*, 1932, 194, 1155—1157).—The aureole of a drop of aq. $K_2Cr_2O_7$ on gelatin shows no discontinuity; that of aq. $AgNO_3$ shows turbidity which decreases parabolically, and may be stratified (cf. A., 1917, ii, 454; 1931, 563). On applying an electric field the aureole of $K_2Cr_2O_7$ is deformed as if attracted by the anode, that of $AgNO_3$ the reverse (cf. A., 1929, 1382).

C. A. SILBERRAD.

Water-gas equilibrium. J. R. PARTINGTON and W. G. SHILLING (*J.S.C.I.*, 1932, 51, 82T).—A reply to criticisms by Bryant (cf. A., 1931, 1233) of the authors' previous paper (*J.S.C.I.*, 1925, 44, 149T, 242T).

Electrolytic dissociation. II. K. FREDENHAGEN (*Z. physikal. Chem.*, 1932, 159, 81—98; cf. A., 1931, 430, 799).—A reply to Hammerschmid and Lange's criticisms (A., 1931, 1010).

R. CUTHILL.

[Electrolytic dissociation.] H. HAMMERSCHMID and E. LANGE (*Z. physikal. Chem.*, 1932, 159, 100—109).—A reply to Fredenhagen (cf. preceding abstract).

R. CUTHILL.

[Electrolytic dissociation.] K. FREDENHAGEN (*Z. physikal. Chem.*, 1932, 159, 110—114).—A reply to Hammerschmid and Lange (cf. preceding abstract).

R. CUTHILL.

Activity coefficients of silver ion in aqueous solutions of some strong electrolytes. I. J. B. CHLOUPEK and V. Z. DANEŠ (*Coll. Czech. Chem. Comm.*, 1932, 4, 124—138).—Activity coeffs. in Ag_2SO_4 solutions up to saturation at 25° have been calc. from e.m.f. measurements on cells with liquid junctions, using various salt bridges, and agreement with the Debye-Hückel equation is reported.

C. W. DAVIES.

Dilute hydrochloric acid solutions and the Debye-Hückel theory. N. F. HALL (*J. Amer. Chem. Soc.*, 1932, 54, 831—832).—Carmody's determinations (this vol., 342) give 0.46 as the mean val. of $-\log \gamma/m^{1/2}$, the difference between which figure and the rather lower Debye-Hückel val. may be accounted

for by uncertainties in the e.m.f. measurements. The data give no support to Davies' view that the limiting val. of the ratio is nearer 0.38.

C. J. WEST (c).

Acidity of acids and their chemical alteration by solvents. A. HANTZSCH and W. LANGBEIN (*Z. anorg. Chem.*, 1932, 204, 193—207; cf. A., 1929, 666).—Conductivities and rates of decomp. of $N_2CH \cdot CO_2Et$ by solutions of a no. of strong acids in AcOH have been measured with a view to determine their relative acidities. Both methods agree in showing the following order of decreasing acidity: $HClO_4$, $CCl_3 \cdot SO_3H$, $C_6H_4Me \cdot SO_3H$, $Ph \cdot N_2 \cdot C_6H_4 \cdot SO_3H$, H_2SO_4 , $(OMe)_2C_6H_3 \cdot SO_3H$, $C_6H_3Me_2 \cdot SO_3H$, HNO_3 , $C_2(CO_2H)_2$, $CCl_3 \cdot CO_2H$. The influence of various solvents on the acidity of $CCl_3 \cdot CO_2H$, as judged from the action on $N_2CH \cdot CO_2Et$, was also studied. The results are discussed.

F. L. USHER.

Hydration of the solute ions of the lighter elements. L. H. FLINT (*J. Washington Acad. Sci.*, 1932, 22, 97—119).—Calculations are based on the assumption that ionisation involves unit change in the equiv. wt. of an element.

C. W. DAVIES.

Behaviour of amphoteric ions and multivalent ions towards far-distant charges in electrolyte solutions. G. SCATCHARD and J. G. KIRKWOOD (*Physical Z.*, 1932, 33, 297—300).—Mathematical.

J. W. SMITH.

Thermodynamic properties of aqueous sodium chloride solutions from 0° to 40°. H. S. HARNED and L. F. NIMS (*J. Amer. Chem. Soc.*, 1932, 54, 423—432).—From measurements of the e.m.f. of the cell $Ag|AgCl|NaCl(M)|Na \ Hg|NaCl(0.1M)|AgCl|Ag$, the activity coeffs. of NaCl in aq. solution have been calc. from 0.05 to 4.0M, and used to compute the relative partial mol. heat content and the partial mol. heat capacity between 0° and 40°.

F. D. ROSSINI (c).

Iodine monochloride in hydrochloric acid solution. J. H. FAULL, jun., and S. BÆCKSTRÖM (*J. Amer. Chem. Soc.*, 1932, 54, 620—621; cf. A., 1926, 128).—Experimental evidence is adduced to show that there is little, if any, I⁺ in aq. ICl (cf. A., 1930, 1520). In HCl solution there is considerable formation of ICl_2' .

L. KELLEY (c).

Constitution of ammoniacal copper salt solutions. F. ROSENBLATT (*Z. anorg. Chem.*, 1932, 204, 351—364).—Optical data show that when a Cu diethylenediamine salt, which forms in H_2O the diaquo-salt $[Cu en_2(H_2O)_2]X_2$, is dissolved in aq. NH_3 containing increasing quantities of NH_3 , 1 mol. of H_2O is gradually replaced by NH_3 to form $[Cu en_2(H_2O)(NH_3)]X_2$. This is independent of the nature of X. Approx. 1/4 of the original salt is changed in N aq. NH_3 , 1/2 in 3N, and 3/4 in 7N. Only 3 mols. of C_5H_5N are taken up by $CuCl_2$ in solution. NH_3 with a Cu salt forms the tetrammine quantitatively at first, but this gradually changes to the pentammine with increasing concn. of NH_3 . There appear to be two forms of the tetrammine with different light absorption coeff. They are probably the diaquo-salt $[Cu(NH_3)_4(H_2O)_2]X_2$ and the anhyd. salt $[Cu(NH_3)_4]X_2$. The configuration of the complex salts is discussed.

M. S. BURR.

Peptides of tervalent amino-acids. II. Titration constants of tyrosyltyrosine and glycyltyrosine. J. P. GREENSTEIN (J. Biol. Chem., 1932, 95, 465—475; cf. this vol., 71).—Electrometric titration of glycyl- and tyrosyl-tyrosine solutions with HCl and NaOH indicates that the dissociation of the $C_6H_4\cdot OH$ group is increased by the proximity of the NH_2 and decreased by that of the CO_2H group. The free NH_2 and CO_2H groups are weaker in the tyrosine peptides than in the free NH_2 -acid; the isoelectric points of the former are more acid than that of tyrosine.

H. DAVSON.

Organic acid iron solutions. III. Complex-colloid equilibrium. N. J. HARRAR and F. E. E. GERMANN (J. Physical Chem., 1932, 36, 688—695).—The most important of the factors determining the properties of these org. Fe complexes is the strength of the acid. The solutions may contain several complexes. The ions present range from Fe^{+++} for very strong acids, through green $[Fe_3(RCO_2)_6]^{+++}$ for strong acids, $[Fe_3(RCO_2)_6]^{++}$ for weak acids, red $[Fe_3(RCO_2)_6(OH)]^+$, and $[Fe_3(RCO_2)_6(OH)_2]$ to colloidal $Fe(OH)_3$ for very weak acids.

I. J. PATTON (c).

System: nitric oxide-nitrogen peroxide. I. R. H. PURCELL and G. H. CHEESMAN (J.C.S., 1932, 826—834).—V. p. over both liquid and solid phases in the system $NO-NO_2$ have been determined between 100° and 300° abs., and are used to interpret the properties of N_2O_3 .

F. L. USHER.

Two-component salt mixtures of lead nitrate with sodium or potassium nitrate. H. M. GLASS, K. LAYBOURN, and W. M. MADGIN (J.C.S., 1932, 874—880).—The f.-p. curves are both of the simple eutectic type. Immiscibility in the solid state is confirmed by photomicrographs. The temp. of incipient decomp. rises with dilution of $Pb(NO_3)_2$ in each mixture.

F. L. USHER.

Higher aliphatic compounds. II. Systems hexadecyl iodide-octadecyl iodide and hexadecane-octadecane. J. C. SMITH (J.C.S., 1932, 737—741; cf. A., 1931, 684, 911).—The m.-p. curve of mixtures of $C_{16}H_{33}I$ and $C_{18}H_{37}I$ shows a eutectic point at 20.1° (22 mol.-% of $C_{18}H_{37}I$) and the presence of an equimol. compound. There is evidence of polymorphism of $C_{16}H_{33}I$. Pure $C_{16}H_{33}I$ has m. p. 23.33° and $C_{18}H_{37}I$ 32.94° . M.-p. and f.-p. curves of mixtures of $C_{16}H_{34}$ and $C_{18}H_{38}$ indicate formation of mixed crystals. Both substances are polymorphic. $C_{16}H_{34}$ has m. p. 18.1° (metastable 16.2°), and $C_{18}H_{38}$ 27.90° (metastable 27.3°).

F. L. USHER.

Thermal dissociation of metal oxides, sulphides, and halides. A. F. KAPUSTINSKY (Z. Elektrochem., 1932, 38, 114—117).—A method is described for determining equilibria between H_2 , on the one hand, and compounds of metals with O, S, Cl, Br, I, etc. on the other, by making use of the principle that at equilibrium the partial pressure on each side of a semi-permeable membrane of Pt, Pd, and Ir is the same. The method has been tested and found satisfactory by determining the equilibrium ratio of p_{H_2S}/p_{H_2} at different temp. for H_2 in contact with Ag_2S .

M. S. BURR.

Thermal dissociation of oxides and peroxides. III. Lithium and potassium peroxides. M. BLUMENTHAL (Rocz. Chem., 1932, 12, 119—134).—The dissociation pressures of Li_2O_2 ($43-198^\circ$) and K peroxides ($198-703^\circ$) have been determined by a dynamic method; the data are reproduced by a Nernst's equation: $\log p = Q/4.571T + 1.75T + ET/4.571 + 2.8$. For Li_2O_2 Q is 13.6 kg.-cal. and E is -0.0710 ; for $2K_2O_4 \rightarrow 2K_2O_3 + O_2$ $Q = +9.9$ kg.-cal., $E = -0.0145$; for $2K_2O_3 \rightarrow 2K_2O_2 + O_2$ $Q = +13.0$, $E = -0.0125$; and for $2K_2O_2 \rightarrow 2K_2O + O_2$ $Q = +53.0$, $E = +0.0329$.

R. TRUSZKOWSKI.

Oxides. VI. Oxides of manganese. A. SIMON and F. FEHÉR (Z. Elektrochem., 1932, 38, 137—148).—The dissociation pressure curve for Mn_2O_7 shows a marked discontinuity at 10° where the O_2 pressure is 7 mm. Above this temp. the pressure rises rapidly. The pressures obtained are not equilibrium vals., which are established too slowly to be determined. Above 14° , however, the system is so far above the transition point that explosive decomp. to MnO_3 may take place. The isobaric dissociation curve of Mn_2O_7 at 3 mm. pressure indicates that the oxide breaks down directly into MnO_2 without the formation of any intermediate oxides. Mn_2O_7 is slightly sol. in MnO_2 . Calculation from thermochemical data of the true equilibrium pressure at 10° gives a val. of the order of 10^{50} mm. The isobaric dissociation curve of MnO_2 at approx. 10 mm. shows the successive formation of Mn_2O_3 , Mn_3O_4 , and MnO , and no other intermediate oxides, but the course of the curve indicates the formation of solid solutions. The formation of MnO is practically complete at 1300° . The following heats of dissociation (kg.-cal.) have been calc.: $2Mn + 3.5O_2$, 170; $2MnO_2 + 1.5O_2$, 82; $2Mn_2O_3 + O_2$, 26; $4Mn_3O_4 + O_2$, 54; $6MnO + O_2$, 72. These are not in all cases in agreement with calorimetric measurements.

M. S. BURR.

Dissociation of lithium and potassium carbonates. J. T. HOWARTH and W. E. S. TURNER (J. Soc. Glass Tech., 1931, 15, 360—364T; cf. A., 1931, 800).—The recorded pressures in mm. Hg (K_2CO_3 in parentheses) are: 800° 3.1, 850° 8.1, 900° 17.4, 950° 32.7 (1.2), 1000° 65.2 (2.1), 1050° 89.1 (4.6), 1100° 134.4 (7.4), 1150° (9.2), 1200° (10.3), 1250° (11.7), 1300° (15.1), 1350° (19.6), 1400° (35.6).

M. PARKIN.

Redetermination of thermal dissociation equilibria of inorganic compounds. II. Determination of dissociation equilibria of strontium carbonate by means of high-temperature vacuum balance. S. TAMARU and K. SIOMI (Z. physikal. Chem., 1932, 159, 227—230; cf. this vol., 124).—The dissociation pressure, p , between 800° and 1250° may be represented by $\log p = -49,090/4.575T + 9.933$; p reaches 1 atm. at 1250.5° . Since p is independent of the composition of the solid phase, neither basic carbonate nor a solid solution of oxide in carbonate is formed.

R. CUTHILL.

Thermal analysis of the system $AlBr_3-C_5H_5N$. V. A. PLOTNIKOV and S. S. VALJASNY (J. Gen. Chem. Russ., 1931, 1, 823—825).—The m.-p. diagram indicates the formation of the compounds, $Al_2Br_6\cdot C_5H_5N$, m. p. 83° , $2Al_2Br_6\cdot 3C_5H_5N$, and

$\text{AlBr}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$, m. p. 98° . In the electrolysis of $\text{AlBr}_3\text{-C}_5\text{H}_5\text{N}$ mixtures of m. p. $<45^\circ$ Al is deposited on the cathode.

R. TRUSZKOWSKI.

Calcium oxide-phosphoric acid compounds. M. A. BREDIG, H. H. FRANCK, and H. FULDNER (Z. Elektrochem., 1932, 38, 158—164).—A phase diagram for $\text{Ca}_3\text{P}_2\text{O}_8\text{-CaO}$ has been constructed from the available data. X-Ray spectra reveal two cryst. forms of pure $\text{Ca}_3\text{P}_2\text{O}_8$, β and γ , transition point about 1180° . A third form, α , may be due to the formation of mixed crystals with a hydrate or with CaO giving an apatite structure. At higher temp. it gives oxyapatite. Tetracalcium phosphate, $\text{Ca}_4\text{P}_2\text{O}_9$, is a fourth cryst. type which, by maintaining at temp. between 700° and 1400° , is completely transformed into the oxyapatite form of the α -phase. In the system $\text{Ca}_3\text{P}_2\text{O}_8\text{-CaO-SiO}_2$, X-ray examination reveals the presence of silicocarnotite, $\text{Ca}_3\text{P}_2\text{O}_8 \cdot 2\text{CaO} \cdot \text{SiO}_2$, which is still stable when maintained at a temp. of 1000° and requires a temp. of 1400° for its formation. Under certain conditions a further cryst. type of unknown constitution is obtained.

M. S. BURR.

Calcium cyanamide. III. Hydrolytic equilibrium of the alkaline-earth cyanamides. H. H. FRANCK and C. FREITAG (Z. Elektrochem., 1932, 38, 240—247).—The val. of $K_p = p_{\text{H}_2\text{O}}/p_{\text{NH}_3}^2$ for the reaction $\text{M}^{\text{CN}}\text{CN}_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{M}^{\text{CO}_3} + 2\text{NH}_3$ has been determined. The results are expressed by: $\log K = -\log T + 4.2$, where S is 12,580, 13,720, and 14,850 for Ca, Sr, and Ba, respectively.

M. S. BURR.

Thermal analysis of artificial aluminosilicates. J. K. DELIMARSKI (Ukrain. Chem. J., 1931, 6, [Tech.], 175—185).—The temp.-time curve for Al_2O_3 prepared by ignition of $\text{Al}(\text{NO}_3)_3$ exhibits a sharp rise between 900° and 1000° ; this phenomenon is not observed with Al_2O_3 obtained from other sources. Aluminosilicates prepared by mixing aluminates and silicates in alkaline solution exhibit an exothermic effect between 900° and 1000° ; this effect is rendered less marked if alkalis are present in the complex. It is concluded that the ppt. obtained from such alkaline solutions is a compound and not a mixture of Al_2O_3 and SiO_2 .

R. TRUSZKOWSKI.

Equilibria between solid and liquid in mixtures of derivatives of malic and tartaric acids. J. TIMMERMANS and (MME.) VESSELOVSKY (Bull. Soc. chim. Belg., 1932, 41, 53—63).—Eutectics are formed between *d*- and *l*-tartaric acids and *l*-aspartic acid; *d*- and *l*-chlorosuccinic acids and *l*-asparagine; *l*-malamide and *d*-tartaric acid amide; Me *l*-tartrate and Me *l*-malate; and between *d*- and *l*-Me tartrate and Me *l*-chlorosuccinate. *l*-Malamide forms an equimol. compound with *d*-tartaric acid amide, and this occurs probably also with Me *d*-tartrate and Me *l*-malate. In general, in a binary mixture containing the amide or Me ester of malic acid and the amide or Me ester of tartaric acid, a eutectic mixture is formed only if both compounds are dextro- or laevo-rotatory; otherwise a racemic mixture is formed. This generalisation does not apply to mixtures containing other acids or their derivatives.

H. F. GILLBE.

Singular folds of the ternary system $\text{Na}_2\text{O-H}_2\text{Br}_2\text{-H}_2\text{O}$. V. I. NIKOLAEV and M. I. RAVITSCH (J.

Gen. Chem. Russ., 1931, 1, 785—791).—The solid phases consist of NaBr and NaBr· $2\text{H}_2\text{O}$ at 25° and 45° , and of NaBr alone at 65° . Below -22° NaBr· $2\text{H}_2\text{O}$ and NaBr· $5\text{H}_2\text{O}$ crystallise out.

R. TRUSZKOWSKI.

Heterogeneous equilibria in the system $\text{CdCl}_2\text{-KCl-H}_2\text{O}$. H. HERING (Compt. rend., 1932, 194, 1157—1160).—KCl·CdCl₂ crystallises anhyd. above 36.5° and with H_2O below. $4\text{KCl} \cdot \text{CdCl}_2$ is decomposed by H_2O to form KCl·CdCl₂· H_2O between -8.1° and 12.9° , and KCl·CdCl₂ between 12.9° and 60° ; it melts with separation of KCl at 461° . KCl· $3\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$ exists from the ternary eutectic (-10.3°) to about 107° ; it is decomposed by H_2O to KCl·CdCl₂· H_2O hydrated below 28.8° , anhyd. above. A thermal diagram is given (cf. A., 1905, ii, 375; 1914, ii, 205, 428; 1916, ii, 122; 1923, ii, 534).

C. A. SILBERRAD.

Composition of the systems [formed by] ammonium chloride with nickel, cobalt, cupric, magnesium, manganese, and zinc chloride. B. SREBROV (Kolloid-Z., 1932, 58, 298—302).—Analysis of the crystals obtained from solutions containing NH_4Cl and the above heavy metal chlorides shows that the Cl content is never stoichiometric and is always in excess. The H_2O content is small and very variable and bears no relation to that of the heavy metal chloride. The H_2O and Cl are regarded as in inner adsorption.

E. S. HEDGES.

Atomic number and heat of formation. W. A. ROTH and G. BECKER (Z. physikal. Chem., 1932, 159, 1—26).—The following heats of formation at const. pressure at 20° have been determined: Ga_2O_3 , 255.8 ; SiO_2 (α -quartz), 207.8 ; TiO_2 (rutile), 218.7 ± 0.3 ; ZrO_2 , 258.1 ± 0.6 ; HfO_2 , 271.5 ; ThO_2 , 292.6 ± 1.4 ; Nb_2O_5 , 460.4 ; GeO_2 , 127.3 ± 0.5 kg.-cal. The following heats of formation have been calc.: SiCl_4 , 154.0 ; TiCl_4 , 185 ; ZrC , 45 ; ThC_2 , 45.7 kg.-cal. A crit. examination of the heats of formation of oxides and chlorides of elements in groups 1—6 of the periodic classification has shown that only in exceptional cases is there any linear relation between the at. no. and the heat of formation.

R. CUTHILL.

Physical chemistry of rhenium. W. A. ROTH and G. BECKER (Z. physikal. Chem., 1932, 159, 27—39).—The integral heats of dissolution in H_2O of Re_2O_7 , KReO_4 , and KMnO_4 have been determined at about 20° at various concns. Conductivity measurements show HReO_4 to be a strong acid and the mobility of ReO_4^- at 18° is 44 ± 1 . The heat of neutralisation of HReO_4 aq. with KOH is 13.5 ± 0.1 kg.-cal. at infinite dilution. At 20° and const. pressure the heat of formation of Re_2O_7 is 295.5 ± 2 , from which the heat of formation of KReO_4 is 262 kg.-cal. A saturated aq. solution of KReO_4 at 18° is $0.0329N$.

R. CUTHILL.

Thermochemistry of sulphur dioxide. W. A. ROTH and H. ZEUMER (Z. Elektrochem., 1932, 38, 164—170).—New thermal data for SO_2 are as follows: Heat of vaporisation at 21° , 5.68 ± 0.01 kg.-cal. Heat of dissolution of gaseous SO_2 (by three different methods) for the concn. range N (mol. H_2O to 1 mol. SO_2) $37\text{—}7570$, $Q = 5.920 + 1.75 \log N + 0.20875(\log N)^2$, mean deviation 0.02 kg.-cal. The vals. are higher

than those deduced from the temp.-solubility curve. The curve for heat of neutralisation of gaseous SO_2 with aq. KOH for N 42—3400 has a slight min. for which a complete explanation cannot be offered. The heat of ionisation of the first stage of H_2SO_3 is 4.34 and of the second 2.3 kg.-cal. The true heat of dissolution of SO_2 without ionisation is 6.70 kg.-cal. ($v=8-128$), practically the same as for CO_2 . The wt. of 1 litre of SO_2 at 20.3° and 750 mm. is 2.6609 g. The heat of neutralisation of HNO_3 , 7.751 H_2O with aq. NaOH at 21° for N 225—320 was found to be 14.44 ± 0.01 kg.-cal. M. S. BURR.

Thermochemistry of sulphur dioxide. W. A. ROTH and H. ZEUMER (Z. Elektrochem., 1932, 38, 248; cf. preceding abstract).—The striking variation of the heat of neutralisation of $(\text{SO}_2) + 2\text{KOH}$, aq. with concn. is probably due to the difference in the heats of dilution of KOH, aq. and K_2SO_3 , aq.

M. S. BURR.

Heats of formation of nitrides. II. Heats of nitrogenation of lithium, aluminium, beryllium, and magnesium. B. NEUMANN, C. KROGER, and H. HAEBLER (Z. anorg. Chem., 1932, 204, 81—96; cf. A., 1931, 432).—Direct measurements by the method previously described gave the following results: Li_3N $47,166 \pm 308$, AlN $57,400 \pm 750$, Be_3N_2 $133,470 \pm 620$ g.-cal. Vals. obtained for Mg_3N_2 depended on the crucible material, being higher when the Pt crucible was lined with MgO . Mn and Cr absorb N_2 readily in presence of Li_3N , but the product is a complex compound of Li_3N with the other nitride.

F. L. USHER.

Pyrolysis, densities, and heats of dissolution and hydration of iodine pentoxide and its hydrates. E. MOLES and A. PÉREZ VITORIA (Anal. Fis. Quim., 1932, 30, 99—119).—Thermal decomp. of HIO_3 yields at 70° $3\text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and at 200° I_2O_5 ; no other hydrate appears to exist. Decomp. of I_2O_5 commences at 275° , irrespective of the presence of decomp. products. HIO_3 has d 4.6504 (lit. 4.869), and $3\text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$ d 4.734. The heats of dissolution of HIO_3 , $3\text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$, and I_2O_5 are -2697 , -9227 , and -601 g.-cal., respectively; the heat of formation of $3\text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$ from I_2O_5 is thus 937 g.-cal., and that of HIO_3 from I_2O_5 2096 g.-cal. H. F. GILLBE.

Absorption determinations in pure liquids and solutions of electrolytes in the range of short electric waves. J. MALSCH (Ann. Physik, 1932, [v], 12, 865—888).—A new method for the direct determination of the heat developed by absorption of high-frequency radiation by liquids is described, and results are given for a series of alcohols and other org. liquids. The wave-lengths used were 76, 48, and 28 m. Results for alcohols are in good agreement with the dipole theory. The applicability of the method to the abs. determination of the high-frequency conductivity of solutions of electrolytes is discussed with reference to results obtained with solutions of AgNO_3 in EtOH and FeCl_3 in EtOH. The results are in agreement with the Debye-Falkenhagen theory.

A. J. MEE.

Electrical conductivity method for determining effective capillary dimensions of wood. A. J. STAMM (J. Physical Chem., 1932, 36, 312—325).—The

ratio of effective capillary length to the effective continuous capillary cross-section has been determined by means of measurements of the resistance of salt solutions filling the wood structure, and by combination with hydrostatic flow data the average radius of the effective capillaries in various kinds of wood has been determined. F. URBAN (c).

Physico-chemical study of the rare-earth sulphates. B. BRAUNER and E. ŠVAGR (Coll. Czech. Chem. Comm., 1932, 4, 49—68).—The electrical conductivities of aq. solutions of the normal and acid sulphates of Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Er, and Th have been measured and the basicity of the normal sulphates has been determined by the rate of inversion of sucrose and the rate of hydrolysis of MeOAc. Experimental results are given, but discussion of them is reserved for a further paper.

E. S. HEDGES.

Mobility of the gelatinate ion. A. L. FERGUSON and A. W. SCHLUCHTER (J. Gen. Physiol., 1932, 15, 477—485).—Comparison of the boundary potentials for the two systems $\text{H}_2[\text{NaOH}][\text{NaOH} + x \text{ g. gelatin}]\text{H}_2$, and $\text{H}_2[\text{NaOH}][\text{KCl}][\text{NaOH} + x \text{ g. gelatin}]\text{H}_2$, with the corresponding vals. given by the Henderson formula indicates that the mobility of the gelatinate ion is about 20.

A. LAWSON.

Some experimental support for Stern's theory of the electrolytic double layer. J. ST. L. PHILPOT (Phil. Mag., 1932, [vii], 13, 775—795).—The capacity per sq. cm. at const. potential of the electrolytic double layer on Hg was measured with a dropping Hg electrode in aq. HCl and NaCl. The results agree with Stern's equation (Z. Elektrochem., 1924, 30, 508).

H. J. EMELÉUS.

Stick antimony electrode: preparation and calibration. L. R. PARKS and H. C. BEARD (J. Amer. Chem. Soc., 1932, 54, 856—864).—In unstirred solutions in contact with air this electrode gives reproducible readings rapidly. When the solution is in equilibrium with Sb and Sb_2O_3 , $E_c = 0.030 + 0.5915p_{\text{H}}$ between p_{H} 2 and 7. Stirring of the solution causes errors. J. H. MOORE (c).

Problem of the sodium amalgam electrode in dilute solutions. J. ST. L. PHILPOT, N. L. ROSS-KANE, and J. H. WOLFENDEN (Phil. Mag., 1932, [vii], 13, 795—805).—The disturbing factors in c.m.f. measurements with a Na amalgam electrode in aq. NaCl at high dilutions have been investigated. A mechanism for the electrode process is suggested.

H. J. EMELÉUS.

Composition of manganese amalgam and manganese-silver alloys in relation to the electrode potential of manganese. H. D. ROYCE and L. KAHLBERG (Trans. Amer. Electrochem. Soc., 1931, 59, 91—103).—A Mn-Ag alloy containing 31 at.-% Mn ($e_h = -0.295$ volt in 0.5N- MnCl_2) displaced Cu readily and Ni and Co slowly from their 5% sulphate solutions, but did not displace Zn, Cd, or Fe. An alloy with 29 at.-% Mn ($e_h = -0.04$ volt in 0.5N- MnCl_2) did not displace Ag nor any of the above metals from their sulphate solutions (cf. Siebe, A., 1920, ii, 39). The micro-structure of the 31% alloy shows crystals of Ag_2Mn in a eutectic of Ag_2Mn

+Ag, and the electromotive behaviour of this alloy is considered to be determined by Ag_2Mn . By subjecting Mn amalgam to increasing pressures, Hg is expressed and the composition of the amalgam is a linear function of pressure up to a crit. val. above which little further change in composition occurs. At room temp. the crit. pressure is about 100,000 lb. per sq. in. and the amalgam then consists of Mn_2Hg_5 , but at 90° the crit. pressure is about 140,000 lb. per sq. in. and the composition then corresponds closely with MnHg . At room temp. the liquid phase in equilibrium with Mn_2Hg_5 contains 0.0031% of Mn. The conditions for determining the electrode potential of Mn from measurements of the potentials of amalgam electrodes (cf. A., 1926, 1104) are discussed. H. J. T. ELLINGHAM.

Role of indifferent electrodes in aqueous solutions which contain no specific oxidation-reduction compounds. N. NEKRASSOV (Z. Elektrochem., 1932, 38, 186—199).—Oxidation-reduction potentials have been measured at various indifferent electrodes, such as smooth or platinised Pt in wires or plates, Au, etc., in a number of mineral and org. acid and alkaline solutions saturated with air. The potential varies with the form of the electrode, the nature of the surface, the previous treatment, e.g., whether anodically or cathodically polarised, the p_{H} of the solution, and the partial pressure of O_2 in the surrounding atm. The electrode is not merely a passive agent in the passage of O_2 into the ionic state OH^- , because it influences the e.m.f. of the adjacent layer of solution. The electrode does not behave strictly as an O_2 electrode, but as an oxide electrode. M. S. BURR.

Quartz electrodes. I. B. VON LENGYEL [with T. MATRAI] (Z. physikal. Chem., 1932, 159, 145—160; cf. A., 1931, 570).—Phase boundary potentials between quartz glass and aq. solutions of various electrolytes have been measured. When the electrolyte concn. exceeds a certain crit. val., which depends on the valency of the cation, the quartz behaves as a metallic electrode. The potential is then determined by the cation of the electrolyte, and is unaffected by the anion or the presence of non-electrolytes. Its variation with electrolyte concn. shows that the potential is not a χ -potential, but a galvanic potential at the junction between the solution and an adsorption layer on the electrode. Light is thrown on the mode of production of this potential by correlation with existing ζ -potential data for the system. R. CUTHILL.

Preparation and reproducibility of the quinhydrone electrode. L. R. MORGAN, O. M. LAMBERT, and M. A. CAMPBELL (Trans. Amer. Electrochem. Soc., 1932, 61, 199—220).—The reproducibility of quinhydrone electrodes with Pt, Pt-Ir, Pt-Rh, Au, Au-plated Pt, lead pencil graphite, and arc carbons has been studied in 0.1M-HCl and 0.01M-HCl+0.09M-KCl saturated with quinhydrone at 25° . The effects of size of electrode, methods of cleaning, drying, and sealing it into glass, the conditions under which the solution is prepared, and methods of stirring the solution are examined. Half-elements with a probable accuracy of 0.05 mv. can

be prepared simply by immersing Pt, Au, or lead pencil graphite in either of the above solutions without stirring during use. For precision work Pt wire or foil of 1 sq. cm. surface is immersed in either of the above solutions through which a current of N_2 is being passed. Reproducibility may be much less satisfactory in solutions of notably different concns., even below p_{H} 8. A bibliography of the quinhydrone electrode is appended. H. J. T. ELLINGHAM.

Concentration cell with ternary electrolyte. K. MASAKI (Bull. Chem. Soc. Japan, 1932, 7, 35—44).—The e.m.f. of cells of the type $\text{M}|\text{MCl}, \text{M}'\text{Cl}_2 (c_1)|\text{M}'\text{Cl}_2 (c_2), \text{MCl}|\text{M}$, where M is Ag or Hg and M' is Zn, Sr, Ba, Ca, or Mg, and of the type $\text{M}, \text{Hg}|\text{MCl} (c_1)|\text{MCl} (c_2)|\text{MHg}$, where M is Zn, Ba, or Ca, have been determined. The results agree satisfactorily with those calc., especially for the more dil. solutions. H. F. GILLBE.

Effect of pressure on the e.m.f. of the Weston standard cell. T. C. POULTER and C. RITCHIEY (Physical Rev., 1932, [ii], 39, 816—820).—Pressures of 1—12,000 atm. increased the e.m.f. by 0.05 volt; factors affecting the change are discussed.

N. M. BLIGH.
Potentiometric acid-base measurements with a rigid reference electrode. F. L. HAHN (Z. Elektrochem., 1932, 38, 136—137).—A Ag plate coated electrolytically with AgBr and placed in a solution of Cl^- may be used as a reference electrode in place of the Hg_2Cl_2 electrode. The titration of pyridine in KCl (0.1N in Cl^-) by 0.1N-HCl may be made by using such an Ag|AgBr electrode in conjunction with a quinhydrone electrode. It should be useful in simplifying potential measurements with the glass electrode. M. S. BURR.

Effect of dissolved CO_2 on the p_{H} of water. H. T. BYCK (Science, 1932, 75, 224).—The curve p_{H} -log partial pressure of CO_2 has been plotted from data for the PbCO_3 equilibrium. L. S. THEOBALD.

Determination of hydrogen exponent by means of the step photometer. II. A. JANKE and F. SEKERA (Biochem. Z., 1932, 245, 362—387; cf. A., 1929, 1348).—With suitably chosen indicators p_{H} may be determined within the range 2.5—10.0 by the use of the step photometer. Since tables are provided, colour standards are not required.

W. MCCARTNEY.
Potentiometric titration of aluminium salts, and colloid chemistry of aluminium hydroxide. B. P. NICOLSKY and V. I. PARAMONOVA (Z. physikal. Chem., 1932, 159, 47—67).—Theory and experiment indicate that the p_{H} of a mixture of aq. NaOH with an equiv. amount of an Al salt is a linear function of the logarithm of the Al concn. The salt anions contained in the ppt. are not chemically combined as basic salts, but merely adsorbed. This leads to a theory of the structure of the $\text{Al}(\text{OH})_3$ micelle which explains the effect of the salt anion and of foreign salts on the form of the titration curve, and the effect of the anion on the position of the isoelectric point. R. CUTHILL.

Titration curves for aluminium salts with alkalis. H. L. DAVIS and E. C. FARNHAM (J. Physical Chem., 1932, 36, 1057—1074).—Previous results

(cf. A., 1913, ii, 721, 963) have been substantially confirmed. Neither the beginning nor the end of the pptn. of Al_2O_3 is signalled by an inflexion point on the curve, for the position of such points varies with the experimental conditions. Alkalis exert a dispersive action on Al_2O_3 , which is influenced by concn. and temp., and also by the anions present, since the latter affect the adsorption of the peptising OH^- .

I. J. PATTON (c).

Electro-titration of strong acids in the presence of salts of weak bases. K. DREWSKI (Rocz. Chem., 1932, 12, 112—118).—Two breaks should appear in the p_{H} -NaOH curve obtained in the electrotitration of strong acids in the presence of their salts with weak bases, corresponding with the neutralisation of free and bound acid, respectively. The first break is imperceptible when the salt is to a large extent hydrolysed, and a method of procedure for determining the free acid in these circumstances is described.

R. TRUSZKOWSKI.

Influence of temperature on oxidation potentials of mixtures of ferric and ferrous chlorides in hydrochloric acid solution. S. R. CARTER and T. J. GLOVER (J. Physical Chem., 1932, 36, 679—687).—Data for cells at 20° and 60° containing mixtures of FeCl_3 and FeCl_2 in 0.1—10.02*N*-HCl indicate that the temp. coeff. decreases with increasing acid concn. The potentials for mixtures containing a much greater proportion of FeCl_3 than of FeCl_2 rise with the temp. at all acid concns., but for mixtures containing a high proportion of FeCl_2 a rise in temp. raises the potential at low acid concns. and depresses it at high acid concns.

J. R. HILL (c).

Oxidation-reduction. XVII. Neutral-red. W. M. CLARK and M. E. PERKINS (J. Amer. Chem. Soc., 1932, 54, 1228—1248; cf. A., 1931, 1013).—Approx. data for neutral-red are: E_0 , 0.237; pK_r , 5.96; pK_r , 4.95; pK_0 , 6.32. For dimethylamino-methylphenazine E_0 is approx. 0.208. The instability of the potentials is attributed to the formation of a fluorescent substance, which has the composition of leuco-neutral-red but different dissociation consts., and, whilst resisting oxidation in neutral or slightly alkaline solution, is oxidised to neutral-red in distinctly acid solution. Titration in acid solution gives a val. of E_0' characteristic of the neutral-red system. Because of the lack of stability, neutral-red can be used only as an oxidation-reduction indicator for approx. comparisons. The data suggest an *ortho*-quinone structure for neutral-red base.

C. J. WEST (c).

Reversibility of the oxidation-reduction system of carbohydrate solutions. R. WURMSER and (Mlle.) N. MAYER (Compt. rend., 1932, 194, 888—890).—The vol. of CO_2 formed at 45° (in 21 days and in 3 months) by oxidation of a reduced carbohydrate solution (obtained by heating 0.5*N*-glucose with 0.1*N*-NaOH at 100°/vac. until the solution is neutral and its potential is const.) with methylene-blue and with $\text{K}_3\text{Fe}(\text{CN})_6$ is, respectively, 0.1 mol. and 0.4 mol. CO_2 per mol. of H_2 oxidised. The larger vol. of CO_2 formed in the latter case indicates that the reversible oxidation of the reduced carbohydrate is prolonged by an irreversible phase which explains the

observed disparity between the two S-shaped potential curves obtained during the oxidation and reduction of the oxidation-reduction system (A., 1928, 846).

J. W. BAKER.

Oxidation-reduction potential. I. Cystine. II. Thioglycolic and thiolactic acids. J. C. GHOSH, S. N. RAYCHAUDHURI, and S. C. GANGULI (J. Indian Chem. Soc., 1932, 9, 43—54).—I. The electrode potentials obtained by the partial reduction of cystine *in situ* at a Hg surface in the absence of air are recorded. In neutral and alkaline solution, the results are expressed by $E = 0.0793 - (RT/F) p_{\text{H}} - (RT/F) \log ([\text{XSH}]/\sqrt{[\text{XS}\cdot\text{SX}]})$, where X is $\cdot\text{CMe}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, corresponding with the equilibrium $2\text{XSH} \rightleftharpoons \text{XS}\cdot\text{SX} + 2\text{H}^+ + 2e^-$. This equation does not hold when $p_{\text{H}} < 7$; the H^+ ions suppress the ionisation of the SH group, so that the reactions $\text{XSH} = \text{XS}^- + \text{H}^+$, $2\text{XS}^- = \text{XS}\cdot\text{SX} + 2e^-$ cannot occur.

II. Thioglycolic and thiolactic acids give the same oxidation-reduction potentials as cystine. This, together with the identity of the Raman spectra, indicates that the force binding H to S is independent of the group X.

D. R. DUNCAN.

Oxidation-reduction potentials in arylarsinic acid-arsenoxide systems. P. M. BARANGER (Bull. Soc. chim., 1932, [iv], 51, 203—212).—Reproducible potentials are recorded for seven arylarsinic acids containing phenolic groups. Amongst these there is no relation between reducibility and trypanocidal activity.

C. W. DAVIES.

Reduction of nitroguanidine. I. Oxidation potential of the nitro-nitroso-guanidine system. G. B. L. SMITH and V. J. SABETTA (J. Amer. Chem. Soc., 1932, 54, 1034—1039).—The reduction of nitro-guanidine to nitrosoguanidine is a reversible reaction. The normal oxidation potential is 0.88 volt (free energy 40.7 kg.-cal.) in acid solution. The nitro-nitroso-guanidine electrode may prove useful as a indicator in the alkaline region. Nitroguanidine is not reducible by H_2 in strongly alkaline solution.

C. J. WEST (b).

Hydrogen overvoltage on alloys. H. FLOOD (Z. physikal. Chem., 1932, 159, 131—134).—Stranski's theory of crystal growth (A., 1931, 288) affords an explanation of Raeder's observations on H overvoltage on alloys (A., 1929, 402; 1930, 21).

R. CUTHILL.

Limiting current density in the electro-deposition of noble metals. S. GLASSTONE (Trans. Amer. Electrochem. Soc., 1931, 59, 105—112).—Assuming that the limiting c.d. to which metal deposition from a salt solution of normality N can occur with 100% current efficiency is determined solely by diffusion rates, the relation $d = 0.027\lambda$ is deduced on the basis of Fick's law, and is shown to hold for CdSO_4 , argento-, cadmi-, and mercuri-cyanides, and cuprammonium salts. Very low vals. of d observed for cupricyanide solutions are attributed to variation in the ratio Cu/CN causing the polarisation to rise so as to permit H_2 evolution at a relatively low c.d., and not to slowness of dissociation of the complex ion.

H. J. T. ELLINGHAM.

Electrochemical behaviour of gold in hydrochloric and hydrobromic acid solutions. G.

GRUBE and T. MORITA (Z. Elektrochem., 1932, 38, 117—131; cf. A., 1929, 1403).—C.d.—potential curves, at 20° and 50°, for anodic dissolution and cathodic separation of Au in aq. HCl containing HAuCl_4 indicate that rise of temp. and increase of concn. of free acid cause a diminution in polarisation at anode and cathode. The depolarising action of HCl may be explained if polarisation is due to the formation of a layer of the products of hydrolysis of HAuCl_4 at the electrodes. Similar behaviour is observed in aq. HBr and HAuBr_4 . The equilibrium $3\text{AuBr}_2' \rightleftharpoons 2\text{Au} + \text{AuBr}_4' + 2\text{Br}'$ has been investigated and the following reduction potentials have been determined at 60°: ${}_0E_h$ of $\text{Au}[\text{AuBr}_2']$, 0.96; $\text{Au}[\text{AuBr}_4']$, 0.87; $\text{AuBr}_4'[\text{AuBr}_2']$, 0.82 volt. By the electrolytic transference of Au in aq. HBr the solution around the anode is supersaturated with univalent Au to an even greater extent than in aq. HCl and the separation of finely divided Au takes place in accordance with the above equation. M. S. BURR.

Electrolytic crystallisation processes. IV. Formation of single crystals. V. KOHLSCHÜTTER and A. TORRICELLI [with A. GOOD] (Z. Elektrochem., 1932, 38, 213—227).—By applying a very small e.m.f. to a cell consisting of Ag electrodes in 3N- AgNO_3 , so that a current just passes, a single crystal nucleus is formed. The current gradually increases as the crystal grows. The ratio of current strength to time is const. while the crystal growth is regular. Variations in the manner of growth are indicated by changes in the ratio. A momentary stoppage of the current causes passivation at the individual crystal and formation of a new crystal. For the deposition of equal quantities of Ag the no. of individuals increases with the ratio of current strength to time. The nature of the deposit, whether of sharply-defined crystals or granular, depends on whether the time is short or long. Other factors come into play such as different rates of growth at different crystal surfaces and the existence of differences of potential between different parts of the deposit, and also between the deposit and the electrodes.

M. S. BURR.

Theory of the separation of chromium from aqueous chromic acid solutions. V. E. MÜLLER, J. V. ROBU, and W. HARTMANN (Z. Elektrochem., 1932, 38, 205—211).—Experiments with Cr-plated Cu wires show that the electrolytic separation of Cr from aq. H_2CrO_4 takes place with the same current efficiency in the presence of HClO_4 as of H_2SO_4 , but a higher cathode potential is required in the former case because of the greater difficulty experienced by ClO_4' in passing through the basic chromate diaphragm at the surface of the electrode and thus bringing about its dissolution (A., 1930, 304). No separation takes place in the presence of H_3PO_4 . The much greater facility with which reduction takes place at a C electrode compared with platinised Pt cannot be due entirely to the rough surface, but is explained by the absence of the primary diaphragm at the surface of C. A sudden jump in e.m.f. just before H_2 evolution, however, is probably due to a secondary, and more strongly basic, Cr chromate diaphragm which is formed in all cases at some distance from the

electrode and is due to the depletion of the solution of H' . The metal of the cathode probably enters into the formation of the primary diaphragm, which would explain the absence of the latter in the case of C. M. S. BURR.

Passivity of chromium. III. A new theory. E. MÜLLER (Z. physikal. Chem., 1932, 159, 68—80; cf. A., 1931, 571).—The rate of liberation of H_2 from an acid of given normality by active Cr increases as the radius of the acid anion decreases. If in acid of such concn. as would normally render it passive the Cr is made active by cathodic polarisation and then anodically polarised, passivity supervenes when the anode potential reaches a certain crit. val., which is the more positive the smaller is the acid anion. The oxide film theory of the passivity of Cr is discarded. It is suggested that H_2O must be able to penetrate into the lattice surface and loosen the electronic linkings before the metal will dissolve. With Cr this is possible only if the H_2O mols. are pressed in by electrostatic forces, as in activation by cathodic polarisation; O_2 , oxidising agents, and anodic polarisation destroy the negative charge required to force the H_2O into the lattice. There are, however, certain points in the lattice where H_2O may enter freely, leading to self-polarisation of the metal. If the number of such points is great, the metal will gradually acquire a negative charge large enough to activate it, the activation by scratching of passive Cr in contact with acid thus being explained. The acid anions offer a frictional resistance both to the emergence of the metal ions from the lattice and to the entrance of H' into the double layer. R. CUTHILL.

Mechanism of unimolecular reactions. A. GANGULI (J. Indian Chem. Soc., 1931, 8, 753—765).—The author's theory (A., 1931, 1130) that activation results from absorption of radiation followed by collision is applied to existing data. C. W. DAVIES.

Efficiency of reaction $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$, and its bearing on reaction between H and O. G. VON ELBE and B. LEWIS (J. Amer. Chem. Soc., 1932, 54, 552—554).—For the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ the stationary concn. of OH is about 5.6×10^{13} radicals per c.c., from which the collision efficiency at 40° is about 10^{10} . The upper limit of the heat of activation is 14,100 g.-cal. Other possible reactions of OH radicals are much less probable than the above.

E. J. ROSENBAUM (c).

Theory of gaseous explosions and oxidation of hydrogen sulphide. H. A. TAYLOR (J. Physical Chem., 1932, 36, 1051—1055; cf. A., 1931, 1240).—A reply to criticism (Thompson, this vol., 344). From the exact equation for $\log_e(p/T)$ of Semenov's theory of gaseous explosions, it is shown that the approx. form $\log(p/T) - A/T + B$ is more accurate than $\log p - A/T + B$, but gives for the oxidation of H_2S $A=2010$, whereas the exact equation, using $E=20,000$ g.-cal., gives $A=1950$. Semenov's relation $9.9A$ is corrected to $E=9.2A$.

H. A. BEATTY (c).

Inflammation of mixtures of hydrogen sulphide and air. P. LAFFITTE and G. BARET (Bull. Soc. chim., 1932, [iv], 51, 281—284; cf. A., 1930, 38).—The ignition temp. of H_2S -air (1.5—60%

H₂S) show a min. (292°) for 14% H₂S; there is a period of induction which is the longer the lower is the temp. At temp. below that of inflammation luminescence is observed which is the more intense the higher is the concn. of H₂S: both the duration of luminescence and the period of induction by which it is preceded are the longer the lower is the temp.

C. W. DAVIES.

Rate of dissociation of nitrogen tetroxide. P. D. BRASS and R. C. TOLMAN (J. Amer. Chem. Soc., 1932, 54, 1003—1020).—The velocity coeff. at 25° under 1 atm. pressure is $2-8 \times 10^4 \text{ sec.}^{-1}$

P. H. EMMETT (c).

Thermal dissociation of nitrous oxide. O. R. WULF (J. Amer. Chem. Soc., 1932, 54, 833—834).—A preliminary discussion of the rate of thermal decomp.

C. J. WEST (c).

Thermal decomposition of methane. T. S. WHEELER (Rec. trav. chim., 1932, 51, 342—344).—If the first stage of the thermal decomp. of CH₄ at about 1000° in presence of SiO₂ surfaces is a homogeneous bimol. reaction, C₂H₄ and not C₂H₂ is probably the product.

E. S. HEDGES.

Kinetics of the oxidation of gaseous acetone. E. W. R. STEACIE (Canad. J. Res., 1932, 6, 265—279).—The effect of varying temp., pressure, proportion of reactants, and area of wall surface, and of addition of N₂, on the velocity and products of the reaction between COMe₂ and O₂ at 350—500° has been investigated. The oxidation is a homogeneous short-chain reaction, apparently initiated by a bimol. process, the concns. of COMe₂ and O₂ having approx. equal effects on the velocity. Probably an unstable peroxide is first formed; this breaks down, forming AcOH and HCO₂H, which then suffer oxidation and decomp., mainly to CO and H₂O. D. R. DUNCAN.

Thermal decomposition of gaseous diethyl ether at high pressures. D. M. NEWITT and M. A. VERNON (Proc. Roy. Soc., 1932, A, 135, 307—315).—At pressures above 2 atm. the thermal decomp. of Et₂O takes place according to the equations: (1) Et₂O = CH₃O + CH₄ + C₂H₄, CH₃O = H₂ + CO, C₂H₄ + H₂ = C₂H₆, and (2) Et₂O = MeCHO + C₂H₆, MeCHO = CH₄ + CO. The second type of decomp. is favoured by high initial pressures. Pressure-time curves for all initial pressures show that the reaction is unimol., but the velocity coeffs., calc. from the time of half change at different pressures, show a departure from unimolecularity, *k* increasing with the initial pressure.

L. L. BIRCUMSHAW.

Thermal decomposition of isopropylamine. H. A. TAYLOR (J. Physical Chem., 1932, 36, 670—672; cf. A., 1931, 175, 1240).—The reaction resembles the pyrolysis of NH₂Pr, being homogeneous and unimol. at pressures above 150 mm. The energy of activation is 42,600 g.-cal., explainable on the basis of an activation and rupture of a single vibrational linking, probably between C and N.

I. J. PATTON (c).

Anhydride-aldehyde-ester systems: rate of formation of butyridene diacetate. C. C. COFFIN and P. A. MILLER (Proc. Nova Scotian Inst. Sci., 1931, 18, 1—10).—The uncatalysed reaction between Ac₂O and PrCHO in the liquid state at 138—180° is

strictly homogeneous, reversible, and free from side reactions. Traces of mineral acids and more than 2% of AcOH catalyse the reaction. The f.-p. curve of the system reveals the existence of a highly associated 1:1 mol. compound with m. p. —20°. The compound exists at higher temp. and is responsible for the large negative heat of mixing observed at 20°, although the chemical reaction is exothermic. No measurable reaction occurs after 6 months at room temp.

E. S. HEDGES.

Effect of various iodides on the stability of hydriodic acid. W. J. HUSA and P. S. SHATTUCK (J. Amer. Pharm. Assoc., 1932, 21, 114—121).—The rate of decomp. of HI is increased by exposure to air and/or light (especially λ 4600—6000 Å.), rise in temp., and increase in concn. FeI₂ and MnI₂ (0.5M) rapidly accelerate the decomp. of 0.1N-HI; Na, Sr, NH₄, Ca, K, and Li iodides also accelerate, in decreasing order, whereas Mg, Cd, Zn, and Ba iodides retard the rate of decomp. Only FeI₂ and MnI₂ were effective at concns. of 0.1M, 0.01M, and 0.001M. The rate of decomp. is decreased by decreasing [HI] by either dilution or salt formation.

E. H. SHARPLES.

Allotropy of phosphorus. II. Velocity of conversion of white into red phosphorus. A. A. VEDENSKI and A. V. FROST (J. Gen. Chem. Russ., 1931, 1, 917—925).—The velocity of conversion of white into red P at 175—373° indicates that the reaction is of the unimol. type. Above 400° it becomes more complex, owing to the greater proportion of P present as vapour, and variations observed in the val. of the velocity coeff. above 400° indicate that a dynamic equilibrium exists between the various allotropes of white P.

R. TRUSZKOWSKI.

Hydrolysis and dissociation of xanthates. K. SCHAUM, P. SIEDLER, and E. WAGNER (Kolloid-Z., 1932, 58, 341—348).—The rate of hydrolysis and the degrees of dissociation of some xanthates have been measured. Under the conditions existing in flotation practice the hydrolytic decomp. is only a few % after several days.

E. S. HEDGES.

Reaction of alkyl bromides with pyridine. C. R. NOLLER and R. DINSMORE (J. Amer. Chem. Soc., 1932, 54, 1025—1034).—The total rates of reaction with C₅H₅N and the rates of formation of C₅H₅N.HBr have been determined for the seven bromides from EtBr to BuBr. The results indicate that the removal of HBr and quaternary salt formation are simultaneous independent reactions. The order of the relative rates of salt formation is primary > secondary, whereas for the removal of HBr the order is *tert.* > secondary > primary. The method of removing H halides from org. compounds by means of *tert.* amines appears to be applicable to *tert.* and less successfully to secondary halides, but not to primary halides. Under the present experimental conditions, the Ladenburg rearrangement does not take place to an appreciable extent. Rearrangement of *iso.*- to *tert.*-BuBr seems to occur during the reaction and probably accounts for the anomalous behaviour of Bu²Br.

C. J. WEST (c).

Thermal decomposition of lead tetramethyl. J. H. SIMONS, R. W. McNAMEE, and C. D. HURD (J.

Physical Chem., 1932, 36, 939—948).—The decomp. has been studied at normal and at reduced pressures. Both a homogeneous gas reaction and a wall reaction occur. At low temp., C, tarry substances, and some isobutylene are formed. I. J. PATTON (c).

Reaction rate of potassium iodide with dibromides of ethylene dibromide type. R. T. DILLON (J. Amer. Chem. Soc., 1932, 54, 952—960).—The reactions with $C_2H_4Br_2$ and $C_2H_6Br_2$ at 30°, 60°, and 75° are kinetically bimol. In EtOH solution 1 mol. of dibromide reacts with 3 mols. of KI. Increase of the ionic strength of the medium by addition of neutral salts slightly reduces the rate of reaction of I⁻ with non-ionised dibromides, but appreciably increases the rate of reaction with ionised dibromides. Velocity and temp. coeffs. for the reaction of KI with various other dibromides have been calc. from existing data. P. H. EMMETT (c).

Rate of oxidation of stannous salt by oxygen and the electrical conductivity of mixtures of sulphuric acid and stannous sulphate. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1932, 7, 56—68).—The rate of oxidation of $SnCl_2$ solution containing NaOH at first increases to a max. at about 0.18N-NaOH and then falls slowly as the NaOH concn. is increased; in presence of Na_2CO_3 the rate is very small and const. On addition of HCl to a $SnCl_2$ solution the rate of oxidation rises to a const. val. at about 0.5N-HCl, and rises again slightly at about 1.5N, whilst with H_2SO_4 there is a max. at about *N*. In solutions containing H_2SO_4 and $SnSO_4$ the conductivity increases with the concn. of the latter if the H_2SO_4 concn. is less than 0.6N, whereas at higher H_2SO_4 concns. the reverse effect obtains. This phenomenon is ascribed to the formation of complexes, probably $H_2Sn_2(SO_4)_3$ and $H_2Sn(SO_4)_2$, and on the assumption that the rate of oxidation of Sn^{++} by O_2 is small it is shown that the influence of HCl and H_2SO_4 is due to the formation of complexes of this type. The acceleration of the oxidation produced by NaOH is caused by the formation of stannite, whilst the relative retardation at higher NaOH concns. is a result of the diminished rate of dissolution of O_2 by the solution. H. F. GILLBE.

Kinetics of decomposition of trichloroacetic acid in aqueous solution. A. N. KAPPANNA (Z. physikal. Chem., 1932, 158, 355—364).—The decomp. in 0.001—5.0M solutions at 70°, 80°, and 90° follows the unimol. law, but the velocity coeff., *k*, slowly falls as the initial concn. of acid is increased, although it is not affected by addition of HCl. The mechanism suggested is $CCl_3CO_2H + nH_2O \rightarrow$ intermediate complex $\rightarrow CHCl_3 + CO_2 + nH_2O$ which, if *n* is assumed to be 6, quantitatively explains the variation in *k*. The energy of activation of the acid, calc. from the temp. coeff., is 37,400 g.-cal. R. CUTHILL.

Kinetics of bimolecular reactions in solutions. V. A. HOLTZSCHMIDT and K. F. TRECHLETOV (J. Gen. Chem. Russ., 1931, 1, 875—879).—The velocity coeffs. of the reaction between $NPhMe_2$ and allyl bromide have been determined at 21.6°, 30.6°, and 40.1° in EtOH, $COMe_2$, $COPhMe$, and $PhNO_2$. A comparison of the results with those for the systems C_5H_5N -allyl

bromide, and $NPhMe_2-CH_2PhBr$ indicates that the energy of activation is diminished in all solvents by substituting C_5H_5N for $NPhMe_2$ or CH_2PhBr for allyl bromide. The factor *A* in Arrhenius' equation, $k = Ae^{-E/RT}$, varies within wide limits, and is able to affect the val. of *k* to the same extent as is the exponent *E*. R. TRUSZKOWSKI.

Addition of halogens to unsaturated acids and esters. IV. Rate of addition of bromine to cinnamic acid in acetic acid. D. M. WILLIAMS (J.C.S., 1932, 979—984; cf. A., 1928, 412).—From 15° to 25°, using AcOH containing 0.2% of H_2O , the reaction is at first approx. bimol., after which the coeffs. develop an upward trend. This deviation from the bimol. type becomes more marked with rise of temp., and is due to the catalytic action of HBr formed by nuclear substitution. An increase in the H_2O content of the AcOH to 0.7—10% raises the velocity and changes the character of the reaction in that the bimol. coeffs. now fall with time, both these effects becoming more marked as the $H_2O\%$ is increased. A possible explanation of these facts is to be sought in the effect of HBr derived from nuclear substitution on the equilibrium $Br_2 + H_2O = HBr + HOBr$, combined with the assumption that HOBr is a better catalyst than HBr. N. H. HARTSHORNE.

Temperature increment of the reaction velocity in heterogeneous reactions. I. K. FISCHBECK and K. SCHNAIDT (Z. Elektrochem., 1932, 38, 199—205).—In endothermic reactions in heterogeneous systems, such as vaporisation, sublimation, and some cases of dissociation of solids, the temp. increment of the reaction velocity (or heat of activation) is equal to the heat of reaction. It follows that the heat of activation of the reverse process, which depends simply on the no. of contacts between mols., must be zero. The behaviour of a 3-phase equilibrium between two kinds of crystals and a gas depends on all the phase boundaries, and not on the boundary between the two solid phases only. Determinations of the dissociation of $CdCO_3$ in a current of N_2 at 299—324° give a temp. increment of 37 kg.-cal. if calc. from the initial rate of evolution of CO_2 . The heat of dissociation is only 22 kg.-cal. The dissociation velocity diminishes more quickly with increasing decomp. than corresponds with the calc. surface diminution. M. S. BURR.

Reduction of copper oxide by hydrogen. J. S. LEWIS (J.C.S., 1932, 820—826).—There is no incubation period and no, or only a very short, induction period in the reduction of $CuO + H_2$, nor is the reaction autocatalytic. Previous opinions to the contrary have been based on experiments in which the CuO surface was modified by adsorbed H_2O . If this H_2O be removed by the addition of P_2O_5 , the rate of reduction is directly proportional to the H_2 pressure over a wide range. Gases with a residual affinity for CuO , e.g., CO_2 , SO_2 , C_2H_2 , H_2S , and NH_3 , have an inhibiting effect similar to that of H_2O , whilst N_2 , CH_4 , N_2O , and C_5H_{12} vapour exert little more than their dilution effect. The addition of metallic Cu to the CuO does not increase the rate of reaction, from which it is concluded that the $Cu-CuO$ interface has no influence on the rate. N. H. HARTSHORNE.

Oxidation of methane and the function of surfaces in gaseous reactions. H. W. THOMPSON and C. F. KEARTON (J.C.S., 1932, 933—941).— $\text{CH}_4\text{--O}_2$ mixtures cease to explode with a spark if the pressure is below a certain val., which depends on the composition of the mixture, passing through a min. at about 20 mol.-% CH_4 . The addition of A, N_2 , CO_2 , SO_2 , and of CCl_4 vapour raises, in general, this pressure limit, and this effect appears to be due to their hindering the diffusion of active centres to the vessel walls where deactivation occurs. The phenomenon is believed to be related to the lower pressure limit for the spontaneous inflammation of $\text{CH}_4\text{--O}_2$ mixtures found by Neumann and Serbinoff (this vol., 127) in the same way that the corresponding phenomena with $\text{H}_2\text{--O}_2$ mixtures are related.

N. H. HARTSHORNE.

Thermal decomposition of benzophenone diazide. G. KORNFIELD and A. STERN (Z. physikal. Chem., 1932, 159, 40—46).—From the v. p. at 80° and 98° the calc. mol. heat of vaporisation is 14,700 g.-cal. The decomp. of the vapour into diphenyltetrazole and N_2 is heterogeneous, the heat of activation being about 14 kg.-cal. When the liquid is present the reaction is still heterogeneous, probably occurring at the liquid surface, but the velocity is much greater and the heat of activation only very small.

R. CUTHILL.

Catalysis of autoxidation: antioxygenic properties of cobalt: theory of the action. C. DUFRAISSE and D. NAKAE (Compt. rend., 1932, 194, 880—882).—The catalytic effect of 1% of Co, CoCl_2 , CoBr_2 , CoI_2 , CoO , Co_2O_3 , CoCO_3 , CoSO_4 , $\text{Co(NO}_3)_2$, and Co acetylacetonate on the autoxidation of acraldehyde, PhCHO , furfuraldehyde, styrene, turpentine, and 10% aq. Na_2SO_3 has been examined. As a rule it is pro-oxygenic, especially as regards the acetylacetonate with hydrocarbons, acraldehyde, and PhCHO . The first seven are antioxygenic to furfuraldehyde, and CoI_2 to PhCHO and acraldehyde. Thus Co, like Fe (cf. A., 1931, 177), can act in both ways. The impossibility of isolating the intermediate oxidation product of the catalyst assumed to be formed is a natural result of its extreme activity in passing on O and no objection to the theory. There is also no reason why the catalyst should act as a reducer: e.g., O_2 itself is antioxygenic towards P.

C. A. SILBERRAD.

Autoxidation of stannous and cuprous chlorides by air. G. W. FILSON and J. H. WALTON (J. Physical Chem., 1932, 36, 740—749).—The autoxidation of SnCl_2 occurs in the extended phase, as is shown by the high temp. coeff. and by the fact that increasing the liquid-gas interface does not increase the rate. Within limits, the rate increases with increase in acid concn., and is directly proportional to $[\text{H}^+]$ between p_{H} 0.2 and p_{H} —0.25. Within certain limits, the rate of autoxidation of CuCl is independent of the acid concn. The catalytic effect of a no. of salts on the autoxidation of SnCl_2 has been investigated, CuCl_2 being outstanding.

I. J. PATTON (c).

Influence of the azide ion on the catalysis of hydrogen peroxide in presence of potassium iodide. E. OLIVERI-MANDALÀ and L. IRRERA (Gaz-

zeta, 1932, 62, 34—39; cf. A., 1930, 170).—The velocity of decomp. of H_2O_2 by KI is accelerated in presence of small amounts of NaN_3 , the sp. action of which is approx. equal to that of NaCl. The effect, therefore, appears to be entirely due to the Na^+ ion.

O. J. WALKER.

Influence of sulphuric acid on the oxidation of aqueous ferrous sulphate by atmospheric oxygen. E. M. MICHELSON (J. Gen. Chem. Russ., 1931, 4, 905—909).—In the absence of H_2SO_4 the velocity of oxidation of aq. FeSO_4 increases to an extent exactly proportional to the concn. of FeSO_4 , whilst in non-acidified solutions the abs. val. of oxidation is greater, but not exactly proportional to concn. The depressive effect of addition of H_2SO_4 is not proportional to its concn., being much greater for the first few c.c. of acid added than for further portions. It is concluded that the action of H_2SO_4 is due partly to inhibition of hydrolysis and partly to its action on unhydrolysed mols. of FeSO_4 .

R. TRUSZKOWSKI.

Cuprammonium solutions. I, II. Cuprammonium salt as oxidation catalyst. N. ISHII (J. Soc. Chem. Ind. Japan, 1932, 35, 69—72B, 72—74B).—I. When a cuprammonium solution containing sucrose is shaken with O_2 at 20° the sucrose is oxidised to the corresponding aldehyde, with evolution of CO_2 , and subsequently HNO_2 is formed from the NH_3 present. The HNO_2 probably exists in the solution in the form of a double Cu salt, since when the absorption of O_2 is complete the solution will no longer dissolve cellulose.

II. Dissolution of cellulose in a cuprammonium solution reduces proportionately the concn. of catalytically active cuprammonium salt. The rate of nitrite formation is proportional to the concn. of the free salt present, and 1 mol. of HNO_2 is produced per mol. of salt.

H. F. GILLBE.

Effect of neutral salts on inversion of sucrose by acids. H. COLIN and (MLLE.) A. CHAUDUN (Compt. rend., 1932, 194, 1074—1076).—Using the previous method (cf. A., 1931, 802), the concn. of added salt being always 0.1N, and the acid $\text{H}_2\text{C}_2\text{O}_4$, the vals. of k'/k with KCl , KNO_3 , K_2SO_4 , $\text{K}_2\text{C}_2\text{O}_4$, and KOAc are respectively 1.28, 1.28, 0.63, 0.09, 0.01, those of $p_{\text{H}} - p'_{\text{H}}$ (k' , p' refer to the solutions with the salt added) 0, 0, —0.20, —1.09, —1.67; corresponding figures with HCl are 1.08, 1.22, 0.77, 0.32, 0.08; and 0, 0, —0.10, —0.42, —0.96. Thus in all cases addition of salt causes an increase in the p_{H} , but more so with a weak acid, together with a more rapid variation in the rate of hydrolysis (cf. B., 1925, 31).

C. A. SILBERRAD.

Catalytic oxidation of carbohydrates and related compounds by oxygen in presence of iron pyrophosphates. E. F. DEGERING (J. Biol. Chem., 1932, 95, 409—412; cf. this vol., 147).—The conclusion of Spoehr (A., 1926, 385) that HCO_2Na does not reduce the ferric form of the catalyst to the ferrous form is confirmed, so that HCO_2H can be determined as an end product in the oxidation of simple sugars. No CO_2 is formed from MeOH , CH_2O , HCO_2H , or HCO_2Na , and CH_2O does not give HCO_2H .

by treatment with O_2 in the presence of ferric pyrophosphates.
H. DAYSON.

Influence of ethylene glycol on some reactions. L. M. YOUNG and H. M. TRIMBLE (J. Physical Chem., 1932, 36, 830—841).—The decomp. of $CO(NH_2)_2$ by urease, the fermentation of glucose and sucrose by yeast, and the inversion of sucrose by invertase are almost completely inhibited at 30° by about 75% of $C_2H_4(OH)_2$, whilst 20% reduces the rate by about two thirds. The degree of inhibition is independent of the extent of reaction except in the fermentation experiments, where for high concns. of $C_2H_4(OH)_2$ it increases with time. The effects, both catalytic and inhibitory, on the inversion of sucrose catalysed by HCl or H_2SO_4 are irregular. H. A. BEATTY (c).

Catalytic decomposition and oxidation of ammonia with identical catalysts. I. E. ADAMUROV and T. I. SOKOLOVA (J. Appl. Chem. Russia, 1931, 4, 191—200).—The heat of activation of NH_3 corresponds with $NH_3 \rightarrow N + H_2 + H$; decomp. precedes oxidation. Oxidation catalysts must also catalyse the decomp. of NH_3 .

CHEMICAL ABSTRACTS.

Dynamics and catalysis of the thermal decomposition of hydrogen carbonates. IV. Calcium hydrogen carbonate. R. STUMPER (Z. anorg. Chem., 1932, 204, 365—377).—The presence of $NaCl$, KCl , KNO_3 , Na_2SO_4 , K_2SO_4 , $BaCl_2$, $MgCl_2$, and $MgSO_4$ has an inhibiting action on the decomp. of $CaH_2(CO_3)_2$, the influence of the sulphates being greater than that of the chlorides. The rate of decomp. decreases exponentially as the concn. of added salt increases. $CaCl_2$ and $CaSO_4$ have a marked accelerating action. The org. colloids agar-agar, gum arabic, starch, gelatin, dextrin, tannic acid, and humic acid have a delaying action. Suspensions of insol. powders, such as metals, oxides, salts, and different varieties of C, had an accelerating action in 38 cases out of 44. The following 6, in the order of increasing effect, delayed decomp.: Bi_2O_3 , $NiCO_3$, SiO_2 , TiO_2 , U, and UO_2 . M. S. BURR.

Oxidation of phosphorus vapour at low pressure in presence of platinum and tungsten. H. W. MELVILLE and E. B. LUDLAM (Proc. Roy. Soc., 1932, A, 135, 315—333).—A Pt filament at 200° induces the oxidation of P vapour, and the velocity of reaction is proportional to the O_2 pressure. The reaction probably takes place on the surface of the filament, as no glow is emitted. A is without influence on the reaction rate. With a W filament at 500° the rate is proportional to the O_2 and P vapour pressures and is increased by the presence of Ne and of A, and by using wider reaction tubes. The equation $-dp_O/dt = kp_F p_O [1 + \mu p_X / (p_F + p_O)] d^2 \times e^{-U/RT}$, (where p_F , p_O , p_X are the pressures of P, O_2 , and inert gas, k is a const., $\mu = 0.46$ for A, and 0.20 for Ne, and d is the diameter of the tube), fits the observations. The apparent heat of activation is 16 kg.-cal. Au, Ag, and Mo behave similarly to W. The pressure of O_2 in these experiments is smaller than the lower explosion limit. L. L. BIRCUMSHAW.

Hydrogenation catalyst. Mechanism of the catalysis. III. M. BOURQUEL [with R. COURTEL,

BELIS, and (MLLE.) V. GREDY] (Bull. Soc. chim., 1932, [iv], 51, 253—280; cf. A., 1931, 1017).—In the hydrogenation of acetylenic hydrocarbons by colloidal Pd the whole is quantitatively converted into olefines before any ethylenic linking is attacked. The hydrogenation of some substances is a zero order reaction, but with others the rate increases irregularly during the reaction. For a given reaction the initial rate alone is reproducible; this is dependent on the nature, but not on the concn., of the reducible substance, is proportional to the wt. of catalyst, and sometimes to the pressure of H_2 .

A kinetic analysis of several hypotheses leads to the following suggested mechanism. The Pd takes up H_2 to give a film, Pd_nH_n , which exposes the surface arrangement $H \cdot Pd \cdot H$ to the org. phase; the reducible substance is adsorbed (at its point of attack) on this and can evaporate from it in an activated state, in which it may either combine with H_2 or suffer deactivation or stereomutation.

C. W. DAVIES.

Preparation of copper-chromium oxide catalysts for hydrogenation. R. CONNOR, K. FOLKERS, and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1138—1145).—The method of prep. of Cu-Cr oxide catalysts by pptn. and decomp. of Cu NH_4 chromate is modified and improved so that larger yields of a considerably more active catalyst are obtained. It is advantageous to incorporate Ba, Ca, or Mg into the Cu-Cr oxide catalysts. Addition of one of these elements stabilises the catalyst against reduction and consequent deactivation, and apparently enhances its activity. These elements also modify the relative rates of competitive hydrogenation such as are encountered in the prep. of $CH_2Ph \cdot CH_2 \cdot OH$ from $CH_2Ph \cdot CO_2Et$, so that larger yields of the alcohol are obtained. Cu-Cr oxide catalysts are also prepared by decomp. of oxalates, by mechanical mixture of Cu and Cr oxides, by decomp. of their nitrates, by the combination of Cu and Cr oxides, and by decomp. of pptd. Cu, Cr, and NH_4 carbonates. All the products containing Cu⁺⁺ catalyse hydrogenation. The most active catalyst of this group is prepared by decomp. of co-pptd. Cu, Cr, Ba, and NH_4 carbonates; its activity is similar to those (better) obtained by decomp. of the corresponding chromates. C. J. WEST (b).

Methanol condensation as modified by alkali catalysts. G. T. MORGAN, D. V. N. HARDY, and R. A. PROCTER.—See B., 1932, 250.

Methyl alcohol catalysts. V. A. PLOTNIKOV and K. N. IVANOV (J. Gen. Chem. Russ., 1931, 1, 826—844).—Cu does not catalyse the reaction of reduction of CO to MeOH by H_2 ; ZnO has a fair catalytic activity, but when the passage of the gases over the catalyst is rapid, the products are chiefly hydrocarbons; the same applies to Cu-ZnO mixtures, and to Cr_2O_3 , which catalyses the reaction $2CO + 2H_2 \rightarrow CH_4 + CO_2$. The binary catalyst Cu- Cr_2O_3 (98:2) gives 58% yields of MeOH, together with 26.8% of CH_4 , 13% of CO_2 , and 2.3% of higher hydrocarbons, at 265° . ZnO- Cr_2O_3 (11:1) mixtures give good yields of MeOH when the rate of flow of gas is small; at high rates of flow the chief products

are hydrocarbons. Under such conditions Cu-ZnO-Cr₂O₃ (82 : 16 : 2) catalysts give 92% yields of MeOH (7% CH₄) at 257° and 162 atm. A probable intermediate product is Cu carbonyl, which is stable under high pressures of CO. The action of catalysts may vary with the duration of contact with the substrates. R. TRUSZKOWSKI.

Mechanism of catalytic decomposition of esters by nickel. III. J. N. PEARCE and H. J. WING (J. Physical Chem., 1932, 36, 703—712; cf. A., 1927, 215).—The first break in the ester mol. is assumed to take place between the alkyl group and the C of the CO₂H group of the acid: $R\cdot CH_2\cdot CO_2C_nH_{2n+1} = R\cdot CH_2\cdot \rightarrow + \leftarrow CO_2C_nH_{2n+1}$. The radicals then add H and the formate undergoes further decomp. The decomp. by Ni at 152°, 200°, 250°, and 300° of HCO₂Me, HCO₂Et, MeOAc, EtOAc, and EtOH was studied. The almost complete absence of CO₂ from the decomp. products, the rapid inactivation of the catalyst, and the formation of H₂O from the acetates support the above mechanism.

CHEMICAL ABSTRACTS (c).

Reactions of acetaldehyde over various oxide catalysts. M. E. KINSEY and H. ADKINS (Ind. Eng. Chem., 1932, 24, 314—317).—The reaction products resulting from the passage of 270 c.c. per hr. of a mixture of MeCHO and EtOH (2 : 1) in an atm. of H₂ at 200 atm. over 30 c.c. of catalyst at 300 ± 5° were examined for the following oxide catalysts: Cu-Cr, Cd-Cr, Ag-Cr, Cu-Cr-Ba, Co-Cr, Cr, Cu-Mo, Zn-Cr, Zn-Cr+Na₂SO₄, Cu-V, Mg-Cr, Fe-Cr, Mn-Cr, Ni-Cr; glass beads and steel balls. In the case of the Ni catalyst decomp. of MeCHO into gaseous products occurred to 35—45%. The yields of BuⁿOH and C₆H₁₃OH and of acetic, butyric, and hexoic acids with the catalysts are tabulated. The catalysts containing Cr were prepared by the decomp. of the NH₄ chromates in the case of Cu, Zn, Mn, Mg, Ni, Ag, Co, and Cd.

H. INGLESON.

Catalytic production of acetophenone. I. T. LAKOMKIN (J. Appl. Chem. Russia, 1931, 4, 176).—A correction (cf. A., 1931, 354).

CHEMICAL ABSTRACTS.

Catalytic decomposition of azomethane, s-dimethylhydrazine, and ethylamine. Thermal decomposition of s-dimethylhydrazine. P. H. EMMETT and R. W. HARKNESS (J. Amer. Chem. Soc., 1932, 54, 538—548).—Over Fe catalysts for the NH₃ synthesis azomethane decomposes rapidly at 250°, forming NH₃, H₂, and small amounts of CH₄, C₂H₆, and N₂. There are produced first NH₂Me, H₂, Fe₃N, and C, and the NH₂Me then decomposes and the Fe₃N is partly reduced by the H₂. Under similar conditions NH₂Me decomposes quantitatively at 250° into H₂, NH₃, and C, whilst dimethylhydrazine at 320° decomposes into the same products, with some CH₄, C₂H₆, and N₂. The homogeneous decomp. of dimethylhydrazine is a complex first order reaction, with an energy of activation of 57 kg.-cal. per g.-mol. The reaction NHMe·NHMe = 2CH₄ + N₂ apparently accounts for about 60% of the products of reaction, the remainder including additional N₂, a substance sol. in H₂O, and C₂H₄. S. LENHER (c).

Catalysts for high-pressure hydrogenation of phenols and hydrocarbons. H. TROPSCH.—See B., 1932, 297.

Direct production of magnesium-aluminium alloys by electrolysis of fused salts. R. WEINER (Z. Elektrochem., 1932, 38, 232—240).—Mg-Al alloys may be prepared by electrolysis of fused carnallite with the addition of 2% CaF₂ at 600—640°, using a molten Al cathode. The most favourable cathode c.d. is 1—5 amp. per sq. cm. The current efficiency is 85—90%. The e.m.f. is not much affected by temp. but depends on the c.d. and, for the above val. at 600°, is 5.5 volts. The energy consumption is 13—15 kw.-hr. per kg. of Mg. The Mg content of the cathode may be raised to 90%. C.d.-potential curves indicate that the change in composition of the cathode does not appreciably affect the course of the electrolysis or the current efficiency. The results obtained are reproducible on a large as well as on a small scale. M. S. BURR.

Optical study of the passivity of iron and steel. L. TRONSTAD (Kong. Norske Vidensk. Selsk. Skr., 1931, 3—247; Chem. Zentr., 1931, ii, 3444—3445).—Changes probably involving the removal of the passive layer occur on cathodic polarisation of Fe and steel in alkaline solution, but the surface layer of "rustless" steel is more stable. In neutral solution rusting occurs except with resistant austenitic rustless steels; in acid solution the layer is partly removed. Passivation is attended by optical changes corresponding with the formation of an oxide layer, n 3.0, 30 Å. thick. By repeated passivation and activation thicker layers are obtained. The effect of anodic polarisation was studied microscopically. The simple oxide theory of passivation is supported. (Cf. this vol., 343.) A. A. ELDRIDGE.

Fully organised anodic layers on aluminium. J. E. LILIENFELD, L. W. APPLETON, W. M. SMITH, and J. K. NIEH.—See B., 1932, 348.

Electrochemistry of chromium. II. Electrolysis of chloride. A. V. PAMFILOV, V. A. GREKK, and A. K. TROITSKAJA (J. Gen. Chem. Russ., 1931, 1, 803—812).—The deposits of Cr obtained by the electrolysis of CrCl₂-CrCl₃ solutions of various concns. (0.5—10% Cr) and alkalinities (0—0.3N-KOH) were in most cases contaminated with oxides. In certain cases a bright, metallic, but non-adherent deposit was obtained, but the usual product was a grey or black powder. R. TRUSZKOWSKI.

Influence of alternating current on the current efficiency in the electrolytic separation of metals. N. ISGARISCHEV and N. KUDRJAVZEV (Z. Elektrochem., 1932, 38, 131—135; cf. A., 1925, ii, 548).—The superposition of a.c. on d.c. in the electrolytic separation of Cu decreases the d.c. efficiency, the effect increasing as the a.c. frequency diminishes. The effect is still more marked in the case of Ni. The addition of gum arabic without the use of a.c. diminishes the efficiency at first, but, as the amount added is increased, a min. is reached and the efficiency then begins to increase. The reverse is observed when a.c. is employed in conjunction with gum arabic and a max. is obtained. M. S. BURR.

Glacial acetic acid as a solvent for electro-deposition of metals. X-Ray diffraction study of structure of deposits of arsenic, antimony, and bismuth. C. W. STILLWELL and L. F. AUDRIETH (J. Amer. Chem. Soc., 1932, 54, 472—478).—Solutions of the chlorides were electrolysed. The nature of the Sb deposit is not affected by a change in c.d. from 0.01 to 0.07 amp. per sq. cm. At low temp. and with higher concns. amorphous Sb is obtained; at temp. above 50° deposits are cryst., but burnt. As is always obtained in the amorphous form, while Bi is always cryst. E. G. VANDEN BOSCHE (c).

Electrochemical oxidation of ketones. W. E. BRADT and C. J. OPP (Trans. Amer. Electrochem. Soc., 1931, 59, 81—90).— COMe_2 in aq. H_2SO_4 solution has been electrolysed under various conditions in a diaphragm cell with a Pt gauze anode, and a preliminary examination made of the gaseous and dissolved oxidation products.

H. J. T. ELLINGHAM.
Reductivity of hydrogen. II. Chloroacetic acid. G. R. HOOD and H. C. IMES (J. Physical Chem., 1932, 36, 927—929).—The efficiency of the electrolytic reduction of $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ to AcOH and HCl increases as the cathode potential is raised from 0.80 to 1.25 volts. L. N. SAGER (c).

Condensation of hydrocarbons by electric discharge. VII. M/N ratio for methane, ethylene, and acetylene. S. C. LIND and G. R. SCHULTZE (Trans. Amer. Electrochem. Soc., 1931, 59, 141—156).—The gases are submitted to an ozoniser type of discharge, and comparative vals. of the ratio of the no. of reacting mols. to the no. of ion pairs (M/N ratio) determined. For CH_4 and C_2H_2 vals. of this ratio are in the same proportion as in α -ray condensation (A., 1931, 60), but the val. for C_2H_4 is exactly twice as high. Taking the product of M/N and the mol. ionisation as the basis of comparison brings the results for CH_4 , C_2H_6 , and C_2H_4 into line, but throws out that for C_2H_2 . In C_2H_2 condensation the solid reaction product is found to have a negative catalytic wall effect, and it is possible that some other inhibitor may be present. H. J. T. ELLINGHAM.

Radiation hypothesis of chemical reactions, and concept of threshold wave-length. G. G. RAO and N. R. DHAR (J. Physical Chem., 1932, 36, 646—651).—It is suggested that the photochemical threshold of a reaction corresponds with the energy of activation of the dark reaction. Extrapolating to zero quantum yield a curve representing the variation of quantum yield with wave-length gives a threshold wave-length for four reactions agreeing closely with the energy of activation of the dark reactions.

R. H. EMMETT (c).
Photosensitised explosion of hydrogen and oxygen by chlorine. R. G. W. NORRISH (Proc. Roy. Soc., 1932, A, 135, 334—348).—A mixture $2\text{H}_2 + \text{O}_2$ can be exploded by the photosensitive action of Cl_2 between 25° and 340°. A sharp limit of pressure exists for each particular temp., above which the explosive combination of H_2 and O_2 occurs and below which the H_2 and Cl_2 unite to form HCl . The limiting pressure of Cl_2 increases rapidly as the lower temp. are approached. The explosion takes place at room

temp. and is not of the same type as the photosensitised explosion of H_2 and O_2 by NH_3 studied by Haber. L. L. BIRCUMSHAW.

Photochemical reaction between hydrogen peroxide and hydrogen or carbon monoxide in the gas phase. G. VON ELBE (J. Amer. Chem. Soc., 1932, 54, 821—822).—Preliminary results, best explained by assuming dissociation of H_2O_2 into OH radicals, are reported. C. J. WEST (c).

Photolysis of aqueous solutions of H_2O_2 . M. QURESHI and M. K. RAHMAN (J. Physical Chem. 1932, 36, 664—669).—When solutions at 30° in quartz vessels are exposed to the light of a Hg arc the reaction rate is proportional to the square root of the light intensity. As the concn. falls the quantum efficiency rises from 7 to a max. of 11 at a concn. of 0.09M, then falls gradually to 3.

E. J. ROSENBAUM (c).
Photochemical decomposition of phosphine. H. W. MELVILLE (Nature, 1932, 129, 546).— PH_3 shows continuous absorption from 220 to 185 μ , and 3 diffuse bands, without fine structure, in the region 220—230 μ . Light from Zn or Al sparks readily decomposes PH_3 into H_2 and red P. In the Hg photosensitised reaction the rate of decomp. is approx. 10 times that of NH_3 , and decreases with a decrease in diameter of the reaction tube. A alone is without effect, but O_2 increases the rate of decomp., which is still further increased by the addition of A. The results partly explain previous observations (A., 1931, 47) obtained with a $\text{PH}_3\text{--O}_2$ mixture.

L. S. THEOBALD.
Notable [photographic] sensitisations. LÜPPO-CRAMER (Z. wiss. Phot., 1932, 30, 313—320).—The effect of bathing an emulsion in CuSO_4 (1%) solution before development is (1) a partial destruction of the latent image, and (2) in metol, quinol, etc. developers, but not in "glycine" or pyrogallol, considerable sensitisation to red light. (2) is caused by oxidation products of the developer, their production being accelerated by Cu ions. Rhodamine dyes inhibit the effect (2). J. LEWKOWITSCH.

Action of nuclei of silver iodide at emulsification. LÜPPO-CRAMER (Z. wiss. Phot., 1932, 30, 311—313).—Similarly to the action of AgI in AgBr emulsions, the presence of THI at the emulsification of HgI_2 (from HgCl_2 and KI) in gelatin reduces the grain-size of the HgI_2 . J. LEWKOWITSCH.

Lattice energy and photochemical decomposition of silver halides. II. S. E. SHEPPARD and W. VANSELOW (Z. wiss. Phot., 1932, 30, 273—311).—Theoretical. The application of Sommerfeld's electron gas theory of metals to photo-ionisation in ionic crystals is criticised. The conception of the virtual field (lattice potential) of metals gives better agreement between observed and calc. limits of light absorption than Pauling's "electronic affinity of crystals." The deformation of anions by cations with bigger outer electron shells tends to reduce the absorption limits. Adsorption effects are ascribed to weakening of the lattice. J. LEWKOWITSCH.

Photolysis of potassium cuprioxalate. H. L. DUBE and N. R. DHAR (J. Physical Chem., 1932, 36,

626—632).—The photolysis in sunlight in the presence of FeCl_3 and uranyl nitrate as sensitizers is zero mol., and the temp. coeff. 1.1—1.23. The reaction is brought about by ultra-violet light. The quantum yield is less than 1 and is higher in the presence of a sensitizer. O_2 retards the reaction more than does CO_2 . Whilst a slight excess of $\text{K}_2\text{C}_2\text{O}_4$ has no effect, a large excess accelerates the reaction. Increasing the amount of sensitizer increases the reaction rate to a max., then reduces it. It is assumed that an activated mol. of cuprioxalate forms a mol. of activated CuC_2O_4 . Since pptd. CuC_2O_4 is not decomposed by light, an activated mol. must absorb more energy from the sensitizer in order to decompose.

E. J. ROSENBAUM (c).

Photochemical interaction of C_2H_2 and H_2O . R. LIVINGSTON and C. H. SCHIFFLETT (J. Physical Chem., 1932, 36, 750—751).—When C_2H_2 was passed through H_2O and then exposed to the light of a Hg arc, neither aldehydes nor acids could be detected. A saturated aq. solution of C_2H_2 after irradiation did not give reactions for acids, aldehydes, ketones, or alcohols, but a white inert, insol. substance, probably a polymeride of C_2H_2 , was formed on the walls of the vessel.

E. J. ROSENBAUM (c).

Photosynthesis in tropical sunlight. III. Synthesis of formaldehyde. IV. Synthesis of sugars and complex nitrogenous substances. A. R. RAJIVANSI and N. R. DHAR (J. Physical Chem., 1932, 36, 567—574, 575—585; cf. A., 1931, 920).—III. When CO_2 was passed through solutions of various org. and inorg. photosensitizers, the most effective of which were MnCl_2 and CoCO_3 , exposed to tropical sunlight, amounts of CH_2O up to about 0.00005% by vol. were formed; nascent CO_2 gave CH_2O even in absence of a catalyst. The yields were slightly greater in ultra-violet light. CH_2O was also found in aq. NaHCO_3 containing catalysts after exposure to sunlight in glass vessels.

IV. The temp. coeff. of sugar formation in sunlight in aq. CH_2O containing photosensitizers is 1.2 between 30° and 40°. Hexamethylenetetramine was detected in solutions of $\text{CH}_2\text{O} + \text{NH}_3$ exposed with photocatalysts. NO_2' was formed when air was passed into H_2O in a quartz vessel. E. J. ROSENBAUM (c).

Attempted photosynthesis of carbohydrates *in vitro* with visible light. F. P. ZSCHELLE, jun. (J. Amer. Chem. Soc., 1932, 54, 973—976).—Repetition of Baly's experiments (A, 1927, 1040) gave negative results.

E. J. ROSENBAUM (c).

Photochemical decomposition of organic acids. W. C. PIERCE and G. MOREY (J. Amer. Chem. Soc., 1932, 54, 467—472).—The rate of decomp. of malonic acid and Na malonate varies with the concn. much less rapidly than would correspond with proportionality, and the velocity coeff. for the acid is about five times that for the salt. Between 3° and 70° the temp. coeff. is 1.07. At low concns. the fraction of light absorbed is proportional to the concn. The acid absorbs much more light than the salt. AcOH yields on decomp. equiv. amounts of CO_2 and CH_4 , with small amounts of CO and unsaturated hydrocarbons, whereas the chief products from EtCO_2H are CO_2

and C_2H_2 . The first step in the decomp. is the elimination of CO_2 .

E. J. ROSENBAUM (c).

Photochemical reaction between quinine and dichromic acid. I. Quantum yields. G. S. FORBES, L. J. HEIDT, and C. G. BOISSONNAS (J. Amer. Chem. Soc., 1932, 54, 960—973).—The photochemical oxidation of quinine sulphate in presence of varying amounts of H_2SO_4 was studied at several concns., wave-lengths, and light intensities. The quantum yield decreases as the light intensity and the dilution of the H_2SO_4 increase, and, for wave-lengths $< 405 \text{ m}\mu$, as the quinine concn. increases. Normally the dark reaction is negligible. The extinction coeffs. are additive. The temp. coeff. is 1.12 ± 0.03 . In light of wave-length 436 $\text{m}\mu$ no photolysis occurs, although the $\text{H}_2\text{Cr}_2\text{O}_7$ absorbs strongly. Activation of the quinine is apparently the decisive factor in the reaction, the first step possibly being the absorption of a quantum by the quinoline group of the quinine mol.

E. J. ROSENBAUM (c).

Starch hydrolysis as affected by light. II. A. E. NAVEZ and B. B. RUBENSTEIN.—See this vol., 543.

Photochemistry of ergosterol. E. H. REERINK and A. VAN WIJK (Strahlentherapie, 1931, 40, 728—732; Chem. Zentr., 1931, ii, 2632).—Irradiation of well-stirred, O_2 -free solutions of ergosterol with ultra-violet light of wave-length 284—300 $\text{m}\mu$ gives, at a definite stage, a certain quantity of a transformation product, *L*, which is considered to be identical with vitamin-D. Longer irradiation alters *L* still further. Irradiation with light of shorter wave-length (254 $\text{m}\mu$) is not suitable for producing *L* or for the prep. of a second substance *S* which is simultaneously produced.

L. S. THEOBALD.

Effect of ultrasonic radiation on indicators. S. LIU and H. WU (J. Amer. Chem. Soc., 1932, 54, 791—793).—Twelve indicator solutions saturated with air or O_2 faded when exposed to ultrasonic radiations either when buffered or unbuffered. Since gas-free solutions and solutions saturated with H_2 did not fade, it appears that indicator mols. are destroyed by oxidation under the influence of ultrasonic radiation.

C. J. WEST (c).

Chemical effects produced by radon on system hydrogen-sulphur-hydrogen sulphide. E. C. TRUESDALE and S. C. LIND (J. Amer. Chem. Soc., 1932, 54, 516—538).—The synthesis and decomp. of H_2S by α -ray ionisation has been studied at 37—270°. The synthesis, the mechanism of which is complex, has a marked temp. coeff. above 234°. The decomp., the temp. coeff. of which is less than unity (cf. A., 1920, ii, 214), may be explained by the ion cluster mechanism, and is more efficient than the synthesis.

L. WALDBAUER (c).

Solid polyiodides of potassium. H. W. FOOTE and W. M. BRADLEY (J. Physical Chem., 1932, 36, 673—678).—The solubility of mixtures of KI and I_2 in CHCl_3 and in PhMe shows that between 25° and 0.7° no solid binary additive product of KI and I_2 exists. A compound $\text{KI}_4\text{I}_2 \cdot 3\text{C}_6\text{H}_6$ exists.

I. J. PATTON (c).

Composition of precipitated copper sulphide. I. M. KOLTHOFF and E. A. PEARSON (J. Physical

Chem., 1932, 36, 642—645).—CuS pptd. at room temp. from aq. CuSO₄ with H₂S is practically pure. After ageing for 7 days under aq. H₂S it contains about 2% Cu₂S. CuS pptd. from boiling solutions contains about 5% Cu₂S. F. URBAN (c).

Promoting action of copper sulphide on speed of precipitation of zinc sulphide. So-called coprecipitation of zinc with copper sulphide. I. M. KOLTHOFF and E. A. PEARSON (J. Physical Chem., 1932, 36, 549—566).—The pptn. of the ZnS occurs, not at the same time as, but after that of the CuS, this being a consequence of fine state of division of the CuS and the adsorption of H₂S. The amount of ZnS pptd. increases with the speed of pptn. and age of the CuS, the amount of shaking, the time of keeping, and the acid dilution. High temp. and ageing seem to reduce the particle size of the CuS. Cysteine and PhSH accelerate the pptn. of ZnS in absence of CuS, but inhibit the pptn. in presence of CuS. The effect of surfaces on the speed of pptn. from a supersaturated solution is shown by the fact that finely-divided solids, such as powdered glass and filter-paper, promote the pptn. of ZnS. The solubility product of ZnS indicates that pptn. should occur at acid concns. up to 1*N*. F. E. BROWN (c).

Apparent formation of copper carbonyl. E. H. BOOMER, H. E. MORRIS, and G. H. ARGUE (Nature, 1932, 129, 438).—The passage of H₂ and CO₂ or of water-gas over a catalyst of Cu, Al, and Zn (1 : 1 : 1) yields a liquid which is colourless when blown from the high-pressure condenser. An evolution of gas and the formation of a yellow ppt. containing Cu as the only metal then occur after a period which depends, apparently, on the amount of H₂O present. The evolution of gas is increased by the addition of H₂O, acid, or alkali. These results indicate the presence of a compound with properties similar to those expected of a Cu carbonyl. No evidence of the formation of a carbonyl was obtained with the above catalyst at 1 atm. and various temp.

L. S. THEOBALD.

New synthesis of copper aluminate, CuAl₂O₄. S. HOLGERSSON (Z. anorg. Chem., 1932, 204, 378—381).—CuAl₂O₄ is prepared by dissolving Cu(NO₃)₂·6H₂O and Al₂(SO₄)₃·18H₂O in H₂O in equimol. proportions, evaporating to dryness, and heating in a Pt crucible for 5 hr. at 950° in an electric furnace. X-Ray measurements give a 8.064 Å., which agrees with earlier measurements, and the mol. vol. 65.5 Å³.

M. S. BURR.

Cupric carbonate. V. AUGER and (MME.) POULENC-FERRAND (Compt. rend., 1932, 194, 788—790).—Benrath and Essers' experiments (cf. A., 1926, 367, 695) were repeated. Only hydrated salts such as K₂Cu(CO₃)₂·H₂O, with more basic salts, and, by complete hydrolysis, nodules of malachite were obtained. The alleged K₆Cu(CO₃)₄ is identical with K₂Cu(CO₃)₂. CuCO₃ was not formed.

C. A. SILBERRAD.

Silver ferrites. III. Structure and polymerisation of brown ortho-ferric hydroxide. A. KRAUSE and M. CIOKÓVNA (Z. anorg. Chem., 1932, 204, 20—28; cf. A., 1931, 1253).—Ag ferrite made by adding a mixture of Ag and Fe^{III} nitrates to boiling

aq. NaOH has the formula Ag₃H(FeO₂)₄, but if AgNO₃ is added to Fe^{III} hydroxide which has been boiled for 3 min. with aq. NaOH the resulting ferrite has Ag : Fe = 1 : 1. This behaviour is explained by assuming that the simple orthohydroxide, H₄Fe₄O₈, has 3 acidic OH groups, the fourth possessing a basic character. This substance polymerises in presence of NaOH in such a way that one of the terminal OH groups is always basic, so that the ratio Ag : Fe approaches 1 the more nearly the greater is the degree of polymerisation. The influence of concn. of NaOH on the complexity of the resulting hydroxide has been studied and the results are discussed.

F. L. USHER.

Silver ferrite. IV. Structure of ferric hydroxide by silver ferrite synthesis. A. KRAUSE, Z. CZAPSKA, and J. STOCK (Z. anorg. Chem., 1932, 204, 385—394).—The possibility of forming silver ferrite with γ-FeO₂H or ferrous acid, and not with α-FeO₂H (A., 1931, 695, 1253), has been utilised for the analysis of samples of yellow Fe^{III} hydroxide prepared by different methods. The different forms of Fe^{III} hydroxide may be classified as follows: (1) Ortho- and polyortho-hydroxides with a chain structure. (2) Yellow Fe hydroxide with a ring structure (meta-hydroxide) including ferrous acid (HFeO₂)_n, which may either be amorphous or give the X-ray interference data of γ-FeO₂H, and goethite preps. (Fe₂O₃·H₂O)_n, to which α-FeO₂H and amorphous goethite belong.

M. S. BURR.

Separation of metals without an external source of current. A. KUTZELNIGG (Z. Elektrochem., 1932, 38, 154—158).—A survey of the different methods for depositing a thin layer of one metal upon another, with special reference to Au, Ag, Cu, and Sn, without the use of an electric current applied externally.

M. S. BURR.

Reduction of magnesia by silicon. G. GIRE (Compt. rend., 1932, 194, 884—886).—Reduction takes place when a finely powdered and strongly compressed mixture is heated in vac. at 1280—1320°.

C. A. SILBERRAD.

Formation of a halogen-free apatite from basic calcium phosphates. G. TROMEL (Z. physikal. Chem., 1932, 158, 422—432).—There is no evidence of the formation of a compound 3Ca₃P₂O₈·CaO in the system CaO-P₂O₅, and from crystal structure considerations it is unlikely that such an oxyapatite can exist. On heating basic Ca phosphates at 1050—1100° hydroxyapatite results, e.g., Ca₁₂P₆O₂₇·H₂O → Ca₁₀P₆O₂₄(OH)₂+2CaO. The H₂O is obtained from the air and is completely expelled from the reaction product only at 1400° or above. Fluoro-apatite has m. p. 1660°.

R. CUTHILL.

Synthesis of calcium silicates. III. S. NAGAI and K. AKIYAMA (J. Soc. Chem. Ind. Japan, 1932, 35, 65—67B; cf. this vol., 350).—The effect of heating mixtures of CaCO₃ (3 mols.) and SiO₂ (2 mols.) at temp. between 900° and 1600° for 1 hr. has been studied. The total Ca silicate content in the product rises from 19% at 900° to 75% at 1300° and to 79% at 1600°. At all temp. above about 1200° the ratio of combined CaO to combined SiO₂ is approx. 2. The product obtained at or above 1400° disintegrates

on cooling as a result of decomp. into $2\text{CaO} \cdot \text{SiO}_2$ and CaO of the small quantity of $3\text{CaO} \cdot \text{SiO}_2$ formed and of the transformation of α - and β - $\text{CaO} \cdot \text{SiO}_2$ into the γ -form. $3\text{CaO} \cdot \text{SiO}_2$ can be obtained only by heating the mixture at above 1600° for several hr. If a mixture containing from 5% to 20% of a mixture of 2CaCO_3 and Fe_2O_3 be heated at 1450° for 2–4 hr., the $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ which is formed at 1400° and melts at 1450° acts as a flux and leads to the formation of a product containing 60–70% of $3\text{CaO} \cdot \text{SiO}_2$.

H. F. GILLBE.

Anhydrite and its formation. L. CHASSEVENT (Compt. rend., 1932, 194, 786–788).—Gypsum heated in a current of dry air to below 300° gives "sol. anhydrite," readily rehydrated; on heating similarly to above 300° the product is "insol. anhydrite," rehydrated very slowly (cf. B., 1922, 659A; A., 1926, 1217). If, however, gypsum (or the hemihydrate or "sol. anhydrite") is heated in steam "insol. anhydrite" is formed at all temp. above 150° . Insol. anhydrite is therefore the stable form at 150° . These facts reconcile the author's observations (*loc. cit.*) with those of van 't Hoff (cf. A., 1904, ii, 35).

C. A. SILBERRAD.

Preparation of anhydrous chlorides and metallic couples. S. D. NICHOLAS (Nature, 1932, 129, 581). The action of H_2O on a metallic salt mixed with a metal lower [?] in the electropotential series often proceeds with violence, especially in the case of the chloride. Typical cases are given by Zn and Al, respectively, in contact with HgCl_2 , PbCl_2 , or Cu_2Cl_2 . Such mixtures readily detect traces of H_2O in org. liquids. Excess of Al heated with PbCl_2 , Cu_2Cl_2 , or AgCl readily yields AlCl_3 . ZnCl_2 and SnCl_4 are similarly obtained from Zn and Cu_2Cl_2 , and Sn and Cu^{II} oxychloride, respectively. Mg and Cu_2Cl_2 give Cu explosively on heating. Effective metallic couples are made in a similar way, e.g., Al and HgCl , in the prep. of CH_2Ph_2 .

L. S. THEOBALD.

Reaction between barium sulphate and alumina at high temperatures. H. S. BOOTH and R. WARD (J. Physical Chem., 1932, 36, 961–984).—Reaction, yielding $\text{BaO} \cdot \text{Al}_2\text{O}_3$, becomes appreciable above 1000° , but is not complete below 1238° , Tammann and Jander's equations being applicable between these temp. The temp. at which rapid reaction sets in is close to that at which γ - Al_2O_3 changes into corundum. The rate increases with the proportion of Al_2O_3 in the reaction mixture. The mechanism involves rapid reaction at the points of contact between BaSO_4 and Al_2O_3 , slower reaction due to diffusion of BaSO_4 through the reaction product, diffusion of the latter into the Al_2O_3 , and change of γ - Al_2O_3 into corundum.

I. J. PATTON (c).

Mercury purification. B. MOORE.—See B., 1932, 348.

Voltaite-like sulphates. B. GOSSNER and E. FELL (Ber., 1932, 65, [B], 393–395; cf. A., 1930, 1386).—The prep. of voltaites containing Ti-Fe^{II} , Ti-Mg , Ti-Cd , Rb-Cd , and $\text{NH}_4\text{-Mg}$ is recorded. In all cases Fe^{III} is partly replaced by Al. The structure of voltaites is discussed.

H. WREN.

Oxycyanogen. II. Free radical. H. HUNT J. Amer. Chem. Soc., 1932, 54, 907–910; cf. A.,

1931, 1043).—*Oxycyanogen*, $(\text{OCN})_x$, m. p. $-12+5^\circ$, has been prepared by the action of I on AgOCN in CS_2 or CCl_4 solution. In Et_2O or EtOH solution IOCN resulted (cf. A., 1931, 832). A solution of $(\text{OCN})_x$ is stable up to 100° in a closed tube, liberates I from KI, but will not displace Br. An oxidising solution, possibly containing percyanic acid, HO_3CN , resulted on electrolysis of a solution of KOCN in MeOH which was not anhyd. (cf. A., 1925, ii, 568).

W. C. FERNELIUS (c).

Hexafluorodisilane. W. C. SCHUMB and E. L. GAMBLE (J. Amer. Chem. Soc., 1932, 54, 583–590).—The prep. is described in detail (cf. A., 1931, 1140), and v. p. between -79° and -4° are reported. On hydrolysis, H_2 , silicic acid, H_2SiF_6 , silico-oxalic acid, and HF are formed. Interaction of C_2Cl_6 and ZnF_2 at ordinary pressures does not give C_2F_6 . Si_2Cl_6 has been prepared by chlorination of Ca-Si and Ca-Mn-Si alloys.

A. L. HENNE (c).

Alkali aluminosilicates. VI. Role of water in permutites. E. GRUNER [in part with E. HIRSCH] (Z. anorg. Chem., 1932, 204, 321–341; cf. this vol., 120).—Certain regularities are observed in the H_2O content of permutites. If a mol. is the H_2O content of an alkali permutite at 100° , $(a+1)$ mol. is the H_2O content in an atm. saturated with H_2O vapour. The hydrated ion introduced into the permutite by base exchange contains b mol. H_2O . Thus the H_2O content of the hydrated permutite is $(a+1+b)$ under saturated H_2O vapour and is $(a+2)$ at 100° . The formula of the hydrated permutite is $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}][\text{R}^{\text{I}}(\text{H}_2\text{O})_x] \dots \text{H}_2\text{O}$ under saturated H_2O vapour (x max. 6; 4 in the case of Cu). At 100° it is $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}][\text{R}^{\text{II}}(\text{H}_2\text{O})_2]$. All permutites are dehydrated between 100° and 700° . The dehydration t - x curves of $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{Na}_2$ and $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{Ba}$ are identical, and those of other permutites, even the hydrated ones, are of similar form after excess of H_2O has been removed. In the thermal decomp. of $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}](\text{NH}_4)\text{H}$, evolution of NH_3 begins at 150° , but only after about 1.5 mols. of H_2O have been removed. Subsequently, the two are evolved together in equal mol. proportions, but dehydration is slower than for $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{Na}_2$. This is explained by assuming an equilibrium $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_9]\text{NH}_3 \rightleftharpoons [\text{Al}_2\text{Si}_2\text{H}_3\text{O}_9]\text{NH}_4$. The evolution of NH_3 is complete at 500° . The v.-p. curves of Na and Ba permutites are also identical. The isothermal decomp. of all permutites is "zeolitic." $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}](\text{NH}_4)\text{H}$ gives off some H_2O before H_2O and NH_3 are evolved in equimol. proportions. The process is completely reversible. By observing the action of liquid NH_3 on permutites 7 different groups have been distinguished: (a) normal with 2 mols. of SiO_2 , e.g., $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{Na}_2$; (b) hydrated, with 2 mols. of SiO_2 , e.g., $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}][\text{Ca}(\text{H}_2\text{O})_6] \dots \text{H}_2\text{O}$; (c) acid, including aluminosilicic acid, e.g., $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{KH}$; (d) anhydrides, e.g., $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_9]\text{NH}_3$; (e) with more than 2 mols. of SiO_2 , e.g., $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{Na}_2 \dots \text{H}_4\text{SiO}_4$; (f) additive compounds, e.g., $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{Na}_2 \dots \text{H}_2\text{O}$, $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{Na}_2 \dots \text{NH}_3$, $[\text{Al}_2\text{Si}_2\text{H}_4\text{O}_{10}]\text{H}_2 \dots \text{H}_2\text{O}_2$; (g) substitution permutites obtained by anionic exchange, e.g., $[\text{Al}_6\text{Si}_6\text{H}_{10}\text{O}_{28}(\text{OH})_2]\text{Na}_6$ gives $[\text{Al}_6\text{Si}_6\text{H}_{10}\text{O}_{28}(\text{SH})_2]\text{Na}_6$, etc.

M. S. BURR.

Investigation of hydrated peroxides [titanium peroxide]. M. BILLY and (Mlle.) I. SAN-GALLI (Compt. rend., 1932, 194, 1126—1128).—To a series of solutions of 117 mg. of TiO_2 in the form of acid solutions of titanic chloride or sulphate, diluted to 200—2000 c.c., are added at 0° and 15° , increasing amounts of H_2O_2 . The mixtures are diluted to a fixed vol., neutralised with the same excess of BaCO_3 , when the hydrated peroxide is pptd., excess of H_2O_2 is determined, and the O_2 combined calc. by difference. This latter is plotted against the amount of O_2 added as H_2O_2 , and shows that Ti_2O_5 is formed, which then forms $\text{Ti}_2\text{O}_5 \cdot 3\text{H}_2\text{O}_2$ (cf. A., 1921, ii, 456). Similar results were obtained with $\text{Ce}(\text{NO}_3)_3$ and Mo, but Cu as hydroxide or phosphate does not combine with H_2O_2 . C. A. SILBERRAD.

Germanium. XXXVII. Germanium dioxide gel. Preparation and properties. A. W. LAUBENGAYER and P. L. BRANDT (J. Amer. Chem. Soc., 1932, 54, 549—552).—By interaction of $\text{Ge}(\text{OEt})_4$, prepared from NaOEt and GeCl_4 , with EtOH and H_2O , a firm gel of GeO_2 results. Its adsorptive power for C_6H_6 , CCl_4 , and Et_2O is of the same order as that of SiO_2 gel. It adsorbs 19.1% H_2O , after removal of which the adsorptive power for C_6H_6 vapour is appreciably lower, indicating that a change in structure is caused by the adsorbed H_2O .

M. McMAHON (c).

Preparation of germanium tetrabromide and tetraiodide. A. W. LAUBENGAYER and P. L. BRANDT (J. Amer. Chem. Soc., 1932, 54, 621—623).—By modifying the method used for the prep. of GeCl_4 (A., 1925, i, 1108) GeBr_4 was prepared directly from GeO_2 and HBr with a yield of about 90% of purified product. GeI_4 , m. p. 146° , was similarly obtained by action of HI on GeO_2 with yields of 80% and 85%. M. McMAHON (c).

Anhydrous combinations of thorium oxy-chloride and alkali chlorides. E. CHAUVENET and J. TONNET (Compt. rend., 1932, 194, 1078—1079).—Solutions of the constituents in definite proportions were mixed, evaporated to dryness, heated at 350° in HCl , and then at 100° in CO_2 . The density and the heat evolved (in kg.-cal.) in the reaction $\text{ThOCl}_2(\text{sol.}) + \text{MCl}(\text{sol.})$ were determined (figures given in this order). The existence of the following is established ($\text{X} = \text{ThOCl}_2$): $\text{X} \cdot \text{LiCl}$ 3.88, 15.13 (cf. A., 1909, ii, 589); $\text{X} \cdot \text{NaCl}$ 3.862, 4.33; $\text{X} \cdot \text{KCl}$ 3.567, 7.69; $\text{X} \cdot \text{RbCl}$ 3.90, 13.3; $\text{X} \cdot \text{CsCl}$ 3.91, 11.86. C. A. SILBERRAD.

Complex nitrites. I. II. Double nitrites of potassium and nickel, and of potassium and cobalt. A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1931, [vi], 14, 435—441, 511—515).—I. The triple nitrites containing K, an alkaline-earth metal, and Co or Ni have a monometric structure of the $\text{K}_3\text{Co}(\text{NO}_2)_6$ type, with 4 mols. in the unit cell. The following vals. of a and d , respectively, were obtained: $\text{K}_2\text{Ca}[\text{Ni}(\text{NO}_2)_6]$ 10.29, 2.75; $\text{K}_2\text{Sr}[\text{Ni}(\text{NO}_2)_6]$, 10.49, 2.88; $\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$, 10.67, 3.02; $\text{K}_2\text{Ca}[\text{Co}(\text{NO}_2)_6]$, 10.17, 2.86; $\text{K}_2\text{Sr}[\text{Co}(\text{NO}_2)_6]$, 10.23, 3.10; $\text{K}_2\text{Ba}[\text{Co}(\text{NO}_2)_6]$ 10.45, 3.20. The X-ray diagrams of the corresponding nitrites containing Cu instead of Co or Ni contain lines characteristic of two isomorphous monometric lattices.

II. The supposed compounds

$6\text{KNO}_2 \cdot 3\text{Co}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ and $2\text{KNO}_2 \cdot \text{Co}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ consist of $\text{K}_3\text{Co}(\text{NO}_2)_6$ mixed with $\text{Co}(\text{OH})_2$. The compound $\text{K}_4\text{Ni}(\text{NO}_2)_8$ has a monometric lattice (a 10.49 Å.) and appears to be isomorphous with $\text{K}_3\text{Co}(\text{NO}_2)_6$ (a 10.32 Å.), although the two mols. do not contain the same no. of atoms. O. J. WALKER.

Reduction of nitrites to hydroxylamine by sulphites. G. K. ROLLEFSON and C. F. OLDERSHAW (J. Amer. Chem. Soc., 1932, 54, 977—979; cf. A., 1918, i, 482).—The yield of $\text{NH}_2\text{OH} \cdot \text{HCl}$ is increased by using KNO_2 and K_2CO_3 instead of the Na salts. K hydroxylaminedisulphonate, $\text{HON}(\text{SO}_3\text{K})_2 \cdot 2\text{H}_2\text{O}$, the solubility of which is 0.075 mol. per litre at 0° , is pptd., then hydrolysed separately in 0.5N-HCl. The temp. should be kept below 0° and the p_{H} adjusted with a suitable acetate buffer.

W. C. FERNELIUS (c).

Decomposition of ammonium nitrate. M. S. SHAH and T. M. OZA (J.C.S., 1932, 725—736).—The effect of temp., pressure, mass, and of the addition of ThO_2 , Na_2SO_4 , As_2O_5 , and CuSO_4 on the thermal decomp. of carefully dried NH_4NO_3 , initially in a vac., has been studied. The NH_4NO_3 first dissociates thus: $\text{NH}_4\text{NO}_3 = \text{NH}_3 + \text{HNO}_3$, after which the consecutive reactions $\text{NH}_3 + 3\text{HNO}_3(\text{gaseous}) = (\text{N}_4\text{O}_6 + 3\text{H}_2\text{O}) = 4\text{HNO}_2 + \text{H}_2\text{O}$; $4\text{NH}_3 + 4\text{HNO}_2 = (4\text{NH}_4\text{NO}_2) = 4\text{N}_2 + 8\text{H}_2\text{O}$ occur. When HNO_3 is formed in quantity, N_2O_4 and N_2O_3 are evolved together with the N_2 . In all cases the main product is N_2O , produced probably by the decomp. of molten NH_4NO_3 thus: $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$. N. H. HARTSHORNE.

Influence of chlorine and bromine on the glow of phosphorus. J. KREJČI and F. SCHACHERL (Coll. Czech. Chem. Comm., 1932, 4, 107—123).—The effect of the dry halogens on the upper pressure limit of the autoxidation of P in O_2 and air is similar to that of NO_2 (A., 1931, 17), although about 0.1 as large, and an equation of the same form is followed. Probably reaction chains are broken by Cl_2 through the reaction $\text{Cl}_2 + \text{O} \rightarrow \text{Cl}_2\text{O}$; presence of H_2O greatly raises the upper pressure limit, in accordance with the known reactions $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$; $\text{HOCl} \rightarrow \text{HCl} + \text{O}$. C. W. DAVIES.

Hexametaphosphates. P. PASCAL and (MME.) R  CHID (Compt. rend., 1932, 194, 762—764).—On heating equimol. amounts of Na_2HPO_4 and NH_4NO_3 very slowly (in 8 hr.) to 270 — 280° and keeping the mixture at that temp. for several days, then dissolving in H_2O and pptg. with EtOH a well cryst. salt, $\text{Na}_6(\text{PO}_3)_6 \cdot 10\text{H}_2\text{O}$, is obtained, quite different from the trimetaphosphate ordinarily produced (cf. A., 1924, ii, 856). The anhyd. salt melts at 852° , and on cooling forms a porcelainic, non-hygroscopic, micro-cryst. mass. It is stable to heat, and in solution at room temp., but when heated in dil. solution it passes directly into NaH_2PO_4 , the reaction being unimol. Its solution ppts. most heavy metals, but not Zn, the ppts. being usually well cryst. Those from salts of Pb, Fe, and Co are sol. in excess. The name normal crvst. hexametaphosphate is proposed.

C. A. SILBERRAD.

Phosphorous oxide. III. Action of water on phosphorous oxide. L. WOLF, W. JUNG, and M.

TSCHUDNOWSKY (Ber., 1932, 65, [B], 488—491; cf. A., 1929, 662, 897).— H_3PO_3 is the sole product when P_2O_3 is caused by vigorous shaking to react rapidly with an excess of cold H_2O . Slow reaction (without shaking) between P_2O_3 and H_2O yields primarily H_3PO_3 , which reacts with unchanged P_2O_3 , giving H_3PO_4 and yellow phosphorus suboxide (?), P_2O . With hot H_2O the change does not differ in principle from the "slow reaction." The PH_3 produced is due to local overheating of H_3PO_3 accelerated by the solid suboxide. H. WREN.

Reduction of phosphates. H. H. FRANCK and H. FULDNER (Z. anorg. Chem., 1932, 204, 97—139).—The reactions occurring during the technical reduction of $\text{Ca}_3\text{P}_2\text{O}_8$ by C have been studied up to a temp. of 1850° . Below 1550° the chief reactions are (1) $\text{Ca}_3\text{P}_2\text{O}_8 + 8\text{C} = \text{Ca}_3\text{P}_2 + 8\text{CO}$, and (2) $3\text{Ca}_3\text{P}_2\text{O}_8 + 5\text{Ca}_3\text{P}_2 = 24\text{CaO} + 16\text{P}$, and CaO is the only solid product. Above 1550° increasing amounts of Ca_3P_2 are formed, and finally CaC_2 , although even at 1850° an appreciable proportion of Ca_3P_2 remains undecomposed. Pressures of $(\text{CO} + \text{P}_n)$ over a mixture of $\text{Ca}_3\text{P}_2\text{O}_8$, Ca_3P_2 , CaO, and C, and of P_n over the same mixture without C, have been measured, and from these the equilibrium pressure of CO over $\text{Ca}_3\text{P}_2\text{O}_8$, Ca_3P_2 , and C has been calc. The heat of formation of Ca_3P_2 (123—133 kg.-cal.) calc. from the data thus obtained agrees with that measured directly (120 ± 2.5 kg.-cal.). Addition of SiO_2 not only increases the velocity of the reaction, but also, by fixing the CaO formed, prevents the attainment of equilibrium between the gaseous and solid products, and thus leads to a practically quant. yield of P at 1450° . The non-occurrence of silicophosphate as an intermediate product was established. $\text{Ca}_3\text{P}_2\text{O}_8$ at 1400° can form mixed crystals with CaO containing 13.5% of the latter substance. F. L. USHER.

Internally complex compounds of quinquivalent niobium and tantalum. A. ROSENHEIM and E. ROEHRICH (Z. anorg. Chem., 1932, 204, 342—350).—The following compounds of Nb^V have been obtained: *pyrocatechol niobates*, $\text{K}_2\text{H}[\text{NbO}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 2\text{C}_6\text{H}_4(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ (the Na salt gives an uncrystallisable syrup), $(\text{NH}_4)_2\text{H}[\text{NbO}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 0.5\text{C}_6\text{H}_4(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_3[\text{NbO}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$, $(\text{CN}_3\text{H}_6)_2\text{H}[\text{NbO}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 6\text{H}_2\text{O}$, $(\text{CN}_3\text{H}_6)_2(\text{NH}_4)[\text{NbO}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$, $(\text{C}_2\text{ON}_4\text{H}_6)_2\text{H}[\text{NbO}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 0.5\text{C}_6\text{H}_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $[\text{Cd}(\text{NH}_3)_6]\text{H}[\text{NbO}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 6\text{H}_2\text{O}$, and also a corresponding Zn ammine salt mixed with NH_4 salt; *guanidinium pyrogallol niobate*, $(\text{CN}_3\text{H}_6)_2\text{H}[\text{NbO}(\text{C}_6\text{H}_3\text{O}_3)_3] \cdot 6\text{H}_2\text{O}$, and an analogous *gallic acid* compound which remains in solution; *acetylacetone niobates*, $\text{K}_2\text{H}[\text{NbO}(\text{C}_5\text{H}_7\text{O}_2)_3] \cdot 1.5\text{C}_5\text{H}_8\text{O}_2$, and $(\text{CN}_3\text{H}_6)_2\text{H}_2[\text{NbO}(\text{C}_5\text{H}_7\text{O}_2)_3]$. The compounds show no analogy with those of Sb^V (A., 1931, 1254). Ta^V forms the following *pyrocatechol tantalates*: $\text{K}_2\text{H}[\text{Ta}_2\text{O}(\text{C}_6\text{H}_4\text{O}_2)_6] \cdot 3\text{C}_6\text{H}_4(\text{OH})_2 \cdot 10\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{H}[\text{Ta}_2\text{O}(\text{C}_6\text{H}_4\text{O}_2)_6] \cdot 3\text{C}_6\text{H}_4(\text{OH})_2 \cdot 7\text{H}_2\text{O}$, $(\text{CN}_3\text{H}_6)_3\text{H}[\text{Ta}_2\text{O}(\text{C}_6\text{H}_4\text{O}_2)_6] \cdot \text{C}_6\text{H}_4(\text{OH})_2 \cdot 11\text{H}_2\text{O}$, and $(\text{C}_2\text{ON}_4\text{H}_6)_3\text{H}[\text{Ta}_2\text{O}(\text{C}_6\text{H}_4\text{O}_2)_6] \cdot 0.5\text{C}_6\text{H}_4(\text{OH})_2 \cdot 14\text{H}_2\text{O}$.

NbCl_5 reacts with salicylic acid and salicylaldehyde to form the compounds $\text{Nb}(\text{OH})_3(\text{O}-\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ and $\text{Nb}(\text{OH})_3(\text{O}-\text{C}_6\text{H}_4\cdot\text{CHO})_2$, respectively. It also forms compounds, too hygroscopic to be analysed, with other derivatives of salicylic acid such as the Me ester. M. S. BURR.

Reduction of sulphur dioxide with hydrogen and carbon monoxide. E. TERRES, K. SCHULTZE, and H. FORTKORD.—See B., 1932, 339.

Decomposition of dithionates. G. TAMMANN and W. BOEHME (Z. anorg. Chem., 1932, 204, 143—144).—Heating curves for dithionates of K, Na, NH_4 , Mg, Ba, and Zn show that SO_2 is evolved in a single stage, and there is no indication of the existence of an acid intermediate between $\text{H}_2\text{S}_2\text{O}_6$ and H_2SO_4 . F. L. USHER.

Esters of selenic acid. J. MEYER and W. HINKE (Z. anorg. Chem., 1932, 204, 29—32).—Conflicting statements with regard to the tendency of Me and Et selenates to explode when heated have been reconciled by showing that these esters, prepared in two ways, can be distilled without decomp. at pressures below 25 mm., but decompose explosively at 145° . Me_2SeO_4 may be conveniently prepared from H_2SeO_4 and a solution of diazomethane in Et_2O . F. L. USHER.

New class of amines. Double selenocyanammines. IV. G. SPACU and V. ARMEANU. V. Simple selenocyanammines. G. SPACU and C. G. MACAROVICI (Bul. Soc. Stiinte Cluj, 1931, 6, 64—78, 95—138; Chem. Zentr., 1931, ii, 2711—2712).—IV. The following have been prepared: $[\text{Hg}(\text{SeCN})_4][\text{Hg en}_2]$, $[\text{Ag}(\text{SeCN})_2][\text{Ag en}]$, $[\text{Cd}(\text{SeCN})_4][\text{Cu en}_2]$, $[\text{Cd}(\text{SeCN})_4][\text{Ni en}_2]$, $[\text{Cd}(\text{SeCN})_4][\text{Cd en}_2]$, $[\text{Cd}(\text{SeCN})_4][\text{Co en}_2]$, $[\text{Cd}(\text{SeCN})_4][\text{Hg en}_3]$, $[\text{Mn}(\text{SeCN})_6][\text{Ni en}_3]_2$, $[\text{Mn}(\text{SeCN})_6][\text{Cu en}_3]_3$.

V. The following NH_3 , en, benzidine (Bd), and toluidine (Td) compounds have been prepared: $[\text{en}_2 \text{CoCl}_2\text{SeCN}]$, $[\text{Co en}_2\text{CO}_3]\text{SeCN}$, $[\text{Cr en}_3](\text{SeCN})_3$, $[\text{Cu en}_2](\text{SeCN})_2$, $[\text{Cu en}_3](\text{SeCN})_2(\text{SeCNK})$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{SeCN})$, $[\text{Ni}(\text{NH}_3)_6](\text{SeCN})_2$, $[\text{Cd}(\text{NH}_3)_4](\text{SeCN})_2$, $[\text{Ni}(\text{NH}_3)_4](\text{SeCN})_2$, $[\text{Cd}(\text{NH}_3)_2](\text{SeCN})_2$, $[\text{CoBd}_2](\text{SeCN})_2$, $[\text{NiBd}_3](\text{SeCN})_2$, $[\text{CdBd}](\text{SeCN})_2$, $[\text{MnBd}_3](\text{SeCN})_2 \cdot \text{H}_2\text{O}$, $[\text{ZnBd}_2(\text{H}_2\text{O})_2](\text{SeCN})_2 \cdot 2\text{H}_2\text{O}$, $[\text{MgBd}_3](\text{SeCN})_2 \cdot 4\text{H}_2\text{O}$, $[\text{CdTd}(\text{H}_2\text{O})](\text{SeCN})_2 \cdot 5\text{H}_2\text{O}$, $[\text{CoTd}](\text{SeCN})_2$, $[\text{NiTdH}_2\text{O}](\text{SeCN})_2$, $6\text{H}_2\text{O}$, $[\text{NiTdH}_2\text{O}](\text{SeCN})_2$, $[\text{CoTd}(\text{C}_5\text{H}_5\text{N})_4](\text{SeCN})_2$, $[\text{NiTd}(\text{C}_5\text{H}_5\text{N})_4](\text{SeCN})_2$, $[\text{NiTd}(\text{C}_5\text{H}_5\text{N})_4](\text{SeCN})_2$, $[\text{NiTd}(\text{C}_5\text{H}_5\text{N})_5](\text{SeCN})_2$, $[\text{CdTd}](\text{SeCN})_2$, $[\text{ZnTd}_2](\text{SeCN})_2$, $[\text{MnTd}_2(\text{H}_2\text{O})_4](\text{SeCN})_2$, $\text{Pb}(\text{SeCN})\text{OH}$. A. A. ELDRIDGE.

Red permolybdates. K. GLEU (Z. anorg. Chem., 1932, 204, 67—80).—By the action of H_2O_2 on a solution of K_2MoO_4 made alkaline with NH_3 a red anhyd. cryst. *K permolybdate*, K_2MoO_8 , is formed. The substance explodes by percussion or slight heating, and is decomposed rapidly in solution, more slowly when dry. In acid solution the active O appears as H_2O_2 . In a similar manner Zn tetrammine permolybdate, $\text{Zn}(\text{NH}_3)_4\text{MoO}_8$, has been prepared. It has similar chemical properties but is not explosive.

These preps. must be carried out at -12° to -18° . Structural formulæ are discussed. F. L. USHER.

Preparation of uranium for Aston's determination of isotopes. A. VON GROSSE (Z. anorg. Chem., 1932, 204, 184—186; cf. A., 1931, 1349).—A description of the prep. and purification of UF_6 used by Aston in examining the mass spectrum of U.

F. L. USHER.

Oxyacids of fluorine. L. M. DENNIS and E. G. ROCHOW (J. Amer. Chem. Soc., 1932, 54, 832—833).—Preliminary details of the method of prep. of HFO_3 and HFO are given. C. J. WEST (c).

Preparation of iodine-free bromine. G. M. KARNS and H. C. DONALDSON (J. Amer. Chem. Soc., 1932, 54, 442—444; cf. A., 1929, 1410; 1930, 1628).—I-free Br of sufficient purity for microchemical work can be prepared by washing Br several times with H_2O . L. KELLEY (c).

Starch-iodide reaction. R. G. TURNER and M. Z. WEEKS (J. Amer. Chem. Soc., 1932, 54, 829—830).—Polemical against Remington, McClendon, and von Kolnitz (A., 1931, 699). C. J. WEST (c).

Metal carbonyls. XII. Reaction of iron carbonyl with bases and formation of iron carbonyl hydride. W. HIEBER and F. LEUTERT [with (FRL.) E. SCHMIDT]. **XIII. Mechanism of decomposition reactions of iron carbonyl hydride.** Preparation of iron tetracarbonyl. W. HIEBER [with H. VETTER and H. KAUFMANN]. **XIV. Chemical behaviour of nickel carbonyl compared with [that of] iron pentacarbonyl.** W. HIEBER and H. KAUFMANN (Z. anorg. Chem., 1932, 204, 145—164, 165—173, 174—183; cf. this vol., 134).—XII. Aq. $\text{Ba}(\text{OH})_2$ and NaOMe in MeOH each react with $\text{Fe}(\text{CO})_5$ to give $\text{Fe}(\text{CO})_4\text{H}_2$ and BaCO_3 (1 mol.) or MeNaCO_3 (1 mol.). H_2O is essential to the reaction, which can serve to detect traces present in MeOH or EtOH . $\text{Fe}(\text{CO})_4\text{H}_2$ is readily dehydrogenated by mild oxidising agents, forming $[\text{Fe}(\text{CO})_4]_3$. The reaction is quant. with alkaline MnO_2 , which, however, does not react in neutral or acid solution. The mode of linking of the H atoms, which are not acidic, is discussed.

XIII. The various types of decomp. observed in alkaline solutions of $\text{Fe}(\text{CO})_5$ are traceable to the great reactivity of the $\text{Fe}(\text{CO})_4\text{H}_2$ primarily formed. By the action of air $\text{Fe}(\text{CO})_3$ or one of its derivatives is produced, and this very readily gives rise to a mixture of di- and penta- or di- and tetra-carbonyls. Similarly, $\text{Fe}(\text{CO})_4$ may form an unsymmetrical mixture. On acidifying, further reactions ensue, in which varying proportions of Fe^{2+} , CO , H_2 , $\text{Fe}(\text{CO})_4\text{H}_2$, $[\text{Fe}(\text{CO})_4]_3$, and $\text{Fe}(\text{CO})_5$ are produced. An almost quant. yield of $[\text{Fe}(\text{CO})_4]_3$ may be obtained by gentle oxidation of alkaline $\text{Fe}(\text{CO})_5$, preferably with an aq. suspension of MnO_2 , or with H_2O_2 containing $\text{CO}(\text{NH}_2)_2$.

XIV. $\text{Ni}(\text{CO})_4$ does not react with alkali, whether aq. or alcoholic, but the mixture is extremely sensitive to O_2 . N_2H_4 , aq. or anhyd., has a slight action on $\text{Ni}(\text{CO})_4$, but no carbonate is formed.

F. L. USHER.

Action of alkali alkoxides on iron pentacarbonyl. F. FEIGL and P. KRUMHOLZ (Monatsh., 1932,

59, 314—327).— $\text{Fe}(\text{CO})_5$ and NaOMe in Et_2O (containing a little MeOH) suspension give the colourless, readily oxidised compound (I), $\text{Fe}(\text{CO})_5\text{NaOMe}$; in presence of excess of MeOH , the compound, $\text{Fe}(\text{CO})_5\cdot 2\text{NaOMe}\cdot 2\text{MeOH}$, results. $\text{Fe}(\text{CO})_5\cdot \text{NaOEt}$ (cf. Hock and Stuhlmann, this vol., 32) and (I) are decomposed by H_2O , yielding about 50% of $\text{Fe}(\text{CO})_5$. The reaction occurring between $\text{Fe}(\text{CO})_5$, NaOR , and H_2O is: $\text{Fe}(\text{CO})_5 + 2\text{NaOR} + \text{H}_2\text{O} = \text{Fe}(\text{CO})_4\text{HNa}\cdot \text{ROH} + \text{NaRCO}_3$ (cf. Hieber and Leutert, A., 1931, 810). The compounds $\text{Fe}(\text{CO})_4\text{HNa}\cdot \text{MeOH}$ and $\text{Fe}(\text{CO})_5\text{HNa}\cdot \text{EtOH}$ with HgCl_2 give $\text{Fe}(\text{CO})_4\text{Hg}_2\text{Cl}_2$; this and the compounds described by Hock and Stuhlmann (A., 1930, 47) are derivatives of $\text{Fe}(\text{CO})_4\text{H}_2$. HgCl_2 and an excess of $\text{Fe}(\text{CO})_4\text{H}_2$ give $\text{Fe}(\text{CO})_4\text{Hg}$, converted by HI (d 1.7) into $\text{Fe}(\text{CO})_4\text{H}_2$ and a little $[\text{Fe}(\text{CO})_4]_3$. $\text{Fe}(\text{CO})_5$ and $M\text{-Ba}(\text{OH})_2$ afford the salt, $[\text{Fe}(\text{CO})_4\text{H}]_2\text{Ba}$. H. BURTON.

Transformation from blue to rose cobaltous hydroxide. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1932, 36, 722—734).—X-Ray analysis shows that $\text{Co}(\text{OH})_2$ exists in two isomeric cryst. forms, the α form being green or blue, and the β form rose. $\alpha\text{-Co}(\text{OH})_2$, the unstable form, dissolves in alkali, from which it is reprecipitated as the less sol. β form. The $\alpha \rightarrow \beta$ transformation can be prevented by strongly adsorbed substances in the solution from which the α form separates. The transformation is delayed indefinitely by small amounts of various sugars, which are strongly adsorbed even in very low concns., and retarded by Co salts, $\text{Ni}(\text{OH})_2$ simultaneously pptd., gelatin, and sulphates. $\text{Co}(\text{OH})_2$ in contact with a solution of CoCl_2 changes in colour from green to blue to lavender. X-Ray analysis shows the blue and green substances to be mixtures of $\alpha\text{-Co}(\text{OH})_2$, $\beta\text{-Co}(\text{OH})_2$, and a basic salt, $\text{CoCl}_2\cdot 3\text{CoO}\cdot 3\cdot 5\text{H}_2\text{O}$. The lavender compound formed on long keeping is the pure basic salt.

H. B. WEISER (c).

Complex salts of cobalt with a double shell. R. GRAF (Z. anorg. Chem., 1932, 204, 187—192).—By the action of H_2O_2 on a solution of Co borate in aq. NH_3 red crystals of NH_4 cobaltic aquo-pentammine octoborate decahydrate $\{[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}][\text{B}_8\text{O}_{14}]\}\cdot \text{NH}_4\cdot 10\text{H}_2\text{O}$ are formed. The K salt has also been prepared. NH_4 and K salts of the analogous hexammine compounds form yellow and deep orange crystals, respectively. A structural formula is given in which the cobaltamine complex, with co-ordination no. 4, is shown as the nucleus of a larger complex.

F. L. USHER.

Synthesis and X-ray investigation of nickel chromite, NiCr_2O_4 . S. HOLGERSSON (Z. anorg. Chem., 1932, 204, 382—384).—Dark green NiCr_2O_4 is prepared by heating NiO and Cr_2O_3 together in mol. proportions for 5 hr. at approx. 1000° , using KCl or B_2O_3 as a flux. By X-ray measurements with a Cr anticathode a is 8.32 and the calc. mol. vol. is 71.5 \AA^3 .

M. S. BURR.

Sedimentation analysis and its application to chemical, agricultural, and technical problems. S. ODÉN (Svensk Kem. Tidskr., 1932, 44, 2—15, 35—43, 65—79).—A theoretical and historical survey of the subject is given, and the various types of

apparatus employed are described. Examples of the results of mechanical analysis (distribution of grain-size) of a no. of clays, soils, and sands, as well as of technical products such as emery, graphite, and cement are given. The formation of ppts. in solutions takes place in 5 stages (*a*) formation of nuclei, (*b*) development of these to form primary particles, (*c*) formation of aggregates, (*d*) changes undergone by reversible aggregates, (*e*) ageing, but all these stages are not necessarily passed through in every pptn. The formation of a no. of ppts. such as the sulphates of Ba, Sr, Ca, and Pb under differing conditions has been studied, and the results are plotted and tabulated. Photomicrographs of cryst. ppts. are given.

H. F. HARWOOD.

Quantitative spectroscopy with special reference to the "ratio quantitative" system. S. J. LEWIS (Chem. and Ind., 1932, 271—274).—Details of the "ratio quant." method of quant. analysis by means of the spectrum are given. The complete quant. analysis of any material can be carried out with a margin of error of 10%. For extremely minute quantities, which can scarcely be detected chemically, the method is of special use.

A. J. MEE.

Combined indicator for acidimetry. B. GROAK (Biochem. Z., 1932, 244, 294—295).—The combination consists of saturated alcoholic Me-red solution (100 c.c.) and 1% aq. solution of methylene-blue (4 c.c.). At the end-point the indicator is colourless. Microburettes or 0.002*N* solutions should be used and titrations carried out hot since CO₂ interferes.

W. MCCARTNEY.

Determination of the hydrogen-ion concentration of gas-rich fluids. B. GROAK (Biochem. Z., 1932, 245, 61—66).—A suitable electrode and its use are described.

P. W. CLUTTERBUCK.

Photographic record of p_H in liquid reactions. P. JOLIBOIS and G. FOURETIER (Compt. rend., 1932, 194, 1072—1074).—The system HgCl electrode|liquid under examination|H or quinhydrone electrode, is used, but resistance is diminished by making the H electrode of Pt foil in a reversed bell jar, and the HgCl electrode of Hg, the surface (1 sq. cm.) being powdered over with HgCl and covered with agar jelly saturated with KCl, and this covered with a thin porous plate of alundum; the galvanometer circuit includes a resistance of 50,000 ohms. The quantity of added reagent is measured as before (cf. this vol., 491). The method is illustrated by the neutralisation of H₃PO₄, aq. with NaOH, aq.

C. A. SILBERRAD.

Accurate colorimetric p_H determination. E. B. G. CAMERON (Internat. Sugar J., 1932, 34, 64).—The max. accuracy obtainable with purchased colour standards and indicator solutions was 0.4 p_H .

J. P. OGILVIE.

Determination of water by distillation with liquids having $d > 1$. I. Tetrachloroethane. H. LUNDIN (Svenska Bryggarefor. Manadsbl., 1931, 40, 283—289; Chem. Zentr., 1931, ii, 3409—3410).—An apparatus and its application to the analysis of press yeast are described.

A. A. ELDRIDGE.

Determination of water by distillation with liquids having $d < 1$. Toluene or xylene. H.

LUNDIN and M. LUNDIN (Svenska Bryggarefor. Manadsbl., 1931, 40, 289—293; Chem. Zentr., 1931, ii, 3410).—An apparatus and its application to the analysis of hops are described.

A. A. ELDRIDGE.

Dolch's moisture determination method. B. RASSOW and A. RECKELER (Angew. Chem., 1932, 45, 266—267).—Dolch's method (Z. Oberschl. Berg-Hüttenmann. Ver. Kattowitz, 1929) is based on the fact that a mixture of EtOH and petroleum separates into two phases at a definite H₂O content and the temp. at which separation occurs is a function of the H₂O content of the EtOH. An apparatus is described whereby the process may be applied to determine H₂O in absorbent substances such as cotton etc. The results obtained are slightly higher than by drying at 105° or by distillation with PhMe, but are believed to be more trustworthy, since the "bound" H₂O is extracted by the EtOH.

E. S. HEDGES.

Titration of peroxide in the presence of alkali oxalates. W. FEHRE (Arh. Hemiju, 1932, 6, 47—52).—H₂C₂O₄ is pptd. by BaCl₂ and H₂O₂ is determined in the filtrate by titration with KMnO₄. This method cannot be applied in the presence of org. substances other than H₂C₂O₄.

R. TRUSZKOWSKI.

Fractional reaction for chlorine. G. T. MICHALTSCHISCHIN (Ukrain. Chem. J., 1931, 6, [Sci.], 183—189).—To 1—2 c.c. of solution, containing Cl', Br', I', CN', CNS', and Fe(CN)₆^{III or IV} 2—3 c.c. of conc. aq. Ni(NO₃)₂ or Zn(NO₃)₂ are added in order to ppt. CN' and Fe(CN)₆^{III or IV}. KMnO₄ is then added in excess, in order to convert I' into IO₃' and CNS' into CN' and SO₄', 2—3 c.c. of saturated aq. Ba(NO₃)₂ are added, and the solution is filtered. The filtrate is decolorised by acidification with HNO₃ and addition of H₂O₂, and 4—5 c.c. of 2% AgNO₃ are added. The ppt. of AgBr and AgCl is washed once with H₂O, and a further 2 c.c. of 2% AgNO₃ are added. 4—5 c.c. of aq. (NH₄)₂CO₃ are added to the suspension, which is boiled a few min., and filtered. Should <0.21—0.35 mg. of Cl' be present, a ppt. of AgCl appears in the filtrate on acidification with HNO₃.

R. TRUSZKOWSKI.

Detection of chloride in presence of bromide. Reaction for bromates. R. MONTEQUI and G. PUNCEL (Anal. Fis. Quím., 1932, 30, 132—139).—Berg's original method, oxidation of the HBr by HBrO₃ in presence of COMe₂, is tedious and liable to lead to large errors if traces only of Cl are present. In the procedure recommended, 2 c.c. of 7.2*N*-H₂SO₄ and 3 c.c. of COMe₂ are added to 5 c.c. of the solution to be tested, the whole is heated just to the b. p., and a 5% solution of KBrO₃ in 2*N*-H₂SO₄ is added dropwise. The whole is diluted with cold H₂O to 30—40 c.c., and 8—10 drops of conc. HNO₃ and 2—3 drops of AgNO₃ solution are added to detect Cl'. The method takes only 2—3 min. and will detect 0.2% of Cl'; it serves also to indicate approx. the quantity of Br' present. BrO₃' may be detected by a solution containing 0.25 g. fuchsin and 250 c.c. HCl (d 1.19) per litre, with which it yields a transient intense reddish-violet coloration or a dark red ppt. which is soluble in CHCl₃; the limit of sensitivity is about 0.002 mg. (KBrO₃). Br' may be detected by oxidation, preferably with a 0.25% solution of chloramine-*T*, in

presence of the fuchsin reagent; 0.0005 mg. of KBr in 5 c.c. of solution may thus be detected.

H. F. GILLBE.

Determination of bromides in presence of iodides and chlorides. A. G. BAITCHIKOV (J. Chem. Ind. Russ., 1931, 8, Nos. 15—16, 54—58).—50 c.c. of CHCl_3 are added to 50—100 c.c. of solution (4—20 mg. Br) containing NaCl, NaBr, and NaI. 50% H_2SO_4 is added, in quantity depending on the NaCl content, and 0.2% KMnO_4 is added to a permanent coloration. The CHCl_3 layer is separated after shaking, and the aq. layer is twice extracted with fresh portions of CHCl_3 . The combined CHCl_3 extracts, containing Br with a little Cl_2 , are shaken with 50% H_2SO_4 and Na_2SO_3 , thus converting Br and Cl_2 into NaBr and NaCl. The aq. layer is again treated with KMnO_4 , and again thrice extracted with CHCl_3 . 10—15 c.c. of H_2O and 2—3 c.c. of 2% KI are added to the CHCl_3 extract, and I thus liberated is titrated with 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$. This method gives an accuracy of 3—4%.

R. TRUSZKOWSKI.

Determination of small quantities of iodides in the presence of bromides and chlorides. L. W. WINKLER (Z. anal. Chem., 1932, 87, 116—119).—The substance containing 2—10 mg I' is dissolved in 10 c.c. of H_2O , 1 g. of KBr is added, followed by 2 c.c. of CCl_4 , and the solution is titrated, with vigorous shaking, with 0.01N-KBrO₃ until the CCl_4 layer, which first becomes rose-coloured, again becomes colourless; 1 c.c. $\text{KBrO}_3 = 0.6346$ mg. I.

A. R. POWELL.

Dichromate as a standard in iodometry. R. V. TEIS (J. Gen. Chem. Russ., 1931, 1, 845—855).—The vol. of $\text{Na}_2\text{S}_2\text{O}_3$ necessary to titrate acid solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ to which KI has been added increases with time when 2% KI is present, and decreases when 1% KI is present. The increase is due to oxidation of HI by atm. O_2 , and the decrease to loss of I by volatilisation. Trustworthy figures are obtained only by using O_2 -free solutions and performing the titration in an atm. of CO_2 .

R. TRUSZKOWSKI.

Determination of reducing substances of different degrees of activity and of iodides in their presence. S. V. GORBATSCHIEV and I. A. KASATKINA (J. Appl. Chem. Russia, 1931, 4, 520—522).—In one portion of the solution the total quantity of substances of which the oxidation products have a potential > that of ICl is determined; the titration is repeated with another portion after removal of iodides with AgCl.

CHEMICAL ABSTRACTS.

Nephelometric determination of sulphate. H. A. J. PIETERS and J. HOVERS (Chem. Weekblad, 1932, 29, 188—189).—Five tubes containing graded standards are mounted on a vertical pillar which may be rotated so that each solution in turn is brought into position for comparison with the solution under examination.

H. F. GILLBE.

Rapid volumetric determination of nitrates. P. SZEBERÉNYI (Z. anal. Chem., 1932, 87, 357—358).—If a nitrate is heated in HCl solution with excess of a Sn^{II} salt, the reactions $2\text{KNO}_3 + 10\text{HCl} + 4\text{SnCl}_2 = \text{N}_2\text{O} + 5\text{H}_2\text{O} + 2\text{KCl} + 4\text{SnCl}_4$ and $\text{KNO}_3 + 9\text{HCl} + 4\text{SnCl}_2 = \text{NH}_3 + 3\text{H}_2\text{O} + \text{KCl} + 4\text{SnCl}_4$ occur, and the excess of Sn^{II} salt may be titrated with iodine. The

relation between the nitrate and the Sn^{II} solution, which does not vary much with the amount of the latter in excess, is determined empirically.

R. CUTHILL.

Influence of carbonates and of the amount of dry residue on the accuracy of nitrate determinations by Grandval and Lajoux' method. B. A. SKOPINTZEV (J. Appl. Chem. Russia, 1931, 4, 716—721).—Alkalinity should be < 0.5 c.c. of 0.1N- H_2SO_4 ; the dry residue should be dissolved completely.

CHEMICAL ABSTRACTS.

Potentiometric determination of nitrites with potassium permanganate and with hydrogen peroxide. E. JIMENO and J. IBARZ (Anal. Fis. Quím., 1932, 30, 128—131).— NO_2' may be accurately determined potentiometrically with KMnO_4 solution, despite the slowness of the reaction. For the potentiometric determination of NO_2' with H_2O_2 it is advisable to employ an excess of H_2O_2 and to titrate the excess with KMnO_4 .

H. F. GILLBE.

Very sensitive reagent for hydrazine and analogous compounds. E. MONTIGNIE (Bull. Soc. chim., 1932, [iv], 51, 127).—The reducing action of SeO_2 on compounds containing the $\text{NH}\cdot\text{NH}_2$ group can be applied to the detection of traces of $\text{NHPh}\cdot\text{NH}_2$ and N_2H_4 with a sensitivity of 0.00025 g. for 5 c.c. of 4% SeO_2 ; with compounds containing the $\text{NH}\cdot\text{NH}\cdot$ group the sensitivity is less marked, being 0.0001 g. for semicarbazide hydrochloride, and 0.001 g. for phenylsemicarbazide. Conversely, 2—3 drops of $\text{NHPh}\cdot\text{NH}_2$ in 10 c.c. of $\text{H}_2\text{O} + \text{HCl}$ indicate the presence of 0.0003 g. of Se.

R. BRIGHTMAN.

Mass analysis. II. Colorimetric determination of phosphoric acid. III. Colorimetric determination of phosphoric acid in fertilisers. N. E. PESTOV (J. Chem. Ind. Russ., 1931, 8, No. 15—16, 22—36; No. 20, 15—22).—II. Applying the following modification of Deniges' colorimetric method the mean relative deviation from the gravimetric method is 0.28%. Not more than 0.16 mg. P_2O_5 per 100 c.c. of final solution should be taken, with a standard of 0.1 mg. set at 40—50. The coloration obtained is stable during 2 hr., and turbidity due to separation of $\text{Sn}(\text{OH})\text{Cl}$ is avoided by adding 100 mg. of HCl together with 100 mg. of NH_4 molybdate and 2 g. of H_2SO_4 , and keeping for 40 min. before adding SnCl_2 (1 c.c., containing 5 mg. Sn). The intensity of coloration is not exactly proportional to the P_2O_5 content, and a series of empirical formulæ is given for the calculation of the theoretical from the observed colorimeter reading, for various parts of the scale, and in the presence of various substances, such as citric acid, salts, alkali, etc.

III. A more detailed account of the above method.

R. TRUSZKOWSKI.

Blue colorimetric method for the determination of phosphorus. H. D. CHAPMAN (Soil Sci., 1932, 33, 125—134).—The SnCl_2 reagent used in the Truog and Meyer method (A., 1929, 1158) oxidises slowly even when covered by a layer of paraffin, but if stored in narrow bottles, deterioration is not serious within several months. The blue colour produced by silicomolybdate is readily formed in solutions of low acidity, and 0.5 p.p.m. SiO_2 may invalidate P

determinations in this condition. With suitable acid-molybdate reagents, the error due to 700 p.p.m. SiO_2 may be negligible. If the test solution is diluted to its final vol. and the addition of SnCl_2 is delayed the P colour may be affected by small amounts (1 p.p.m.) of Fe^{++} . This effect is minimised by immediate addition of reagent. SO_4^{--} , NO_3^- , and Cl^- affect the accuracy of the test only when present in very high proportions. A. G. POLLARD.

Biological detection of arsenic. A. F. LERRIGO (Analyst, 1932, 57, 155—158).—A résumé of the literature dealing with the liberation of volatile As compounds by the action of micro-organisms and enzymes. Volatile As compounds could not be obtained by the use of type cultures or natural mixed cultures. T. MCLACHLAN.

Determination of silicic acid in apatites and phosphorites. V. TISCHTSCHENKO and M. M. RAINES (J. Appl. Chem. Russia, 1931, 4, 523—526).—Schrenk and Ode's method (B., 1930, 55) is satisfactory. CHEMICAL ABSTRACTS.

Manometric analysis of gas mixtures. I. Determination, by simple absorption, of carbon dioxide, oxygen, and nitrogen in mixtures. D. D. VAN SLYKE and J. SENDROY, jun. II. [Determination of] carbon dioxide by the isolation method. D. D. VAN SLYKE, J. SENDROY, jun., and S. H. LIU. IV. [Determination of] hydrogen and oxygen by combustion. V. [Determination of] hydrogen by absorption with Paal's picrate-palladium solution. D. D. VAN SLYKE and M. E. HANKE. VI. [Determination of] carbon monoxide by absorption with blood. J. SENDROY, jun. (J. Biol. Chem., 1932, 95, 509—529, 531—546, 569—585, 587—597, 599—611).—I. Using the const.-vol. blood-gas apparatus (A., 1924, 872), CO_2 and O_2 are determined by absorbing with *N*-NaOH and 30% $\text{Na}_2\text{S}_2\text{O}_4$ in 2*N*-KOH, respectively, and noting the decrease in pressure. The usual error in analysis of air is ± 0.05 vol.-%, but a trace of N_2 in a 50-c.c. sample of O_2 or CO_2 can be determined more accurately by measuring its pressure at 0.5 c.c. vol. The experimental procedure depends on the proportion of N_2 present.

II. CO_2 is absorbed by shaking with alkali. The residual gases are ejected, the CO_2 is liberated with acid, and determined as in the determination of plasma CO_2 (A., 1924, ii, 872). The CO_2 in 200—300 c.c. of air can be determined to within 0.0003 vol.-%; with respired air containing about 5% CO_2 the accuracy is ± 0.05 vol.-% (cf. A., 1923, i, 162).

IV. Pressure measurements were made in the usual manometric apparatus and the gases combusted in a separate chamber, explosive mixtures being burnt under reduced pressure. In the micro-method, with 1.5 c.c. sample, the max. error is $\pm 0.2\%$; with 30 c.c. it is $\pm 0.05\%$ for H_2 and $\pm 0.03\%$ for O_2 . Combustible organic gases can similarly be determined, with CO_2 analyses as in I and II.

V. The H_2 , free from CO_2 and O_2 , is absorbed by 0.2 c.c. of reagent containing 2% of colloidal Pd and 3.5% of picric acid in 0.154*N*-NaOH. The max. error is 0.2% of total gas. The method is untrustworthy in presence of O_2 .

VI. CO is absorbed from the O_2 -free gas, in the manometric apparatus, with reduced ox blood, then liberated with acid ferricyanide and determined by the method of Sendroy and Liu (A., 1930, 942). In concns. of 0.05—0.30% the max. error is $\pm 5\%$.

J. B. BATEMAN.

Determination of traces of carbon monoxide in ethylene. H. S. BOOTH and M. B. CAMPBELL—See B., 1932, 250.

Titration of [total] alkalis in water. J. TILMANS and E. NEU.—See B., 1932, 290.

Errors involved in determination of minute amounts of sodium by the magnesium uranyl acetate method. E. R. CALEY (J. Amer. Chem. Soc., 1932, 54, 432—437).—Amounts of Na as small as 0.2 mg. may be determined satisfactorily by the direct Mg uranyl acetate method (A., 1929, 900; 1931, 56). Still smaller amounts may be determined in special cases by the use of unusually small vols. of solution and reagent. The use of a more conc. reagent leads to high results with the usual procedure and does not favour the quant. pptn. of minute quantities of Na. W. T. HALL (c).

Physical method of determining potassium chloride in sylvites. E. CORNEC and H. KROMBACH (Compt. rend., 1932, 194, 784—786).—The lowering of temp. on dissolving (at 20° in a Dewar flask with agitation) 10 g. of sylvite in 100 c.c. of saturated aq. NaCl is determined. The apparatus is standardised by determining the lowering due to a solution of pure KCl, to the amount of which it is almost linearly proportional. The error does not exceed 0.3% KCl, but is relatively greatest for poor sylvites, and can be reduced by a second standardisation with a poor sylvite of known composition.

C. A. SILBERRAD.

Determination of potassium by means of per-rhenic acid. H. TOLLERT (Z. anorg. Chem., 1932, 204, 140—142; cf. A., 1930, 1392).—The procedure, for which precise directions are given, closely resembles that followed when using HClO_4 . Solubilities of K, Na, and Ba per-rhenates in 90% EtOH are given. The method is not recommended for general laboratory practice, but is useful when the quantity of K is too small to be determined satisfactorily as KClO_4 . F. L. USHER.

Extension of isoamyl alcohol separation of alkali and alkaline-earth metals to lithium, rubidium, and caesium. H. YAGODA (J. Amer. Chem. Soc., 1932, 54, 984—988).—When Ba, Sr, Ca, Mg, Na, K, Li, Rb, and Cs bromides are dissolved in a min. vol. of hot H_2O , treated with 10 c.c. of isoamyl alcohol, conc. to 1 c.c., and treated with 1 drop of 8*N*-HBr and 1 c.c. of isoamyl alcohol, only Mg, Sr, Ca, and Li bromides remain dissolved. After washing the ppt. with isoamyl alcohol containing a little HBr, it is treated with 95% EtOH, which dissolves Ba and Na bromides and traces of the others, and from this solution BaCl₂ and NaCl are pptd. with conc. HCl. The Mg is removed as MgO from the first filtrate by adding conc. HNO_3 , evaporating to dryness, and igniting. After adding H_2O and evaporating the filtrate to dryness with HNO_3 $\text{Sr}(\text{NO}_3)_2$ remains,

and is dissolved in hot H_2O , then pptd. by boiling with 2 c.c. of isoamyl alcohol. From the solution of Ca and Li nitrates the Ca is pptd. as oxalate, and then the Li as stearate. W. T. HALL (c).

Volumetric determination of alkaline-earth carbonates. A. V. FILOSOFOV (J. Appl. Chem. Russia, 1931, 4, 532—534).—In titrations with standard HCl and NaOH solutions boiling should be limited to <3 min. CHEMICAL ABSTRACTS.

Fractional reaction for strontium. E. P. GARMASCH (Ukrain. Chem. J., 1931, 6, [Sci.], 177—181).—The solution, containing ± 2.2 mg. % of Sr, is made slightly acid with AcOH, and excess of K_2CrO_4 is added. The filtrate is then boiled with $(NH_4)_2SO_4$, when a ppt. of $SrSO_4$ indicates the presence of Sr. This reaction is applicable in the presence of the metals of all 5 analytical groups. Ca may be detected in the filtrate from $SrSO_4$ by the formation of a ppt. with $Na_2C_2O_4$. R. TRUSZKOWSKI.

Fractional reaction for barium. A. V. LARIONOV (Ukrain. Chem. J., 1931, 6, [Sci.], 191—193).—Excess of aq. NH_3 is added to the solution, containing all the ordinary cations, the mixture is boiled and filtered, the filtrate is made acid with AcOH, and NaOAc is added. Saturated aq. K_2CrO_4 is now added, yielding a ppt. of $BaCrO_4$ and Ag_2CrO_4 . The latter ppt. is dissolved by addition of aq. NH_3 , leaving cryst. $BaCrO_4$. In this way ± 14 mg. Ba can be detected in 1 c.c. of solution. R. TRUSZKOWSKI.

Separation of cations of last three groups in analysis without ammonium sulphide. A. S. KOMAROVSKI and V. J. GOREMYKIN (Z. anal. Chem., 1932, 87, 339—342).—The filtrate from the H_2S group after removal of excess of H_2S is boiled with a mixture of 20% aq. NaOH, 10% aq. Na_2CO_3 , and a c.c. of 3% aq. H_2O_2 , the filtrate containing Zn, Al, and Cr. The ppt. is boiled with aq. $(NH_4)_2CO_3$ and aq. NH_3 , the Ni and Co dissolving as complex salts. On dissolving the residue in a mixture of HNO_3 and H_2O_2 , then neutralising with Na_2CO_3 and boiling with aq. NH_3 , NH_4Cl , and H_2O_2 , Fe and Mn remain as a ppt., whilst the alkaline-earth metals are in solution. Alternatively, the ppt. after removal of Zn, Cr, and Al may be boiled with aq. $NH_2OH \cdot HCl$, aq. NH_3 , and NH_4Cl , when Fe remains undissolved. After evaporating the filtrate with HNO_3 , Mn is separated by addition of NH_4Cl , aq. NH_3 , and H_2O_2 . On boiling the filtrate with an excess of aq. $(NH_4)_2CO_3$ and aq. NH_3 Ca, Sr, and Ba separate, whilst Ni, Co, and Mg remain in solution. R. CUTHILL.

Gravimetric determination of beryllium by means of guanidine carbonate, and its separation from Fe^{+++} , UO^{++} , Th^{+++} , Zr^{+++} , Ti^{+++} , WO_4^{--} , MoO_4^{--} , VO_4^{--} , CrO_4^{--} , AsO_4^{--} , SbO_3^{--} , and Cu^{+} . III. A. JILEK and J. KOŤA (Coll. Czech. Chem. Comm., 1932, 4, 97—106).—Be in the presence of the radicals named can be determined by the method previously described (A., 1931, 1024), except that with VO_4^{--} or WO_4^{--} the solution before pptn. must be neutral instead of slightly acidic. C. W. DAVIES.

Fractional reaction for magnesium. E. V. VASILIEVA (Ukrain. Chem. J., 1931, 6, [Sci.], 195—197).—A reagent, prepared by dissolving $(NH_4)_2C_2O_4$

in saturated aq. $K_3Fe(CN)_6$, and adding 0.1 of the vol. of aq. NH_3 , is added to the solution, containing ± 0.12 mg. of Mg per c.c., as long as a ppt. forms, the mixture is filtered, and Na phosphate is added to the filtrate, when a cryst. ppt. indicates the presence of Mg. R. TRUSZKOWSKI.

Determination of magnesium by means of 8-hydroxyquinoline. H. FREDHOLM (Svensk Kem. Tidskr., 1932, 44, 79—85).—A modification of Berg's method (A., 1927, 639), which gives more accurate results. The neutral solution of the Mg salt is heated at 90—100°, and a few g. of NH_4Cl are added. A solution of 1 g. of 8-hydroxyquinoline in 100 c.c. of 0.1N-NaOH is then added dropwise until a slight excess is present. After cooling, the solution is filtered, the ppt. well washed with warm water containing a little NH_3 , and redissolved in 2N-HCl. After the addition of KBr and a few drops of 0.2% Me-red, 0.1N-KBrO₃ is added until a yellow colour is obtained. KI is then added, and the free I titrated with 0.1N- $Na_2S_2O_3$. Alkalies, Ba, and Sr do not interfere, but in the presence of much Ca the pptn. with 8-hydroxyquinoline must be repeated.

H. F. HARWOOD.

Qualitative separation of zinc and aluminium. E. CHIRNOAGA (Bull. Math. Phys. Bucarest, 1931, 11, 190).—Since Zn is frequently pptd. with Al in qual. analysis, NaOH is added to the solution until the ppt. first formed just dissolves. $(NH_4)_2S$ then ppts. Zn as sulphide, whilst Al remains in solution as $NaAlO_2$. A. J. MEE.

Volumetric determination of zinc in zinc oxide and chloride. I. TANANAEV (J. Appl. Chem. Russia, 1931, 4, 686—695).—The methods of Cone and Cady and of Kolthoff are satisfactory only if the Zn concn. of the solution examined is approx. equal to that of the solution used for standardising the $K_4Fe(CN)_6$ solution. Preferably $K_4Fe(CN)_6$ is added in excess, and the excess titrated with indigo as indicator. For standardising $K_4Fe(CN)_6$ with $KMnO_4$ Me-violet and tropæolin OO are recommended as indicators.

CHEMICAL ABSTRACTS.

Quantitative separations by thermal decomposition of anhydrous mixtures of metal sulphates. H. H. WILLARD and R. D. FOWLER (J. Amer. Chem. Soc., 1932, 54, 496—516; cf. Wohler and Grünzweig, A., 1913, ii, 597).—Mixtures of the non-isomorphous sulphates of Fe^{III} and Zn, Al and Zn, and Be and Al may be separated by heating at such a temp. that one sulphate is converted into an insol. basic sulphate or oxide, whilst the other is unchanged. Anhyd. mixed crystals of the sulphates of Ni and Co, Be and Zn, Be and Mg, La and Pr, and Nd and Pr decompose into mixed crystals of basic sulphates or oxides, so that no separation is possible. $Ce_2(SO_4)_3$ mixed with the anhyd. isomorphous sulphates of La, Pr, and Nd is preferentially decomposed into CeO_2 , because of difference in the lattices of CeO_2 and the rare-earth sesquioxides. The mixed nitrates of Pr and La decompose at 400—450° into PrO_2 and a solid solution of La_2O_3 in Pr_2O_3 . A considerable separation of these oxides may then be achieved by conversion into sulphates and extraction with H_2O .

L. KELLEY (c).

Volumetric determination of the lead ion by the oxalate method from the viewpoint of the rules of remainders and of substitution. N. A. TANANAEV and V. S. KOZARENKO (Ukrain. Chem. J., 1931, 6, [Sci.], 199—206).—More accurate results are obtained by back-titrating excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ added to $\text{Pb}(\text{NO}_3)_2$ than by treating the washed ppt. of PbC_2O_4 with H_2SO_4 and titrating the product with KMnO_4 . The best results ($\pm 0.2\%$) are given by adding 50 c.c. of $0.1N\text{-(NH}_4)_2\text{C}_2\text{O}_4$ to 25 c.c. of $0.1N\text{-Pb}(\text{NO}_3)_2$, boiling, cooling, adding H_2O to 100 c.c., filtering, and titrating 25 c.c. of filtrate with $0.1N\text{-KMnO}_4$. R. TRUSZKOWSKI.

Determination of lead peroxide. III. Bromo-potentiometric method. A. V. PAMFILOV and E. G. IVANCEVA.—See B., 1932, 259.

Volumetric determination of thallium. A. J. BOGORODSKI and M. V. TROTSKI (J. Gen. Chem. Russ., 1931, 1, 895—899).—To 1—5 c.c. of solution, containing 0.005—0.26 g. of $\text{Tl}(\text{NO}_3)_3$, 1 c.c. of 15% KOH , 30 c.c. of $0.1N\text{-KI}$, 40 c.c. of $0.1N\text{-KIO}_3$, and H_2O to 110 c.c. are added, the solution is filtered to remove pptd. TlI , and 4 c.c. of 33% H_2SO_4 are added to 100 c.c. of filtrate, which is then boiled to remove liberated I . Excess of KIO_3 is then determined by adding 0.5—1 g. of KI to the cooled solution and titrating with $0.025N\text{-Na}_2\text{S}_2\text{O}_3$. The method gives results 0.2—0.3% lower than the actual figures. R. TRUSZKOWSKI.

Titration of copper with sodium sulphide, and detection of small amounts of dissolved sulphides. A. BORNTRAGER (Z. anal. Chem., 1932, 87, 342—352).—After addition to 20 c.c. of the Cu solution, containing 0.05 g. of Cu , of sufficient aq. NH_3 to redissolve the ppt. first formed, followed by 50 c.c. of H_2O , the standard Na_2S solution is gradually added with continuous and vigorous shaking until the supernatant liquor is no longer blue in colour and addition of the Na_2S solution does not produce a brown colour. 2 c.c. of the solution are then filtered and tested with AcOH and $\text{K}_4\text{Fe}(\text{CN})_6$, titration being continued until no reaction for Cu is obtained in this way. The Na_2S solution should be preserved under a layer of petroleum, and not exposed to strong light. The titration is not affected by $\text{Na}_2\text{S}_2\text{O}_4$. Attempts to use internal and external indicators to detect the end-point have not been very successful. R. CUTHILL.

Influence of substituents on the solubility and stability of complex metal compounds of 8-hydroxyquinoline derivatives. R. BERG (Z. anorg. Chem., 1932, 204, 208—214; cf. A., 1930, 1546).—The influence of CO_2H , SO_3H , Ph , OMe , and halogens substituted in various positions in 8-hydroxyquinoline has been studied. The most useful from an analytical point of view are the 5 : 7-dichloro-, 5 : 7-dibromo-, and 5-chloro-7-iodo-derivatives, all of which form very insol. compounds with Cu , Fe , and Ti .

F. L. USHER.

5 : 7-Dibromo-8-hydroxyquinoline, a new specific reagent for copper, iron, and titanium in quantitative analysis. R. BERG and H. KÜSTEN-MACHER (Z. anorg. Chem., 1932, 204, 215—221; cf. preceding abstract).—The pptn. limits for Cu , Fe , and Ti are $1 : 10^6$, $1 : 5 \times 10^5$, and $1 : 10^6$, respectively. A

process of separation is based on the fact that $\text{H}_2\text{C}_2\text{O}_4$ prevents the pptn. of Fe and Ti , and tartaric, malonic, or citric acid that of Ti only. Detailed directions are given for procedure when other metals are present.

F. L. USHER.

Electrochemical detection of minimal amounts of mercury. E. SCHMIDT and E. TORNOW (Chem. Ztg., 1932, 56, 187—188, 206—207).—The solution is electrolysed for $\frac{1}{4}$ hr. between a C anode and small Al cathode; Hg is detected by its promotion of rapid oxidation at the Al surface. Ag , Cd , Cu , and As^{V} do not interfere; As^{III} may do so, but not if 1—2% NaCl is added. 0.001 mg. Hg can be detected.

C. W. DAVIES.

Determination of small quantities of mercury in air. E. V. ALEXEEVSKI (J. Appl. Chem. Russia, 1931, 4, 411—414).— Hg is absorbed in Cl_2 solution, pptd. with Cu , and determined by a micro-colorimetric method. CHEMICAL ABSTRACTS.

Interference of chlorine and ammonium salts with colorimetric determination of small amounts of mercury with diphenylcarbazone. V. MAJER (Z. anal. Chem., 1932, 87, 352—356).—Free Cl_2 and HCl in a solution of HgCl_2 in which Hg is to be determined colorimetrically are most readily removed by concn. over P_2O_5 and soda-lime in a desiccator. The solution should not evaporate quite to dryness, otherwise some Hg is lost. If NH_4 salts are present, the Hg is separated on Cu after removal of excess of Cl , then distilled off and reconverted into HgCl_2 . R. CUTHILL.

Analysis of aluminium sulphate. W. D. BANCROFT, H. L. DAVIS, and E. C. FAENHAM (J. Physical Chem., 1932, 36, 515—522).—The SO_3 may be determined as BaSO_4 provided that a little HCl is added to prevent hydrolysis, and the Al_2O_3 by ignition over the blow-pipe. At 400—500° the H_2O is lost without appreciable volatilisation of SO_3 . W. T. HALL (c).

Influence of iron and chromium on the [caesium] alum reaction for aluminium. B. V. J. CUVELIER (Natuurwetensch. Tijds., 1932, 14, 41—43).—Formation of Cs alum cannot be employed for the micro-detection of Al in presence of Fe or Cr , as these metals form similar crystals, but if aq. NH_3 is added the reaction products may be differentiated if the ratio $\text{Al} : \text{Fe}$ or $\text{Al} : \text{Cr}$ does not exceed 1 : 2 or 1 : 3, respectively. If KHSO_4 is used instead of CsHSO_4 , 0.05 mg. of Al in 0.05 c.c. of solution may be detected if the $\text{Al} : \text{Fe}$ or $\text{Al} : \text{Cr}$ ratio does not exceed 1 : 40 or 1 : 50, respectively. If the Fe is removed by extraction as FeCl_3 by Et_2O , and the Cr^{III} is oxidised to CrO_4^{II} , the Cs alum reaction is satisfactory with $\text{Al} : \text{Fe}$ and $\text{Al} : \text{Cr}$ ratios of 1 : 2000. H. F. GILLBE.

Electroanalytical determination of gallium. I. E. REICHEL (Z. anal. Chem., 1932, 87, 321—332).—To the solution of $\text{Ga}_2(\text{SO}_4)_3$ are added 10—40 g. of $(\text{NH}_4)_2\text{SO}_4$ per 0.1 g. of Ga , then the p_{H} is adjusted to 10.4—10.8 with aq. NH_3 . Electrolysis, with Pt electrodes and a current of 5 amp., is started at 60—65°, the temp. gradually being raised to 75—80° as electrolysis proceeds. A certain amount of Pt is dissolved from the anode and deposited on the cathode, necessitating the application of a suitable correction.

The Ga deposited alloys with the Pt, but can largely be removed by treatment with HNO_3 .

R. CUTHILL.

Use of potassium manganate in volumetric analysis. H. GALL and M. DITT (Z. anal. Chem., 1932, 87, 333—338).—A solution of K_2MnO_4 in 50% aq. KOH does not change in composition on keeping. For the determination of H_3PO_3 the neutral, or preferably alkaline, solution is boiled gently for 10 min. with a distinct excess of K_2MnO_4 , then there is added $\text{H}_2\text{C}_2\text{O}_4$ approx. equiv. in amount to the K_2MnO_4 , and after acidification with H_2SO_4 the excess of $\text{H}_2\text{C}_2\text{O}_4$ is titrated with K_2MnO_4 at 60° . H_3PO_2 may be determined similarly. To determine Mn the solution is gradually added to an excess of K_2MnO_4 at 80 – 90° , and the mixture then heated for 3–4 min. almost at the b. p. After filtering off the pptd. MnO_2 , the excess of K_2MnO_4 is determined as before.

R. CUTHILL.

Determination of manganese in ferrous products. L. MALAPRADE (Bull. Soc. chim., 1932, [iv], 51, 241—248).—When the amount of Mn is less than 1%, the HPO_3 used in Travers' method (A., 1926, 704) must be replaced by H_3PO_4 . After oxidation to MnO_4' , excess of H_2O_2 is added and back-titration effected with KMnO_4 . Manganic salts react with H_2O_2 according to the equation $\text{Mn}_2\text{O}_3 + \text{H}_2\text{O}_2 = 2\text{MnO} + \text{O}_2 + \text{H}_2\text{O}$.

C. W. DAVIES.

Separation of iron from thorium. N. I. MATVEEV (J. Appl. Chem., Russia, 1931, 4, 275—282).— Fe^{III} is pptd. with $(\text{NH}_4)_2\text{S}$ in ammoniacal tartrate solution; Th is pptd. from the filtrate with cupferron, the AcOH solution being buffered.

CHEMICAL ABSTRACTS.

Formaldoxime, a sensitive reagent for metals of the iron group and especially for manganese. Various applications (mineral waters etc.). G. DENIGES (Compt. rend., 1932, 194, 895—897).—Details are given relative to the sp. colour, its lability and sensitivity to various experimental conditions, by means of which formaldoxime [3 g. $(\text{CH}_3\text{O})_3$, 7 g. $\text{NH}_2\text{OH}\cdot\text{HCl}$, and 15 c.c. H_2O boiled until a clear solution is obtained] is employed, in the presence of NaOH, as a sensitive reagent for the colorimetric determination of small quantities of Mn, Ni, Co, Fe^{III} , and Cu^{II} . The reaction is especially sensitive for Mn (0.1 mg. per litre) owing to the stability of the colour towards heat and may be used for the determination of Mn in mineral waters.

J. W. BAKER.

Iodometric determination of chromium and manganese in presence of each other by means of persulphate. J. H. VAN DER MEULEN (Rec. trav. chim., 1932, 51, 369—373).—One portion of the solution is oxidised to MnO_4' and $\text{Cr}_2\text{O}_7''$ by $\text{K}_2\text{S}_2\text{O}_8$ in presence of HF, H_3PO_4 , and Ag_2SO_4 , excess of $\text{S}_2\text{O}_8''$ is removed by boiling, and the liquid titrated with I and $\text{Na}_2\text{S}_2\text{O}_3$. Another portion is treated similarly, with omission of HF and H_3PO_4 , thus forming $\text{Cr}_2\text{O}_7''$ and only a little MnO_4' , which is pptd. as MnO_2 by excess of MnSO_4 . The MnO_2 is filtered off and $\text{Cr}_2\text{O}_7''$ is determined in the filtrate. The difference of the two results represents the MnO_4' .

E. S. HEDGES.

Determination of tin in tin pyrites containing cassiterite. B. HIRSCH.—See B., 1932, 348.

Determination of titanium as dioxide by means of guanidine carbonate in presence of tartrate. A. JÍLEK and J. KOŤA (Coll. Czech. Chem. Comm., 1931, 4, 72—80).—Ti is quantitatively pptd. as TiO_2 in the presence of tartrate by treating the neutral or feebly acid solution at boiling temp. with a considerable excess of guanidine carbonate. The ppt. retains some of the precipitant, which is removed by ignition.

E. S. HEDGES.

Thermostat for temperatures below that of the laboratory. L. RAMBERG (Chem. Fabr., 1932, 89).—A Hg thermoregulator operates a telephone relay which controls the cooling liquid flowing through the coil by stopping or starting the motor of the operating pump. The periods of rest and running should be about equally long to minimise lag. The control is to 0.01° .

C. IRWIN.

Xenon lamp, a source of light for the extreme ultra-violet. P. HARTECK and F. OPPENHEIMER (Z. physikal. Chem., 1932, B, 16, 77—80).—A low-tension lamp filled with a mixture of a little Xe with Ne or Ar, and capable of emitting through a fluorite window 3×10^{17} quanta per sec. of wave-lengths 1295 and 1469 Å., is described.

R. CUTHILL.

Photographic method of recording reactions between electrolytes. P. JOLIBOIS and G. FOURTIER (Compt. rend., 1932, 194, 872—874).—A specially shaped capillary tube, which also acts as an agitator, through which by centrifugal force a sample of the reacting mixture is driven, forms part of one circuit, enabling its conductivity to be continuously recorded. The solution to be added is in a burette with an arrangement whereby the air pressure above the liquid varies proportionally to the amount of liquid that has flowed out; change in this pressure moves a column of Hg in which a Pt wire dips, thus altering the resistance of a second circuit of which this forms part.

C. A. SILBERRAD.

Application of the electrometer triode to the measurement of high resistance. J. A. C. TEEGAN and N. HAYES (Nature, 1932, 129, 508).

L. S. THEOBALD.

Basic law of the wet- and dry-bulb hygrometer at temperatures from 40° to 100° . J. H. AWBERRY and E. GRIFFITHS (Proc. Physical Soc., 1932, 44, 132—142).—Tables are given for converting wet- and dry-bulb readings into relative humidities, which were determined by dew-point and by gravimetric methods.

C. W. GIBBY.

Absolute manometer. F. W. LANE, F. N. T. HAMERSCHLAG, and E. J. ROEHL (J. Amer. Chem. Soc., 1932, 54, 1020—1021).—The manometer is easily filled and cleaned, and gives a direct comparison between the attained and a Torricellian vac.

H. J. WING (c).

Water-tight seal for very hygroscopic substances examined by the rotation method. B. BRUNOVSKI (Z. Krist., 1932, 81, 475—477).

C. A. SILBERRAD.

Gas-liquid reaction tower [for laboratory use]. E. F. DEGERING (Ind. Eng. Chem., 1932, 24, 181).—

The tower and gas inlet are sealed to a Buchner funnel containing a sintered glass plate. The perforations give under low gas pressure a spray of small bubbles.
C. IRWIN.

Comparison of gaseous densities by the method of balancing columns. A. H. SNELL and A. N. SHAW (Canad. J. Res., 1932, 6, 309—321).—The method has been improved, mainly by the use of a Toepler micromanometer, a sensitivity of 10^{-7} g. per c.c. being obtained with 12-m. columns, even without the use of a thermostat. The sources of error and the application of the method to hygrometry and the analysis of binary gas mixtures are discussed in detail.

D. R. DUNCAN.

Apparatus for preparing membranes. G. FLORENCE (Bull. Soc. chim., 1932, [iv], 51, 72—73).—An apparatus for preparing uniform collodion cylinders consists of a silvered bronze cylinder mounted in a hollow shaft. Collodion is introduced by side openings, the cylinder rotated, and a current of air (dry or moist) is admitted through the hollow shaft. Finally the cylinder is immersed in H_2O , when a uniform membrane is readily detached.

R. BRIGHTMAN.

Catalyst chamber. S. YUSTER (J. Physical Chem., 1932, 36, 1056).—A catalyst chamber for use in gas reactions is described. It may be conveniently disconnected for change of catalyst.

L. H. REYERSON (c).

Improved apparatus for micro-electroanalysis. B. L. CLARKE and H. W. HERMAN (J. Amer. Chem. Soc., 1932, 54, 877—885).—Cells with Pt electrodes are described, one for large vols. of liquid, the other for small vols. The determination of Zn in aq. $Al_2(SO_4)_3$, Pb in $ZnSO_4$ and in $Ni(NO_3)_2$ solutions, Cu in H_2O and aq. $Ni(NO_3)_2$, and impurities in

reagents, when the substance to be determined is present in minute amount, is described. The determination of traces of Ni, Sn, and Zn in small vols. of solution is carried out in the smaller cell.

L. T. FAIRHALL (c).

Surface tension meters. K. GRANT (J. Sci. Instr., 1932, 9, 108—109).—A thin vertical plate dips into the liquid and lies partly within a narrow channel formed in the containing vessel; the surface tension of the liquid, which tends to draw the plate further into the channel, is opposed either by wts. at the end of a lever or by the torque of a wire. The apparatus is suitable chiefly for detecting and measuring changes of surface tension caused by temp. differences, contamination, films of liquid or gas, etc.

H. F. GILLBE.

Double capillary method for measurement of interfacial tension. G. L. MACK and F. E. BARTELL (J. Amer. Chem. Soc., 1932, 54, 936—942).—Apparatus for the precise determination of the interfacial tension between H_2O and a small amount of a liquid of higher or lower d is described. In one apparatus the interfaces are brought so nearly to the same level by means of H_2O levels in large reservoirs that it is not necessary to know the d of the non-aq. liquid very accurately or to calibrate more than a short length of the capillaries. In another apparatus no wide meniscus is measured, but the d of the liquids must be known accurately and the entire length of the long capillary must be calibrated.

F. E. BROWN (c).

Preparation and mounting of deliquescent substances. N. WOOSTER and A. J. P. MARTIN (Nature, 1932, 129, 582).

L. S. THEOBALD.

High-pressure technique. F. G. KEYES.—See B., 1932, 291.

Geochemistry.

Maxima of the intensity of the solar radiation at various regions of the earth's surface. L. GORCZYNSKI (Rev. Chim. Pura Appl., 1931, [iii], 6, 1—15).—Max. vals. of the solar radiation, for tropical ocean, ocean in temperate zone, on land at or above sea level, and in the upper atm. are recorded. The low vals. at sea level are due to absorption by H_2O vapour; this effect is noticeably greater in the tropics.

H. F. GILLBE.

Physico-chemical constants and radioactivity of the water of Corgas [Portugal]. P. FORJAZ (Rev. Chim. Pura Appl., 1931, [iii], 6, 15—16).—The H_2O contains 0.2404 g. of solids and 13.1 c.c. of N_2 and inert gases per litre; traces only of HCO_3' , Fe, and Mg are present. Its radioactivity is 0.61 millimicrocurie per litre. Various physical consts. are given.

H. F. GILLBE.

Relation between composition of mud and of Salt Lake brine. V. I. NIKOLAIEV (J. Appl. Chem. Russia, 1931, 4, 627—632).—Mud of the salt lakes gradually adsorbs $CaSO_4$ and $Ca(HCO_3)_2$, K salts, and Br, but not Na.

CHEMICAL ABSTRACTS.

Origin of diamond in the South and West African coasts. E. REUNING (Neues Jahrb. Min., 1931, A, 64, Beil.-Bd., 775—828; Chem. Zentr., 1931, ii, 3455).

Analysis of a Canadian cyrtolite. O. B. MUENCH (Amer. J. Sci., 1932, [v], 23, 273).—A sample from Ontario contained 0.529% U, 0.431% Pb, and 0.08% Th, whence the age of the mineral is calc. to be 571×10^6 years.

C. W. GIBBY.

Melting of granite. R. W. GORANSON (Amer. J. Sci., 1932, [v], 23, 227—236).—Granite from stone Mt., Atlanta, Georgia, becomes completely liquid (apart from hematite) at $700 \pm 50^\circ$ in the presence of H_2O vapour at a pressure of 980 bars. The liquidus of the dry granite is calc. to be at $1050 \pm 50^\circ$.

C. W. GIBBY.

Occurrence of iron ore in Minas Geraes, Brazil. E. A. SCHEIBE (Arch. Eisenhüttenw., 1931—1932, 5, 391—406).—The geology of the Fe ore deposits between Queluz and Bello Horizonte is discussed in detail. In the primary deposits there are two distinct types of ore, viz., (a) pure itabirite consisting of

stratified red hæmatite with >68% Fe and <0.03% P containing local inclusions of magnetite, and (b) micaceous Fe schist consisting of finely-banded massive deposits of thin layers of specular Fe ore interspersed with quartz and containing 45% Fe with 0.02% P. The only important secondary ore is the so-called "canga," which consists of a relatively thin conglomerate or glassy layer of ferruginous minerals containing 60% Fe and <0.2% P. The southern portion of the deposit contains much dolomitic limestone and high-grade Mn ore. In some parts there are thin intrusive seams of eruptive rock containing Au.

A. R. POWELL.

Constitution of oolitic minerals [of Lorraine]. J. P. AREND (Compt. rend., 1932, 194, 990—993; cf. this vol., 360).—11 analyses are given of the oolitic and gangue portions of four vertically successive beds, and of the pisolitic, oolitic, and gangue portions of the pea-ore (Bohnerz). The relative proportions of oolite and gangue in each are also stated. The variations depend mainly on the accessibility of O_2 to the various beds. The changes are accompanied by an increase in d and consequent diminution in vol.

C. A. SILBERRAD.

Average chemical composition of different rock types. A. JOHANNSEN (Jahrb. Min. Beil.-Bd., 1931, 64, 505—516; Chem. Zentr., 1931, ii, 3196).—A division of rocks into 4 classes with subdivisions.

L. S. THEOBALD.

Mineralogy of Brazil. Occurrence of anatase, zircon, and a vanadium niobate in N. Brazil. E. RIMANN (Jahrb. Min. Beil.-Bd., 1931, 64, 423—436; Chem. Zentr., 1931, ii, 3196).—Anatase, zircon, and a vanadium niobate (ochre-red in colour, strong lustre, and high refractivity), probably of Y, were isolated from an opal. The spectrum showed strong lines of Y in addition to those of V and Nb. La, Ce, Ta, and weak U and Pb lines were also present.

L. S. THEOBALD.

Zeolite minerals of the basalts of the Platten Lake region in Hungary. B. MAURITZ (Jahrb. Min. Beil.-Bd., 1931, 64, 477—494; Chem. Zentr., 1931, ii, 3196).—Phillipsite, apophyllite, chabasite, thaumasite, heulandite, natrolite, and calcite were found in the rock-cavities.

L. S. THEOBALD.

Steenstrupine. F. MACHATSCHKI (Jahrb. Min. Beil.-Bd., 1931, 64, 235—250; Chem. Zentr., 1931, ii, 3195—3196).—Steenstrupine has $a:c$ 1:1.0836; the structure is not similar to that of eudialyte. The formula is $X_3YZ_3(O,OH,F)_{12}$, where X is Na, Ca, Ce, La, and Di, Y is Mn^{++} , Mn^{+++} , Fe^{+++} , Al, and Z is Si and P. Powder photographs give a 9.47, and c 15.39 Å, whilst rotation photographs give average vals. of a 9.64 and c 15.25 Å. The unit cell, wt. 4.195×10^{-24} g., d 3.31, has 5 units of the above formula. Attempts to recrystallise altered steenstrupine occurring in the metamictic condition failed.

L. S. THEOBALD.

Composition of garnets. B. GOSSNER (Jahrb. Min. Beil.-Bd., 1931, 64, 225—233; Chem. Zentr., 1931, ii, 3195).—Deviations from the normal ratio $SiO_2:M'O:M''O_3$ in certain garnets are discussed. Almandine from Dillenberg, near Neu-Albenreuth, has the composition SiO_2 37.00, Al_2O_3 20.36, Fe_2O_3

2.09, FeO 30.80, MnO 7.57, MgO 1.52, and CaO 0.98%; d 4.232. Melanite from Fraskati has the composition SiO_2 35.08, Al_2O_3 4.77, Fe_2O_3 21.37, FeO 2.10, TiO_2 3.60, CaO 33.10, MgO 0.39, and MnO 0.41%.

L. S. THEOBALD.

Aragonite from the rock-cavities of the lower Rhine basalts. K. OBENAUER (Jahrb. Min. Beil.-Bd., 1931, 64, 437—442; Chem. Zentr., 1931, ii, 3195).—Crystallographic measurements of 50 aragonite crystals gave (4, 13, 0), (140) (150) (160) and (350) as new, mostly vicinal, faces.

L. S. THEOBALD.

Pseudoabsorption. F. CORIN (Bull. Soc. franç. Min., 1931, 54, 57—63; Chem. Zentr., 1931, ii, 3194).—Pseudoabsorption in calcite appears to be a complicated process due to other properties besides polarisation, reflexion, and refraction. A calcite from Eysden showed strong pleochroism (brownish-black to colourless) which is traceable to very fine inclusions, probably of argillaceous matter.

L. S. THEOBALD.

Simple sliding of anorthite. O. MUGGE and F. HEIDE (Jahrb. Min. Beil.-Bd., 1931, 64, 163—170; Chem. Zentr., 1931, ii, 3195).—Numerous thin laminae were formed about (010) when homogeneous, regular, twinning-free crystals of anorthite were embedded in clay or $NaNO_3$ and submitted to pressures of approx. 25,000 kg. per sq. cm. The striations are anomalous and indicate a simple sliding process.

L. S. THEOBALD.

Rare minerals in pegmatite, Pointe du Bois, Manitoba. T. L. WALKER (Univ. Toronto Stud. Geol. Ser., 1931, No. 30, 9—13).—The triphylite contained: Li_2O 8.36, Na_2O 0.12, K_2O 0.44, H_2O 0.99, MgO 0.23, CaO 0.65, FeO 21.70, MnO 21.13, P_2O_5 46.41, insol. 0.20%. The columbite contained FeO 14.77, MnO 2.17, CaO 2.66, MgO 0.45, Nb_2O_5 52.26, Ta_2O_5 26.41, TiO_2 0.49, SiO_2 0.13, ZrO_2 0.65, H_2O 0.21%.

CHEMICAL ABSTRACTS.

Lattice dimensions of certain monoclinic amphiboles. G. GREENWOOD and A. L. PARSONS (Univ. Toronto Stud. Geol. Ser., 1931, No. 30, 29—39).—Pargasite (from Pargas, Finland) has a 9.88, b 17.70, c 10.92 Å; hornblende (from Anakie, Victoria) has a 9.88, b 17.85, c 5.443 Å. There are at least 2 types of end-members for the monoclinic amphiboles: a pure meta- and a pure ortho-silicate. In certain specimens in which the unit cell is doubled along the c axis, double-salt formation between meta- and ortho-silicate is postulated.

CHEMICAL ABSTRACTS.

Orthoclase lavas of the volcanoes of Tibesti. A. LACROIX (Compt. rend., 1932, 194, 757—761).—Throughout the massif of Tibesti the oldest and newest lavas are basaltic, those of intermediate age are leucocratic. The orthoclase varieties of these last include rhyolitoids containing numerous spherulites. They are rich in alkali, and include comendites, d 2.395, and pantellerites, d 2.420, passing into trachytes; elsewhere occur microgranites and an obsidian rich in fayalite, and also calco-alkaline rhyolites containing in places much bronzite. The phonolites include varieties containing ægyrine and/or nepheline. Among the trachytes occur a latite, and a rock resembling doreite. The dyke rocks

include a microsphenite closely resembling rhombophyry, a micro-akerite, and (probably) two rocks akin to doréite. Magmatic formulae are given.

C. A. SILBERRAD.

Pyroxene from Hiva Oa, Marquesas Is., and the formula of titaniferous augite. T. F. W. BARTH (Neues Jahrb. Min., 1931, A, 64, Beil.-Bd., 217—224; Chem. Zentr., 1931, ii, 3095).—The pyroxene contained SiO_2 47.11, TiO_2 3.75, Al_2O_3 3.00, Fe_2O_3 3.84, FeO 12.20, MgO 16.65, CaO 13.54, Na_2O 0.22, and K_2O 0.03%; n_a 1.695, n_β 1.701, n_γ 1.728 (all ± 0.003).

A. A. ELDRIDGE.

Crystallography of artificial cassiterite. H. HIMMEL and M. M. PORTER (Neues Jahrb. Min., 1931, A, 64, Beil.-Bd., 27—33; Chem. Zentr., 1931, ii, 3094).

Cassiterite. H. HIMMEL (Neues Jahrb. Min., 1931, A, 64, Beil.-Bd., 67—70; Chem. Zentr., 1931, ii, 3094).—Vals of n are recorded.

A. A. ELDRIDGE.

Origin of the silver of Kongsberg from the electrochemical point of view. L. TRONSTAD (Tidsskr. Kjem. Berg., 1932, 12, 15—18, 28—31).—Primary Ag may have been formed in three ways, (a) by the contact of argentiferous solutions with certain minerals (pyrites etc.) whereby local currents are generated, (b) by electrolytic pptn. as a result of currents set up by contact of the Ag solutions with minerals which under these conditions give a conducting, sparingly-sol. metallic or sub-metallic ppt. (Becquerel effect), and (c) by "capillary electric" pptn. during the passage of Ag solutions through porous rocks. Secondary Ag, especially as wire Ag, may be formed as a result of thermo-electric action, or from effects due to concn. differences. The conclusion is reached that the "cross rule" (i.e., that Ag is found only where the lodes are intersected by the fahlbands) is not of universal application, but that there is a possibility of Ag being pptd. at other points.

H. F. HARWOOD.

Crystal structure of some natural and synthetic apatite-like substances. S. B. HENDRICKS, M. E. JEFFERSON, and V. M. MOSLEY (Z. Krist., 1932, 81, 352—369).—Analyses of the following are given (in this order) (a) fluorapatite from Quebec (cf. A., 1931, 551), (b) chlor- α -apatite from Krageroe, (c) naphtha-extracted bone, (d) (c) steamed for 225 hr. under 40 lb. pressure, (e) $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ from $\text{Na}_3\text{PO}_4 + \text{Ca}(\text{NO}_3)_2$, dried at 50° , (f) hydroxyapatite from $\text{Ca}_3(\text{PO}_4)_2$ hydrolysed with NH_4 citrate (cf. B., 1931, 199): CaO 52.40, 52.97, 34.40, 50.96, 47.76, 49.99; MgO 0.46, 0.29, 0.32, 0.67, 0, 0.11; P_2O_5 40.30, 40.50, 26.13, 38.47, 40.48, 38.68; F 3.26, 0.17, 0, 0, 0, 0; Cl 1.16, 4.13, 0, 0, 0, 0; CO_2 1.51, 0, 3.09, 1.50, 0, 0.12; $\text{Na}_2\text{O} + \text{K}_2\text{O}$ 0, 0.32, 0.54, 0.69, 0.56, 1.01; SiO_2 3.08, 1.16, 0.09, 0, 0, 0.54; Fe_2O_3 0.60, 0.18, 0.09, 0.13, 0, 0.13; loss at 1000° 1.95, 0.48, 37.61, 8.30, 10.97, 8.56; total (less CO_2 and O equiv. to $\text{F} + \text{Cl}$) 100.2, 100.8, 99.09, 99.22, 99.77, 99.02%. a and c (in Å.), d and no. of mols. in unit cell are (b) 9.52, 6.85, 3.25, 2; (c) 9.27, 6.95, 3.25, 2; (e) 9.25, 6.88, 3.01, 2; (f) 9.40, 6.93, 3.08, 2; oxyapatite $\text{Ca}_{10}(\text{PO}_4)_6$ 9.38, 6.93, 3.17—3.20, 2; pyromorphite 9.95, 7.31, 7.04, 2; mimetite 10.24, 7.43, 7.23, 2; vanadinite 10.31, 7.34, 6.86, 2 (cf. A., 1931, 817). It is con-

cluded that F in fluorapatite can be replaced isomorphously by CO_3 , OH, SO_4 , SiO_4 , O, Cl, Br, or I, thus explaining the occurrence in phosphate rock of minerals such as voelkerite, wilkeite, dahllite, podolite, staffelite, collophanite, etc.

C. A. SILBERRAD.

Structure of fibrous sphalerite of the Aachen lead-zinc deposits and the effect of its iron content on the formation of minerals. H. EHRENBURG (Neues Jahrb. Min., 1931, A, 64, Beil.-Bd., 397—422; Chem. Zentr., 1931, ii, 3316—3317).

Titaniferous augite from Mt. Lobau. P. J. BEGER (Neues Jahrb. Min., 1931, A, 64, 71—106; Chem. Zentr., 1931, ii, 3095).—Optical data are recorded.

A. A. ELDRIDGE.

New crystals of kipushite. H. BUTTGENBACH (Bull. Acad. roy. Belg., 1932, [v], 18, 43—51).—A detailed description of new crystals of kipushite, a hydrated basic phosphate of Cu and Zn, is given.

C. W. GIBBY.

Radium content of Portuguese minerals and rocks. G. COSTANZO (Rev. Chim. Pura Appl., 1931, [iii], 6, 17—20).—The Ra content of the various Portuguese minerals examined varied from 0.4 to 12.6 g. per 10^{12} g. The highest figures were obtained for granites, and considerably exceeded those for granites from other regions, whilst the lowest were obtained for schists.

H. F. GILLBE.

Composition of lithiophilite from Mangualde [Portugal]. A. M. DE JESUS (Rev. Chim. Pura Appl., 1931, [iii], 6, 20—23).—The mineral has a composition approx. corresponding with $\text{MO}_2\text{M}'\text{O}_2\text{P}_2\text{O}_5$, where M is Mg, Ca, Li_2 , or Na_2 , and M' is Mn or Fe. It contains Li_2O 8.04%, Na_2O 1.33%, $\text{CaO} + \text{MgO}$ 2.16%.

H. F. GILLBE.

Relationships of the granites to the rhyolites in S.E. Missouri. W. A. TAAR (Science, 1932, 75, 265).—Evidence has accumulated showing that the granites in S.E. Missouri are younger than the rhyolites and have been injected into them.

L. S. THEOBALD.

Differentiation and sequence [of the eruptive rocks] in the Bohemian Midland Mountains. H. KNORR (Tsch. Min. Petr. Mitt., 1932, 42, 318—370).—104 analyses of igneous rocks of Tertiary age from northern Bohemia are tabulated, including 14 new analyses of trachyte, sodalite-syenite, essexite, and nepheline-basalt. The differentiation of the several rock types from an original basaltic-basanitic magma is traced.

L. J. SPENCER.

Gold and bismuth in the spathic iron veins of Siegerland. J. M. HUTTENHAIN (Tsch. Min. Petr. Mitt., 1932, 42, 285—317).—The FeCO_3 veins of the Siegen district, on the borders of Westphalia and Rheinland, contain gold of two generations. The earlier is contained in an invisible form, perhaps as sulphide, in pyrite (6.23 g. per ton). The later generation occurs as minute particles of free Au in association with Bi minerals (Bi, Bi_2S_3 , klaprothite, etc.). They belong to different phases of the hydrothermal processes (arising from a hidden mass of igneous rock) which deposited the material in the veins.

L. J. SPENCER.

Spectroscopic investigation of Brazilian tourmaline. G. O. WILD (Zentr. Min., Geol., Palaont., 1931, 327—330; Chem. Zentr., 1931, ii, 2589).—The red and the rose-coloured tourmaline from the mines near the bridge between Arassuahy and Itinga, and the green rocks of the Barra de Selinas, Minas Geraes, have been investigated with a quartz spectrograph and C arc. Ga, Sn, Na, Ca, and Li are present in the red rocks, but Mg is absent. The green tourmaline showed the principal Fe lines, and strong lines due to Mn, Li, Ca, and Mg, but not Ga. A rose-coloured rock showed no Mg lines. L. S. THEOBALD.

Occurrence of telluride minerals at Kalgoorlie. F. L. STILLWELL (Proc. Austral. Inst. Min. Met., 1931, [ii], No. 84, 115—190).—A description of the following minerals and of their occurrence is given, together with their associated ores: PbTe, HgTe, NiTe₂, xCuTe, yCu₂Te, Ag₂Te, Au₂Te, 3Ag₂Te, AuAgTe₂, (AuAg)Te₂, Au(Ag)Te₂, (PbAu)(STeSb)₁₋₂. C. W. GIBBY.

Constitutional formulæ of spinels. H. RHEIN-BOLDT (Rec. trav. chim., 1932, 51, 356—360).—A lecture. E. S. HEDGES.

Quantitative mineralogical composition of Tertiary sands in the subsoil of Hamburg and its neighbourhood. H. MÜLLER (Zentr. Min., 1931, 278—296; Chem. Zentr., 1931, ii, 2590).—The following sedimentary types have been distinguished (i) pyrite-ilmenite-corundum, (ii) rutile-ilmenite-corundum, (iii) cyanite-ilmenite-corundum, and (iv) amphibole-ilmenite-corundum. These types agree with the sedimentation cycle revealed by the felspar contents of the individual horizons. L. S. THEOBALD.

Nature of clay. F. H. NORTON and F. B. HODG-DON (J. Amer. Ceram. Soc., 1932, 15, 191—205).—The particle spacing (calc. from the bulk- α) of a no. of plastic and non-plastic materials was determined for varying conditions of pressure and H₂O content. All materials at the low pressures (80 kg. per sq. cm.) have a crit. H₂O content (pores half-filled) below which addition of H₂O causes little change in vol., but above which the particles re-orient themselves into a closer packing with a more or less sudden decrease in vol. A saturation point is reached at higher H₂O contents. The non-plastic materials are distinguished only by the absence of drying shrinkage. At high pressures (up to 800 kg. per sq. cm.) the particle spacing is proportional to the logarithm of the pressure and a marked elastic return is found on releasing the pressure. The min. particle spacing at high pressures occurs at the saturated point, and beyond this point additional H₂O forms thick films around the particles of such stability that they are not influenced by pressures of 800 kg. per sq. cm. and the drying shrinkage is also unaffected. Bentonite gave results which indicate close packing of plate-like particles. The plasticity of clays is due to the adsorption on the surface of the particles of a film of H₂O about 3×10^{-5} cm. thick which provides both the cohesion and lubrication. J. A. SUGDEN.

Genesis of coals. II—IV. E. BERL and A. SCHMIDT.—See B., 1932, 245.

Soil charting in the U.S.A. H. KELLER (Z. Pflanz. Düng., 1932, 24, A, 38—44).—The val. of American methods is discussed. A. G. POLLARD.

Organic Chemistry.

Number of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins. C. M. BLAIR [with H. R. HENZE] (J. Amer. Chem. Soc., 1932, 54, 1098—1106; cf. A., 1931, 1147, 1148).—Theoretical. No direct or simple relationship exists between the no. of stereoisomeric and non-stereoisomeric mono-substitution products of the paraffins and their C content. Recursion formulæ are advanced for calculating the no. of stereoisomeric and non-stereoisomeric primary, *sec.*, and *tert.* mono-substitution products from their C content, but their use involves the knowledge of the total no. of isomerides, both stereoisomeric and non-stereoisomeric, of every smaller C content.

C. J. WEST (b).

Preparation of pure ethane, methane, and hydrogen, and analysis of their mixtures. W. E. MACGILLIVRAY (J.C.S., 1932, 941—952).—A column for the purification of CH₄ and C₂H₆ by fractional distillation of the liquefied gases is described. The column is adapted to the analysis of large samples of complex mixtures of hydrocarbons (e.g., CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and C₄H₁₀) (cf. B., 1929, 583, 799). Pure C₂H₆ is prepared from the commercial gas by passing it (at 10 atm.) over heated Cu turnings and then over SiO₂ gel cooled in liquid air. Mixtures of CH₄ and

C₂H₆ can be analysed accurately by the explosion method provided certain precautions (e.g., the use of a grease-free pipette; short washing of the exploded mixture with 10% H₂SO₄) are observed. With mixtures of H₂, CH₄, and C₂H₆, a satisfactory procedure is to oxidise the H₂ over Pd-black at 80—90°, and then explode the residual mixture.

H. BURTON.

Transformation of saturated acyclic hydrocarbons into ethylenic hydrocarbons. C. MATIGNON, A. KLING, and J. FLORENTIN (Compt. rend., 1932, 194, 1040—1043).—Pyrogenic decomp. of C_nH_{2n+2} \rightarrow H₂ + C_nH_{2n} in the presence of Cu- or Ni-pumice predominates at lower temp., is favoured by short duration of contact with the catalyst, but is limited by attainment of equilibrium ($n-2$, $k=12.6$ at 600°). Thus decomp. of C₂H₆ (Ni) at 600° affords C₂H₄, H₂, C₂H₂, and CH₄ in the proportions 14.2, 22.0, 51.0, and 12.8%, respectively, with 42 sec. contact, the vals. for 6.6 min. contact being 12.7, 40.7, 0, and 49.9%. Decomp. of C₃H₈ (Cu) affords negligible amounts of C₂H₄ at 500°, formation of C₃H₆ being favoured (at all temp.) by short contact, whilst the formation of CH₄ and C₂H₄ becomes the predominant reaction for prolonged contact periods. Decomp. of C₄H₁₀ \rightarrow C₂H₄ + C₂H₆—16.4 g.-cal. does not occur below 520°

(Cu), but increases rapidly with rise of temp., becoming predominant at 600°, when secondary reactions of the type $C_2H_4 \rightarrow CH_4 + C$ appear. At 500° the reaction $C_4H_{10} \rightarrow C_3H_6 + CH_4 - 17$ g.-cal. is predominant, whilst about 20% decomp. $\rightarrow C_4H_8 + H_2 - 32.7$ g.-cal. occurs.

J. W. BAKER.

Polymerides and polymerisation. V. Influence of methyl and phenyl substitution on the polymerisability of butadiene. G. S. WHITBY and W. GALLAY (Canad. J. Res., 1932, 6, 280—291).—The polymerisation of methyl- and phenyl- Δ^{γ} -butadienes by heat and chemical agencies (usually H_2SO_4 ; $SbCl_5$ and $SnCl_4$ are less satisfactory) has been examined. The presence of unsubstituted H atoms on the terminal C atoms facilitates polymerisation, at least three being necessary for the formation of a synthetic rubber. Ph groups favour dimeride formation, but inhibit further polymerisation. The following dimethylbutadienes were prepared from the alcohols named by the dehydrating action of HBr, $KHSO_4$ generally giving poorer yields (cf. A., 1914, i, 646): $\beta\gamma$ -, b. p. 69—70°, from pinacol; $\alpha\gamma$ -, b. p. 76—77°, from δ -methyl- Δ^{β} -penten- γ -ol; $\alpha\beta$ -, b. p. 76—79°, from γ -methyl- Δ^{β} -penten- δ -ol; $\alpha\delta$ -, b. p. 80—82°, from Δ^{β} -hexene- δ -ol; $\alpha\alpha$ -, b. p. 76—77° (shown to be different from the $\alpha\gamma$ -compound), from β -methylpentane- $\beta\delta$ -diol. By the action of heat the following dimerides were obtained: $\beta\gamma$ -dimethylbutadiene gave one dimeride, b. p. 95°/17 mm.; the $\alpha\beta$ -compound gave two, b. p. 97—100°/16 mm. and 103—110°/16 mm.; the $\alpha\alpha$ -gave two, b. p. 94—97°/16 mm. and 105—108°/16 mm.; the $\alpha\gamma$ -gave one, b. p. 90—92°/16 mm.; the $\alpha\delta$ -gave two, b. p. 90°/20 mm. and 96—98°/20 mm. Higher polymerides were also obtained. The $\beta\gamma$ - and $\alpha\gamma$ -compounds gave white elastic solids, the $\alpha\beta$ -gave a gel, the $\alpha\delta$ -gave a gel at 100° and an oil at 150°, and the $\alpha\alpha$ -gave an oil. Dehydration of ϵ -methyl- Δ^{β} -hexene- δ -ol by HBr yielded β -methyl- $\Delta^{\beta\delta}$ -hexadiene, b. p. 97—99°, whilst the $\alpha\alpha\gamma$ -compound, b. p. 92°/749 mm., resulted from simple distillation of $\beta\delta$ -dimethyl- Δ^{β} -penten- δ -ol. The dimeride of the $\alpha\alpha\delta$ -compound had b. p. 92—95°/8 mm., that from the $\alpha\alpha\gamma$ - 87—89°/8 mm., this compound also yielding higher oily polymerides. Dehydration of $\gamma\delta$ -dimethylhexane- $\gamma\delta$ -diol by a trace of dil. H_2SO_4 yielded $\gamma\delta$ -dimethyl- $\Delta^{\beta\delta}$ -hexadiene, b. p. 71—73°/100 mm. This polymerised on heating to the dimeride, b. p. 127—123°/14 mm., and higher polymerides. $\alpha\gamma$ -Diphenylbutadiene could not be obtained, its dimeride, m. p. 167°, being produced by the interaction of $MgMeI$ and Ph styryl ketone followed by alkaline hydrolysis. The filtrate, after separation of the dimeride, when refluxed with Ac_2O , yielded Ph β -phenylpropyl ketone, m. p. 74°. Me styryl ketone, treated similarly, gave the dimeride of γ -methyl- α -phenylbutadiene, b. p. 180—185°/2 mm. Neither of these dimerides could be polymerised further. The $\alpha\gamma$ -diphenyl compound polymerised to a grey powder, m. p. 243—250°, under the action of $SbCl_5$ in $CHCl_3$ and to an oil on heating. Tetraphenyltetramethyleneglycol was dehydrated by conc. HCl in boiling AcOH to $\alpha\alpha\delta\delta$ -tetraphenylbutadiene, m. p. 202°. This and the $\alpha\beta\gamma\delta$ -compound (A., 1914, i, 266) yielded only traces of polymeride under the action of heat or

chemical agencies. The dimerides are ring compounds combining with 2 mols. of I.

D. R. DUNCAN.

Reaction of alkyl bromides with pyridine. C. R. NOLLER and R. DINSMORE.—See this vol., 474.

Fluorination of hexachloroethane under pressure. H. S. BOOTH, W. L. MONG, and P. E. BURCHFIELD (Ind. Eng. Chem., 1932, 24, 328—331).— C_2Cl_6 when heated with SbF_3 and $SbCl_5$ under elevated pressure at about 300° yields solid $\alpha\alpha\alpha\beta\beta$ -pentachloro- β -fluoroethane, b. p. 136.8°, $\alpha\alpha\beta\beta$ -tetrachloro- $\alpha\beta$ -difluoroethane, b. p. 91°, C_2Cl_4 , b. p. 119°, $\alpha\alpha\beta$ -trichloro- $\alpha\beta\beta$ -trifluoroethane, b. p. 46.5°, and smaller amounts of gases probably C_2F_6 , C_2F_5Cl , and $C_2F_4Cl_2$.

H. INGLESON.

Preparation of allyl chloride from allyl alcohol and hydrochloric acid. G. T. PILUGIN (Ukrain. Chem. J., 1931, 6, [Sci.], 213—216).—The best yields (78%) are obtained by heating 1 mol. of allyl alcohol with 2 mols. of HCl (d 1.19) at 100° for 15 hr. in a sealed tube.

R. TRUSZKOWSKI.

[Reaction of] **nitrosyl chloride with alcohols and aldehydes.** F. A. LEE and E. V. LYNN (J. Amer. Pharm. Assoc., 1932, 21, 125—128).—All aliphatic monohydric alcohols give nitrites on treatment with NOCl, preferably in presence of pyridine. Nitrites have been prepared from the following: EtOH; CMeEt₂.OH, b. p. 24°/10 mm.; CEt₃.OH, b. p. 36°/10 mm.; CEt₂Pr.OH, b. p. 48°/10 mm. Thymol and antipyrine gave the nitroso-compounds and PhCHO gave BzCl and BzOH. No nitrites were obtained from $C_3H_5(OH)_3$, $C_2H_4(OH)_2$, menthol, chloreton, trimethylene chlorohydrin, or $CH_2Ph.OH$ (cf. A., 1927, 544).

E. H. SHARPLES.

Hexadienol, octatrienol, and decatetraenol. T. REICHSTEIN, C. A. ANN, and G. TRIVELLI [with L. D. VAN DER BEEK and VASS] (Helv. Chim. Acta, 1932, 15, 261—268).—The preps. of *n*-hexadienal (I), b. p. 58—68°/12 mm. ($CaCl_2$ compound), *n*-octatrienal, b. p. 57—68°/0.5 mm. (II), and *n*-decatetraenal (III), b. p. 90—105°/0.5 mm. ($NaHSO_3$ compound, m. p. 95—98°), from crotonaldehyde and MeCHO are modified. (III) with Ag_2O gives the corresponding acid, m. p. indef. (Me ester, m. p. 139—141.5°). (I) with $Al(OPr^i)_3$ and Pr^iOH [but not with $Al(OEt)_3$] forms sorbyl alcohol, b. p. 76—77°/12 mm., m. p. 30.5—31.5° ($CaCl_2$ compound; diphenylurethane, m. p. 78—79°; 3:5-dinitrobenzoyl derivative, m. p. 85° gives with α -naphthylamine a compound, m. p. 89—90°), reduced catalytically ($Pd-CaCO_3$) in Et_2O to pure *n*-hexyl alcohol. (II) and (III) give similarly *n*-octatrienol, m. p. 99.5—100.5° (reduced to pure *n*-octyl alcohol), and *n*-decatetraenol, m. p. 122—124° (together with much oily material), respectively. All three alcohols are unstable in the air.

R. S. CARR.

Reduction of acetylenic carbinols with titanium trichloride. R. S. SWEET and C. S. MARVEL (J. Amer. Chem. Soc., 1932, 54, 1184—1190).—The expected hexasubstituted ethanes are not always produced from acetylenic carbinols by reduction with $TiCl_3$. γ -Methyl- γ -ethyl- Δ^{α} -pentinene with $MgEtBr$ and $COPh_2$ gives 71% of diphenyl- $(\gamma$ -methyl- γ -ethyl- Δ^{α} -

pentinyl)carbinol (I), b. p. 154—156°/0.5 mm., the bromide of which with Ag yields 51.5% of a hydrocarbon (II), $C_{42}H_{48}$, m. p. 105—106°. (II) does not absorb O_2 from the air, does not rearrange when heated alone or with $AcOH-HCl$, yields a coloured Na derivative with 40% Na-Hg (no evidence of cleavage obtained), and is oxidised by $K_2Cr_2O_7$ in $AcOH$ to an unidentified acid, m. p. 135—136°. *Tri(isopropylethynyl)carbinol*, b. p. 118—121°/1 mm., could not be converted into the bromide and the corresponding ethane, whilst *tri(cyclohexylethynyl)carbinol* decomposes on attempted distillation. *Diphenyl-tert.-butylethynylcarbinol* and 20% $TiCl_3$ in $EtOH$ at 60—65° give 24.7% of a hydrocarbon, m. p. 150—151°, identical with that obtained by rearrangement of tetraphenyldi-*tert.*-butylethynylethane; in another case, the main product was $\alpha\alpha$ -diphenyl- $\delta\delta$ -dimethyl- Δ^5 -penten- γ -one, unaffected by $TiCl_3$ at 60° for 2 hr. (I) and $TiCl_3$ give 44% of (II). *Tri(tert.-butylethynyl)carbinol* and $TiCl_3$ give a compound, $C_{38}H_{56}Cl_2$, m. p. 175—176°, which is unchanged by boiling 10% $EtOH-KOH$. Treatment with $NaNH_2$ in xylene affords a hydrocarbon, m. p. 171—172°, identical with that from the rearrangement of hexa-*tert.*-butylethynylethane, which decolorises only a little Br in CS_2 , gives no colour with $C(NO_2)_4$ in $AcOH$, is not oxidised by 5% $KMnO_4$, and with 40% Na-Hg gives a dark brown solution, from which an acid could not be obtained by the action of CO_2 . Definite compounds were not obtained from various other acetylenic carbinols and $TiCl_3$.

C. J. WEST (b).

Preparation of epichloro- and epibromohydrins. G. BRAUN (J. Amer. Chem. Soc., 1932, 54, 1248—1250).—Epichlorohydrin is prepared in 80% yield from dichlorohydrin, 88% $Ca(OH)_2$, and H_2O at room temp.; epibromohydrin is obtained similarly in 90% yield, from dibromohydrin. C. J. WEST (b).

Synthesis of polyhydroxylic compounds. W. CHARLTON and J. KENNER (J.C.S., 1932, 750—755).—Attempts to extend Piloty and Ruff's synthesis of glycerol (A., 1897, i, 453) to other polyhydroxy-compounds are described. γ -Nitropropyl alcohol and CH_2O (or paraformaldehyde) in dil. aq. K_2CO_3 at 30° give β -nitro- β -hydroxymethylbutane- $\alpha\delta$ -diol (I), m. p. 59—61° (triacetate, b. p. 210°/20 mm.; tribenzoate, m. p. 145—147°), converted by $EtOH-NaOEt$ into the Na salt (II) of β -nitrobutane- $\alpha\delta$ -diol. Reduction of (I) with 2.5% Na-Hg in aq. $Al_2(SO_4)_3$ gives a gum, which when oxidised with HgO in $EtOH$, and then treated with $NHPh-NH_2$, $AcOH$ affords the osazone, m. p. 99—101°, of α -keto- γ -hydroxybutaldehyde, also formed by successive treatment of (II) with dil. HCl (in absence or presence of $SnCl_2$) and $NHPh-NH_2$. (II) and PhN_2Cl give CH_2O and ω -nitro- α -hydroxypropionaldehydephenylhydrazone, m. p. 103—104°, whilst (II) and Cl_2 in Et_2O afford β -chloro- β -nitrobutane- $\alpha\delta$ -diol, m. p. 62—66°. $MeNO_2$ and $OEt-CH_2-CHO$ in dil. aq. K_2CO_3 yield γ -nitro- α -ethoxypropan- β -ol, b. p. 128°/20 mm., which with CH_2O gives (owing to the reversibility of the initial reaction) $NO_2-C(CH_2OH)_3$, also formed similarly from CH_2O and α -nitropropan- β -ol or β -nitrolactic acid.

H. BURTON.

Acetalisation of polyhydric alcohols with mono- and di-ketones. N. FROSCHL and A. HEUBERGER.—See this vol., 514.

Ribosephosphoric acid from xanthylic acid. P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1932, 95, 755—764).—Xanthylic acid (cf. this vol., 71) is kept in 10% aq. solution for 3—4 days at 50°, cooled, pptd. by $HgSO_4$, Hg and SO_4 are removed from the filtered solution, and sufficient $Ba(OH)_2$ is added to render it slightly alkaline. On concn. in a vac. to a small vol. and addition of an equal vol. of $EtOH$, Ba ribosephosphate is pptd. The product is purified by dissolving in H_2O , centrifuging, and re-pptg. with $EtOH$ or by conversion into the brucine salt. Oxidation of crude Ba ribosephosphate by $Ba(OI)_2$ and treatment of the resulting solution, freed from Ba^{++} and SO_4^{--} , with a $MeOH$ solution of brucine yields a tribrucine salt of a phosphoribonic acid, not identical with that obtained from inosinic acid (A., 1911, i, 408). Ribosephosphoric acid from xanthylic acid yields 1 : 4- and 1 : 5-methylglucosides, indicating that in this acid the 4 and 5 positions are free.

P. O. HOWITT.

Chlorination of methanetrissulphonic acid. H. J. BACKER (Rec. trav. chim., 1932, 51, 374—380; cf., A., 1930, 1556).— $CH(S_3OK)_3.Cl_2$, and a little I heated at 200° for 10 hr. give *K* chloromethanetrissulphonate, converted through the strychnine and Ba salts into the acid (+4½ H_2O), m. p. 160—165° [anhyd. acid, m. p. 180—182° (decomp.); Li, Na, Rb, Cs, Tl, and NH_4 salts]. With PCl_5 the acid gives SO_2 and a liquid, b. p. 103—105°/2 mm., converted by H_2O into a solid, m. p. 103—104°, or under different conditions SO_2 , and a liquid, b. p. 109—110°/6 mm., converted slowly by moist air into a solid, m. p. 41—42°.

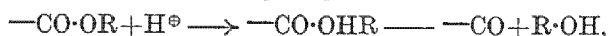
A. A. LEVI.

Effect of replacement of methyl by alkyl and aryl on the stability of the xanthate molecule. (MISS) I. M. McALPINE (J.C.S., 1932, 906—912).—*Menthyl Pr³ xanthate* (I), m. p. 48°, $[\alpha]_D^{25} -77.6^\circ$ in C_6H_6 , is unaffected by boiling 40% aq. KOH , but is hydrolysed by $EtOH-KOH$ to menthol, and partly hydrolysed by $EtOH-Ba(OH)_2$ to menthol and the "stable" form of (I), which, unlike (I), can be distilled unchanged. Thermal decomp. of (I) by (a) heating alone, (b) vac. distillation, and (c) heating in various solvents gives (a) (at 170°) menthene, Pr^3SH , and COS ; (b) menthene and the "stable" form; (c) menthene and (in $PhNO_2$, $BuOH$, and ethylene dibromide) the "stable" form. (I) is more readily converted into the "stable" form and less readily decomposed than the corresponding Me ester (A., 1931, 847). *Menthyl benzyl xanthate* (II), m. p. 46.5—47°, $[\alpha]_D^{25} 43.5^\circ$ in C_6H_6 , is hydrolysed slightly by 40% KOH , completely by $EtOH-KOH$, and partly by $EtOH-Ba(OH)_2$ ("stable" form not produced). Thermal decomp. affords (a) and (b) menthene; (c) menthene and (in ethylene dibromide only) a little of the "stable" form, which, however, undergoes decomp. in $PhNO_2$ above 140°. (II) shows a greater rate of decomp. in org. solvents and a smaller tendency towards transformation than the Me ester. *Menthyl p-nitrobenzyl xanthate*, m. p. 60°, -35.2° in C_6H_6 , decomposes in ethylene dibromide at 135° to menthene and 5% of a "stable" (?) form, which, however, decomposes

on vac. distillation. The menthene recovered from the decomp. experiments shows considerable variation in rotation. The xanthates are prepared by Tschugaev's method (A., 1900, i, 129). H. BURTON.

Hydrolysis and decomposition of menthyl and bornyl dixanthides. (Miss) I. M. McALPINE (J.C.S., 1932, 912—918).—Menthyl dixanthide (I) is hydrolysed (to menthol) by 40% aq. KOH, EtOH-KOH, and EtOH-Ba(OH)₂, whilst bornyl dixanthide (II) is hydrolysed only by the EtOH-alkalis; "quasi-stable" forms, which decompose on vac. distillation, are produced using EtOH-Ba(OH)₂. Thermal decomp. of (I) by heating alone, in vac., and in various solvents gives menthol, menthene, CS₂, COS, and S, whilst (II) similarly affords borneol, bornylene, camphene, CS₂, COS, and S; (I) decomposes more readily than (II). "Stable" forms are not produced, but in ethylene dibromide, compounds which are stable in this solvent but decompose on vac. distillation are formed. The dixanthides are much less thermostable than the xanthates (A., 1931, 847; preceding abstract), but are more stable than the sulphonates (A., 1927, 364; 1928, 1253). The rotation of the recovered menthene varies according to the method of decomp. H. BURTON.

Mechanism of hydrolysis of carboxylic esters with special reference to acid hydrolysis. E. H. INGOLD and C. K. INGOLD (J.C.S., 1932, 756—760).—Hydrolysis of α -methylallyl and crotyl acetates, first with 0.2N-H₂SO₄ at 61—62° and then (after upwards of 90% hydrolysis) with 0.2N-KOH, gives the respective alcohols, indicating that during the hydrolysis there is no liberation of α -methylallyl or crotyl cations, otherwise equilibrium mixtures would result (cf. Burton, A., 1928, 880). The following mechanism for acid hydrolysis is favoured:



$\text{CO} + \text{H}_2\text{O} \longrightarrow -\text{CO}_2\text{H} + \text{H}^+$; the point of fission suggested by Lapworth (J.C.S., 1912, 101, 273) is confirmed. α -Methylallyl alcohol is obtained by alkaline hydrolysis of its acetate (cf. Prévost, A., 1928, 1211) by dil. KOH (end concn.—0.2N) at 60°. Alkaline hydrolysis undoubtedly proceeds thus: $-\text{CO}\cdot\text{OR} + \text{OH}^- \longrightarrow -\text{C}(\text{OH})(\text{OR})\text{O}^- \longrightarrow \text{CO}_2\text{H} + \text{RO}^-$; $\text{RO}^- + \text{H}_2\text{O} \longrightarrow \text{R}\cdot\text{OH} + \text{OH}^-$. H. BURTON.

Freudenberg's method for determining acetyl groups. H. BREDERECK (Angew. Chem., 1932, 45, 241—242).—The micro-adaptation of the method (A., 1925, ii, 446) presents certain difficulties especially in the case of *N*-Ac compounds. The technique is modified to permit a more prolonged hydrolysis, successive additions of EtOH being made to the reaction mixture, and the AcOEt distilled in several stages. A. G. POLLARD.

Sorbyl chloride. T. REICHSTEIN and G. TRIVELLI (Helv. Chim. Acta, 1932, 15, 254—260).—Like furfuryl chloride, but unlike 5-methylfurfuryl chloride or allyl derivatives, sorbyl chloride (I), b. p. 45.5°/12 mm. (from sorbyl alcohol, pyridine, and SOCl₂ in dry Et₂O), reacts "abnormally" with conc. aq. KCN to yield α -methylhexadienonitrile, b. p. about 60—80°/12 mm., hydrolysed by KOH-EtOH

to α -methylhexadienoic acid, m. p. 102.5—103.5°, b. p. about 130°/12 mm., the C skeleton of which is proved by hydrogenation (PtO₂) in dry Et₂O to α -methyl-*n*-hexoic acid. The constitution of (I) is proved by oxidation (O₃ in cyclohexane, followed by KMnO₄) to CH₂Cl·CO₂H (OPh·CH₂·CO₂H). (I) reacts with cold aq. AgNO₃ and with AgOBu^t in Et₂O affords a mixture of esters, b. p. about 40—50°/0.15 mm., reduced catalytically (PtO₂) to a mixture of α - and β -*n*-butyl *n*-hexyl ethers, which after hydrolysis and oxidation by alkaline KMnO₄ yields *n*-hexoic acid and COMeBu^t. R. S. CAHN.

Component glycerides of partly hydrogenated fats. I. Alterations in glyceride structure produced during progressive hydrogenation of olive and cottonseed oils. T. P. HILDITCH and E. C. JONES (J.C.S., 1932, 805—820).—The oils are partly hydrogenated (Ni-kieselguhr catalyst) and the amounts of fully-saturated glycerides in the resulting products determined essentially by the method previously described (A., 1928, 152). The mixtures of fatty acids obtained by hydrolysis of the partly reduced products and their component fully-saturated glycerides are analysed by the ester-fractionation method (cf. A., 1931, 1178 and previous abstracts). The general constitutions of the partly reduced products are determined from these results. The selective conversion of linoleic into oleic or isooleic groups (before further reduction of these groups) causes little increase in the amount of fully-saturated glycerides until the linoleo-glycerides have disappeared; even then, the increase is only relatively slow until the final stages of hydrogenation are reached. The predominating action in the earlier stages is the conversion of triolein into oleostearins; only one double linking is hydrogenated in each effective contact between the catalyst and triolein mol. Dioleo-glycerides are then reduced preferentially to the mono-oleo-compounds. Mono-oleo-glycerides containing palmito-groups are reduced to palmitostearins in preference to the conversion of oleodistearins into tristearin. H. BURTON.

Structure of couepic acid. J. VAN LOON and A. STEGER (Rec. trav. chim., 1932, 51, 345—348; cf. A., 1931, 1034).—A reply to Rossmann (this vol., 366). The evidence is considered to support a triolefinic structure for couepic acid. A. A. LEVI.

Polymerisation of methyl esters of higher unsaturated fatty acids. X. Influence of temperature and diluent. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 77—82).—The ratio of intra- to inter-mol. condensation of the esters (b. p. 215—234°/6 mm.) of the unsaturated acids of sardine oil increases with rise in temp. and with addition of paraffin (m. p. 68—72°). The velocity of both reactions is increased by rise of temp. R. S. CAHN.

Oxidation of unsaturated compounds. VI. Synthesis of γ -bromothreonic [γ -bromo- α -3-dihydroxybutyric] acid. Configuration of dihydroxybutyric acids. G. BRAUN (J. Amer. Chem. Soc., 1932, 54, 1133—1137; cf. A., 1930, 1271).—Oxidation of γ -bromocrotonic acid, m. p. 74°, with Ba(ClO₄)₂ in H₂O containing osmic acid

gives 70% of γ -bromo- $\alpha\beta$ -dihydroxybutyric acid (I), m. p. 107°, the configuration of which is proved by its conversion into *dl*-tartaric acid by oxidation with HNO_3 . Reduction of (I) with H_2 and Pd gives *dl*- $\alpha\beta$ -dihydroxybutyric acid, m. p. 74° (70% yield), showing that the latter has the same configuration as *dl*-tartaric acid; consequently the *dl*-erythro- $\alpha\beta$ -dihydroxybutyric acid, m. p. 81.5°, has a configuration corresponding with mesotartaric acid. Treatment of (I) with AgOAc gives good yields of *dl*-threonic acid, m. p. 98–99°. C. J. WEST (b).

Catalytic reduction of chlorides of dibasic acids. N. FRÖSCHL and A. MAIER [with (in part) A. HEUBERGER] (Monatsh., 1932, 59, 256–274).—Catalytic reduction (Pd-charcoal unless stated otherwise) of dibasic acid chlorides usually gives some aldehydo-monocarboxylic acid (after hydrolysis); occasionally one of the $\cdot\text{COCl}$ groups is converted into $\cdot\text{CH}_2\cdot\text{OH}$. Addition of "sulphured" quinoline (Rosenmund and Zetsche, A., 1921, ii, 320) influences the time but not the course of the reaction. $(\text{COCl})_2$ in C_6H_6 at 40–50° gives only gaseous products (CO is detected), thus supporting the *as*-structure. Succinyl chloride in PhMe at 120° and tetrahydronaphthalene at 170° affords mainly γ -butyrolactone and a little β -aldehydopropionic acid, whilst dibromo-succinyl chloride yields γ -butyrolactone and succinic anhydride (isolated by distillation of the reaction mixture). $\text{CH}_2(\text{COCl})_2$ in C_6H_6 at 90° furnishes α -aldehydo- Δ^2 -propene- $\alpha\gamma$ -dicarboxylic acid (?), m. p. 83°, formed by self-condensation of the intermediate $\text{CHO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Adipyl chloride is reduced to δ -aldehydovaleric acid and cyclopentenecarboxylic acid; an Os-charcoal catalyst is better than Pd-charcoal. Suberyl chloride gives ζ -aldehydoheptic acid (*p*-nitrophenylhydrazide *p*-nitrophenylhydrazone, decomp. 220°), whilst *p*- $\text{C}_6\text{H}_4(\text{COCl})_2$ affords (probably) *p*-hydroxymethylbenzoic acid (cf. Rosenmund *et al.*, A., 1922, i, 39). H. BURTON.

[Attempted] syntheses of agaric acid. N. FRÖSCHL and J. HARLASS (Monatsh., 1932, 59, 294–299; cf. Passerini and Banti, A., 1931, 1036).—The Na derivative of Et acetonedicarboxylate and cetyl iodide in boiling EtOH give Et α -cetylacetonedicarboxylate, m. p. 38.5° (*Cu* derivative, m. p. 27°), which could not be made to undergo addition of HCN. Prolonged interaction of Mg, Et α -bromostearate (I), and Et oxaloacetate (II) affords the *Mg* derivative, m. p. 115–117°, of (II); Et α -iodostearate, m. p. 22° [from (I) and KI in EtOH], (II), and Mg give Et α -stearylstearate, m. p. 28–29°. H. BURTON.

α -Thio-, α -thionyl-, and α -sulphone-dibutyric acids. R. AHLBERG (Svensk Kem. Tidskr., 1932, 44, 48–58; cf. A., 1924, i, 832).—The prep. of α -thiodibutyric acid and the method of separation of its stereoisomeric forms are described. Four forms are possible, but only two are known, and attempts to prepare the others in a pure state have failed. Oxidation of the two inactive α -thiodibutyric acids in aq. COMe_2 solution with H_2O_2 yields *meso*- and *r*- α -thionyldibutyric acids, respectively, which can be further oxidised with alkaline KMnO_4 to α -sulphone-dibutyric acids. The valency directions of the S atom in these compounds are discussed. H. F. HARWOOD.

Photosynthesis in tropical sunlight. III. Formaldehyde. IV. Sugars and complex nitrogenous substances. A. R. RAJVANSI and N. R. DHAR.—See this vol., 480.

Reactions of acetaldehyde over various oxide catalysts. M. E. KINSEY and H. ADKINS.—See this vol., 478.

Electrochemical oxidation of ketones. W. E. BRADT and C. J. OPP.—See this vol., 479.

General method of condensing ketones. V. GRIGNARD and J. COLONGE (Compt. rend., 1932, 194, 929–933).—Treatment of 2 mols. of ketone with a mixture of equiv. portions of MgEtBr and NH_2Ph in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ affords a hydroxy-ketone in good yield. COEt_2 , COPr_2 , COMePr^2 , *Me tert.*-butyl ketone afford, respectively, δ -methyl- γ -ethylheptan- γ -ol- ϵ -one, b. p. 101–102°/16 mm., d_4^{20} 0.926; ϵ -ethyl- δ -propylnonan- δ -ol- ζ -one, b. p. 135–137°/16 mm., d_4^{20} 0.894; $\beta\gamma\zeta$ -trimethylheptan- γ -ol- ϵ -one, b. p. 97–98°/16 mm., d_4^{20} 0.909; $\gamma\zeta\zeta$ -pentamethylheptan- γ -ol- ϵ -one, b. p. 103–105°/15 mm. J. L. D'SILVA.

Preparation of diacetyl. S. C. J. OLIVIER (Bull. Soc. chim., 1932, [iv], 51, 99–107).— Ac_2 (98–99% purity) is obtained by passing Et nitrite into COMeEt in Et_2O and 20% MeOH-HCl in a freezing mixture. The crude oximino-derivative, m. p. 72–74° (yield 66%), isolated by addition of 33% NaOH , affords 82% of Ac_2 on treatment with NaNO_2 and dil. H_2SO_4 at 15°; purification through the compound, $\text{Ac}_2\cdot 2\text{H}_3\text{PO}_4$, m. p. 60–69.5°, followed by distillation, affords Ac_2 , m. p. –2.4°, b. p. 88–89°/750 mm., d_4^{20} 0.9904, which polymerises much less readily and after several days is 97% pure, falling to 88.7% and 71.2% after 97 and 227 days, respectively. R. BRIGHTMAN.

Dioximes. LXXXVI. E. DURIO and M. A. ROLLIER (Gazzetta, 1932, 62, 148–154).—The dissociation of oximinoketones $2\text{R}\cdot\text{C}(\text{NOH})\cdot\text{CO}\cdot\text{R}' \rightarrow \text{R}\cdot\text{CO}\cdot\text{CO}\cdot\text{R}' + \text{R}\cdot\text{C}(\text{NOH})\cdot\text{CR}'\cdot\text{NOH}$ occurs only when R and R' are aliphatic and is a bimol. reaction.

E. E. J. MARLER.

Dioximes. LXXXIV. A. VIANELLI (Gazzetta, 1932, 62, 131–138).—Only two forms of diacetyl-glyoxime peroxide exist; those described by Tryller (A., 1895, i, 201) and Ponzio (A., 1923, i, 853) are identical, have m. p. 145°, and are probably 4:5-diacetyl-1:2:3:6-dioxidiazinedioxime, $\text{CMe}(\text{NOH})(\text{C}_2\text{O}_2\text{N}_2)\cdot\text{CMe}\cdot\text{NOH}$ (*Bz* derivative, m. p. 165°; diperoxide, m. p. 187°), and that described by Behrend (A., 1893, i, 303), m. p. 189–190°, is probably diacetylfuroxandioxime, $\text{CMe}(\text{NOH})[(\text{C}_2\text{ON}_2)\text{O}]\text{CMe}\cdot\text{NOH}$ [*Bz* derivative, m. p. 220° (decomp.)]. E. E. J. MARLER.

Attempted photosynthesis of carbohydrates in vitro with visible light. F. P. ZSCHEILE, jun.—See this vol., 480.

Detection of reducing carbohydrates. P. K. BOSE (Z. anal. Chem., 1932, 87, 110–114).—Carbohydrates containing the group $\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{O}$ give a violet coloration when warmed with 2 c.c. of 25% aq. Na_2CO_3 to which is added 1 drop of a 1% solution of *o*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$. The method will detect

0.006 mg. of the reducing carbohydrate in 1 c.c. of solution. Aldehydes, except CH_2O , do not interfere.

A. R. POWELL.

Volumetric determination of reducing sugars using iodide and thiosulphate. P. VOKULOV (Ukrain. Chem. J., 1931, 6, [Sci.], 173—175).—The solution (2—2.5 c.c.) is boiled for 4 min. with 5 c.c. of 7% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and the filtrate and washings are acidified with 10% H_2SO_4 , after which 5 c.c. of 20% KI are added, and the mixture is shaken for 1.5 min. Free I is titrated with 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$, and the result is subtracted from that of a blank determination.

R. TRUSZKOWSKI.

Influence of hydrochloric acid on optical rotation of glucose. M. SCHENK (Helv. Chim. Acta, 1932, 15, 409—411).—The vals. of $[\alpha]_D^{25}$ and $[\alpha]_D^{50}$ are determined for solutions of glucose in HCl (d 1.004—1.209); the latter agree with those of Zechmeister (A., 1923, i, 183) and Willstätter (A., 1913, i, 955; except at d 1.209).

H. A. PIGGOTT.

Graduated determination of methoxyl and acetyl. K. FREUDENBERG and K. SOFF (Annalen, 1932, 494, 68—72).—The (glucosidic) OMe group in α -methylglucoside, tetramethyl- β -methylglucoside, heptamethyl- β -methylcellobioside, and related compounds (this vol., 501) is eliminated by treatment with 2N-HCl and AcOH (1:1) at 100°; the resulting MeOH (or MeCl) is distilled in CO_2 into HI at 100° contained in a Zeisel apparatus.

Four of the Ac groups in penta-acetyl- d -catechin are determined by the procedure previously described (A., 1923, ii, 884; 1925, ii, 446) using (a) KOAc (cf. Perkin, J.C.S., 1905, 87, 108), (b) K stearate (+ a little stearic acid), or (c) brucine in place of $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_3\text{H}$ (I); the fifth (non-phenolic) Ac is then determined in (b) and (c) by addition of (I). The O-Ac groups in a mixture of mannitol hexa-acetate (II) and NHAcPh are determined by (a) (8 distillations necessary), and in a mixture of (II) and $\text{NHAc} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (which must be first neutralised) by (b) (6 distillations necessary). Six Ac groups are eliminated from the so-called hepta-acetylmethylmaltoside (A., 1930, 1412) by (b) (5 distillations) and the seventh by (I).

H. BURTON.

Reactivity of the methylated sugars. VI. Action of dilute alkali on 3-methylglucose. D. J. LODER and W. L. LEWIS (J. Amer. Chem. Soc., 1932, 54, 1040—1054; cf. this vol., 145).—The conversion of 3-methylglucose (I) into 3-methylfructose (II) with aq. $\text{Ca}(\text{OH})_2$ at 35° confirms the recorded position of the Me group in (II). The "enediol" of (I) resembles that of glucose rather than that of tetramethylglucose. The absence of a high I-absorbing product in the reaction mixture indicates that the 2:3-monomethylenediol is not formed. The equilibrated solution contains about 64% of aldose and 32% of (II); indirect evidence is given for the formation of about 3% of saccharic acid. The Me group is eliminated (as MeOH) from (I) by dil. alkali, slowly at 35°, but rapidly at 100°. Details are given of the prep. of (I) through diisopropylideneglucose and its 3-Me derivative, and of (II) through α -diisopropylidenefructose and its 3-Me derivative. Brucine 3-methylgluconate has m. p. 146—148°, $[\alpha]_D^{25}$ -16.7° in

H_2O . (I) can be determined in presence of (II) iodometrically. The original should be consulted for details.

C. J. WEST (b).

Method of preparing 2-methylglucose. Synthesis of 2:6-dimethylglucose. J. W. H. OLDHAM and J. K. RUTHERFORD (J. Amer. Chem. Soc., 1932, 54, 1086—1091).—The 3:5:6-Bz₃ derivative of isopropylideneglucose is hydrolysed and the resulting 3:5:6-tribenzoylglucose converted into its γ -methylglucoside. Methylation and debenzoylation gives 2-methyl- γ -methylglucoside, hydrolysed by dil. H_2SO_4 to 2-methylglucose (I). The β -methylglucoside of (I) and $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Cl}$ give 90% of 3:4:6-tri- p -toluenesulphonyl-2-methyl- β -methylglucoside, m. p. 168—169° (decomp.), $[\alpha]_D +13.8^\circ$ in CHCl_3 , converted by NaI into 6-iodo-3:4-di- p -toluenesulphonyl-2-methyl- β -methylglucoside, m. p. 184—185°, $[\alpha]_D +26.6^\circ$ in CHCl_3 , and thence (cf. this vol., 254) into 3:4-di- p -toluenesulphonyl-2-methyl- β -methylglucoside 6-nitrate, m. p. 157—158°, $[\alpha]_D -3.4^\circ$ in CHCl_3 , which is reduced to 3:4-di- p -toluenesulphonyl-2-methyl- β -methylglucoside, m. p. 137—140°, $[\alpha]_D -17.8^\circ$ in CHCl_3 . This with MeI and Ag_2O gives 3:4-di- p -toluenesulphonyl-2:6-dimethyl- β -methylglucoside, m. p. 155—157°, identical with the product isolated from starch. The β -methylglucoside of (I) yields a benzylidene derivative, m. p. 170—171°, $[\alpha]_D -69.2^\circ$ in CHCl_3 , methylated to benzylidene-2:3-dimethyl- β -methylglucoside, m. p. 132—135°, thus confirming the constitutions of the compounds used.

C. J. WEST (b).

Further attempts to synthesise sucrose. J. C. IRVINE and E. T. STILLER (J. Amer. Chem. Soc., 1932, 54, 1079—1083; cf. A., 1930, 197).—Attempts to synthesise sucrose octa-acetate from glucose and γ -fructose tetra-acetates (new methods of prep. given) by various methods [including that of Pietet and Vogel (A., 1928, 510, 741)] were unsuccessful; the compounds isolated were isosucrose octa-acetate, glucose penta-acetate, and isotrehalose octa-acetate (either individually or in admixture). The non-crystalline products of the condensation are complex mixtures containing acetylated diglucoses and difructoses, hexose penta-acetates, isosucrose octa-acetate, and at least one additional glucofructose acetate; evidence for the presence of sucrose octa-acetate was not obtained.

C. J. WEST (c).

Hydrolysis of maize starch and its amyloses with reference to the production of gentiobiose. T. C. TAYLOR and D. LIFSCHITZ (J. Amer. Chem. Soc., 1932, 54, 1054—1063).—Glucose heated in 0.06M-HCl for 30 min. under 3 atm. gives about 1.5% of gentiobiose (I). Whole maize starch under the same conditions gives some (I); maize β -amylose, which constitutes 85% of the starch, does not afford (I), but the α -amylose gives similarly a solution of low sp. rotation from which the osazone of (I) has been isolated. The production of (I) from the starch appears to be by direct scission of a polysaccharide in the insol. α -amylose fraction of the starch, rather than by condensation of glucose. C. J. WEST (b).

Glucoside formation in the commoner monoses. P. A. LEVENE, A. L. RAYMOND, and R. T. DILLON (J. Biol. Chem., 1932, 95, 699—713).—

The sugar (*d*-glucose, -galactose, -mannose, -fructose, -lyxose, -ribose, -xylose; *l*-arabinose or -rhamnose) dissolved in anhyd. MeOH is treated with anhyd. MeOH-HCl at room temp. and at 76°. For each sugar the proportion of furanoside rises to a max. and then decreases, the time required to attain the max. val. being characteristic for each sugar. The sp. rates of formation of furanoside and pyranoside and their ratio are also different for each sugar.

F. O. HOWITT.

Croton-seed [*Croton Tiglimum*, L.]. I. Crotonoside (6-amino-2-hydroxypurine-*d*-riboside). E. CHERBULIEZ and K. BERNHARD (Helv. Chim. Acta, 1932, 15, 464—471).—*Crotonoside* (+2H₂O), m. p. 248° (corr.) when rapidly heated (*picrate*, decomp. above 210°), is isolated from croton seed by extraction with MeOH and identified by hydrolysis with 5% H₂SO₄ as the *d*-riboside of 6-amino-2-hydroxypurine (*hydrochloride*, decomp. above 250°; *hydrobromide*, decomp. above 214°; *nitrate*, decomp. above 250°; *picrate*, decomp. above 260°). Identification of the purine depends on the properties of its sulphate and its behaviour with diazo-compounds in alkaline medium.

H. A. PIGGOTT.

Synthesis of saligenin-β-*d*-galactoside. B. HELFERICH and R. GOOTZ (Ber., 1932, 65, [B], 407—409).—*o*-Tolyl-β-*d*-galactoside tetra-acetate is converted by Br in anhyd. CHCl₃ in presence of NaHCO₃ and under the influence of powerful irradiation into α-bromo-*o*-tolyl-β-*d*-galactoside tetra-acetate, m. p. 149—150°, [α]_D²⁰ +60.0° in CHCl₃, transformed by Ag₂CO₃ in boiling aq. CMe₂ into saligenin-β-*d*-galactoside tetra-acetate, m. p. 139—140° (corr.), [α]_D¹⁸ +2.8°, also obtained in poor yield from saligenin and acetobromogalactose by Robertson's method. Treatment of the acetate with NaOMe in MeOH affords saligenin-β-*d*-galactoside, m. p. 215—218° (corr.), [α]_D¹⁸ -33.9° in H₂O, hydrolysed by emulsin to saligenin and galactose.

H. WREN.

Colouring matter of the flowers of the mullen (*Flores verbasci*). L. SCHMID and E. KOTTER (Monatsh., 1932, 59, 341—356).—The colouring matter [described by Klein (A., 1922, i, 1099) as anthochlor], obtained by extraction of the fat-freed flowers with hot EtOH or by extraction with AcOH and pptn. with Et₂O, is a glucoside of α-crocetin.

H. BURTON.

[Hydrolysis of polysaccharides.] K. FREUDENBERG and W. KUHN (Ber., 1932, 65, [B], 484—487; cf. A., 1930, 1025).—A reply to Klages (this vol., 370).

H. WREN.

Lignin and cellulose. XVIII. Cellulose and starch. K. FREUDENBERG, K. FRIEDRICH, and I. BUMANN [with K. SOFF]. XIX. Synthesis of the methylated cellotriose, decamethyl-β-methylcellotrioside. K. FREUDENBERG and W. NAGAI (Annalen, 1932, 494, 41—62, 63—68).—XVIII. Details are given (cf. A., 1930, 1412; 1931, 337) for the separation of decamethyl-β-methylcellotrioside (I), b. p. 215—225°/0.1 mm., m. p. 118—119°, [α]_D¹⁸ -16.8° in H₂O, -11.28° in CHCl₃, -15.5° in MeOH, and tridecamethyl-β-methylcellotetraoside (II), b. p. 260—270°/0.1 mm., m. p. 139°, [α]_D¹⁸ -16.1° in H₂O, -9.8° in CHCl₃, -15.5° in MeOH, from the product

obtained by methylation of the acetate mixture (freed partly from cellobiose octa-acetate) produced when cotton ("verbandswatte") is acetylated with Ac₂O, AcOH, and H₂SO₄ at 0—30°. Undecamethylmalto-triose, b. p. 215—225°/0.1 mm., [α]_D¹⁸ +129.9° in CHCl₃, and tetradecamethylmalto-tetraose, b. p. 260—270°/0.1 mm., [α]_D¹⁸ +146° in CHCl₃, are obtained similarly (cf. A., 1931, 337) from starch. (I) and (II) are both hydrolysed to 2:3:6-trimethyl- and 2:3:4:6-tetramethyl-glucose. The vals. of [M]_n/n (*n*=no. of units) for the above and related compounds agree well with those calc. from the expression $[M]_n/n = [M]_2 - [M]_\infty / \infty + 2 \times (n-1)/n([M]_\infty / \infty - [M]_2/2)$, where *n* ≥ 2, [M]₂ is the mol. rotation of the corresponding disaccharide derivative, and [M]_∞/∞ is the rotation-contribution of a single unit of a polysaccharide (built up of the same units) and is approx. the same as that of the middle unit of a pentasaccharide. The results are explicable only by the recurrence of the same linking in all these substances. Contrary to Pringsheim and von Meerkatz (Z. physiol. Chem., 1915, 105, 173), cellobiose (*thiosemicarbazone*, decomp. about 170°) is oxidised by HgO in H₂O + CaCO₃ at 100° to cellobionic acid (*Ca* and *brucine* salts).

XIX. Crude heptamethylcellobiose 1-chlorohydrin, prepared from heptamethylcellobiose by Allison and Hixon's method (A., 1926, 386), and trimethyl-β-methylglucoside in presence of Ag₂CO₃, CaCl₂, and CCl₄ give a mixture of products from which decamethyl-β-methylcellotrioside is isolated. The original must be consulted for details.

H. BURTON.

Combination of bio-colloids [with other substances]. IV. Combination with amylopectin and with proteins or protein derivatives. S. J. VON PRZYLECKI and S. DOBROWOLSKA (Biochem. Z., 1932, 245, 388—407; A., 1931, 1437).—Amylopectin is pptd. from starch solution at 80—90° by addition of electrolyte (preferably an acid); the washed ppt. contains no amylose but almost all the P and most of the N. Suspended starch does not combine with glycine, alanine, asparagine, guanidine, creatine, creatinine, uric acid, guanine, peptone, or protein, but amylopectin combines with all but glycine, alanine, and uric acid. The extent of combination depends on the concn. of the reactants, on the *p*_H, and on the chemical nature of the N compound. The possible reasons for combination and failure to combine are discussed.

W. MCCARTNEY.

Cryoscopic determinations of mol. wt. of sugars and inulin in liquid ammonia. L. SCHMID and L. HASCHEK (Monatsh., 1932, 59, 328—334).—Further determinations of the mol. wt. of inulin in liquid NH₃, using an improved form of the apparatus previously described (A., 1925, i, 1386), give the val. 275—363 (limits). Other mol. wts. found are: fructose 152—201, sucrose 335—373, raffinose 488—535.

H. BURTON.

A triphenylmethyl ether of glycogen. L. SCHMID and E. KOTTER (Monatsh., 1932, 59, 335—340).—Glycogen and CPh₃Cl in pyridine at 100° give an insol. compound, (C₁₂H₁₉O₁₆·CPh₃)₂, m. p. 235° (decomp.), unaffected by further treatment with CPh₃Cl and hydrolysed by successive treatment

with CHCl_3 -HCl and H_2O to glycogen and $\text{C}_6\text{H}_5\cdot\text{OH}$. A C_6H_5 ether of inulin could not be prepared.

H. BURTON.

Degradation of cellulose by a new method. H. H. SCHLUBACH, H. ELSNER, and V. PROCHOVNICK (Angew. Chem., 1932, 45, 245—249).—Dry HCl converts cellulose into a mixture of low-mol. glucose anhydrides. Saturation pressure and 20—30° are the most favourable conditions, the process then being complete in 10 hr. The decomp. takes place also in presence of indifferent org. media such as C_6H_6 , but requires a longer time, depending on the nature of the liquid. The reddish-violet, powdery product does not show the original fibre structure. It contains much adsorbed HCl, of which 6—8% remains after leaving in vac. The product is purified by dissolving in a little H_2O and pptg. with $\text{MeOH-Et}_2\text{O}$. A portion which is sol. in this mixture is recovered by adding $\text{C}_6\text{H}_6\text{-EtOH}$ (75:25). The pure product is a white powder which can be separated by H_2O , EtOH , and Et_2O into fractions having different rotations; it consists mainly of 1-, 2-, and 3-mol. anhydrides. The action of HCl on cellulose is differentiated into three stages: depolymerisation, hydrolysis, and reversion. By the same method starch, inulin, mannan, xylan, silk fibroin, wool, horn, and other materials can be degraded into low-mol. anhydrides.

E. S. HEDGES.

New degradation of cellulose. III. H. PRINGSHEIM and K. WARD, jun. (Cellulosechem., 1932, 13, 65—71).—Cellulose acetate treated with PhSO_3H in boiling CHCl_3 containing 2% EtOH affords a product which, after hydrolysis with cold 5% aq. NH_3 (A., 1928, 1226; 1930, 1168) and pptn. of the H_2O -sol. product with EtOH , gives a prep., $[\alpha]_D^{20} +93^\circ$. Re-pptn. from aq. solution with EtOH gives, finally, a more sol. prep. C , $[\alpha]_D^{20} +66$ — 69° . Similar results are obtained with the primary acetate, "Agfa," and an acetate (Ac 44.4%) as starting material and using MeOH in place of EtOH . C is quantitatively hydrolysed by 3% HCl to glucose, and with aq. malt extract at p_H 4.8 suffers 4% and 10% hydrolysis in 2 and 8 days, respectively. Acetylation (Ac_2O -pyridine, or $\text{Ac}_2\text{O-SOCl}_2$) gives an acetate (45% Ac), $[\alpha]_D^{20} +75^\circ$ in CHCl_3 , hydrolysed by cold KOH in MeOH to the original prep., $[\alpha]_D^{20} +69^\circ$. Mol. wt. determinations show that C is not a single entity. Dialysis of C until the effluent gives no reducing sugars on hydrolysis and pptn. with EtOH gives a prep. D , $[\alpha]_D^{20} +88$ — 92° , which gives an acetate, $[\alpha]_D^{20} +88^\circ$ in CHCl_3 , and is not appreciably hydrolysed by enzymes (1.1% and 2.78% in 2 and 8 days, respectively). Methylation of C with 45% KOH and Me_2SO_4 followed by Ag_2O and MeI gives a yellow powder (43.68% OMe), becoming white at 80° and fluid at 120°, which is only partly distillable in a high vac. and probably contains >5 glucose residues. Debye-Scherrer diagrams (A. WEIDINGER) of C (freshly prepared or re-pptd. with EtOH after gelatinisation in H_2O for 1 month) indicate definite cryst. structure, but both these and that of the acetate are quite unlike the cellulose diagram. It is considered that degradation of cellulose has been effected without fission of the glucosidic linkings.

J. W. BAKER.

Molecular structure of polysaccharides. J. C. IRVINE (Chem. and Ind., 1932, 263).—In part a reply to Haworth (this vol., 370). Graded hydrolysis of methylated cellulose affords only 2:3:6-trimethylglucose in the first stage, and then 2:3:4:6-tetramethylglucose from the more resistant fraction. The latter is also obtained (3—5%) by similar hydrolysis of methylated amylose, one fraction of which gives a mixture of 2:3:4:6-tetra- (23—26%), 2:3:6-tri- (55—52%), and 2:3- and 2:6-di- (21%) -methylglucose. Approx. equal proportions of the 2:3- and 2:6-derivatives are obtained when the amylose is methylated directly, but the ratio is 24% and 76%, respectively, when methylation follows preliminary acetylation. Hydrolysis of trimethylinulin with $\text{H}_2\text{C}_2\text{O}_4$ yields, in addition to trimethyl- γ -fructoses, ω -methoxy-5-methylfurfuraldehyde, tetramethyl- γ -fructose (2.7—1.7% yield), and a trimethylanhydrofructose. Caution is urged in applying such results to deductions of the structure of polysaccharoses.

J. W. BAKER.

Chloroacetic esters of cellulose. H. RUDY (Cellulosechem., 1932, 13, 49—58).—Cellulose does not react with $\text{CH}_2\text{Cl-COCl}$ in presence of ZnCl_2 or pyridine, but with $(\text{CH}_2\text{Cl-CO})_2\text{O}$ and conc. H_2SO_4 affords cellulose trichloroacetate, sintering at 85°, $[\alpha]_D^{20} +30.5^\circ$, also obtained from hydrocellulose (obtained by reducing cellulose with HCO_2H), $(\text{CH}_2\text{Cl-CO})_2\text{O}$, and ZnCl_2 . Similarly, di- and trichloroacetic anhydride with hydrocellulose afford cellulose *didi*-, sinters and decomp. 160°, $[\alpha]_D^{20} +21.3^\circ$, and *ditri*-chloroacetate, sinters at 198—200°, $[\alpha]_D^{20} +8.4^\circ$, respectively. The trichloroacetate yields an odour of carbonylamine on warming with NH_2Ph and EtOH-KOH . All three esters are hydrolysed by EtOH-NH_3 to a chloroacetamide and a reducing cellulose. Starch and $(\text{CH}_2\text{Cl-CO})_2\text{O}$ with H_2SO_4 afford an ester, sintering at 85°, $[\alpha]_D^{20} +96.2^\circ$ (containing 25.5% Cl), which on hydrolysis affords a slightly-reducing Cl-free product. Chlorination of cellulose triacetate with PCl_5 in very large excess gives cellulose trichloroacetate, $[\alpha]_D^{20} -13.2^\circ$, unaffected by conc. alkali and NaOEt . 41% HCl is without action during several weeks. Chlorination in sunlight or in presence of PCl_5 or red P affords a series of products containing up to 40.4% Cl. This stage is reached by chlorinating at 130° during 2 hr. in presence of red P. Prolonged action of PCl_5 at 135—140° in a solvent on starch triacetate affords starch *tritrichloroacetate*, very resistant to hydrolysis.

J. L. D'SILVA.

p-Nitrobenzyl halides as reagents for the identification of primary and secondary amines. E. LYONS (J. Amer. Pharm. Assoc., 1932, 21, 224—225).—The completely amino-substituted *p*-nitrobenzyl derivatives of the following amines are described: NH_2Me , m. p. 102°; NH_2Et , m. p. 67°; $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m. p. 108°; $\text{NH}_2\cdot\text{CH}_2\cdot\text{Ph}$, m. p. 144°; $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, m. p. 117°; $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Pr}$, m. p. 114°; $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, chars; NH_2Ph m. p. 168°; NHPhEt , m. p. 67°; NHPh_2 , m. p. 96°; $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, m. p. 210°, *o*-, m. p. 198°, and $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, m. p. 225°, and benzidine, m. p. 228°.

E. H. SHARPLES.

Aliphatic ammono-aldehydes. H. H. STRAIN (J. Amer. Chem. Soc., 1932, 54, 1221—1228).—Evidence is presented to support the postulation that aliphatic imines, hydramides, and Schiff bases are ammono-aldehydes. In addition to the known reactions, it is shown that reactions which should lead to the formation of $\text{CH}_2\text{:NH}$ (ammono-formaldehyde) yield only hexamethylenetetramine (I) (polymerised ammono-formaldehyde). Anhydroformaldehyde-aniline (ammono-formaldehyde acetal) is ammonolysed to (I) and NH_2Ph , whilst NH:CHMe (ammono-acetaldehyde) is nitridised to acetamidine (ammono-acetic acid), and reacts with $\text{CH}_2(\text{CO}_2\text{H})_2$ and N_2H_4 derivatives as do aquo-aldehydes. The formation of pyridines from aldehydes and NH_3 is dependent on the formation of aquo-ammono-aldols. (I) is recovered unchanged when passed through an evacuated glass tube heated to redness (the presence of soda-lime caused no change), it does not react with liquid NH_3 in presence or absence of NH_2Ph or KNH_2 at 210° , and it is not nitridised by I in liquid NH_3 at -33° or by N_3H in liquid NH_3 at $260-270^\circ$. EtCHO and $\text{Ca}(\text{NH}_2)_2$ in liquid NH_3 give a liquid *ammono-aldol* (structure suggested), which is unaffected by dil. HCl and when distilled passes into 3:5-dimethyl-2-ethylpyridine. PrCHO similarly gives a compound, $\text{C}_{12}\text{H}_{26}\text{ON}_2$, convertible into 3:5-diethyl-2-propylpyridine; Pr^iCHO appears to give NH:CHPr^i , rapidly hydrolysed by HCl to the aldehyde; heptaldehyde affords a compound, $\text{C}_{21}\text{H}_{44}\text{ON}_2$, convertible into 3:5-diamyl-2-hexylpyridine, b. p. $355-365^\circ$.

C. J. WEST (b).

Colorimetric determination of glycine. G. KLEIN and H. LINSE (Z. physiol. Chem., 1932, 205, 251—258).—Glycine when treated with a buffered solution of *o*-phthaldialdehyde followed by a mixture of 5 parts of conc. H_2SO_4 and 30 parts of 96% EtOH , gives a green colour, extractable with CHCl_3 , which may be used for colorimetric determination. The reaction is sensitive to 0.05 mg. of glycine. Tryptophan and NH_3 interfere. J. H. BIRKINSHAW.

Physico-chemical behaviour of polypeptides composed of *dl*-alanine. E. ABDERHALDEN and J. HEUMANN (Z. physiol. Chem., 1932, 205, 271—282).—A series of polypeptides of increasing complexity was obtained from *dl*-alanine by coupling in successive stages with *dl*- α -bromopropionyl bromide: *dl*-alanine anhydride, oil; di-(*dl*-alanyl)-*dl*-alanine, becomes yellow at 237° , decomp. 245° , from α -bromopropionyl-*dl*-alanyl-*dl*-alanine, m. p. $170-175^\circ$; tri-(*dl*-alanyl)-*dl*-alanine, m. p. about 245° , from bromo-precursor, m. p. $217-220^\circ$ (becomes brown); tetra-(*dl*-alanyl)-*dl*-alanine, m. p. $280-283^\circ$ (becomes brown), from bromo-precursor, becomes yellow at 231° , m. p. about 241° ; penta-(*dl*-alanyl)-*dl*-alanine, yellow about 270° , decomp. about 280° , from bromo-precursor, m. p. about 240° (decomp.); hexa-(*dl*-alanyl)-*dl*-alanine, decomp. above 280° , from bromo-precursor, m. p. about 243° (decomp.).

By repetition of the same component, polypeptides quickly show colloidal properties, with *dl*-alanine, from the hexapeptide up. The particles of all the colloidal *dl*-alanine chains are strongly hydrated, the H_2O not being removed by drying in high vac., hence

their small adsorptive power. This may explain the high O content of protein. The *dl*-alanine chains contain $\frac{1}{3}$ mol. of H_2O , the *l*-1 mol. The colloidal polypeptide particles swell greatly, are negatively charged and show little movement in the electric field. Electrolytes produce coagulation but no discharge. Halogenoacyl compounds with an uneven no. of constituents are more readily aminated than those with an even no. J. H. BIRKINSHAW.

Tastes of derivatives of *d*-glutamic acid. C. L. TSENG and E. J. H. CHU (Acad. Sin. Mem. Nat. Res. Inst. Chem., 1931, No. 5, 1—18).—Na *d*-glutamate has the most intense meat-like taste; K and NH_3Me salts (both deliquescent) follow, but have an unpleasant after-taste. NH_2Me_2 *d*-glutamate hydrolyses readily; the NHMe_3 salt does not form an aq. solution.

CHEMICAL ABSTRACTS.

Glutamic acid. I. Action of dehydrating agents on *d*-glutamic acid. II. Tastes of some derivatives of *d*-glutamic acid. III. Hydrolysis of acetyl-*d*-glutamic acid. C. L. TSENG and E. J. H. CHU (Nat. Centr. Univ. Sci. Rep., 1931, A., 1, No. 2, 8—10).—I. *d*-Glutamic acid was unaffected by ZnCl_2 at 100° or 140° or by P_2O_5 in CHCl_3 .

III. Na acetyl-*d*-glutamate could not be prepared owing to hydrolysis.

CHEMICAL ABSTRACTS.

Synthesis of *N*-substituted β -aminoaldehydes. C. MANNICH, B. LESSER, and F. SILTEN (Ber., 1932, 65, [B], 378—385).—*iso*-Butaldehyde, NHMe_2HCl , and paraformaldehyde in boiling EtOH afford β -dimethylamino- α -dimethylpropaldehyde, b. p. $142-144^\circ$ (hydrochloride, m. p. $152-153^\circ$; chloroaurate, m. p. 106° ; oxime, m. p. 57° , and its hydrochloride, m. p. 163° ; semicarbazone, m. p. 160° ; *p*-nitrophenylhydrazine hydrochloride, m. p. 174° ; methiodide, m. p. $219-220^\circ$; cyanohydrin). Reduction of the aldehyde by Na-Hg in AcOH yields γ -dimethylamino- β -dimethylpropyl alcohol, b. p. $166-168^\circ$ (hydrochloride, m. p. 136° ; methiodide, m. p. 222° ; benzoate hydrochloride, m. p. 153° ; *p*-nitrobenzoate, m. p. 35° ; *p*-aminobenzoate, m. p. $79-80^\circ$). The aldoxime and boiling Ac_2O give β -dimethylamino- α -dimethylpropionitrile, b. p. $72/14$ mm. (hydrochloride, m. p. 145°), hydrolysed to β -dimethylamino- α -dimethylpropionic acid (hydrochloride, m. p. $150-151^\circ$). *iso*-Valeraldehyde is converted by CH_2O and piperidine hydrochloride into α -piperidinomethyl- α -hydroxymethyl-*iso*-valeraldehyde hydrochloride, m. p. about 145° (decomp.), in 70% yield. *n*-Butaldehyde, NHMe_2HCl , and CH_2O at 75° or room temp. afford α -dimethylamino-methyl-*n*-butaldehyde, b. p. $60/19$ mm. (hydrochloride, m. p. 105°), more complex products, and α -ethylacetaldehyde. EtCHO , NHMe_2HCl , and CH_2O at 85° yield α -dimethylaminomethyl-, b. p. $45/15$ mm., and α -bisdimethylaminomethyl-propaldehyde, b. p. $83/15$ mm. MeCHO , NHMe_2HCl , and CH_2O (1:3:3 mols.) yield β -hydroxy- α -bisdimethylaminomethyl-propaldehyde hydrochloride (+ H_2O), m. p. about 105° , from which dimethylhydroresorcinol removes 1 and 3 mols. of CH_2O in cold and hot solution; it is reduced by Na-Hg in slightly acid solution to $\text{CH}_2(\text{NMe}_2)_2$ and γ -dimethylamino- β -dimethylaminomethylpropyl alcohol, b. p. $95-102/11$ mm. (benzoate, *p*-nitrobenzoate, and *p*-aminobenzoate hydrochlorides, m. p. 242° , 223° ,

and 230°, respectively). The following compounds are similarly prepared: β -diethylamino- α -dimethylpropaldehyde, b. p. 175—177° (semicarbazone, m. p. 124—125°), and γ -diethylamino- β -dimethylpropyl alcohol, b. p. 90—91°/12 mm. (Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 131—132°, 160°, and 196°, respectively); β -piperidino- α -dimethylpropaldehyde, b. p. 95°/12 mm. (hydrochloride, m. p. 164°; chloroaurate, m. p. 116°; chloroplatinate, m. p. 167°; oxime hydrochloride, m. p. 169°; semicarbazone, m. p. 175°; cyanohydrin; methiodide, m. p. 211°), and γ -piperidino- β -dimethylpropyl alcohol, b. p. 140°/39 mm., (hydrochloride, m. p. 204°; Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 152°, 162—163°, and 218°, respectively); α -piperidino-methylhexahydrobenzaldehyde, b. p. 141—142°/15 mm. [hydrochloride, m. p. 165° (decomp.); nitrate, m. p. 164°; oxime hydrochloride, m. p. 178°; methiodide, m. p. 160°], and β -piperidinomethylhexahydrobenzyl alcohol, b. p. 155—157°/15 mm. (hydrochloride, m. p. 181°; methiodide, m. p. 148°; Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 177°, 134°, and 230°, respectively); α -dimethylaminomethylhexahydrobenzaldehyde, b. p. 102—104°/17 mm. (hydrochloride, m. p. 130°; oxime hydrochloride, m. p. 179°; methiodide, m. p. 223°), and β -dimethylaminomethylhexahydrobenzyl alcohol, b. p. 127—129°/20 mm. (hydrochloride, m. p. 144°; methiodide, m. p. 178°; Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 145°, 185°, and 193°, respectively); α -piperidinomethylisovaleraldehyde, b. p. 119—120°/18 mm. [hydrochloride, m. p. 142° (decomp.)], and β -piperidinomethylisoamyl alcohol, b. p. 134—136°/17 mm. (Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 155°, 189°, and 222°, respectively); α -dimethylaminomethyl- α -hydroxymethylisovaleraldehyde, m. p. 149° (decomp.); α -dimethylaminomethylisovaleraldehyde, b. p. 63—66°/13 mm. [hydrochloride, m. p. 120° (decomp.)]; methiodide, m. p. 145°; oxime hydrochloride, m. p. 133°], and β -dimethylaminomethylisoamyl alcohol, b. p. 80°/13 mm. (Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 180°, 176°, and 167°, respectively); β -dimethylaminomethylbutyl alcohol, b. p. 70—71°/14 mm. (hydrochloride, m. p. 81°; Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 159°, 163°, and 163°, respectively); β -dimethylaminomethylpropyl alcohol, b. p. 60—65°/12 mm. (Bz, p-nitro- and -amino-benzoyl ester hydrochlorides, m. p. 142°, 183°, and 165°, respectively); β -bisdimethylaminomethylpropyl alcohol, b. p. 100—102°/12 mm. (Bz and p-nitrobenzoyl ester hydrochlorides, m. p. 196° and 209°, respectively). H. WREN.

β -Methylamino- α -dimethylpropaldehyde and the corresponding alcohol. C. MANNICH and H. WIEDER (Ber., 1932, 65, [B], 385—390).—*iso*Butaldehyde, paraformaldehyde, and $\text{NH}_4\text{Me.HCl}$ afford β -methylamino- α -dimethylpropaldehyde, b. p. 48°/12 mm. [very hygroscopic hydrochloride; perchlorate, m. p. 221° (decomp.); semicarbazone hydrochloride, m. p. 192°; oxime hydrochloride, m. p. 132°], which passes slowly when preserved, partly when distilled

into the compound (I), $\text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_2\text{NMe}$, m. p. 71·5°, $\text{NMe}\cdot\text{CH}\cdot\text{CMe}_2$.

converted by 25% HCl into the aldehyde. The Bz derivative, m. p. 67°, of the aldehyde, its oxime, m. p. 86—87°, semicarbazone, m. p. 90°, and cyanohydrin, m. p. 107·5°, are described. β -Methylamino- α -dimethylpropaldehyde diethylacetal has b. p. 82—83°/12 mm. Reduction of the crude aldehyde with Na-Hg in dil. acid yields γ -methylamino- β -dimethylpropyl alcohol, b. p. 75—77°/12 mm., m. p. 52° (hydrochloride, m. p. 179°; hydrobromide, m. p. 124°; benzoate, b. p. 162°/12 mm., its hydrochloride, m. p. 182°, corresponding carbamide, m. p. 97°, and N-Bz derivative, m. p. 69—70°; p-nitrobenzoate, its hydrochloride, m. p. 207°, and N-p-nitrobenzoyl compound, m. p. 131°; p-aminobenzoate monohydrochloride, m. p. 193°; compound $\text{NH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, m. p. 157°). Et N-methyl-N- γ -hydroxy- β -dimethylpropylcarbamate, b. p. 127°/12 mm., from the alcohol and ClCO_2Et in COMe_2 , is transformed by cold, conc. H_2SO_4 into the lactone, $\text{NMe}\langle\text{CH}_2\cdot\text{CMe}_2\text{CO}\rangle\text{CH}_2$, b. p. 132—133°/12 mm. With $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ at 100° the alcohol affords Et N-methyl-N- γ -hydroxy- β -dimethylpropylaminoacetate, b. p. 137—138°/12 mm., hydrolysed by $\text{Ba}(\text{OH})_2$ to the corresponding acid, m. p. 167°. γ -Methylamino- β -dimethylpropyl alcohol with 35% CH_2O gives 3:5:5-trimethylmetoxazinetetrahydride, $\text{NMe}\langle\text{CH}_2\cdot\text{CMe}_2\text{CHR}\rangle\text{CH}_2$ (R=H), b. p. 40—42°/12 mm. (hydrochloride, m. p. 203°; methiodide, m. p. 210°), and with PhCHO affords 2-phenyl-3:5:5-trimethylmetoxazinetetrahydride (R=Ph), b. p. 124°/12 mm. (hydrochloride; methiodide, m. p. 160°). H. WREN.

Oxycyanogen. II. Free radical. H. HUNT.—See this vol., 482.

Action of primary amines on dicyanodiamidine sulphate. A. PERRET (Compt. rend., 1932, 194, 975—977).—At high temp., dicyanodiamidine sulphate and primary amines afford guanidine sulphate and a s-carbamide the structure of which depends on the amine used. Reaction proceeds easily with NH_2Ph etc., but very weak bases like o-chloroaniline do not react. o- and m-Phenylenediamine afford polymerised carbamides. Aliphatic and aliphatic-aromatic amines show varying capacities for reaction.

J. L. D'SILVA.

Electronic interpretation of reactions applied to halogen organic compounds. N. J. BEABER (Iowa State Coll. J. Sci., 1931, 5, 317—319).—There is no analogy between Grignard reagent formation and Fry's electronic formula for C_6H_6 . For poly-halogeno-aromatic compounds no catalyst is known to facilitate reaction of the second halogen atom to form a di-Grignard reagent.

CHEMICAL ABSTRACTS.

Derivatives of sec.-butylbenzene. R. R. READ, C. A. HEWITT, and N. R. PIKE (J. Amer. Chem. Soc., 1932, 54, 1194—1195).—The following derivatives of sec.-butylbenzene are described: o-, b. p. 123—126°/12 mm., m-, b. p. 132—134°/19 mm., and p- NO_2 , b. p. 142—144°/12 mm.; o-, b. p. 120—122°/16 mm., m-, b. p. 120°/18 mm., and p- NH_2 , b. p. 130—133°/26 mm. o-sec.-Butylphenol has b. p. 116°/21 mm., 227—228° (corr.). C. J. WEST (b).

Comparative stability of isomerides according to their absorption spectra. Intramolecular transpositions. (MME.) RAMART-LUCAS and (MLE.) P. AMAGAT (Bull. Soc. chim., 1932, [iv], 51, 108—126).—The ascending branch of the absorption curve of the propenyl hydrocarbons is nearer the visible region and the intensity of the absorption is much greater than in the isomeric allyl derivatives in the series allylbenzene, propenylbenzene, propenyltoluene, anethole, safrole, isosafrole. The characteristic absorption of two chromophores can be modified when the two chromophores are directly linked, the spectra of the hydrocarbons, $\text{CHAr}:\text{CHMe}$, showing traces of the characteristic spectra of the Ar radical. The isomeride possessing an absorption curve nearest to the visible spectrum possesses the lowest heat of combustion and is the most stable at low temp. The absorption curve of the phenylbutenes is displaced towards the visible region as the double linking approaches the ring. Similarly in the α -diarylethylenes and $\alpha\beta$ -diarylethylenes, the absorption curve of the *s*-hydrocarbon is nearer to the visible region than that of the *as*-isomeride, and accordingly (A., 1928, 881, 1000) the latter isomerises to the *s*-hydrocarbon by heat. Similarly, α -phenyl- Δ^2 -propene has an absorption curve nearer the visible spectrum and a lower heat of combustion than β -phenyl- Δ^2 -propene, and the absorption curve of $\alpha\alpha$ -diphenyl- Δ^2 -propene is nearer the visible than that of $\alpha\beta$ -diphenyl- Δ^2 -propene.

Dehydration of γ -phenylpropan- α -ol at 400—500° over kieselguhr affords mainly methylstyrene with some allylbenzene, although with SO_2Cl in pyridine at room temp. allylbenzene is the main product. Similarly, δ -phenylbutan- α -ol at 500° also affords ethylstyrene. The allylhydrocarbons, $\text{CH}_2\text{Ar}:\text{CH}:\text{CH}_2$, when passed over kieselguhr at 500° isomerise to propenyl derivatives, allylbenzene yielding propenylbenzene, estragole, anethole; safrole, however, yields resinous products and not isosafrole. $\alpha\alpha$ -Diphenylethylene is similarly converted into $\alpha\beta$ -diphenylethylene. Dehydration of the alcohols $\text{CHArR}:\text{CH}_2:\text{OH}$ and $\text{CHArAr}:\text{CH}_2:\text{OH}$ proceeds according to the rules previously described, yielding hydrocarbons with an absorption curve nearer the visible region than the normal hydrocarbons. Dehydration of the alcohols $\text{CRPh}_2:\text{CH}_2:\text{OH}$ gives exclusively the hydrocarbon, $\text{CRPh}:\text{CHPh}$, which has an absorption curve nearer the visible region than the isomeric $\text{CPh}_2:\text{CHR}$.

The following are described: *Et* β -*p*-anisylpropionate, b. p. 152—153°/12 mm.; *Et* β -3:4-methylenedioxyphenylpropionate, b. p. 180°/15 mm.; γ -*p*-anisylpropan- α -ol, m. p. 26°, b. p. 162°/15 mm. (phenylurethane, m. p. 67°), obtained in 40% yield from the ester and 60% yield from the amide by reduction with Na and EtOH; and γ -3:4-methylenedioxyphenylpropan- α -ol, b. p. 180°/13 mm. (phenylurethane, m. p. 97°), yield, 50% from the amide, 25% from the ester. R. BRIGHTMAN.

Rearrangement of certain poly-inenes. Structure of the product obtained by the rearrangement of tetraphenyldi-*tert*-butylethynylethane. D. ALTHAUSEN and C. S. MARVEL (J. Amer. Chem.

Soc., 1932, 54, 1174—1184).—Reactions of the hydrocarbon $\text{C}_{38}\text{H}_{38}$ (I), obtained by the rearrangement of tetraphenyldi-*tert*-butylethynylethane, indicate the indene formula $\left(\text{C}_6\text{H}_4 \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{CMe}_3) \end{array} \text{CH} \right)_2$.

Oxidation of (I) with O_3 gives $\text{CMe}_3\cdot\text{CO}_2\text{H}$, $\text{H}_2\text{C}_2\text{O}_4$, $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, and tarry products; COPh_2 could not be detected. Oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH gives $o\text{-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$; definite products are not obtained using HNO_3 , and (I) is not oxidised by KMnO_4 or H_2O_2 . (I) does not add Br in CCl_4 , is not reduced with H_2 under slight pressure in presence of Pt or Pd catalysts, but with H_2 and a Cu chromite catalyst at 175° under a pressure of 200 atm. gives (mainly) 3-phenyl-1-*tert*-butylhydrindene (II), m. p. 181—182°, $\alpha\alpha$ -diphenyl- $\delta\delta$ -dimethylpentane, b. p. 122—127°/1 mm. (also obtained by reduction of diphenyl-*tert*-butylethynylcarbinol), and the tetrahydro-derivative, m. p. 132—133°, of (I). Reduction of (I) with Na and amyl alcohol gives (II). (I) is not cleaved by 40% Na-Hg; the Na derivative formed is converted by H_2O into the hydrocarbon, $\text{C}_{38}\text{H}_{40}$, m. p. 179.3—180.3° (this vol., 50), which decolorises Br rather rapidly, is not reduced by H_2 and Pt or by Na and amyl alcohol, but with Na and EtOH gives a hydrocarbon, $\text{C}_{38}\text{H}_{42}$, m. p. 181—182°, not identical with (II). Rearrangement of (I) by heating with AcOH-HCl gives a hydrocarbon, $\text{C}_{38}\text{H}_{38}$, m. p. 173—174°, not oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH and not reduced by Na and amyl alcohol. The mechanism of the formation of (I) is discussed.

C. J. WEST (b).

ψ -Halogens. XVIII. Reaction between silver perchlorate and iodine in organic media. New method of substitution by iodine. L. BIRKENBACH and J. GOUBEAU (Ber., 1932, 65, [B], 395—401).— AgClO_4 , I, and C_6H_6 yield PhI ; since the reaction occurs at -80° , direct iodination is improbable and the intermediate production of IClO_4 is postulated. The oxidising action of liberated HClO_4 can be negated by addition of MgO , MgCO_3 , CaO , or CaCO_3 . The following changes have been observed: PhCl to $p\text{-C}_6\text{H}_4\text{ClI}$; PhMe to $o\text{-C}_6\text{H}_4\text{MeI}$; C_{10}H_8 to $1\text{-C}_{10}\text{H}_7\text{I}$; PhOH to $p\text{-C}_6\text{H}_4\text{I}\cdot\text{OH}$. The system $\text{AgClO}_4\text{-Br}$ permits the reactions: C_6H_6 to PhBr ; PhBr to $\text{C}_6\text{H}_4\text{Br}_2(p)$; PhNO_2 to $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$. In the dark at room temp. PhMe is iodinated almost exclusively in the nucleus; in the light much tar is produced, presumably as a result of the formation of $\text{CH}_2\text{Ph}\cdot\text{ClO}_4$. COMe_2 behaves similarly, giving little iodoacetone and much carbonised material. With Et_2O at room temp. a reducing solution results along the lines iodoether \rightarrow ether perchlorate \rightarrow acet-aldehyde semiacetal. MeOH and EtOH yield hypoiodous esters stable at -80° , but eliminating I at room temp.; their production is established by addition of cyclohexene to the mixture of MeOH, I, and AgClO_4 at -80° , whereby 2-iodocyclohexyl Me ether, b. p. 98°/10 mm., results. PhOH probably reacts similarly, but the primary PhIO isomerises rapidly to $p\text{-C}_6\text{H}_4\text{I}\cdot\text{OH}$. The kinetics of the reaction of AgClO_4 and I in org. media are discussed.

H. WREN.

Chloriodotoluenes. H. J. LONG and F. B. DAINS (Univ. Kansas Sci. Bull., 1930, 19, 205—214).

The m. p., b. p., n_D^{23} , d_4^{15} , and m. p. of mononitro-derivative are recorded for 2:3-, 2:4-, 2:5-, 2:6-, 3:2-, 3:4-, 3:5-, 5:2-, 4:2-, and 4:3-chloriodotoluene. 2:5- and 4:3-chloriodotoluene have been obtained by direct iodination of the corresponding chlorotoluene.

CHEMICAL ABSTRACTS.

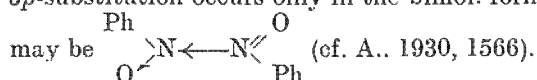
Addition of bromine to $\alpha\beta$ -diphenyl- δ -methyl- $\Delta^{\gamma\gamma}$ -butadiene. H. BURTON (J.C.S., 1932, 748—750).— α -Phenylcinnamaldehyde (convenient prep. given; cf. A., 1919, i, 21) [phenylhydrazone, m. p. 140—141° (lit. 125—126°); *p*-nitrophenylhydrazone, m. p. 205—206°; semicarbazone, m. p. 194—195°] and MgEtI in boiling $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ give, after distillation, $\alpha\beta$ -diphenyl- δ -methyl- $\Delta^{\gamma\gamma}$ -butadiene (I), m. p. 48—49°, which readily absorbs O_2 from air either in EtOH or in the solid state. In accordance with theory (cf. A., 1929, 1270), addition of Br (>1 mol.) to (I) in CCl_4 gives solely the oily $\gamma\delta$ -dibromide, since successive oxidation with O_3 and H_2O_2 affords BzOH as the only acidic product. A definite product could not be isolated by reducing (I) with Na and EtOH or Na-Hg in various media.

H. BURTON.

Relationship of dipole measurements to the stereochemistry of carbon. VI. Dipole measurements with substances containing double linkings. E. BERGMANN, L. ENGEL, and H. MEYER (Ber., 1932, 65, [B], 446—457).—Determination of the dipole moments of the *p*-chlorophenyl-, m. p. 92—93° and 43—44°, and *p*-bromophenyl-, m. p. 107° and 42—44°, -vinyl bromides shows that the compounds of lower m. p. are the *trans* forms (expressed with regard to the polar groups). The applicability of dipole measurements to determination of the angle between the individual valencies in ethylenic compounds is discussed (cf. A., 1930, 979). Measurements are recorded for $\beta\beta$ -dichloro-, $\beta\beta$ -dibromo-, $\beta\beta$ -dinitro- $\alpha\alpha$ -diphenylethylene, $\alpha\alpha$ -di-*p*-chlorophenylethylene, benzophenone, *p*-chloro-, *pp'*-dichloro-, *p*-bromo-, *pp'*-dibromo-benzophenone, benzophenone-anil and *p*-chloroanil, m. p. 92—93°, acridine, phenazine, pyridine, quinoline, and isoquinoline. In COPh_2 , in its *p*-substituted derivatives, and in those of $\alpha\alpha$ -diphenylethylene the angle between the valencies is uniformly about 130°.

H. WREN.

Orienting power of the nitroso-group. D. L. HAMMICK, R. G. A. NEW, and L. E. SUTTON (J.C.S., 1932; 742—748).—The electric dipole moments of PhNO , *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}$, and β -nitroso- $\beta\epsilon$ -dimethylhexane, determined by the method previously described (A., 1931, 1354), are 3.14, 1.80, and 2.51×10^{-18} e.s.u., respectively. These vals. indicate that the NO group causes a negative electromeric effect when substituted in a C_6H_5 ring, which is approx. the same as that for NO_2 and CHO (cf. *loc. cit.*). In view of this and the negative induced effect set up by the negative moment, the NO group will be *m*-directing. It is inferred that *op*-substitution occurs only in the bimol. form, which



H. BURTON.

Reduction of nitro-compounds by aldehydes in ethyl-alcoholic potassium hydroxide solution. E. S. BACON and D. H. RICHARDSON (J.C.S., 1932,

884—888; cf. A., 1926, 515).—*m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ is readily reduced by MeCHO-free 0.5*N*-EtOH-KOH at 60°/96 hr. to 3:3'-dichloroazoxybenzene (50% yield). Of 16 other NO_2 -compounds studied, only *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, and 1- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ give similarly the corresponding azoxy-derivative (in yields of 9.5, 3, and 3%, respectively); complex products are, however, formed (% yield given in parentheses) from *o*- (9) and *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ (19), *m*- (13) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ (59), *m*- (13) and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (68), and 1- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ (93). In presence of MeCHO (0.5*N*), the yields of the corresponding dichloroazoxybenzenes from *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ are 28, 74, and 31%, respectively; an increase is not found for any other compound, but all the substances used give rise to considerable amounts of complex insol. products. *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ thus affords an insol. compound (I), $\text{C}_{26}\text{H}_{24}\text{O}_4\text{NCl}$, decomp. 200°, probably derived from *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{OH}$, the amount formed increasing with rise in the concn. of MeCHO; raising the concn. of KOH causes a greater increase in the yield of 4:4'-dichloroazoxybenzene (II) than of (I). *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ is also reduced by the following aldehydes (concn.=0.5*N*) in 0.5*N*-EtOH-KOH at 60°; the % yield of (II) or 4:4'-dichloroazobenzene (or a mixture of both) is given in parentheses: $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{CHO}$ (30), piperonal (30), EtCHO (25), heptaldehyde (12), PrCHO (9), glucose (8), PhCHO (6), CH_2O (3), $\text{CH}_2\text{Ph}\cdot\text{CHO}$ (2.5). Less than 1% of (II) is formed using cinnamaldehyde, vanillin, anisaldehyde, *o*-OH- $\text{C}_6\text{H}_4\cdot\text{CHO}$, and protocatechualdehyde (large amount of insol. product formed in this case), whilst COMe_2 causes 5% reduction.

H. BURTON.

Reduction of nitrostyrenes to ω -phenylethylamines. A. SKITA and F. KEIL (Ber., 1932, 65, [B], 424—431).—Colloidal H_2O -free solutions of the Pt metals are prepared (I) by dissolving H_2PtCl_6 in abs. EtOH, addition of collodion solution, boiling with $\text{N}_2\text{H}_4\cdot\text{HCl}$, and treating the cold solution with Na wire or by treating the solution with Na followed by H_2 under 3 atm. Conc. colloidal Pt solutions are obtained by adding a few c.c. of above solution to H_2PtCl_6 in EtOH and reducing with H_2 . (II) PdCl_2 in EtOH is mixed with collodion and treated with H_2 under 3 atm. (III) H_2PtCl_6 in abs. EtOH mixed with solution II and reduced by H_2 under 3 atm. gives EtOH-collodion-sol. Pt with a nucleus of colloidal Pd. (IV) Solutions in AcOH are obtained by evaporating solutions I—III in vac. and dissolving the residue in AcOH containing Ac_2O . The preps. are useful in the following cases, in which the presence of H_2O would disturb the course of the change: conversion of AcBz in presence of $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ into Et α -hydroxy- α -phenyl- β -propylaminoacetate; reduction of aceto-, propio-, butyro-, and valero-nitriles to the corresponding primary amine as essentially basic product; conversion of acet- and hept-aldoxime into ethyl- and heptyl-amine as sole basic product; prep. of ω -phenylethylamines from ω -nitro-*p*-methoxy-, -3:4-dimethoxy-, and -3:4:5-trimethoxy-styrene. ω -3:4-Dimethoxyphenylethylamine hydrochloride has m. p. 154°.

H. WREN.

Aryl-hydrocarbon sulphonium compounds. C. COURTOT and P. CHIFFERT (Compt. rend., 1932,

194, 986—988).—In the action of aromatic hydrocarbons with SOCl_2 and AlCl_3 , the triarylsulphonium chlorides were encountered. The following are described: 3:4:3':4', m. p. 99°; 2:4:2':4', m. p. 88°; 2:5:2':5'-tetramethyldiphenyl sulphoxide, m. p. 77.5°. Tri-*p*-tolyl-, m. p. 140°; tri-(3:4-dimethylphenyl)-, m. p. 132°; tri-(2:4-dimethylphenyl)-sulphonium chloride, m. p. 86°. The sulphonium chlorides on heating afford diaryl sulphides and aromatic chloro-compounds. J. L. D'SILVA.

Relationship of dipole measurements to the stereochemistry of carbon. VII. Dipole moment and structure of sulphoxides and sulphones. E. BERGMANN and M. TSCHUDNOVSKI (Ber., 1932, 65, [B], 457—463).—Measurement of the dipole moment of Ph_2 , *p*-chloro-, and *pp'*-dichlorodiphenyl sulphoxides (4.08, 3.94, and 2.74, respectively) leads to the conclusion that the angle at S is the same in all three compounds, but the O of the S:O group does not lie in the plane determined by the S and single linkings proceeding from it. Confirmation of this view is found in measurements of the isomeric thianthrene disulphoxides; since thianthrene has a finite dipole moment its structure cannot be centrosymmetrical. Since the O of the S:O group does not lie in the same plane as the central atom and its single linkings, the hypothesis of a semipolar double linking is not necessary to explain the resolution of unsymmetrically-substituted sulphoxides into optical antipodes. The dipole moments of Ph_2 and *p*-chlorodiphenyl sulphone suggest that the valencies enclose approximately the same angle as those of an (undistorted) methane C atom. *p*-Chlorodiphenyl sulphoxide, b. p. 228°/21 mm., m. p. 45—46°, sulphone, m. p. 92—93°, and *pp'*-dichlorodiphenyl sulphoxide, m. p. 143—145°, appear new. CHPh_3Na and Ph_2 sulphoxide afford CHPh_3 , Ph_2S , and PhSH .

H. WREN.

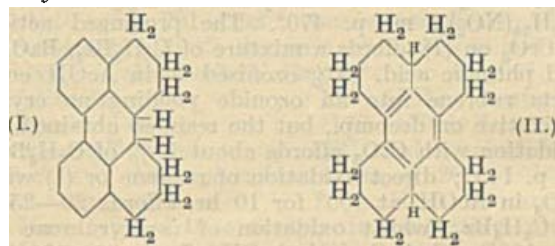
Mechanism of polymerisation processes. III. Dimeric indene. E. BERGMANN and H. TAUBADEL (Ber., 1932, 65, [B], 463—467).—The hypothesis, based on the analogy between indene and styrene, that di-indene is 2:1'-hydrindylindene is indirectly verified. Di-indene is converted by amyl nitrite and NaOEt into an oximino-derivative, $\text{C}_{18}\text{H}_{15}\text{ON}$, m. p. 201° (decomp.). 1:1'-Hydrindylindene, b. p. 190—192°/12 mm., prepared from 1-chlorohydrindene, b. p. 105°/22 mm., and Li-indene, is not identical with di-indene, into which it cannot be isomerised by KOH-EtOH . Anhydrodihydrindone is converted by P and HI into 2:1'-hydrindylhydrind-1-one, m. p. 94°, which could not be catalytically hydrogenated, but possibly affords di-indene when reduced with Na and EtOH. 3-Phenyl-2-methylindone, P, and HI in AcOH afford 3-phenyl-2-methylhydrind-1-one, m. p. 64—65°.

H. WREN.

Use of lithium for synthesis of naphthalene homologues. V. VESELÝ and F. ŠTURSA (Coll. Czech. Chem. Comm., 1932, 4, 139—144).—Methylnaphthalenes are obtained by the action of Me_2SO_4 on the Li compound obtained from 1-halogenonaphthalenes and Li in dry Et_2O in a N_2 atm., diaryls also being formed. The yield of methylnaphthalenes decreases in the order $\text{X}=\text{Cl} > \text{Br} > \text{I}$, and with

2-halogenonaphthalenes diaryls are the sole products except when $\text{X}=\text{Cl}$. Reduction of 1-nitro-2-methylnaphthalene with SnCl_2 affords 4-chloro-2-methyl- α -naphthylamine, converted by diazotisation into 4-chloro-2-methylnaphthalene, b. p. 180—190°/16 mm. (picrate, m. p. 79—80°), similarly converted into 1:3-dimethylnaphthalene. J. W. BAKER.

Perylene and its derivatives. XXXIV. Hydrogenation of perylene. A. ZINKE and O. BENNDORF (Monatsh., 1932, 59, 241—255).—Reduction of perylene with Na and boiling amyl alcohol gives octa- (I), m. p. 119—121°, and tetradeca- (II), m. p. 175—177°, -hydroperylene; the octahydroperylene, m. p. 159—161°, previously described (A., 1929, 803), may be a mixture.



[By N. SCHNIDERSCHITSCH.] Catalytic reduction of perylene using a large amount of Pd-charcoal in AcOH gives (II) (cf. *loc. cit.*), and not a dodecahydroperylene as previously supposed (A., 1931, 730).

Hexahydroperylene (A., 1920, i, 541) (now postulated as the 1:2:3:7:8:9-derivative) is an intermediate in the production of (II); it is reduced by both the above methods to (II). (I) is not reduced further by Na and amyl alcohol, indicating that it is not an intermediate in the prep. of (II) by these reagents; it is reduced catalytically to (II). The formation of (I) is considered to be analogous to the reduction of C_{10}H_8 to tetrahydronaphthalene, whilst the production of (II) is analogous to the production of 1:2:3:4:5:6:7:8-octahydroanthracene. Perylene is considered to exist in two forms, viz., one as previously suggested (A., 1931, 730) and the other with partial valencies (Thiele formulation) at the 3, 6, 9, and 12 positions. (I) and (II) [crystallographic data for both by F. ANGEL] are both dehydrogenated by CuO to perylene. H. BURTON.

Coloured hydrocarbons: a blue hydrocarbon. M. BADOCHÉ (Compt. rend., 1932, 194, 1086—1088).—Hydrolysis of the derivative obtained by the action of Na on 9:11-diphenyl-9:12:10:11-dibenzo-9:11-dihydronaphthacene affords, in addition to the two normal products previously described (this vol., 375), a blue hydrocarbon (I), m. p. 465°, subliming at 260°/0.001 mm. [C, 95.05; H, 4.49%: max. of absorption bands in CHCl_3 at 6100, 5650, and 5200 Å.: reduced by nascent H to (II)], a colourless hydrocarbon (II), and a colourless hydrocarbon, $\text{C}_{36}\text{H}_{24}$ (III), +0.5 C_6H_6 , m. p. 245°, and solvent-free, m. p. 286—287° (replacement of Ph by H). Both (II) and (III) are dehydrogenated by PbO to (I).

J. W. BAKER.

Dissociable organic oxides. Oxidation of rubrene by different oxidising agents. C. DUFRAISSE and L. ENDERLIN (Bull. Soc. chim., 1932,

[iv], 51, 132—144).—Oxidation of rubrene with Caro's acid and KMnO_4 or in C_6H_6 solution with KMnO_4 and 50% H_2SO_4 affords rubrene monoxide (I), $\text{C}_{42}\text{H}_{28}\text{O}$, m. p. 200° (efferv.), solidifying and melting again at 325° (Br-derivative, m. p. above 500°), and dihydroxydihydorubrene (II); with KMnO_4 and 1% H_2SO_4 , (II) alone is formed. CrO_3 in AcOH yields 80%, and 18% HNO_3 85% of (I). (I) is also obtained in 85% yield by reducing the dissociable dioxide with Zn and AcOH . (I) is not attacked by Fe or Zn when dry, but with Fe and AcOH yields rubrene; HI affords ψ -rubrene, but with aq. HI containing traces of I an isomeric oxide appears to be obtained. With H_2SO_4 in C_6H_6 (I) is converted into a satellite of rubrene. With 52% HNO_3 rubrene and (I) yield a $(\text{NO}_2)_2$ -derivative, $\text{C}_{42}\text{H}_{26}(\text{NO}_2)_2$, m. p. 470° . The prolonged action of CrO_3 on (I) affords a mixture of $\text{C}_6\text{H}_4\text{Bz}_2$, BzOH , and phthalic acid. 3% ozonised O_2 in AcOH converts rubrene into an ozonide yielding no cryst. derivative on decomp., but the resin so obtained on oxidation with CrO_3 affords about 10% of $\text{C}_6\text{H}_4\text{Bz}_2$, m. p. 145° ; direct oxidation of rubrene or (I) with CrO_3 in AcOH at 100° for 10 hr. affords 20—25% of $\text{C}_6\text{H}_4\text{Bz}_2$, whilst oxidation of isooxyrubrene at 80 — 100° with CrO_3 and AcOH affords 33—38% of $\text{C}_6\text{H}_4\text{Bz}_2$, thus confirming the presence of the two $\alpha\gamma$ -diphenylindene rings in rubrene. The absence of higher yields of $\text{C}_6\text{H}_4\text{Bz}_2$ is attributed to resinification or further decomp. into BzOH and phthalic acid.
R. BRIGHTMAN.

Effect of aqueous dilution in organic nitrations.
Nitration of aniline. E. MACCIOTTA (Annali Chim. Appl., 1932, 22, 142—148).— H_2O in this reaction has a twofold effect, chemical in taking part in the formation of nitrophenols, and physical in preventing rapid superheating of the reacting mass.

O. F. LUBATTI.

Preparation of disubstituted formamidines and reactions of di-*p*-xylylformamidine. F. B. DAINS and A. E. DAILY (Univ. Kansas Sci. Bull., 1930, 19, 215—219).—Quant. yields of disubstituted formamidines are obtained from 1 mol. of $\text{CH}(\text{OEt})_3$ and 2 mols. of aromatic amine heated at 100 — 120° for 1—2 hr.; di-*p*-xylylformamidine, m. p. 155° , condenses with 4-benzylidene-3-methylisooxazolone to give 3-methyl-4-*p*-xylylaminomethyleneisooxazol-5-one, m. p. 193° ; with *p*-tolylmethylpyrazolone to give 1-*p*-tolyl-3-methyl-4-*p*-xylylaminomethylenepyr-azolone, m. p. 249° ; with Et cyanoacetate to give Et *p*-xylylaminomethyleneacyanoacetate, m. p. 153° ; with CH_3Ac_2 to give *p*-xylylaminomethyleneacetyl-acetone, m. p. 125° ; with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ to give *p*-xylylaminomethyleneacetoaceto-*p*-xylylide, m. p. 140° ; with $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ to give *p*-xylylaminomethylenebenzoylaceto-*p*-xylylide, m. p. 182° ; with $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ to give $\text{CH}_2\text{Bz}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, m. p. 142° ; and with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ to give $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, m. p. 98° .
CHEMICAL ABSTRACTS.

Optically active amines containing no asym-metric atom. S. E. JANSON and [Sir] W. J. POPE (Chem. and Ind., 1932, 316).—*spirocyclo*Heptanedicarboxylic acid (A., 1931, 1054) is converted by Schmidt's method (B., 1930, 939) into dl-diaminospirocyclo-

heptane, b. p. 91 — $92^\circ/12$ mm., m. p. 7 — 8° (Bz_2 derivative, m. p. 223 — 224°). Fractional crystallisation of its *d*-camphor- β -sulphonate from EtOH affords the less sol. *d*-base *d*-camphorsulphonate (hydrochloride, $[\alpha]_{4358} +30^\circ$ in H_2O), whilst the base from the mother-liquor affords the *l*-base *l*-camphor-sulphonate (hydrochloride, $[\alpha]_{4358} -30^\circ$ in H_2O).

J. W. BAKER.

Dimorphism of tetranitrodiphenyl derivatives.
II. J. VAN ALPHEN (Rec. trav. chim., 1932, 51, 361—368; cf. this vol., 267).—3 : 3'-Dichloro-4 : 4' : 6 : 6'-tetranitrodiphenyl (m. p. 184° and 191° ; cf. A., 1917, i, 390) with NaOMe gives 4 : 4' : 6 : 6'-tetra-nitro-3 : 3'-dimethoxydiphenyl, m. p. 244° (Maquenne block), also obtained by heating 1-chloro-4 : 6-dinitro-3-methoxybenzene with Cu at 235° (small yield). The 3 : 3'-diethoxy-compound, m. p. 194° and 208° , is similarly obtained from 3 : 3'-dichloro-4 : 4' : 6 : 6'-tetranitrodiphenyl, which when heated with the appropriate amine gives 3 : 3'-diamino-, m. p. 297° (*loc. cit.*); 3 : 3'-dimethylamino-, explodes above 360° , changes colour in light [nitrated to 3 : 3'-di(methyl-nitroamino)-, decomp. 210° , explodes 225° , which is reconverted into the dimethylamino-derivative by boiling PhOH]; 3 : 3'-diethylamino-, m. p. 315 — 320° (decomp., turns red 270 — 280°); 3 : 3'-di(dimethyl-amino)-, decomp. 270° ; 3 : 3'-di(diethylamino)-, m. p. 210° (Maquenne block, turns red 185° ; on a block preheated to 200° it melts, solidifies, and remelts at 210°); and an NH_2Ph additive compound of 3 : 3'-diphenylamino-4 : 4' : 6 : 6'-tetranitrodiphenyl, m. p. 278° (Maquenne block) (cf. *loc. cit.*).
A. A. LEVI.

Action of dibasic acids on 2 : 2'-diaminodi-phenyl. S. SAKO (Mem. Coll. Eng. Kyushu, 1932, 6, 307—325).—The oxalate, decomp. 148° , of 2 : 2'-diaminodiphenyl (I) heated in *m*-cresol at 85 — 90° (bath) gives the oxalyl derivative, decomp. 179° , of (I), which is pptd. unchanged from its solution in conc. H_2SO_4 by H_2O , and is readily hydrolysed by dil. alkali to (I). *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and (I) in H_2O at 100° afford (mainly) the *s*-monophthalyl derivative (II), m. p. 176 — 177° , converted by conc. HCl (not by dil.) at room temp. or by dry HCl in Et_2O , PhMe, xylene, or C_6H_6 (slowly) (not in CHCl_3) into the hydrochloride, decomp. 190° (becomes yellow at about 170°), of 2-amino-2'-phthalimidodiphenyl (III), which when heated in CHCl_3 or H_2O regenerates (II). Dissolution of (II) in 10% Na_2CO_3 and acidification with AcOH affords the unstable acetate (?), m. p. about 80° , decomp. 120° , of (III), but (II) is recovered unchanged by evaporation (vac.) of its solution in AcOH . (II) is converted by 70% H_2SO_4 into the sulphate of (III); diazotisation of the resultant solution followed by KI gives 2-iodo-2'-phthalimidodiphenyl, m. p. 247° (softens at 240°). (II) and Ac_2O furnish 2'-phthalimido-2-acetamidodiphenyl, m. p. 145° ; with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ at 200 — 250° , 2 : 2'-diphthalimidodiphenyl, m. p. 330° , results. (I) and succinic anhydride at 150 — 230° give 2 : 2'-disuccinimidodiphenyl, m. p. 312° ; attempted prep. of the succinyl derivative affords a syrup.
H. BURTON.

Nitration of acyl derivatives of 2 : 2'-diamino-diphenyl. S. SAKO (Mem. Coll. Eng. Kyushu, 1932, 6, 327—351).—2 : 2'-Diacetamidodiphenyl and

HNO_3 (*d* 1.49), alone or in conc. H_2SO_4 , give the 5 : 5'-*dinitro*-derivative, m. p. 250° with darkening (softens at about 240°), hydrolysed by conc. HCl in EtOH to 5 : 5'-*dinitro*-2 : 2'-*diaminodiphenyl* (I), m. p. 303° (decomp.) after softening at 296° (lit. 285°). Hydrolysis of the product, decomp. 117° , from oxalyl-2 : 2'-*diaminodiphenyl* and KNO_3 in conc. H_2SO_4 also gives (I). 2 : 2'-*Disuccinimidodiphenyl* and HNO_3 (*d* 1.48) in conc. H_2SO_4 below 3° give 20% of the 4 : 4'- (II), m. p. $311\text{--}312^\circ$ (decomp.) (softens at 295°), and 60—70% of the 4 : 5'- (III), m. p. $271\text{--}272^\circ$, -*dinitro*-derivatives; the 5 : 5'-derivative is also produced since hydrolysis of the residue after removal of (II) and (III) gives (I). (II) is hydrolysed difficultly by conc. HCl , but more readily by aq. 10% KOH at $60\text{--}80^\circ$, forming 4 : 4'-*dinitro*-2 : 2'-*diaminodiphenyl*, m. p. $249\text{--}250^\circ$ (the Ac_2 derivative, m. p. $237\text{--}238^\circ$, is also hydrolysed difficultly by conc. HCl , but readily by aq. alkali), reduced (as is 2 : 2'-*dinitrobenzidine*) by SnCl_2 and conc. HCl to 2 : 4 : 2' : 4'-*tetra-aminodiphenyl* (*tetrahydrochloride*). (III) is hydrolysed more readily than (II); the resultant 4 : 5'-*dinitro*-2 : 2'-*diaminodiphenyl* (IV) [*acetate*, m. p. 180° (softens at 100°); 2-*Ac*, m. p. 252° (decomp.), and Ac_2 , m. p. 271° (decomp.), derivatives] exists in orange (stable), m. p. $179\text{--}180^\circ$, and yellow (unstable), m. p. $143\text{--}144^\circ$, forms; the latter is obtained by alkaline hydrolysis and by treatment of the above acetate with EtOH , and is converted into the former when heated alone or with MeOH and EtOH . 2 : 4 : 2' : 5'-*Tetra-aminodiphenyl tetrahydrochloride* is prepared. Phthalyl-2 : 2'-*diaminodiphenyl* and KNO_3 in cold conc. H_2SO_4 give a product, hydrolysed to (IV).

H. BURTON.

Diphenyl and its derivatives. X. Influence of certain 2'-substituents on the 2-NH₂-group. L. MASCARELLI, D. GATTI, and M. PIRONA (Atti R. Accad. Lincei, 1931, [vi], 14, 506—511).—The insol. powder always formed during the prep. of 2 : 2'-disubstituted diphenyls (this vol., 152) is diphenyleneiodonium iodide. The known readiness with which a penta-atomic heterocyclic ring with an I atom in the ring is formed is thus confirmed. The ease with which carbazole is formed when a 2'-substituted 2-diazodiphenyl is decomposed by H_2O , CuCl , CuBr , or CuCN indicates that here also the 2'-substituent is expelled from the tervalent N atom. That the 2-substituent of 2 : 2'-disubstituted diphenyls disturbs the reactions of the 2'-substituent is shown by the course followed by various reactions of 2-amino-diphenyl. Preps. of 2-chloro-, -bromo-, -iodo-, -fluoro-, -hydroxy-, and -cyano- from 2-amino-diphenyl are described.

T. H. POPE.

Reaction of diazonium salts on sodium alkyl-dithiocarbamates. A. M. CLIFFORD and J. G. LICHTY (J. Amer. Chem. Soc., 1932, 54, 1163—1166).—Diazonium salts react with Na alkyl-dithiocarbamates, giving (mainly) aryl alkyl-dithiocarbamates. PhN_2Cl and Na dimethyldithiocarbamate give *Ph dimethyldithiocarbamate*, m. p. $94\text{--}95^\circ$; the *o*-, m. p. $81\text{--}82^\circ$, and *p*-tolyl, m. p. $112\text{--}113^\circ$; *p*-bromophenyl, m. p. $120\text{--}121^\circ$, and *p*-nitrophenyl, m. p. 154° , esters are prepared similarly. *Ph*, m. p. 46° , and *p*-tolyl, m. p. $77\text{--}78^\circ$, diethyldithiocarbamates, and *Ph*, m. p. 78° ,

and *p*-tolyl, m. p. $90\text{--}4^\circ$, pentamethylenedithiocarbamates are also prepared. By-products formed in these reactions are aryl disulphides, substituted ammonium alkyl-dithiocarbamates, and (in some cases) an alkylthiocarbamide. Preliminary work shows that the products of interaction of diazonium salts and alkali-metal aliphatic and aromatic carboxylates contain N.

C. J. WEST (b).

Preparation of oximinoacetamidoazobenzene derivatives. C. NAEGELI and A. TYABJI (Helv. Chim. Acta, 1932, 15, 403—409).—The following are prepared by interaction of the hydrochlorides of appropriate aminoazo-compounds with $\text{CCl}_3\text{-CH(OH)}_2$ and NH_2OH in a suitable solvent: 4-oximinoacetamido-, m. p. 214° ; 4-oximinoacetamido-3 : 3'-dimethyl-, m. p. 163° ; 4-oximinoacetamido-2 : 4'-dimethyl-, m. p. $201\text{--}202^\circ$; 4-oximinoacetamido-2 : 3'-dimethyl-, m. p. 198° ; 2-oximinoacetamido-, m. p. 211° ; 4-oximinoacetamido-3 : 4'-dimethyl-, m. p. 202° ; 3-oximinoacetamido-, m. p. $198\text{--}199^\circ$; 4-oximinoacetamido-2-methyl-, m. p. $178\text{--}179^\circ$; 4-oximinoacetamido-3-methyl-, m. p. 173° , and 4-oximinoacetamido-2 : 2'-dimethyl-azobenzene, m. p. 202° .

H. A. PIGGOTT.

New type of true acetylenic derivative, phenoxypropinene [phenoxiallylene]. L. BERT and E. ANDOR (Compt. rend., 1932, 194, 886—888).—Na reacts with $\text{Ph } \gamma\text{-chloro-}\Delta^2\text{-propenyl ether}$ (A., 1926, 44) in PhMe at 110° to give products from which phenyl propargyl ether, b. p. $98^\circ/23\text{ mm.}$ (*Ag* derivative: compound with HgCl_2), is isolated by means of its *Cu* derivative.

J. W. BAKER.

Nitrosation of phenols. XIII. *o*-Chlorophenol. H. H. HODGSON. XIV. Resorcinol isopropyl ether. H. H. HODGSON and H. CLAY (J.C.S., 1932, 866—869, 869—873).—XIII. Nitrosation of *o*-chlorophenol at 15° gives 2-chloro-4-nitrosophenol (40% of theoretical), m. p. 142° (decomp.), and the diazonium salt; the former is regarded as having the nitroso- rather than the previously assigned quinoneoxime structure on account of its comparatively low m. p. and its ready formation of a *picrate*, m. p. $156\text{--}158^\circ$ (decomp.), and analogous compounds with 2 : 4 : 6-trinitro-*m*-cresol, m. p. $147\text{--}5^\circ$ (decomp.), and 3-fluoro-, m. p. 151° (decomp.), 3-chloro-, m. p. 164° (decomp.), 3-bromo-, m. p. 163° (decomp.), and 3-iodo-, m. p. 169° (decomp.)-2 : 4 : 6-trinitrophenols. It readily forms the brownish-red *Ag* salt, *p*-nitrophenylhydrazones, m. p. $184\text{--}185^\circ$ (decomp.), and semicarbazones, decomp. above 150° , of 2-chlorobenzoquinone-4-oxime, and the Me ether of this is obtained from the *Ag* salt and MeI or from the nitrosophenol, NaOH , and Me_2SO_4 .

XIV. Resorcinol *Pr*⁸ ether, b. p. $249\text{--}250^\circ$, prepared in 25% yield by alkylation with NaOPr^8 (1 equiv.) and *Pr*⁸ I in Pr^8OH , gives with HNO_2 a mixture of 4-, m. p. $170\text{--}172^\circ$ (decomp.) (27% of the theoretical), and 6-, dimorphic (green and brown) forms, both m. p. 91° , -nitroso-3-isopropoxyphenols. Oxidation of these with alkaline $\text{K}_3\text{Fe(CN)}_6$ gives the corresponding NO_2 -compounds, m. p. 91° and 44° , respectively, also obtained in admixture by nitration of the *Pr*⁸ ether in Et_2O . 6-Nitro-3-isopropoxyphenol, m. p. 44° , is identified by synthesis from 3-chloro-4-nitro-

phenyl Pr^β ether (from Ag 3-chloro-4-nitrophenoxide and Pr^βI) by the action of NH₃ in aq. EtOH at 160° and diazotisation etc. of the resulting 4-nitro-3-aminophenyl Pr^β ether, m. p. 102—103°. *m*-Nitrophenyl Pr^β ether, b. p. 258—259°/744 mm., is reduced to the corresponding NH₂-compound, b. p. 244—245°/750 mm. (*hydrochloride*, m. p. 175—180°; *Ac* derivative, m. p. 100—101°), the Me₂ derivative of which, b. p. 253—254°/750 mm., is converted by nitrosation into 4-nitroso-3-isopropoxydimethylaniline, m. p. 65° (*hydrochloride*), which is hydrolysed by boiling 5% aq. NaOH to 4-nitroso-3-isopropoxyphenol, m. p. 170—172° (decomp.), and NHMe₂. Resorcinol Pr^β₂ ether could not be nitrosated, and with HNO₃ in Et₂O gave a small yield of 6-nitro-3-isopropoxyphenol.

H. A. PIGGOTT.

Baeyer-Drewson reaction. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1932, 985—987).—The formation of an indigotin derivative from an *o*-nitrophenol by interaction with COMe₂ and aq. NaOH is inhibited by a *m*- or *p*-OH (but not OMe) group except in the presence of two *o*-NO₂ groups. Thus a positive reaction is observed with 2- and 6-nitro- and 2:6-dinitro-3-methoxybenzaldehydes, 2- and 6-nitroveratraldehydes, and 2:6-dinitroisovanillin, but not with 6-nitro-3-hydroxybenzaldehyde or 2- or 6-nitrovanillin. An electronic explanation is advanced.

H. A. PIGGOTT.

Synthesis of thymol, chlorothymol, and homologues of thymol by the intramolecular rearrangement of *m*-tolyl ethers. J. B. NIEDERL and S. NATELSON (J. Amer. Chem. Soc., 1932, 54, 1063—1070).—The intramol. rearrangement of *m*-tolyl Pr^β ether, b. p. 195°, in glacial AcOH and conc. H₂SO₄ gives thymol and 6-isopropyl-*m*-cresol. 6-Chlorothymol is similarly prepared from 6-chloro-*m*-tolyl Pr^β ether, b. p. 231°, whilst 4-*sec*.-butyl-, b. p. 246—250°, and 4-*sec*.-amyl-*m*-cresols, b. p. 143—145°/10 mm., are formed from *m*-tolyl Bu^β, b. p. 212°, and *sec*-amyl ethers, b. p. 235°, respectively. Theories underlying such intramol. rearrangements are discussed, and a mechanism based on the theories of Lapworth (J.C.S., 1898, 73, 445) and Latimer (A., 1930, 9) is given.

C. J. WEST (b).

Catalytic decomposition of phenol silver salts. VI. Intermediate stages. W. H. HUNTER and R. B. WHITNEY (J. Amer. Chem. Soc., 1932, 54, 1167—1173; cf. A., 1921, i, 238).—The existence of radicals of the type C₆H₂X₃O[•] and -C₆H₂X₂O[•] (X=halogen) is supported by the electrolysis of the Ag salts of trihalogenophenols in pyridine; a characteristic blue colour develops rapidly at the anode and the amorphous polyphenylene oxide is produced. Various phenols and amines prevent the normal decomp. of these salts; the presence of these reagents in the reaction between I and alkali trihalogenophenoxides results in the iodination of the inhibiting reagent, except when the solvent is COMe₂. In the last case, iodination of COMe₂ occurs and the final product is the acetonyl ether of the trihalogenophenol. *Tribromoresorcinol Me acetonyl ether*, m. p. 83°; (2:4:6-) *trichloro*-, m. p. 75°, *tribromo*-, m. p. 111·5°, and *tri-iodo*-, m. p. 131·5°, -*phenyl acetonyl ethers* are thus prepared.

C. J. WEST (b).

Substituted phenols and germicidal activity. R. R. READ and E. MILLER (J. Amer. Chem. Soc., 1932, 54, 1195—1199).—A series of substituted phenols, C₆H₄R·OH, containing O in R, has been prepared and their PhOH-coeffs. have been compared with those of *n*-, *sec*-, and *tert*.-Bu·C₆H₄·OH; the activities of various other phenols are also given. The following conclusions are reached: (i) the mass of the group R has little relation to the germicidal activity; (ii) position isomerism has little effect on the bactericidal activity of alkyl- and alkoxy-phenols; (iii) side-chain isomerism affects the activity of alkylphenols markedly (the more compact is the group the lower is the activity); (iv) CH₂R is more effective than OR in enhancing the activity of a phenol; (v) CO₂Me and Ac groups are ineffective in enhancing the activity of PhOH. The following appear to be new: *o*-, m. p. 96—97°, *m*-, m. p. 83—85°, and *p*-, b. p. 202—205°/14 mm., -β-*hydroxyethoxyphenols*; *o*-βγ-*dihydroxypropoxyphenol*, b. p. 245—255°/18 mm.; *quinol Pr ether*, m. p. 55°; C₆H₃(OH)₂(O·CH₂·CH₂·OH), b. p. 195—205°/13 mm.

C. J. WEST (b).

Decomposition products of safrole. II. T. HIRADZUMI (J. Soc. Chem. Ind. Japan, 1932, 35, 48—50B).—Hydrolysis of the benzoates of methoxyisoeugenol (I) and methoxyisochavibetol (II) affords products both of which, on methylation, give isoeugenol benzoate. A m.-p. curve is constructed for mixtures of benzoates (I) and (II) and is used to determine the percentages of these substances in the benzoylated decomp. products of safrole.

J. L. D'SILVA.

Optically active β-keto-α-phenylpropyl alcohol. K. FREUDENBERG (Biochem. Z., 1932, 245, 238).—The compound was synthesised as an intermediate in the formation of ephedrine.

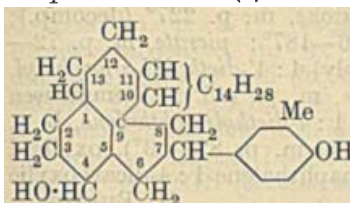
P. W. CLUTTERBUCK.

New colorimetric determination of cholesterol. A. L. BERNOUILLI (Helv. Chim. Acta, 1932, 15, 274—286).—Cholesterol (I), AcCl, and ZnCl₂ in AcOH, with or without CHCl₃, EtOH, or EtOAc, give a red colour, changed by warming for a few min. to a permanent, intense golden-brown, which can be used for determination of (I) in concn. of 1 in 100,000; 1 drop of blood suffices for the test, since by means of a micro-colorimeter 0·005 mg. of (I) can be determined within 0·3%. Phytosterol, ergosterol, and (less accurately) esters of (I) give similar colours and can be similarly determined. Substitution of BzCl for AcCl increases the delicacy of the determination fourfold.

R. S. CAHN.

Constitution of cholesterol. VII. Action of silver and cuprous chlorides on cholesterol. R. DE FAZI, F. MONFORTE, and F. PIRRONE. **VIII. Action of *o*-cresol and hydrochloric acid on cholesterol.** R. DE FAZI and L. DE FAZI GUERCI (Gazzetta, 1932, 62, 108—118, 118—126).—VII. With AgCl cholesterol gives a resin which contains cholesterylene; with CuCl it gives cholesterylene, a compound, m. p. 193°, and a secondary alcohol, C₁₅H₃₀O, m. p. 201° (*Br* derivative, m. p. 152—153°; *Br*₂ derivative, m. p. 166—167°; *Ac* derivative, m. p. 191—193°), which is probably cholesterol without the C₈ side-chain.

VIII. Cholesterol with *o*-cresol in presence of HCl gives a resin, probably *hydrocholesteryl-o-cresol* (annexed formula), and two compounds, $C_{27}H_{47}OCl$, m. p. 158—158.5° (I) and 136—137° (II), probably 13- and 7-chlorodihydrocholesterols, respectively. With KOAc (I) gives *allo*cholesterol and (II) gives cholesterol and a compound, m. p. 138—140°, probably a new isomeride of cholesterol. With $AgNO_3$ (I) gives cholesterol and (II) *metacholesterol*. E. E. J. MARLER.



β -Ergosterol. M. C. HART and H. EMERSON (J. Amer. Chem. Soc., 1932, **54**, 1070—1074).—Fractionation of the isomerised product (after saponification) from α -ergosterol acetate by EtOH gives β -ergosterol (I), m. p. 141°, $[\alpha]_D^{25} + 21.2^\circ$ in $CHCl_3$, purified through its acetate, m. p. 114°, $[\alpha]_D^{25} + 10.0^\circ$ in $CHCl_3$. Catalytic reduction (PtO_2) of (I) in AcOH gives *allo*- α -ergosterol, m. p. 146°, $[\alpha]_D^{25} + 8.0^\circ$ (chloroacetate, m. p. 200—201°, $[\alpha]_D^{25} + 9.0^\circ$ in $CHCl_3$). (I) and $CH_2Cl-COCl$ or $(CH_2Cl-CO)_2O$ give a mixture of the α - and β -chloroacetates; a similar mixture is also obtained from α -ergosterol. The original isomerised product consists of α - and β -ergosterol acetates and the acetate of at least a third isomeride (having a higher sp. rotation than either α - or β -ergosterol). C. J. WEST (b).

Sterols of ergot. III. Occurrence of an isomeride of α -dihydroergosterol. F. W. HEYL (J. Amer. Chem. Soc., 1932, **54**, 1074—1077; cf. A., 1930, 1483).—The mother-liquors after separation of α -dihydroergosterol (I) (*loc. cit.*) contain a third sterol (II), $C_{27}H_{43}OH$, m. p. 135—134° (acetate, m. p. 143—145°, $[\alpha]_D^{25} - 0.5^\circ$), which absorbs 2 atoms of H and gives colour reactions resembling those of (I). The fungisterol of Tanret (A., 1908, i, 637) is a mixture of (I) and (II). Myricyl alcohol and hentriacontane are present in ergot fat. The presence of a fourth sterol is definitely indicated by the fact that dextro-rotatory fractions were separated from extremely sol. (in AcOEt) parts of the fractionation. The readily sol. material gives, after acetylation, fractionation, and treatment with Br, the dibromide, m. p. 173—174°, of a sterol acetate. C. J. WEST (b).

Determination of α -dihydroergosterol in ergosterol from ergot. M. C. HART and H. EMERSON (J. Amer. Chem. Soc., 1932, **54**, 1077—1078).—“Ergosterol” from ergot consists of a mixture of ergosterol and α -dihydroergosterol, the latter amounting to not less than 30% of the material. The composition is determined polarimetrically. C. J. WEST (b).

Difference between *allo*- α -ergosterol and γ -sitosterol. K. BONSTEDT (Z. physiol. Chem., 1932, **205**, 137—140).—*allo*- α -Ergosterol (I) and γ -sitosterol (II) are shown to be different by the m.-p. diagrams when mixed with cholestanol (III). (I) and (III) form mixed crystals, (II) and (III) give a depression of about 10°. The corresponding hydrocarbons were shown to differ by the same method;

stigmastane gives a perceptible depression with γ -sitostane and mixed crystals with *allo*- α -ergostane.

J. H. BIRKINSHAW.

Isomerides of ergosterol and of its hydrogenation products. L. H. DEJUST and (Mlle.) D. VAN STOLK (Bull. Soc. Chim. biol., 1932, **14**, 369—401).—A review.

Lead, barium, and magnesium salts of hydnocarpic and chaulmoogric acids. H. I. COLE (Philippine J. Sci., 1932, **47**, 351—355).—The solubilities of the Pb, Ba, and Mg salts of hydnocarpic (m. p. 77—78°, 120°, and softens from 80°, respectively) and chaulmoogric (m. p. 83°, 123°, and softens from 100°, respectively) acids in EtOH, Et_2O , C_6H_6 , and ligroin (b. p. 30—60°) at various temp. are recorded. They lie between those of typical saturated and unsaturated fatty acids, do not permit separation of these two acids from one another, but indicate possible methods of separating these acids from saturated acids. R. S. CAHN.

Nitration of phenylacetic acid. D. L. YABROFF and C. W. PORTER (J. Amer. Chem. Soc., 1932, **54**, 1199—1204).— CH_2Ph-CO_2H added to HNO_3 (d 1.495; free from N oxides) at 0° gives 14.4% of the *m*- NO_2 -derivative. Optimum conditions are established (cf. Flürscheim and Holmes, A., 1928, 403) for the oxidation of nitrophenylacetic acids, the reduction of the nitrobenzoic acids, and the bromination of the resultant aminobenzoic acids.

C. J. WEST (b).

Mechanism of sulphur lability in cysteine and derivatives. II. Addition of mercaptan to benzamidocinnamic acid derivatives. B. H. NICOLET (J. Biol. Chem., 1932, **95**, 389—392).—Treatment of 2-phenyl-4-benzylidene-5-oxazolone in benzene with *p*-tolylmercaptan and NaOEt in EtOH results in addition of EtOH and the mercaptan to form *Et* α -benzamido- β -*p*-tolylthiol- ϵ -phenylpropionate, m. p. 136° (*Me* ester, m. p. 130—132° indef.; *Bu* ester, glassy solid), showing that the decomp. of compounds of the cysteine type by alkalis is reversible. Attempts to add H_2S instead of mercaptan failed.

H. DAVSON.

Action of phenylthiocarbimide on phenols in presence of aluminium chloride. H. RIVIER and S. KUNZ (Helv. Chim. Acta, 1932, **15**, 376—380).—By reaction of $PhNCS$ with the appropriate phenol in CS_2 in presence of $AlCl_3$ at room temp. are prepared *p*-hydroxythiobenzanilide, (I), m. p. 163—164° (80% yield); *OS*-dimethyl derivative, m. p. 169—170°; 6-hydroxy-m-, m. p. 164—165°, 5-hydroxy-o-, m. p. 175—176°, and 4-hydroxy-m-toluthioanilide, m. p. 139°; 2:4-dihydroxy-, m. p. 175—176°, and 2:4:6-trihydroxy-thiobenzanilide, m. p. 160—161°. α - and β -Naphthol give similarly 1-hydroxy-2-thionaphth-anilide, m. p. 182—183°, and 2-hydroxy-1-thionaphth-anilide, m. p. 99—100°, respectively. Using HCl and $ZnCl_2$ (A., 1929, 697) α -naphthol gives probably 1-hydroxy-4-thionaphthanilide, m. p. 204—205°, yielding with HgO in EtOH 1-hydroxy-4-naphth-anilide, m. p. 144—145°. The constitution of (I) is proved by transformation by alkaline $Pb(OAc)_2$ into *p*-hydroxybenzanilide and by synthesis from *p*-nitrobenzanilide, reduced by $SnCl_2$ and HCl in EtOH to

p-aminobenzanilide, m. p. 135—136°, which with PS_5 in xylene gives *p*-aminothiobenzanilide, m. p. 155°, whence by the diazo-reaction (I) is obtained.

R. S. CAHN.

Hexahydrophthalic acid. R. STOERMER and H. J. STEINBECK (Ber., 1932, 65, [B], 413—418).—The view that inability to effect resolution is incomplete evidence of the *meso* structure of a compound and that more trustworthy data are secured by introducing a group into the mol. with production of an asymmetric substance which is resolved and subsequently caused to lose its activity by being rendered symmetrical is illustrated at the instance of hexahydrophthalic acid.

Me H phthalate is transformed by PCl_5 into the chloride and thence by NH_2Ph into *Me* phthalanilide, m. p. 111° (*nitroso*-derivative, decomp. 94—96°), also obtained from the anilic acid and diazomethane; it readily loses MeOH with formation of phthalanil. *cis*-Hexahydrophthalic anhydride and NH_2Ph in C_6H_6 afford *cis*-hexahydrophthalanilic acid, m. p. 172—173° when rapidly heated, smoothly transformed by boiling 20% KOH - EtOH into the *trans*-anilic acid, m. p. 224—225°. The *cis*-acid is converted by diazomethane in Et_2O into the *Me* ester, m. p. 87°, and by AcCl into *cis*-hexahydrophthalanil, m. p. 132°. *cis*-Hexahydrophthalidialanilide, m. p. 234° (from the acid dichloride and NH_2Ph), is converted by boiling 80% AcOH into the *cis*-anil. *trans*-Hexahydrophthalic anhydride and NH_2Ph yield *trans*-hexahydrophthalanilic acid, m. p. 224—225° (decomp.) (*nitroso*-derivative, decomp. 103°), converted by AcCl into *trans*-hexahydrophthalanil, m. p. 224°, isomerised to the *cis*-anil at 230—240°. Subsequent experiments yielded the *trans*-hexahydrophthalanil, m. p. 195—196°, of Hückel and Müller (A., 1931, 1291). The anil, m. p. 224°, is hydrolysed by boiling aq. Na_2CO_3 to an acid, m. p. 214—215°, from which the original anil is obtained by the action of AcCl . Hydrolysis of the anil, m. p. 195—196°, gives an acid from which the anil is re-formed. Isomerisation of the *trans*-anilic acid, m. p. 224°, could not be effected. *Me* *trans*-hexahydrophthalanilide, m. p. 126°, and *trans*-hexahydrophthalidialanilide, m. p. 303—304° (decomp.), are described. *cis*-Hexahydrophthalanilic acid is resolved by cinchonine in methylal or dioxan; cinchonine *d*-*cis*-hexahydrophthalanilate has m. p. about 152° after softening when placed in a preheated bath or m. p. 205° (decomp.) when slowly heated (consequent on racemisation). *d*-*cis*-Hexahydrophthalanilic acid, m. p. about 142° in preheated bath, $[\alpha]_D^{25} + 14.32^\circ$ in COMe_2 , is very readily racemised when heated (consequently m. p. 170° when slowly heated; m. p. of *r*-acid) or in warm AcOH , but appears optically stable in warm COMe_2 . The highest observed val. is $[\alpha]_D^{25} - 6.93^\circ$ in COMe_2 for the *l*-acid. The *d*-acid is transformed by cold AcCl into inactive *cis*-hexahydrophthalanil. The possibility that inactivity of the anil is due to racemisation of the acid is excluded by the observation that the residual acid retains its activity when the change is not allowed to proceed to completion.

H. WREN.

Preparation of naphthalenedicarboxylic acids. N. FRÖSCHL and J. HARLASS (Monatsh., 1932, 59, 275—288).— α -Naphthyl *Me* ketone, formed together

with a little 2 : 2'-dinaphthyl from C_{10}H_8 , AcCl , and AlCl_3 in CS_2 , is reduced (Clemmensen) to 1-ethylnaphthalene, which with AcCl and AlCl_3 in CS_2 gives 4-ethyl- α -naphthyl *Me* ketone (I), b. p. 170—173°/18 mm. [*p*-nitrophenylhydrazone, m. p. 227° (decomp.); semicarbazone, m. p. 186—187°; picrate, m. p. 72—73°], and a little (probably) 4 : 4'-diethyl- α -naphthyl, m. p. 76—77° (picrate, m. p. 145°). Clemmensen reduction of (I) affords 1 : 4-diethylnaphthalene, b. p. 138—139°/8 mm. (picrate, m. p. 82—83°), oxidised [as is (I)] by HNO_3 to naphthalene-1 : 4-dicarboxylic acid [*Ba* salt (+ $2\text{H}_2\text{O}$)]. H. BURTON.

Transformations of 3-hydroxynaphthalic acid.

K. DZIEWONSKI, W. KAHL, and Z. OLSZEWSKI (Bull. Acad. Polonaise, 1931, A, 531—545).—Interaction of 3-hydroxynaphthalic anhydride with Br in boiling CHCl_3 gives the 4- Br -derivative, m. p. 286° (A., 1929, 186) [*imide*, m. p. 237—238°; *Bz*, m. p. 247—248°, and *Ac*, m. p. 214°, derivatives; *Me* ether, m. p. 216—217°; (1- or 8-)-phenylhydrazone, m. p. 283—284°; *oxime*, m. p. 303°], converted by NaOH at 180° into 3 : 4-dihydroxynaphthalic anhydride, m. p. 324—325° (phenylhydrazone, m. p. 317—318°; *oxime*, m. p. 312°; *Bz*, m. p. 222—223°, and *Ac*, m. p. 217°, derivatives; *Me* ether, m. p. 226—228°); this differs from the previously described dihydroxynaphthalic anhydride (A., 1929, 444), which is therefore the 3 : 5-isomeride. 4-Nitro-, m. p. 235—236° [*imide*, m. p. 310°; *Ac*-derivative, m. p. 167—178°(?), 4-nitroso-, m. p. 214° (decomp.), and 4-benzeneazo-, m. p. 261°, 3-hydroxynaphthalic anhydrides are all converted by reduction into 4-amino-3-hydroxynaphthalic anhydride, m. p. above 360° (*imide*, m. p. above 360°; *Ac* derivative, m. p. 253°), which is hydrolysed by boiling aq. HCl to the 3 : 4-(OH)₂-compound.

H. A. PIGGOTT.

Condensation of phenols and phenolic ethers with acetonedicarboxylic acid. I. β -Substituted glutaconic acids. V. M. DIXIT (J. Indian Chem. Soc., 1931, 8, 787—800; cf. A., 1931, 1056).—Acetonedicarboxylic acid (I), PhOH , and conc. H_2SO_4 at below 10° give β -*p*-hydroxyphenylglutaconic acid (II), m. p. 184° (decomp.) [*acetate*, m. p. 193° (decomp.); *Et* ester, b. p. 268°/25 mm.; monoanilide, m. p. 197° (decomp.)], and a monobasic ketonic acid (not described). (II) is synthesised from *Et* α -bromo- β -*p*-hydroxyphenylglutarate, b. p. 230°/21 mm., by Darbshire and Thorpe's method (J.C.S., 1905, 87, 1714), and from *Et* α -cyano- β -*p*-hydroxyphenylglutaconate, b. p. 269°/18 mm. (prepared by interaction of $n\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$), by Thole and Thorpe's method (J.C.S., 1911, 99, 2187). Reduction of (II) with Na-Hg and aq. NaOH gives β -*p*-hydroxyphenylglutaric acid (III), m. p. 172° (*Et* ester, b. p. 268°/18 mm.), also prepared by hydrolysis of *Et* *p*-hydroxybenzylidenebisacetate, m. p. 136° [formed (cf. Kotz, A., 1907, i, 705) from $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in presence of *p*-hydroxybenzylidenedipiperidyl, m. p. 112°], and of *Et* α -cyano- β -*p*-hydroxyphenylglutarate, b. p. 184°/16 mm. (from *Et* *p*-hydroxycinnamate and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$). Reduction of (II) with red P and HI in AcOH gives *p*-isopropylphenol, m. p. 61°, also formed when (III) is heated with soda-lime. (II)

and H_2O at 150° afford β -*p*-hydroxyphenylcrotonic acid, m. p. 163° , and *p*-isopropenylphenol. Distillation of the NH_4H salt of (II) under 40 mm. gives 2:6-dihydroxy-4-*p*-hydroxyphenylpyridine, m. p. 257° (tribenzoate, m. p. 177° ; sulphate, m. p. 320 – 330° ; oximino-derivative, m. p. 194°). KOH-fusion of β -anisylglutaconic acid (*loc. cit.*) yields $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$. $\alpha\beta$ -Dibromo- β -anisylglutaric acid, m. p. 121° , is resolved by brucine into the *l*-acid, m. p. 123 – 125° , $[M]_{\text{D}}^{25} -46.37^\circ$ in EtOH (brucine salt, m. p. 211°).

The following compounds, which appear to be new, are similarly prepared by way of (I) and PhOMe: *Ba* and *Et* β -anisylglutaconate, b. p. $254^\circ/19$ mm. ($\alpha\text{-CN}$ derivative, b. p. $251^\circ/21$ mm.); β -anisylglutaric acid, m. p. 164° [*Et* ester, b. p. $211^\circ/18$ mm. ($\alpha\text{-Br}$, b. p. $246^\circ/21$ mm., and $\alpha\text{-CN}$, b. p. $177^\circ/20$ mm., derivatives)]; *Et* anisylidenbisacetoacetate, m. p. 116° ; β -anisylcrotonic acid, m. p. 156° ; 2:6-dihydroxy-4-anisylpyridine, m. p. 248° (dibenzoate, m. p. 163° ; sulphate, m. p. 310 – 315° ; oximino-derivative, m. p. 201°).

The following are similarly obtained from $o\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$: β -6-methoxy-*m*-tolylglutaconic acid, m. p. 173° [*Ba* salt; *Et* ester (IV), b. p. $265^\circ/18$ mm.; dibromide, m. p. 286° ; monoanilide, m. p. 201° (decomp.)]; β -6-methoxy-*m*-tolylglutaric acid, m. p. 149° (*Et* ester, b. p. $257^\circ/14$ mm.); 2-methoxy-5-isopropyltoluene, b. p. 231° ; 2-methoxy-5-isopropenyltoluene, b. p. $219^\circ/19$ mm.; 2:6-dihydroxy-4-(6-methoxy-*m*-tolyl)pyridine, m. p. 252° (dibenzoate, m. p. 173° ; sulphate, m. p. above 320° ; oximino-derivative, m. p. 217°); 4-hydroxy-3-methylacetophenone, m. p. 103° ; 4-methoxy-3-methylphenylacetic acid, m. p. 128° . (IV) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ condensed by Kohler and Reid's method (A., 1926, 48), give *Et* α -cyano- β -6-methoxy-*m*-tolyl- $\beta\beta$ -di(carbethoxymethyl)propionate, hydrolysed to 6-methoxy-*m*-tolylmethanetriacetic acid, m. p. 191° (decomp.).

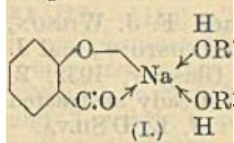
H. BURTON.

Manufacture of derivatives of 1:4:5:8-naphthalenetetracarboxylic acid. W. W. GROVES. From I. G. FARBENIND. A.-G.—See B., 1932, 332.

Reduction of *o*- and *p*-nitrobenzaldehydes and some of their derivatives in neutral solution. W. M. CUMMING, J. G. DUNCAN, H. G. A. ANDERSON, and R. ASHCROFT (J. Roy. Tech. Coll. Glasgow, 1932, 2, 596–600).—Reduction of *o*- and *p*-nitro-benzaldehyde, -benzoic acid, and -benzyl alcohol by Zn and NH_4Cl affords azoxy-compounds, except *o*-nitrobenzaldehyde which affords a compound, $\text{C}_{14}\text{H}_9\text{O}_3\text{N}_3$, m. p. 207 – 208° , probably in virtue of its tautomeric properties. The yields are poor. J. L. D'SILVA.

Chemical evidence of chelation in sodium salts of *o*-hydroxybenzaldehydes. O. L. BRADY and W. H. BODGER (J.C.S., 1932, 952–957).—When warmed in EtOH with NaOEt (1 equiv.) and 1-chloro-2:4-dinitrobenzene, *m*- and *p*-hydroxybenzaldehydes and α -naphthol-4-aldehyde readily form 2:4-dinitrophenyl ethers, m. p. 125° , 105° , and 158° , respectively; salicylaldehyde, its 3-OEt-, 5- NO_2 -, and 5-Br-derivatives, and α -naphthol-2-aldehyde, however, fail to do so under similar conditions. This does not seem to be due to steric hindrance, since derivatives such as salicylaldehydephenylmethylhydrazones, m. p. 69° , and

its 3 -derivative, m. p. 72° , and salicylaldehyde *O*-Me ether readily yield 2:4-dinitrophenyl ethers, m. p. 117° , 164° , and 106° , respectively, under these conditions.



Na salicylaldehyde with 1-chloro-2:4-dinitrobenzene gives Na 2:4-dinitrophenate in 95% EtOH and dinitrophenetole in complete absence of H_2O . It is suggested that this anomalous behaviour is due to chelation of Na salicylaldehyde, e.g., with formation of (I; R=H) in aq. EtOH and of (I; R=Et) in dry EtOH.

H. A. PIGOTT.

Effect of substituents in certain condensations of benzaldehyde. L. C. RAIFORD and W. F. TALBOT (J. Amer. Chem. Soc., 1932, 54, 1092–1097).—*o*-Bromobenzaldehydes do not undergo the benzoin condensation; thus, 5-bromovanillin and 2- and 6-bromoveratraldehydes do not give benzoin. Vanillin is unaffected by KCN, whilst veratraldehyde gives a large amount of unchanged material, some 3:4:3':4'-tetramethoxybenzil, and a little veratric acid. 5-Bromoveratraldehyde, m. p. 59.5° , and KCN give a resin, oxidised to 5:5'-dibromo-3:4:3':4'-tetramethoxybenzil, m. p. 209 – 210° (mono-*p*-bromophenylhydrazones, m. p. 155 – 156°), and 5-bromoveratric acid. 2-Bromoveratraldehyde, m. p. 85 – 85.5° , is obtained by methylation of 2-bromovanillin. 5-Bromovanillin and COMe_2 in AcOH–conc. HCl give di-(5-bromo-4-hydroxy-3-methoxystyryl) ketone, m. p. 230 – 231° ; 6-bromo-4-hydroxy-3-methoxystyryl Me ketone, m. p. 153 – 154° (formed in dil. NaOH), and di-(6-bromo-4-hydroxy-3-methoxystyryl) ketone, m. p. 255 – 256° , are prepared from 6-bromovanillin. 5-Nitro-4-hydroxy-3-methoxystyryl Me ketone has m. p. 156° .

C. J. WEST (b).

Dioximes. LXXXIII. G. PONZIO (Gazzetta, 1932, 62, 127–131).—Nitrogen tetroxide converts phenylchloroglyoxime (A., 1931, 223) into phenylchloroglyoxime peroxide, $\text{Ph}(\text{C}_2\text{O}_2\text{N}_2)\text{Cl}$, m. p. 66 – 67° , which with aqueous EtOH–NaOH gives phenylethoxy- and phenylhydroxy-glyoxime peroxides (A., 1903, i, 764). Methylchloroglyoxime similarly gives methylchloroglyoxime peroxide. E. E. J. MARLER.

Dioximes. LXXXV. G. LONGO (Gazzetta, 1932, 62, 139–147).—Phenylcarbimide with glyoximes gives dicarbanil derivatives of methyl- $\text{R}[\text{C}(\text{NO}\cdot\text{CO}\cdot\text{NHPh})]_2\text{R}'$ [m. p. 156 – 157° (decomp.)], dimethyl- [m. p. 195 – 196° (decomp.)], β -phenylmethyl- [m. p. 175 – 176° (decomp.)], α -phenyl- [m. p. 136° (decomp.)], β -phenyl- [m. p. 146 – 147° (decomp.)], α -methylbenzoyl- [m. p. 141 – 142° (decomp.)] and β -methylbenzoyl- [m. p. 153 – 154° (decomp.)] glyoximes, and with aminoglyoximes gives dicarbanil derivatives $\text{CR}(\text{NO}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, of amino- [m. p. (172° decomp.)], methylamino- [m. p. 191 – 192° (decomp.)], and β -phenylamino- [m. p. 190° (decomp.)] glyoximes, dicarbanil derivatives, $\text{CR}(\text{NO}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{C}(\text{N}\cdot\text{OBz})\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$, of benzoylmethyl- [m. p. 179 – 180° (decomp.)] and benzoylphenyl- [m. p. 185° (decomp.)] aminoglyoximes and a tricarbonyl derivative, $\text{CPh}(\text{NO}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{C}(\text{NH}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh})\cdot\text{C}(\text{N}\cdot\text{CO}\cdot\text{NHPh})$, m. p. 161 – 162° (decomp.), of α -phenylaminoglyoxime.

In the glyoximes, $\text{R}[\text{C}(\text{N}\cdot\text{OH})]_2\text{R}'$, the two oximino-

groups appear to be equivalent in both the α - and β -forms, but not in the aminoglyoximes
 $R[C(N\cdot OH)]_2NH_2$. E. E. J. MARLER.

Acyl derivatives of hydrazine. F. J. WILSON, (MISS) J. M. STRATTON, A. Y. LIVINGSTONE, and J. CHAPMAN (J. Roy. Tech. Coll. Glasgow, 1932, 2, 590—595).—A summary of work already abstracted (cf. A., 1931, 486, 613, 850). J. L. D'SILVA.

Friedel-Crafts reaction in the aliphatic and hydroaromatic series. F. UNGER (Ber., 1932, 65, [B], 467—472).—Contrary to Hopff (this vol., 44), hexa- and tetra-hydroacetophenone are not obtained by the action of $AlCl_3$ and $AcCl$ on cyclohexane, the products being derived from methylcyclopentane and -pentene. Reaction is effected at 10—28° and at -18° to 28°. The identified products are: Et α -diacetoacetate, b. p. 104—105°/17 mm., converted by $p\text{-NO}_2\cdot C_6H_4\cdot NH\cdot NH_2$ in 50% $AcOH$ into Et 1-*p*-nitrophenyl-3:5-dimethylpyrazole-4-carboxylate, m. p. 149.5—150°; stable 2-acetyl-1-methylcyclopentane, b. p. 55.5—56°/15 mm., 168°/763 mm. (semicarbazone, m. p. 162.5—163°; *p*-nitrophenylhydrazone, m. p. 102.5°); 2-acetyl-1-methyl- Δ^1 -cyclopentene, b. p. 71.5°/14.5 mm., 185°/744 mm. (semicarbazone, m. p. 221°; oxime, m. p. 85—85.5°; *p*-nitrophenylhydrazone, m. p. 162°), hydrogenated in presence of Pd-C and MeOH to labile 2-acetyl-1-methylcyclopentane (semicarbazone, m. p. 161.5—162.5°, yielding the stable ketone when distilled with oxalic acid). H. WREN.

Friedel-Crafts syntheses in the aliphatic and hydroaromatic series. H. HOPFF (Ber., 1932, 65, [B], 482—484; cf. this vol., 44).—In agreement with Nenitzescu and Ionescu (this vol., 49) the product of the action of $AcCl$ and $AlCl_3$ on cyclohexane is found to be 2-acetyl-1-methylcyclopentane. CO and cyclohexane give 2-methylcyclohexanone, not hexahydrobenzaldehyde as stated (*loc. cit.*). H. WREN.

Acetalisation of polyhydric alcohols with mono- and di-ketones. N. FRÖSCHL and A. HEUBERGER (Monatsh., 1932, 59, 289—293).—COPhMe reacts slowly with glycerol in presence of $ZnCl_2$ and dry HCl, forming α -methylbenzylidene-glycerol, b. p. 142°/16 mm. (27% yield); $COPh_2$ does not react under the same conditions, nor does $COMe_2$ with sucrose. *d*-Mannitol and acetylacetone give a viscous compound, $C_{11}H_{20}O_7$; only one of the CO groups reacts. H. BURTON.

Haloform reaction. V. Influence of α -bromine atoms. R. C. FUSON, P. H. LEWIS, and R. N. DU PUIS (J. Amer. Chem. Soc., 1932, 54, 1114—1120; cf. this vol., 164).—Two α -Br atoms in aryl Me ketones retard the haloform reaction, thus rendering difficult halogenation or cleavage of the halogenated product. Evidence indicating that the apparent rates of these reactions may be dependent on solubility factors is given. Successive treatment of 2:4:6-tribromoacetophenone (I) with $MgEtBr$ and Cl_2 gives 38% of 2:4:6-tribromophenacyl chloride (II), m. p. 98—98.5°, converted, as is (I), by 10% $NaOBr$ into $\alpha\alpha\alpha$:2:4:6-hexabromoacetophenone (III), m. p. 115—115.5°. (I) is unaffected by aq. $NaOCl$ but in presence of pyridine, $\alpha\alpha\alpha$ -trichloro-2:4:6-tribromoacetophenone

(IV), m. p. 73—73.5°, also obtained from (II) and $NaOCl$, results. Hot conc. $NaOH$ causes very slow decomp. of (IV) and (III), the normal cleavage product being isolated only from (IV). Prolonged treatment of (I) with $NaOCl$ in aq. pyridine gives 2:4:6-tribromobenzoic acid. 2:4:6-Tribromo-3-hydroxyacetophenone, m. p. 127.5°, formed by bromination of $m\text{-OH}\cdot C_6H_4\cdot Ac$, gives with $NaOBr$ an alkali-insol. product from which no pure compound could be isolated. 2:4:6-Tribromo-3-cyanoacetophenone, m. p. 115° (41% yield from the NH_2 -derivative), could not be hydrolysed. C. J. WEST (b).

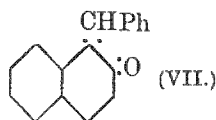
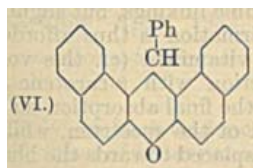
Indones. XII. Halogeno-derivatives of 3-phenyl-2-ethylindone. R. DE FAZI (Gazzetta, 1932, 62, 101—107).—2:3-Dichloro-3-phenyl-2-ethylindone, and the two isomeric 3:3'-dibromo-3:3'-diphenyl-2:2'-diethyl diketodi-indanyls, (I) and (II) previously described (A., 1930, 779) have m. p. 113—114°, 111—112°, and 153—155.5°, respectively. When heated with Cu for 45 min. (I) and (II) are converted into a different pair of isomeric dibromodiphenyldiethyl diketodi-indanyls, m. p. 160—162° and 145—147°, respectively. E. E. J. MARLER.

Reactivity of positively activated hydrogen atoms. VII. Condensation reactions of aldehydes with substances containing active methylene groups. W. DILTHEY and H. STEINBORN (J. pr. Chem., 1932, [ii], 133, 219—256; cf. A., 1931, 842).—The mechanism previously (*loc. cit.*) postulated for the condensation of 1 mol. of aldehyde with 1 mol. of substance containing an active CH_2 group in presence of primary or secondary amines is supported by the following facts. Deoxybenzoin (I) (1 or 2 mols.), $PhCHO$, and NH_2Ph , when kept in EtOH at room temp. for several weeks, give β -anilino- $\alpha\beta$ -diphenylpropionophenone (65% yield), also obtained from (I) and $CHPh\cdot NPh$ (II) under similar conditions, but not from NH_2Ph and benzylidenedeoxybenzoin; anisaldehyde and piperonal similarly afford β -anilino- α -phenyl- β -anisylpropionophenone (also obtained without NH_2Ph), m. p. 156°, and β -anilino- α -phenyl- β -3:4-methylenedioxyphenylpropionophenone, m. p. 153—155°, respectively; acetylacetone with $PhCHO$ and NH_2Ph , or with (II) gives α -anilino- $\beta\beta$ -diacetyl ethylbenzene, $CHPh(NHPh)\cdot CHAc_2$. (I) with CH_2O and NH_2Ph gives a resin. β -Piperidino- $\alpha\beta$ -diphenylpropionophenone, m. p. 155°, is obtained from (I) (1 or 2 mols.), $PhCHO$, and piperidine (1.25 mols. or a few drops), or (I) and $CHPh(NC_5H_{10})_2$ (III) in EtOH at room temp., or from benzylidenedeoxybenzoin (IV) and excess of piperidine without, but not with, EtOH; when heated in $AcOH$, this substance gives (IV), also obtained from β -chloro- $\alpha\beta$ -diphenylpropionophenone and piperidine (excess) in C_6H_6 . β -Piperidino- α -phenyl- β -*p*-anisyl- (m. p. 149°), and - β -3:4-methylenedioxyphenyl- (m. p. 159°)-propionophenone, and β -piperidino- α -phenylbutyrophenone were prepared from (I), piperidine, and the appropriate aldehyde in EtOH, but not in C_6H_6 ; similar experiments yielding *p*-anisylidene- (m. p. 113°) and piperonylidene- [stereoisomerides, m. p. 135—136° and 125—126° (lit. 128—129° and 119—120°)]-deoxybenzoin are described. Et acetoacetate and acetylacetone with $PhCHO$ and piperidine (not in EtOH or C_6H_6) give $Et_2\ \alpha\gamma$ -diacetyl- β -phenylglutarate and

α -piperidino- $\beta\beta$ -diacetyethylbenzene, m. p. 85° (lit. 93°), respectively. Poor yields of δ -phenyl- $\beta\eta$ -heptadione, m. p. 163°, were obtained from acetylacetone and (III) in C_6H_6 . Acetylacetone with anis- and *m*-nitrobenzaldehyde and piperidine give resins. $NHPhMe$, $NPhMe_2$, and $NPhEt_2$ did not bring about condensation of (I) with various aldehydes. Piperidine and $NHET_3Cl$, but not NEt_3 , isomerise *Et* maleate to *Et* fumarate, whence it is inferred that *tert.* bases bring about condensations as salts, NHR_3X , combining with aldehydes to form substances of the type $R\cdot CH(OH)\cdot NR_3X$.

Compounds of the type $Ar\cdot CH(NRR')\cdot CH_2\cdot COAr$ (A) will not react with compounds (B) containing active CH_2 groups, whence it is concluded that condensation of 1 mol. of aldehyde with 2 mols. of (B) proceeds by dissociation of (A) into base and arylidene-ketone, the latter reacting with a second mol. of (B). This view is supported by the following facts. β -Piperidino- α -benzoyl- β -phenylpropionophenone (V), m. p. 118—119°, is obtained from (a) benzoylacetone (1 or 2 mols.), $PhCHO$, and piperidine (1.25 mols. or a few drops), (b) benzylidenbenzoylacetone and piperidine [excess of which forms (III)], or (c) benzoylacetone and (III) in ligroin; similar experiments in C_6H_6 or without a solvent give $\gamma\epsilon$ -dibenzoyl- δ -phenyl- $\beta\eta$ -heptadione (mixture of isomerides, m. p. variable from 183—185° to 213—214°). (V) in cold $AcOH$ gives benzylidenbenzoylacetone, also formed (with piperidine picrate) by picric acid in C_6H_6 , or (with benzoylacetone) by benzoylacetone in $PhCHO$ or $AcOH$ (hot or cold) (but not in $EtOH$). (V) in cold $EtOH$ gives a substance, m. p. 107—108°. Resins are formed from benzoylacetone, piperidine, and anisaldehyde, piperonal, or *m*-nitrobenzaldehyde in C_6H_6 -ligroin. Decomp. of (V) is much more rapid in $EtOH$ than in C_6H_6 , and does not take place in ligroin.

β -Naphthol and $PhCHO$ in hot $AcOH$ give phenyl-2:2'-dihydroxy-1:1'-dinaphthylmethane, m. p. 204—205° (cf. A., 1901, i, 207), in hot $AcOH$, phenyldibenzoxanthene (VI), and a mixture of both compounds



in cold HCl - $AcOH$. Additive products of the type $OH\cdot C_{10}H_7\cdot CHPh\cdot NR_2$ do not react with β -naphthol, but in hot $AcOH$ slowly decompose yielding the bis-compound. It is considered that condensation proceeds by way of the substance (VII), which could not, however, be isolated. By condensation of β -naphthol, piperidine, and the appropriate aldehyde in $EtOH$ the following were prepared: 1-(α -piperidyl-*p*-methoxybenzyl)- (m. p. 137—139°), 1-(α -piperidyl-3:4-methylenedioxybenzyl)- (m. p. 141—143°), and 1-(α -piperidyl-*o*-chlorobenzyl)- (double m. p. 160—161° and 200—210°)- β -naphthol. Colour developed by these substances in hot $EtOH$ or $AcOH$ is believed to be due to reversible, partial dissociation to (VII). The red colour given by the bis-compound in hot, conc. H_2SO_4 is believed to be due to oxidation to the carbinol. R. S. CAHN.

Pinacol-pinacolin rearrangement. Relative migration aptitudes of aryl groups. W. E. BACHMANN and F. H. MOSER (J. Amer. Chem. Soc., 1932, 54, 1124—1133).—The migration aptitudes of a group in a *s*-benzpinacol is a characteristic property of that group and is not dependent on the pinacol. 4'-Phenyl-2-, b. p. 283—285°/20 mm., m. p. 107—109°, and -3-methyl-, b. p. 234°/10 mm., m. p. 80—81°; 4-methoxy-4'-phenyl-, m. p. 165—167°, and 4-chloro-4'-phenyl-, b. p. 300°/10 mm., -benzophenones are prepared by the Friedel-Crafts reaction from Ph_2 and the requisite acyl chloride. Reduction of substituted benzophenones with $Mg+MgI_2$ gives the corresponding pinacols (4—98% yield); the following are new: *s*-4:4'-4'''-diphenyl-2:2'- and -3:3'-dimethylbenzpinacols, m. p. 182—183° and 174—175°, respectively; *s*-4:4'-dimethoxy-4':4'''-diphenylbenzpinacol, m. p. 172—174°; *s*-4:4'-dichloro-4':4'''-diphenylbenzpinacol, m. p. 190—191°; *s*-4:4'-dimethoxy-4':4 -dimethylbenzpinacol, m. p. 175—176°. The structures and amounts of the products formed by rearrangement of the pinacols are determined by fission of the pinacols (with $EtOH-KOH$) into triarylmethanes and acids. Migration of the *p*-tolyl and Ph groups occurs to the extent of 94 and 6%, respectively, with 4:4'-dimethylbenzpinacol. 4:4'-Diphenyl-4'-methyltriphenylmethane (I), m. p. 162—163°, and 4-phenyl-4':4''-dimethyltriphenylmethane, m. p. 123—125°, are obtained from 4':4'''-diphenyl-4:4'-dimethylbenzpinacol, which when heated with I in $AcOH$ gives 30% (isolated) of *p*-tolyl *p*-tolylid(diphenyl)methyl ketone, m. p. 227—229°. *p*- $MeC_6H_4\cdot MgBr$ and $CO(p-PhC_6H_4)_2$ give 58% of 4:4'-diphenyl-4'-methyltriphenylcarbinol, m. p. 143—144°, reduced by Zn and $AcOH$ to (I). With 3:3'-dimethylbenzpinacol migration of the *m*-tolyl and Ph groups is 66 and 34%, respectively. 4':4'''-Diphenyl-3:3'-dimethylbenzpinacol gives 4:4''-diphenyl-3-methyltriphenylmethane, m. p. 144—145° (also obtained by reduction of 4':4''-diphenyl-3-methyltriphenylcarbinol, m. p. 124—125°); migration: *m*-tolyl 13, *p*- PhC_6H_4 87%. With 4:4'-dimethoxybenzpinacol, the % migration is anisyl 96.8, Ph 1.4. 4:4'-Dimethoxy-4':4'''-dimethylbenzpinacol gives 80% of *p*-tolyl dianisyl-*p*-tolylmethyl ketone, m. p. 129—130°; in the rearrangement, the *p*-tolyl group migrates to the extent of 3.3%. Migration of the *p*- PhC_6H_4 group occurs to the extent of 3.2% with 4:4'-dimethoxy-4':4'''-diphenylbenzpinacol; 4:4'-dimethoxy-4'-phenyltriphenylmethane, m. p. 118—119°, is produced on fission. 4:4'-Dichloro-4':4'''-dimethylbenzpinacol (migration of *p*-tolyl group, 82%) gives *p*-chlorophenyl-*p*-chlorophenyldi-*p*-tolylmethyl ketone, m. p. 204—205°. 4-Chloro-4':4''-dimethyltriphenylcarbinol, m. p. 94—95°, is converted by HCO_2H into 4-chloro-4':4''-dimethyltriphenylmethane, m. p. 66—68°. 2-Methylbenzpinacol has m. p. 175—176°. Vals. for the migration aptitude of various groups (with respect to Ph) are given. C. J. WEST (b).

Condensation of vanillin substitution products with acetophenone. L. C. RAIFORD and G. V. GUNDY (J. Amer. Chem. Soc., 1932, 54, 1191—1193).—Bromo- and chloro-vanillins condense with $COPhMe$ in presence of $NaOH$ to give Ph substituted-styryl

ketones and vanillylidenediacephophenones. The following are prepared: *Ph* 2-, m. p. 114—115°, 5-, m. p. 124—125°, and 6-, m. p. 172—173°, -bromo-; 5-, m. p. 128°, and 6-, m. p. 165°, -chloro-, 2:5-, m. p. 145—146°, 2:6-, m. p. 159°, and 5:6-, m. p. 158.5—160°, -dibromo-, and 2:5:6-tribromo-, m. p. 174°, -4-hydroxy-3-methoxystyryl ketones: 2-, m. p. 154—155°, 5-, m. p. 150—151°, and 6-, m. p. 137°, -bromo-; 5-, m. p. 151°, and 6-, m. p. 151°, -chloro-; 2:5-, m. p. 134—135°, 2:6-, m. p. 135°, and 5:6-, m. p. 163—164°, -dibromo-, and 2:5:6-tribromo-, m. p. 163°, -vanillylidenediacephophenones.

C. J. WEST (b).

Substances with a mobile methylene-hydrogen atom. M. V. IONESCU (Bull. Soc. chim., 1932, [iv], 51, 171—200).—A lecture.

Benzoin reduction. I. Mechanism of ketone formation. Benzanisoin. S. S. JENKINS (J. Amer. Chem. Soc., 1932, 54, 1155—1163).—A new mechanism of benzoin reduction is advanced. Reduction of benzanisoin with Na-Hg in 95% EtOH gives 61% of hydrobenzanisoin (I), m. p. 133—134°, and a little isohydrobenzanisoin (II), m. p. 109—110°. (I) or (II) heated with 80% AcOH and 20% HCl gives 50% of *Ph p*-methoxybenzyl ketone, m. p. 96.5°, also formed in about 47% yield [together with a little *anisyl benzyl ketone* (III), m. p. 77°] by reducing benzanisoin with Sn and conc. HCl in EtOH containing a little CuSO₄.

(III) [oxime, m. p. 114° (corr.)] is synthesised from CH₃Ph·MgCl and anisamide, and is reduced to β-phenyl-α-anisylethyl alcohol, α-Phenyl-β-anisylethyl alcohol has m. p. 62° (corr.). The trustworthiness of the method of Friedel and Crafts in structural work of this nature is questioned.

C. J. WEST (b).

Fluorene group. Synthesis of 1:2-diaceto-fluorene. K. DZIEWONSKI and A. KLESZCZ (Rocz. Chem., 1932, 12, 167—172).—Fluorene reacts with AcCl in CS₂ solution in the presence of AlCl₃ at 36—38° to yield 1:2-diacetofluorene (I), m. p. 188—190° (diphenylhydrazone, m. p. 250—252°), the dioxime, m. p. 252°, of which is converted by HCl into 1:2-diacetamidofluorene, m. p. 220°. (I) is oxidised to 1:2-diacetofluorenone, m. p. 262° (triphenylhydrazone, m. p. 252°).

R. TRUSZKOWSKI.

Reaction between alizarin and sodium aluminate in aqueous solution. S. MATSUOKA (Bull. Chem. Soc. Japan, 1932, 7, 50—56).—Various proportions of a 0.001*M* solution of alizarin (improved purification described) in PhMe and a 0.0372*M* aq. solution of Na₃AlO₃ have been shaken together at room temp. and the amount of alizarin remaining in the PhMe layer has been determined colorimetrically. Thus the mol. ratio of alizarin and Na₃AlO₃ reacting was determined. The results are taken to indicate that a chemical reaction takes place giving a hydrophile colloid [possibly (C₆H₃(CO)₂C₆H₃(CO)₂)]₃AlNa₃ which also absorbs a further quantity of alizarin.

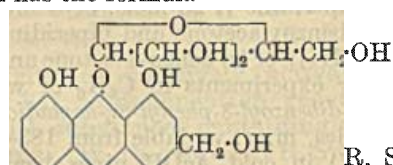
J. W. BAKER.

Anthraquinone series. Synthesis of 1:6- and 1:7-dihydroxy-3-methylanthraquinones. P. C. MITTER and N. N. CHATTERJI (J. Indian Chem. Soc., 1931, 8, 783—786).—4-Nitrophthalic anhydride,

m-cresol, and AlCl₃ at 100—130° give 4-, m. p. 196°, and 5-, m. p. 202—203°, -nitro-2-2'-hydroxy-4'-methylbenzoylbenzoic acids, which when fused with KOH afford *p*- and *m*-NO₂·C₆H₃·CO₂H, respectively. Reduction with FeSO₄ and aq. NH₃ affords 4-, m. p. 218° (decomp.), and 5-, m. p. 237—238°, -amino-2-2'-hydroxy-4'-methylbenzoylbenzoic acids, converted by the usual method into the 4-, m. p. 214—215°, and 5-, m. p. 215—216°, -hydroxy-derivatives, which with oleum and B₂O₃ at 100° (bath) give 1:7-, m. p. 255—256°, and 1:6-, m. p. 213—214°, -dihydroxy-3-methylanthraquinones, respectively. H. BURTON.

Manufacture of anthraquinone [alkoxy-]derivatives. J. Y. JOHNSON. From I. G. FARBERIND. A.-G.—See B., 1932, 301.

Constitution of aloins. L. ROSENTHALER (Arch. Pharm., 1932, 270, 214—217).—From published data and the conversion of "aloemodinanthranol" into the Ac₃ derivative of 1:8-dihydroxy-3-methylanthranol it is concluded that barbaloin or *iso*-barbaloin has the formula



R. S. CAHN.

Spectrometric measurements with carotenoids. H. VON EULER, P. KARRER, E. KLUSMANN, and R. MORF (Helv. Chim. Acta, 1932, 15, 502—507).—The absorption spectra of various carotenoids in CHCl₃ containing SbCl₃ are measured, and those with the carotene structure (carotene, zeaxanthin, leaf-xanthophyll, lutein) are observed to give absorption maxima at λ 590—586; liver oils under the same conditions give max. at λ 620 and 574—570. The absorption is also studied in absence of CHCl₃, and the absorption spectrum of vitamin-A compared with those of a series of conjugated alcohols of increasing (conjugated) chain length and found to lie between those containing 4 and 6 double linkings, but slightly nearer to the former; confirmation is thus afforded of the formula ascribed to vitamin-A (cf. this vol., 200). The Carr-Price reaction with β-carotene is accelerated by heating, and the final absorption max. shifted towards the red end of the spectrum, whilst that of β-carotene itself is displaced towards the blue.

H. A. PIGGOTT.

Saponin series. III. Sapogenins of Panax repens, Maxim., and Aralia chinensis, L. var. M. KOTAKE and Y. KIMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 83—96).—Taragenin from *A. chinensis* is identical with panaxsapogenin. MeOH extracts from the roots of *P. repens* an amorphous panaxsapogenin, whence by MeOH panaxtoxin, cryst., m. p. 212°, is obtained. This is hydrolysed to panaxsapogenin, m. p. about 304°, C₂₉H₄₈O₃ (?C₃₀H₅₂O₃) [not C₃₆H₅₈O₄ (lit.)] (K salt), which affords the following derivatives: by Ac₂O, *Ac* (I), m. p. 261—262° [*Br*-derivative, (II), m. p. 217°], and mixed anhydride of (I) and AcOH, double m. p. 207—210° and 306—310° (III); by AcOH (I); by CrO₃ in AcOH, a substance, C₂₉H₄₄O₄ (?C₂₉H₄₂O₄ or C₃₀H₄₄O₄), m. p. 276—277°; by conc. HNO₃ in

hot AcOH, the substance, $C_{28}H_{40(38)}O_3(NO_2)_2$, dimorphous, m. p. 240—242° and 214—215° (labile), converted by Zn and HCl in EtOH-AcOH into a substance, $C_{28}H_{40}O_5$, m. p. 320°; Br-, decomp. 223° [Ac derivative=(II)]; by HI and P, substances, m. p. 337—338°, $C_{23}H_{34}$ or $C_{30}H_{50}O_3$ (IV), and m. p. 247—248°, $C_{29}H_{46}O_2$ or $C_{30}H_{50}O_2$; by hot HCO_2H (IV). (III), when heated at 210—250°, gives (?) *anhydro-acetylpanaxsapogenin*, $C_{31}H_{48}O_3$, m. p. 316—318°.

R. S. CAHN.

Bitter principle of neem oil. I. R. N. SEN and G. BANERJEE (J. Indian Chem. Soc., 1931, 8, 773—776).—The hot aq. extract of the oil contains a bitter dicarboxylic acid, $C_{55}H_{81}O_{13}S$, m. p. 203—205° (decomp.) (Ag salt; dibromide), containing 4 OMe groups, and its Na salt; a non-bitter S-free compound, decomp. above 270°, is also present. The results differ from those of Watson *et al.* (A., 1923, i, 1163).

H. BURTON.

Isomerisation of terpenes found in turpentine from *Pinus sylvestris*. E. I. LYUBARSKI (J. Appl. Chem., Russia, 1931, 4, 361—370).—The scheme proposed is: $d\text{-}\alpha\text{-pinene} \rightarrow \Delta^3\text{-carene} \rightarrow$ (1) $m\text{-terpinolene} \rightarrow$ *sylvestrene*, or (2) $p\text{-terpinolene} \rightarrow$ *dipentene*. CHEMICAL ABSTRACTS.

Racemisation process of camphene. J. HUBBEN and E. PFANKUCH (Ber., 1932, 65, [B], 491—492; cf. A., 1931, 358).—A question of priority (cf. Lipp, this vol., 398).

H. WREN.

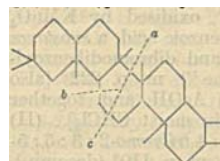
Condensation products of pernitrosocamphor with primary amines. P. SACCARDI and P. LATINI (Annali Chim. Appl., 1932, 22, 88—90).—Condensation of pernitrosocamphor (1) with NH_2Ph yields *camphoranil*, $C_8H_{14} \begin{smallmatrix} CH_2 \\ >C:NPh \end{smallmatrix}$, b. p. 225°/65 mm.; (2) with $N_2H_4 \cdot H_2O$ gives 2 : 2'-azocamphor [*camphorazine*], $\begin{smallmatrix} CH_2 \\ C_8H_{14} \end{smallmatrix} >C:N \cdot \begin{smallmatrix} CH_2 \\ C_8H_{14} \end{smallmatrix}$, m. p. 184°. T. H. POPE.

New condensation product of pernitrosocamphor with *p*-bromoaniline. P. LATINI (Annali Chim. Appl., 1932, 22, 91—93).—This product is *camphor-p-bromoanil*, $\begin{smallmatrix} CH_2 \\ C_8H_{14} \end{smallmatrix} >C:N \cdot C_6H_4Br$, m. p. 50°.

T. H. POPE.

Polyterpenes and polyterpenoids. LXV. Dehydration of triterpenes, sapogenins, and related substances. L. RUZICKA, H. BRÜNGGER, R. EGLI, L. EHLMANN, M. FURTER, and H. HÖSLI [with K. MEYER and M. W. GOLDBERG]. LXVI. Accurate determination of empirical formulae of triterpenes and triterpenoids of acidic character. L. RUZICKA and M. FURTER. LXVII. Determination of number of double linkings in the amyrins. L. RUZICKA, H. SILBERMANN, and M. FURTER (Helv. Chim. Acta, 1932, 15, 431—457, 472—482, 482—490).—LXV. The following are isolated from the products of dehydrogenation of substances of triterpene type with Se at 300—350°: 2 : 7-dimethylnaphthalene (I), sapotalin (II; 1 : 2 : 7-trimethylnaphthalene), the hydrocarbons $C_{14}H_{16}$ (III), m. p. 116° (*picrate*, m. p. 155°; *styphnate*, m. p. 165.5°) (this differs from 1 : 2 : 5 : 7-tetramethyl- and 2 : 7-dimethyl-1-ethyl-naphthalenes), $C_{25}H_{20}$ (IV; $C_{24}H_{18}$?),

m. p. 306—307° (cf. " $C_{30}H_{22}$," A., 1930, 781), $C_{27}H_{28}$ (V), m. p. 138.5°, b. p. 204—206°/0.3 mm. (*dipicrate*, m. p. 203°; *distyphnate*, m. p. 226°; these are partly decomposed into their components by crystallisation from EtOH, but are stable in C_6H_6), C_nH_n , m. p. 250°, and a *naphthol* (VI), $C_{13}H_{14}O$, m. p. 157°. The substances subjected to dehydrogenation were hederagenin [(I), (II), (IV), (VI), C_nH_n], sumaresinolic acid [(I)—(V)], siarsesinolic acid [(II), (III), (V)], betulin [(II), (III)], æscigenin [(II)], oleanolic acid [(I)—(III)], and cyclamiretin [(I), (II)].



Ethylene linkings were detected in all of 17 substances of triterpene type examined by formation of a yellow coloration with $C(NO_2)_4$ in AcOH, EtOH, or $CHCl_3$; other methods failed except with gypsogenin which absorbed H_2 in presence of PtO_2 . They are therefore penta- or perhaps occasionally tetra-cyclic, and on the basis of the isoprene unit and their dehydrogenative degradation (by fission at *a* and *b* or *c*) to 2 : 7-dimethyl- and 1 : 2 : 7-trimethyl-naphthalenes the annexed skeletal structure is tentatively advanced.

LXVI. The mol wt. of triterpene acids is determined within 1% by micro-titration with 0.02*N*-aq. KOH in EtOH, using phenolphthalein as indicator and *d*-pimaric acid as standard. The following corrected formulae are determined by this method and C and H determination; siarsesinolic acid, $C_{30}H_{46}O_4$; sumaresinolic acid, $C_{30}H_{48}O_4$; δ-elemic acid, $C_{30}H_{46}O_3$; oleanolic acid (2 sources), $C_{30}H_{48}O_3$; the formulae of α-elemic acid ($C_{30}H_{48}O_3$) and hederagenin ($C_{31}H_{50}O_4$) are confirmed.

LXVII. An improved prep. of α- and β-amyryn benzoates is described. *Dihydro-d-α-amyrylene*, m. p. 84—85°, $[\alpha]_D^{20} +120.2^\circ$ in C_6H_6 , and *d-β-amyrylene*, m. p. 83—85°, $[\alpha]_D^{20} +131.5^\circ$ in C_6H_6 , are prepared by reduction of the amyrylenes with H_2 and PtO_2 . Vals. of $M [\alpha]_D^{20-17}$ for cryst. *d-α*- and *β*-amyrylenes and their H_2 -derivatives indicate the presence of only one double linking in the present amyryns. α-Amyryn and α-dihydroamyrylene are practically unaffected by BzO_2H , and α-amyrylene absorbs 10 with formation of two monoxides, m. p. 172—173°, and 133°, both of which give a yellow coloration with $C(NO_2)_4$ in $CHCl_3$. The β-derivatives each absorb 10 more than their α-isomerides, and an impure monoxide, m. p. 191—193° [$+xEtOH(?)$, m. p. 162°], is obtained from β-amyryn. β-Amyrylene absorbs 20, but gives only a monoxide, m. p. 162—163°, and a *dehydro*-derivative, m. p. 153—156° (? isomeric monoxide), with a small amount of impure material with a higher O content; all of these give a yellow coloration with $C(NO_2)_4$. The difference in O-absorption between the α- and β-series is ascribed to a difference not of unsaturation but of reactivity.

H. A. PIGGOTT.

Essential oil from *Sciadopitys verticillata*, S. and Z. J. KAWAMURA.—See B., 1932, 321.

Action of bromine on a glycol of the ethylene series. J. SALKIND and V. TETERIN (J. pr. Chem., 1932, [ii], 133, 195—218).—ααδδ-Tetraphenyl-Δ².

butene- $\alpha\delta$ -diol (I) reacts anomalously with Br. Addition of (I) in CHCl_3 to Br in dry CHCl_3 at 0° gives 2:3:4-tribromo-2:3:5:5-tetraphenyltetrahydrofuran dibromide (II), whereas addition of Br in CHCl_3 to (I) in CHCl_3 gives 2:2:5:5-tetraphenyl-2:5-dihydrofuran (Ia), slowly brominated to $\begin{matrix} \text{CPhBr-CPhBr} \\ \text{CHBr-CPh}_2 \end{matrix} > \text{O}, \text{Br}_2$ (II). (II) decomposes slowly alone at 60° , rapidly alone at 130° or in CHCl_3 at 30 – 40° to give much HBr, a little Br, and dibromo-2:3:4:5-tetraphenylfuran ("dibromolepidene") (III), m. p. 192° , oxidised by KMnO_4 in COMe_2 to BzOH , *p*-bromobenzoic acid, a substance (? bromobenzil), m. p. 84° , and dibromodibenzoylstilbene ("dibromo-oxylepidene"), m. p. 222° [also obtained from (III) by Cl_2 in AcOH , and, together with (III), when (I) is kept in moist CHCl_3]. (II) in moist Et_2O gives 2:3:4-tribromo-2:3:5:5-tetraphenyltetrahydrofuran (IV), m. p. 110° (decomp.). (II) and (IV) with Mg afford a little 2:3:4:5-tetraphenyltetrahydrofuran ("lepidene") (V) and much condensation product; the latter only (including a substance, m. p. 234°) is obtained when Zn is used. (V) with KMnO_4 in hot COMe_2 slowly gives dibenzoylstilbene ("oxylepidene") (VI), benzil, and BzOH . (I) with EtOH gives 2-ethoxy-2:3:5:5-tetraphenyl-2:5-dihydrofuran (VII), m. p. 116 – 117° , and a little (VI), whilst MeOH affords similarly 2-methoxy-2:3:5:5-tetraphenyl-2:5-dihydrofuran (VIII), m. p. 128° . (VIII) with AcOH and a drop of HBr at 70 – 80° gives (V). (VII) and (VIII) are interconvertible by EtOH or MeOH and AcOH or NaOH . With AcOH both give (V), and with 80% AcOH and KOAc at 70 – 90° 2-hydroxy-2:3:5:5-tetraphenyl-2:5-dihydrofuran (IX), m. p. 144° , which probably with Br gives the same products as (I). (VII) or (II) with Zn and AcOH give a substance, m. p. 254° , but cannot be reduced catalytically (Pt or Pd). (VII), (VIII), or (IX) with CrO_3 in AcOH (but not with KMnO_4) gives BzOH , COPh_2 , Bz_2 , 2:3-dihydroxy-4-keto-2:3:5:5-tetraphenyltetrahydrofuran (X), m. p. 145 – 146° , and as-dibenzoyldiphenylethylene glycol, $\text{OH-CPh}_2\text{-CBz}_2\text{-OH}$ (XI), m. p. 176° (transformed at 180° into COPh_2 and a substance, probably dibenzoylcarbinol, m. p. 119°). When melted or treated with acids or alkalis, (X) is partly decomposed (to COPh_2 , BzOH , and other products) and partly isomerised to (XI); with aq. NH_3 or EtOH-KOAc it gives a good yield of (XI), which is thus probably formed as a secondary product during the oxidation; with CrO_3 in AcOH (X) yields COPh_2 , BzOH , and (?) α -hydroxy- $\beta\gamma$ -diketo- $\alpha\gamma$ -triphenylpropane, $\text{OH-CPh}_2\text{-COBz}$, greenish-yellow, m. p. 150° [also formed as a secondary product during the oxidation of (VII)]. (VII), (VIII), or (IX) in warm AcOH (not in EtOH) with the appropriate reagent affords (by ring fission) the semicarbazone (m. p. 264°), oxime (m. p. 168°), and hydrazone [m. p. 222° (decomp.)], of α -hydroxy- δ -keto- $\alpha\gamma\delta$ -tetraphenyl- Δ^2 -n-butene; the oxime affords at the m. p. a substance, m. p. 192° , also formed as by-product during the prep. of the oxime; the hydrazone, when heated slightly above the m. p., gives N_2 and α -hydroxy- $\alpha\gamma\delta$ -tetraphenyl- Δ^2 -n-butene, m. p. 191° . (II) is hydrolysed by AcOH and a little H_2O to 4-bromo-2:3-dihydroxy-

2:3:5:5-tetraphenyltetrahydrofuran, m. p. 176 – 178° (decomp.); this with NaOEt gives HBr and a substance, $\text{C}_{28}\text{H}_{22}\text{O}_3$, m. p. 105° , and is further hydrolysed by K_2CO_3 in COMe_2 and a little H_2O to 2:3:4-trihydroxy-2:3:5:5-tetraphenyltetrahydrofuran, m. p. 190° (and another substance, not isolated), oxidised to (X) by CrO_3 in AcOH .

The constitutions of the reaction products are proved by the reactions described above, and it is concluded that Br and (I) form primarily (Ia), which with 2 mols. of Br forms $\begin{matrix} \text{CHBr-CPh}_2 \\ \text{CHBr-CPh}_2 \end{matrix} > \text{O}, \text{Br}_2$; this by loss of Br and wandering of a Ph group gives $\begin{matrix} \text{CPh=CPh} \\ \text{CHBr-CPh}_2 \end{matrix} > \text{O}, \text{Br}_2$, whence (II) is formed. (II) by hydrolysis loses successively the Br attached to O, the *tert.* and *sec.* C atoms; in the formation of the "lepidene" derivatives a second Ph group wanders by the same mechanism. The formation of (IX) is considered to proceed by way of an oxide.

R. S. CAHN.

Constitution of methoxysylvanecarboxylic acid derived from δ -ketorhammonic acid. E. VOTOCEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1932, 7, 87–97).—The OMe-acid (phenylhydrazide, m. p. 130 – 131°) of the ester (I) obtained from δ -ketorhamnonolactone (A., 1929, 1166; improved prep. given) is demethylated by 0.2*N*-HCl to the unstable hydroxy-acid (II), further hydrolysed by Ba(OH)_2 to $\text{H}_2\text{C}_2\text{O}_4$ and Me α -hydroxyethyl ketone (also obtained by decomp. of the OMe-acid by light), since addition of NHPh-NH , affords the osazone of Ac_2 , identical with a synthetic specimen. Distillation of freshly-prepared (II) causes decarboxylation to 4-hydroxy-5-methylfuran, b. p. 63 – $64^\circ/12$ mm., whilst an older specimen gives a substance, b. p. 156 – $158^\circ/12$ mm., which has the same composition and is possibly a polymeride, since it also affords diacetylosazone after hydrolysis. These results, represented thus: $\begin{matrix} \text{CH}_2\text{C(CO}_2\text{H)} \\ \text{C(OH)=CMe} \end{matrix} > \text{O (II)} \rightarrow \text{H}_2\text{C}_2\text{O}_4 + \text{OH-CMe-CMe-OH} \rightarrow \text{OH-CHAcMe}$, can be explained only if (I) is *Et* 4-methoxy-3-methylfuran-2-carboxylate, and not the 3-OMe-derivative as previously suggested.

J. W. BAKER.

5-Methylfurfuryl chloride. T. REICHSTEIN and H. ZSCHOKKE (Helv. Chim. Acta, 1932, 15, 249–253).—5-Methylfurfuryl alcohol, b. p. 81 – $83^\circ/11$ mm., 56 – $60^\circ/0.5$ mm., prepared by reduction of 5-chloromethylfurfuraldehyde (modified prep., b. p. about $90^\circ/1$ mm., cryst.) with Zn and AcOH in EtOH or, better, from 5-hydroxymethylfurfuraldehyde with N_2H_4 and KOH in MeOH , gives with SOCl_2 and pyridine in dry Et_2O 5-methylfurfuryl chloride, unstable, b. p. about 30 – $35^\circ/0.2$ mm. (often with total decomp.). This reacts normally (cf. A., 1930, 611) with aq. KCN to yield 5-methylfuryl-2-acetonitrile (5-methyl-2-cyanomethylfuran), b. p. 79 – $84^\circ/10$ mm., hydrolysed by KOH in MeOH to 5-methylfuryl-2-acetic acid (I), m. p. 61 – 62° . 5-Methylfuroyl chloride, b. p. $82^\circ/11$ mm. (from the acid and SOCl_2), with HCN and pyridine in dry Et_2O gives 5-methylfuroyl cyanide, m. p. 55° , b. p. about $100^\circ/11$ mm., slowly hydrolysed by HCl at room temp. to 5-methylfuroylformic acid, m. p. 90 – 91° , b. p. about $100^\circ/1$ mm. (transformed by crystallisation under

certain conditions into a yellow substance, m. p. 84° or lower), which with N_2H_4 and NaOEt yields (I).

R. S. CAHN.

Applications of furfuraldehyde and other furan derivatives in analytical chemistry. M. WAGENAAR (Pharm. Weekblad, 1932, 69, 286—300).—A review.

Furan-3-carboxylic acid. T. REICHSTEIN and H. ZSCHOKKE (Helv. Chim. Acta, 1932, 15, 268—273).— Et_2 acetonedicarboxylate, $\alpha\beta$ -dichloroethyl ether, and aq. NH_3 , or, better, NaOH, give Et_2 3-carboxyfuryl-2-acetate, b. p. 86—90°/0.2 mm., hydrolysed by KOH to 3-carboxyfuryl-2-acetic acid (I), m. p. 217—218°, the constitution of which is proved by decomp. at about 230° to 2-methylfuryl-3-carboxylic acid. (I) with amyl nitrite and NaOEt forms the *oximino-ester*, an oil, which, when hydrolysed and heated, best with Ac_2O , yields the nitrile, hydrolysed by aq. KOH to furan-2:3-dicarboxylic acid (II). (II) at 250°, or furan-2:4-dicarboxylic acid with boiling quinoline and Cu powder, yields furan-3-carboxylic acid, m. p. 120—121.5°, b. p. 105—110°/12 mm. (*amide*, m. p. 168—169°; *anilide*, m. p. 131—132°), identical with and proving the constitution of the acid prepared from *Euonymus atropurpureus* (cf. J.C.S., 1912, 101, 1044).

R. S. CAHN.

2-Methyl-3-furoic acid. H. GILMAN and R. R. BURTNER (Iowa State Coll. J. Sci., 1931, 5, 189—192).—2-Methyl-3-furoic acid, m. p. 101°, was prepared in 26.9% yield (based on CH_3AcCO_2Et) from CH_3AcCO_2Et , $CH_2ClCHClOEt$, and NaOH; nitration of the Et ester with HNO_3 in Ac_2O gave Et 5-nitro-2-methyl-3-furoate, m. p. 51°, in 28.3% of the theoretical yield. CHEMICAL ABSTRACTS.

Furan derivatives. IV. I. J. RINKES (Rec. trav. chim., 1932, 51, 349—355; cf., A., 1931, 1422).—A general discussion of the nitration of furan derivatives. 2-Acetylfuran with HNO_3 in Ac_2O gives 2-nitrofuran, and 5-nitro-2-acetylfuran [5-nitro-2-furyl Me ketone], m. p. 78.5°, b. p. 127°/10 mm. (*semi-carbazone*, m. p. 250°). Et 5-acetamidofuroate (improved prep.) gives on nitration Et 4-nitro-5-acetamidofuroate (A., 1931, 1422), hydrolysed by warm 1% HCl to Et 4-nitro-5-aminofuroate, m. p. 150°. 3-Nitro-2-methylfuran 5-carboxylic acid (A., 1931, 95) gives a Me ester (*benzylidene* derivative, m. p. 151°). 5-Nitro-2-methylfuran gives a *benzylidene* derivative, m. p. 115° (small yield). The action of NaOCl in MeOH on coumarilamide gives Me coumarylcarbamate, m. p. 139°, converted by HCl into o-hydroxyphenylacetic acid lactone.

A. A. LEVI.

Reduction of hydrofuranamide to tri-2-furfurylamine. H. GILMAN and J. B. DICKEY (Iowa State Coll. J. Sci., 1931, 5, 193—194).—Catalytic reduction (PtO_2) with H_2 in EtOH-AcOH afforded a 38% yield.

CHEMICAL ABSTRACTS.

Coumarinyl-3-acetic acids. B. B. DEY and Y. SANKARANARAYANAN (J. Indian Chem. Soc., 1931, 8, 817—827).—o-OH· C_6H_4 ·CHO, dry Na succinate, and succinic anhydride at 170—180° give coumarinyl-3-acetic acid, m. p. 158° (Me ester, m. p. 77°; *anilide*, m. p. 200°), 3:3'-dicoumarinyl, and o-o-hydroxyphenyl- β -3-coumarinylethylene, m. p. 207° (acetate,

N N

m. p. 177°). Et acetosuccinate, m- $C_6H_4(OH)_2$, and conc. H_2SO_4 in the cold afford (cf. Banerjee, this vol., 520) Et 7-hydroxy-4-methylcoumarinylacetate, m. p. 163° (Me ether, m. p. 80°; Ac derivative, m. p. 98°); the free acid (I) [Ag, Ca (+11 H_2O), and Ba (+16 H_2O) salts; Me ether, m. p. 198°; Me ester, m. p. 122°; *amide*, m. p. 300° (decomp.); *anilide*, m. p. 242°] has m. p. 265°. The Na salt of (I), o-OH· C_6H_4 ·CHO, and Ac_2O at 160—170° give 7-acetoxy-4-methyl-3-coumarinyl-3'-coumarin, m. p. 268°. Similarly, Et acetosuccinate and α -naphthol afford the Et ester, m. p. 139°, of 4-methyl-1:2- α -naphthapyrone-3-acetic acid, m. p. 251° (Ag salt; *anilide*, m. p. 251°); with β -naphthol, 4-methyl-2:1- β -naphthapyrone-3-acetic acid (II), m. p. 199° (Me, m. p. 137°, and Et, m. p. 101°, esters), is produced. (II) is hydrolysed by 2N-NaOH to β -2-hydroxy-1-naphthyl- β -methylitaconic acid, m. p. 154° with loss of H_2O , regenerating (II). Et formylsuccinate and β -naphthol give a product hydrolysed to 2:1- β -naphthapyrone-3-acetic acid, m. p. 265° (Me ester, m. p. 149°).

H. BURTON.

Synthesis of chromones. I. Condensation of halogenophenols and cresols with ethyl alkylacetoacetates. II. Condensation of nitrophenols with ethyl alkylacetoacetates. D. CHAKRAVARTI (J. Indian Chem. Soc., 1932, 9, 25—30, 31—35).—I. o- and p-Halogenophenols heated with Et alkylacetoacetates and P_2O_5 (cf. A., 1918, i, 26) give 8- and 6-halogeno-2-methyl-3-alkylchromones, respectively; these with PhCHO in EtOH-NaOEt afford the corresponding 2-styryl derivatives, the reactivity of the 2-Me group not being influenced by the substituent in the C_6H_5 nucleus (cf. Heilbron *et al.*, J.C.S., 1923, 123, 2569). The following are described: (a) from o- C_6H_4Cl ·OH: 8-chloro-2-methyl-, m. p. 100°, and -2-styryl-, m. p. 109°, -3-propyl-, 8-chloro-2-methyl-, m. p. 160°, and -2-styryl-, m. p. 151°, -3-isopropyl-, 8-chloro-2-styryl-3-ethyl-, m. p. 137°; (b) from p- C_6H_4Cl ·OH: 6-chloro-2-methyl-, m. p. 108°, and -2-styryl-, m. p. 126°, -3-propyl-, 6-chloro-2-methyl-, m. p. 127°, and -2-styryl-, m. p. 159°, -3-isopropyl-, 6-chloro-2-styryl-3-methyl-, m. p. 143°; (c) from 2:4- $C_6H_3Cl_2$ ·OH: 6:8-dichloro-2-styryl-3-ethyl-, m. p. 155—157°; (d) from o- C_6H_4Br ·OH: 8-bromo-2-styryl-3-methyl-, m. p. 200°; 8-bromo-2-methyl-3-propyl-, m. p. 82°; (e) from p- C_6H_4Br ·OH: 6-bromo-2-styryl-3-methyl-, m. p. 152°; 6-bromo-2-methyl-, m. p. 112°, and -2-styryl-, m. p. 129°, -3-propylchromone. p-Cresol, CH_3AcCO_2Et , and cold conc. H_2SO_4 give 3:4:6-trimethylcoumarin, m. p. 165°; with P_2O_5 as the condensing agent (cf. A., 1913, i, 890), 2:3:6-trimethylchromone results. 2:8-Dimethyl-3-ethyl-, m. p. 71—72° (from o-cresol and CH_3AcCO_2Et); 2-styryl-8-methyl-3-ethyl-, m. p. 142°; 2-styryl-3:6-dimethyl-, m. p. 120°; 2-styryl-, m. p. 133°, and 2-m-nitrostyryl-, m. p. 225°, -3:8-dimethylchromone are also prepared. Resorcinol Me ether and CH_3AcCO_2Et with H_2SO_4 or P_2O_5 give 7-methoxy-4-methylcoumarin, also formed from resorcinol Me ether, CH_3AcCO_2Et , and H_2SO_4 .

II. The following chromones are prepared: (a) from p- NO_2 · C_6H_4 ·OH: 6-nitro-2:3-dimethyl- (cf. loc. cit.); 6-nitro-2-styryl-3-methyl-, m. p. 205°; 6-nitro-2-methyl-, m. p. 184°, and -2-styryl-, m. p. 239°.

-3-ethyl-, 6-nitro-2-methyl-3-propyl-, m. p. 125°; 6-nitro-2-methyl-3-isobutyl-, m. p. 96°; (b) from $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$: 7-nitro-2:3-dimethyl-, m. p. 136°; 7-nitro-2-styryl-3-methyl-, m. p. 258°; 7-nitro-2-methyl-3-ethyl-, m. p. 167°; 7-nitro-2-methyl-, m. p. 136°, and -2-m-nitrostyryl-, m. p. 256°, -3-propyl-, 7-nitro-2-methyl-, m. p. 133°, and -2-m-nitrostyryl-, not melted at 270°, -3-isopropyl-, 7-nitro-2-methyl-, m. p. 158°, and -2-m-nitrostyryl-, m. p. 252°, -3-isobutyl-chromones.

Phenols which condense readily (or not at all) with acylacetates in presence of H_2SO_4 to give coumarins, invariably afford chromones when P_2O_5 is used as the condensing agent. Whilst *m*-cresol and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ with P_2O_5 (or H_2SO_4) afford a coumarin, the use of $\text{CHAcR}\cdot\text{CO}_2\text{Et}$ (with P_2O_5) leads to a chromone.

H. BURTON.

Condensation of ethyl acetosuccinate with phenols. S. K. BANERJEE (J. Indian Chem. Soc., 1931, 8, 777—782).—Et acetosuccinate (I) (modified prep. given), α -naphthol, and conc. H_2SO_4 in the cold give *Et* 4-methyl-1:2- α -naphthapyrone-3-acetate, m. p. 137°; the free acid (II), m. p. 258° (*Ag* salt), is decarboxylated to 3:4-dimethyl-1:2- α -naphthapyrone, m. p. 199°, also prepared from α -naphthol and $\text{CHAcMe}\cdot\text{CO}_2\text{Et}$. Similarly, (I) and $m\text{-C}_6\text{H}_4(\text{OH})_2$ afford *Et* 7-hydroxy-4-methylcoumarinyl-3-acetate, m. p. 162° (*Me* ether, m. p. 78°; *Ac*, m. p. 98°, and *Bz*, m. p. 127°, derivatives); the free acid (*Ag* salt; anilide, m. p. 285°) has m. p. 268°. The Na salt of (II), $o\text{-OH}\cdot\text{C}_6\text{H}_3\cdot\text{CHO}$, Ac_2O , and a little I at 120—180° give 3-(3'-coumarinyl)-4-methyl-1:2- α -naphthapyrone, m. p. 311°; the condensation could not be effected with piperidine.

H. BURTON.

Synthetical experiments in the chromone group. V. Chromones derived from 2-phenylacetyl- α -naphthol and 2- β -phenylpropionyl- α -naphthol. U. S. CHEEMA and K. VENKATARAMAN. VI. 2-Styrylchromones. U. S. CHEEMA, K. C. GULATI, and K. VENKATARAMAN (J.C.S., 1932, 918—925, 925—933).—V. 2-Phenylacetyl- α -naphthol, m. p. 96° (*Ac*, m. p. 109°, and *Bz* derivative, m. p. 161°; 2:4-dinitrophenylhydrazone, m. p. 252°), does not react with HCO_2Et and Na, but gives, with Ac_2O and NaOAc , 3-phenyl-2-methyl-, m. p. 203—204°, with Bz_2O and NaOBz , 2:3-diphenyl-, m. p. 206—207°, and with cinnamic anhydride and Na cinnamate, 3-phenyl-2-styryl-1:4- α -naphthapyrone, m. p. 262—263°. 2- β -Phenylpropionyl- α -naphthol (I), m. p. 99° (*Ac*, m. p. 91°, and *Bz* derivative, m. p. 88°; 2:4-dinitrophenylhydrazone, m. p. 223—224°), with HCO_2Et and Na forms a mixture of 3-benzyl- (II), m. p. 149°, and 2-hydroxy-3-benzyl-2:3-dihydro-1:4- α -naphthapyrone, m. p. 172°, which gives (II) when heated with $\text{EtOH}\cdot\text{H}_2\text{SO}_4$. (I) forms with Ac_2O and NaOAc , 3-benzyl-2-methyl-, m. p. 139°, with cinnamic anhydride and Na cinnamate, 3-benzyl-2-styryl-1:4- α -naphthapyrone, m. p. 223°, and with Bz_2O and NaOBz , 3-benzyl- α -naphthafavone, m. p. 187°. The compounds described by Jacobson and Ghosh (J.C.S., 1915, 107, 432, 964, 1055) are probably the isomeric 1:2-naphthapyrones.

2-Benzoyl- α -naphthol forms the corresponding acetate, m. p. 118°, with Ac_2O and NaOAc , but with Ac_2O and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ gives 3:4-diphenyl-1:2- α -naphtha-

pyrone, m. p. 237°. 2-Acetyl- α -naphthol, Ac_2O , and Na β -phenylpropionate afford 3-acetyl-2-methyl-1:4- α -naphthapyrone, m. p. 147°. α -Naphthol, α -acetylphenylacetoneitrile, and ZnCl_2 yield 3-phenyl-4-methyl-1:2- α -naphthapyrone, m. p. 212°.

VI. Phloracetophenone gives with cinnamic anhydride and Na cinnamate 5:7-dicinnamoyloxy-, m. p. 235°, and with *p*-methoxycinnamic anhydride, 5:7-di-*p*-methoxycinnamoyloxy-4'-methoxy-2-styryl-chromone(?), m. p. 240—241°. From respropionophenone and 2-propionyl- α -naphthol and the same anhydrides, the following were prepared: 7-hydroxy-, m. p. 307° (*Ac* derivative, m. p. 159°), and 7-hydroxy-4'-methoxy-2-styryl-3-methylchromone, m. p. 271—272° (*Ac* derivative, m. p. 181°); 4'-methoxy-, m. p. 169°, and 2-styryl-3-methyl-1:4- α -naphthapyrone, m. p. 166°. Condensation of the corresponding ketone with cinnamaldehyde and NaOH affords 2-cinnamylideneacetyl- α -naphthol, m. p. 154°, 2-hydroxy-, m. p. 156—157°, and 2-hydroxy-3:4-dimethoxy-cinnamylideneacetophenone, m. p. 141—142°, which cannot be converted into the 2-styrylchromones.

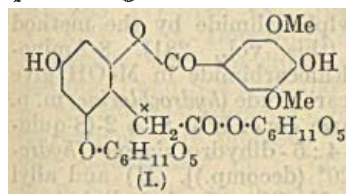
3-Phenyl- and 3-benzyl-2-methyl-1:4- α -naphthapyrones condense with PhCHO , *o*-methoxybenzaldehyde, anisaldehyde, and veratraldehyde to give 3-phenyl-, m. p. 262—263° (dibromide, m. p. 198°), and 3-benzyl-2-styryl-, m. p. 233° (dibromide, m. p. 167°), 3-phenyl-, m. p. 231°, and 3-benzyl-2-*o*-methoxystyryl-, m. p. 200°, 3-phenyl-, m. p. 224—225°, and 3-benzyl-2-*p*-methoxystyryl-, m. p. 216—217°, and 3-phenyl-, m. p. 215—216°, and 3-benzyl-2-(3':4'-dimethoxystyryl)-1:4- α -naphthapyrone, m. p. 215°. 2:3-Dimethyl-1:4- α -naphthapyrone, m. p. 142°, prepared from 2-propionyl- α -naphthol, similarly affords 2-styryl-, m. p. 166°, 2-*p*-methoxystyryl-, m. p. 169°, and 2-(3':4'-dimethoxystyryl)-3-methyl-1:4- α -naphthapyrone, m. p. 204°. 2-Methyl- condenses to give 2-styryl-, m. p. 177°, 2-*o*-methoxystyryl-, m. p. 169°, 2-*p*-methoxystyryl-, m. p. 207°, and 2-(3':4'-dimethoxystyryl)-1:4- α -naphthapyrone, m. p. 211—212°; 7:8-dimethoxy-2-methylchromone yields 7:8-dimethoxy-, m. p. 171°, and 7:8:4'-trimethoxy-2-styrylchromone, m. p. 178°, and 2-methylchromone gives 2-styryl-, m. p. 131°, 4'-methoxy-, m. p. 140°, and 3':4'-dimethoxy-2-styrylchromone, m. p. 165°.

F. R. SHAW.

Vegetable dyes. XXXIX. Carotenoids (α -carotene, zeaxanthin, carotenoids from kiki fruit). P. KARRER, R. MORF, E. VON KRAUSS, and A. ZUBRYS. XL. Oxidative degradation of anthocyanins. Constitution of malvone. P. KARRER and G. DE MEURON (Helv. Chim. Acta, 1932, 15, 490—493, 507—512).—XXXIX. A pure sample of α -carotene, $[\alpha]_{\text{D}}^{25} +330^\circ$ in C_6H_6 , separated from β -carotene by fractional absorption on fuller's earth gave neither geronic nor isogeronic acid on ozonisation, thus confirming the structure previously assigned. Cryst. zeaxanthin and lycopene are isolated from the fruit of *Diospyros Kaki*. Zeaxanthin from *Physalis* is degraded to an optically inactive hydrocarbon, b. p. 226—229°/0.06 mm., by methods similar to those employed for leaf-xanthophyll from the common nettle (cf. A., 1931, 1066), but in this case analysis and formation of a yellow coloration with $\text{C}(\text{NO}_2)_4$, but not hydrogenation, indicate that it is unsaturated. The

relation of zeaxanthin to leaf-xanthophyll is therefore uncertain; the derivation of the latter from α -carotene is confirmed spectrometrically. The nature of the products of reduction of lycopene with Al-Hg is dependent on reaction conditions, and the isolation of a cryst. reduction product containing O is reported.

XL. An almost quant. yield of syringic acid is obtained by hydrolysis of malvone or its NHPH-NH₂ derivative (cf. A., 1927, 1197) with 2N-NaOH at room temp.; in the former case it is accompanied by glucose (1 equiv.). Interaction of NH₃ and malvone in cold abs. EtOH gives an amorphous *amide* and glucose (1 equiv.); the former eliminates a further equiv. of glucose on acid hydrolysis. The tetra-



acetylglucose ester of *p*-methylmandelic acid similarly yields the *amide*, m. p. 153°, and NHPH-NH₂ the *phenylhydrazide*, m. p. 172°, of the acid; the formation of similar derivatives from malvone is regarded as occurring in the same manner and the formula (I), $-\text{H}_2\text{O}$ [or (I), CH-OH in place of CH₂*] is therefore assigned to malvone.

H. A. PREGOTT.

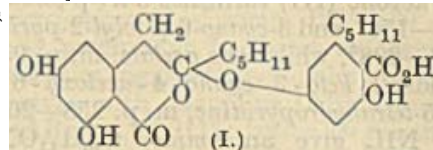
Lichen substances. X. Olivetoric acid. I. Y. ASAHINA and J. ASANO (Ber., 1932, 65, [B], 475—482).—Extraction of the thalli of *Alectoria divergens*, Nyl (mixed with *A. jubata*, Ach), with Et₂O at room temp. and crystallisation of the residue from boiling C₅H₈ affords olivetoric acid (I), C₂₆H₃₂O₈, m. p. 151°, identified by analysis, m. p., and colour reactions with FeCl₃, Ca(OCl)Cl, and Ba(OH)₂ with the product obtained by Zopf from *Parmelia olivetorum*, Nyl, and *Evernia olivetorina*. When treated with boiling 95% HCO₂H or MeOH at 150—200° it gives *olivitol* (II), m. p. 40—41°, and *olivetonide* (III), m. p. 110°. When oxidised with KMnO₄ (II) yields hexoic acid; it is identified as 3:5-dihydroxy-*n*-amylbenzene, obtained synthetically by condensing Et *n*-hexoyleacetate with Et acetonedicarboxylate by Na and fusion of the product with KOH at 250°. (III) does not absorb H₂ in presence of PtO₂, does not react with cold NH₂OH or NH₂·CO·NH·NH₂, but is converted by diazomethane into *olivetonide Me₂ ether* (IV), m. p. 94°; with molten KOH it affords orcinol and *n*-hexoic acid. (IV) and KOH-EtOH give *olivetonide Me₂ ether*, m. p. 93° (*oxime*, m. p. 120°), converted by boiling HCO₂H or Ac₂O into (IV) and smoothly oxidised by KMnO₄ to *n*-hexoic acid and 3:5-dimethoxyphthalic acid, thus

establishing the constitutions (OH)₂C₆H₂ $\begin{smallmatrix} \text{CH}_2\text{C}^*\text{C}_5\text{H}_{11} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$ and CO₂H·C₆H₂(OH)₂·CH₂·CO·C₅H₁₁ for (II) and (I), respectively. (I) is transformed by semicarbazide acetate in cold dil. EtOH quantitatively into *olivetonide anhydride semicarbazone*,

(OH)₂C₆H₂ $\begin{smallmatrix} \text{CH}_2\text{C}^*\text{C}_5\text{H}_{11} \\ \text{CO}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \end{smallmatrix}$ m. p. 266°, and *olivitolcarboxylic acid* (2:4-dihydroxy-6-amylbenzoic acid, m. p. 143°, since it differs from synthetic 2:6-dihydroxy-4-amylbenzoic acid, m. p. 127°). With excess of diazomethane, (I) yields *olivetonide Me₂ ether* and *Me 2:4-dimethoxy-6-amylbenzoate*, b. p.

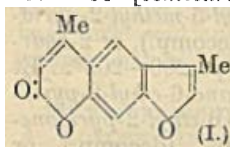
175°/5 mm. With NH₂OH acetate in boiling solution, (I) gives *olivetonide anhydride oxime*,

(OH)₂C₆H₂ $\begin{smallmatrix} \text{CH}_2\text{C}^*\text{C}_5\text{H}_{11} \\ \text{CO}\cdot\text{N}\cdot\text{OH} \end{smallmatrix}$, *olivitol*, and a trace of *olivitolcarboxylic acid*. It therefore has the constitution



H. WREN.

Furocoumarin group. I. Formation of a 3:4'-dimethylfurocoumarin. D. B. LIMAYE (Ber., 1932, 65, [B], 375—377).—4-Methylumbelliferone acetate, m. p. 150°, is converted by AlCl₃ at 120—140° into 6(or 8)-acetyl-4-methylumbelliferone, m. p. 167—168° [*semicarbazone*, m. p. above 300° (decomp.)



after changing colour at about 260°]. It is transformed by NaOEt and CH₂Br·CO₂Et in boiling EtOH into 6(or 8)-acetyl-7-carboxymethoxy-4-methylfurocoumarin, m. p. 212° [*semicarbazone*, m. p. 245° (decomp.); *Et ester*, m. p. 112°], converted by NaOAc and boiling Ac₂O into 3:4'-dimethylfurocoumarin (I), m. p. 176°.

H. WREN.

Ozone fission of nuclear-substituted derivatives of thioindigotin as method of elucidating the constitution of dyes of the thioindigotin series. K. FÜRST and R. POLLAK (Ber., 1932, 65, [B], 390—392).—Ozonisation of 6-chloro-6'-ethoxy-4-methyl-2:2'-bisthionaphthenindigotin suspended in PhNO₂ and treatment of the product with H₂O affords 6-chloro-4-methylthionaphthenquinone and 6-ethoxythionaphthenquinone, m. p. 160°. Similar fission is observed with a mixture of 6:6'-dichloro-4:4'-dimethyl- and 6:6'-diethoxy-2:2'-bisthionaphthenindigotin.

H. WREN.

Stability of pyrrolones to water. R. LUKEŠ (Coll. Czech. Chem. Comm., 1932, 4, 81—86).—Methylsuccinimide is converted by CH₂Ph·MgCl in C₆H₆ into 5-benzyl-1-methylpyrrolone, m. p. 100° (83% yield), readily hydrolysed by boiling 10% H₂SO₄ into 8-phenyl-lævulinic acid. Similar condensation with Zn and CH₂Br·CO₂Et gives *Et 1-methylpyrrolone-5-carboxylate*, m. p. 123°, hydrolysed, not to β-keto-adipic acid, but to AcOH, succinic and lævulinic acids, and CO₂.

J. W. BAKER.

Reactivity of conjugated systems. V. Condensation of hydroxymethylene-ketones with cyanoacetamide. C. BARAT (J. Indian Chem. Soc., 1931, 8, 801—816).—Michael (A) or Knoevenagel (B) condensation of hydroxymethylene-ketones, OH·CH·CR·COR', with CN·CH₂·CO·NH₂ gives 6-substituted (R') 3-cyano-2-pyridones, whilst OAc·CH·CR·COR' affords (A) 6-substituted 2-keto-3-cyano-4-acetoxy-2:3:4:5-tetrahydropyridines (cf. A., 1930, 925; 1931, 1427). Thus, hydroxy-methyleneacetophenone (I) gives 3-cyano-6-phenyl-2-pyridone (II), m. p. 292—293°, accompanied in (B) by much *s*-C₆H₃Bz₃ [not produced when the Na salt of (I) is condensed with the amide in aq. piperidine]. The *acetate*, m. p. 70—72°, of (I) affords 2-keto-3-

cyano-4-acetoxy-6-phenyl-2:3:4:5-tetrahydropyridine, m. p. 235—236°, hydrolysed, as is (II), by 75% H_2SO_4 to 6-phenyl-2-pyridone-3-carboxylic acid, m. p. 300—302° (decomp.), and by fuming HCl at 150—160° to 2-hydroxy-6-phenylpyridine. *p*-Tolyl β -hydroxyvinyl ketone (III) furnishes *s-tri-p-toluoxybenzene*, m. p. 157—158°, and 3-cyano-6-*p*-tolyl-2-pyridone (IV), m. p. 297—298°, whilst the acetate, m. p. 95—96°, of (III) yields 2-keto-3-cyano-4-acetoxy-6-*p*-tolyl-2:3:4:5-tetrahydropyridine, m. p. 258—260°. (III) and aq. NH_3 give an amide, $\text{C}_{10}\text{H}_{11}\text{ON}$, m. p. 103°, which when heated or condensed (A) with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ affords (IV). 6-*p*-Tolyl-2-pyridone-3-carboxylic acid and 2-hydroxy-6-*p*-tolylpyridine have m. p. 288—290° (decomp.) and 200°, respectively. Ph β -hydroxy- α -methylvinyl ketone (V) or the amide, $\text{C}_{10}\text{H}_{11}\text{ON}$, m. p. 182—183° (prepared as above), furnish 3-cyano-6-phenyl-5-methyl-2-pyridone, m. p. 264—265°, hydrolysed to 6-phenyl-5-methyl-2-pyridone-3-carboxylic acid, m. p. 295° (decomp.), or 2-hydroxy-6-phenyl-5-methylpyridine, m. p. 200—202°. Et β -hydroxyvinyl ketone gives 3-cyano-6-ethyl-2-pyridone, m. p. 278—280°, hydrolysed to 6-ethyl-2-pyridone-3-carboxylic acid, m. p. 300—302° (decomp.), or 2-hydroxy-6-ethylpyridine, m. p. 205—206°.

The reaction of the above hydroxymethyleneketones with semicarbazide is studied. In cold aq. EtOH the α -semicarbazone, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}'\cdot\text{CH}\cdot\text{CHR}\cdot\text{COR}'$, is the main product, whilst a cyclic semicarbazone (pyrazole-1-carboxylamide) results at 100° (bath). Condensation in AcOH (cf. Wallach, A., 1904, i, 104) gives the pyrazolecarboxylamide and 5—10% of the disemicarbazone. The α - and cyclic forms are converted by boiling 25% H_2SO_4 into the corresponding pyrazoles. The following are prepared: (I) [α -, m. p. 175—176° (decomp.)], and cyclic, m. p. 135—137° (probably a mixture; cf. von Auwers, A., 1925, i, 1459), semicarbazones; disemicarbazone, m. p. 225° (decomp.) (lit. 238°); pyrazole, $\text{C}_9\text{H}_8\text{N}_2$, m. p. 72—74°; (III) [α -, m. p. 182—184° (decomp.)], and cyclic, m. p. 145—146°, semicarbazones; disemicarbazone, m. p. 218—220° (decomp.); pyrazole, $\text{C}_{10}\text{H}_{10}\text{N}_2$, m. p. 87—88° (sulphate, m. p. 190°); (V) [α -, m. p. 220° (decomp.)], and cyclic, m. p. 124—125°, semicarbazones; pyrazole, $\text{C}_{10}\text{H}_{10}\text{N}_2$, m. p. 118—120°]. H. BURTON.

Bromination of pyridine in the gaseous phase at elevated temperatures. Preparation of 2-bromo- and 2:6-dibromo-pyridine. H. J. DEN HERTOOG and J. P. WIBAUT (Rec. trav. chim., 1932, 51, 381—388).—Bromination of pyridine at 300° in presence of charcoal or pumice gives 3-bromo-, m. p. —29.5°, b. p. 173.7—174°/762 mm. (yield 39%), and 3:5-dibromo-pyridine (I), m. p. 115.5 (? 111.5)—112°, b. p. 222°/755 mm. (yield 13%), higher brominated products, and unchanged pyridine. At 500° 2-bromo- (II), m. p. —40.1°, b. p. 193.5—194°/764 mm. (yield 48%), and 2:6-dibromo-pyridine (III), m. p. 118.5—119°, b. p. 249°/757.5 mm. (yield 36%), are obtained. At higher temp. carbonisation occurs, but no higher brominated products were detected. At 400° (I) and (III) were isolated. (II) when heated with aq. NH_3 at 200° gives 2-aminopyridine (yield 66%). Similar treatment of (III) at 180° gives 2-amino-6-

bromopyridine, m. p. 89—89.5° (yield 70—80%), whilst at 200° it gives 2:6-diaminopyridine.

[With P. H. VAN DER LEY.] By the action of Cl_2 on pyridine at 250° in the presence of asbestos, *pentachloropyridine*, m. p. 125°, 3:5-dichloro- and 2-chloropyridine were obtained. A. A. LEVI.

Quinoline compounds. VI. U. BRAHMACHARI and J. M. DAS-GUPTA (J. Indian Chem. Soc., 1932, 9, 37—42).—The *dihydrochlorides* of 8- α -aminoisopropylamino-6-methoxy-, m. p. 218—220°, -6-methoxy-2-methyl-, m. p. 260°, -6-ethoxy-2-methyl-, m. p. 270°, -6-chloro-, m. p. 212°, -6-chloro-2-methyl-, m. p. 255°, and -2-methyl-, m. p. 275—280°, quinolines are prepared from the requisite 8-aminoquinolines and β -bromopropylphthalimide by the method previously described (this vol., 281). 8-Aminoquinoline (I) and allylthiocarbimide in MeOH give α -8-quinolyl- γ -allylthiocarbimide (*hydrochloride*, m. p. 150°), converted by warm conc. HBr into 2-(8-quinolylamino)-4-methyl-4:5-dihydrothiazole [*hydrochloride*, m. p. 215—220° (decomp.)]. (I) and allyl bromide in boiling aq. Na_2CO_3 afford 8-allylaminoquinoline (*hydrochloride*, m. p. 175°). The *hydrochlorides* of α -6-ethoxy-8-quinolyl- γ -allylthiocarbimide and 8-allylamino-6-ethoxyquinoline have m. p. 160° and 182°, respectively. H. BURTON.

Antiseptic and trypanocidal action of certain styryl- and anil-quinolinecarboxylamides. C. H. BROWNING, J. B. COHEN, J. N. ASHLEY, and R. GULBRANSEN (Proc. Roy. Soc., 1932, B, 110, 249—260; cf. A., 1931, 1187).—2-Methylquinoline-6-carboxylic acid (A., 1884, 1200) yields an Et ester, m. p. 57°, converted into the amide, m. p. 225—227° [*methosulphate*; *methiodide*, m. p. 230° (decomp.); *methochloride*], with aq. NH_3 , *carboxymethylamide*, m. p. 202—204° [*methosulphate*; *methiodide*], with NH_4Me , and *carboxyethylamide*, m. p. 153° [*methiodide*, m. p. 241—242° (decomp.)], with NH_4Et . Similarly were prepared from 2-methylquinoline-5-carboxylic acid (Et ester, m. p. 72°), the amide, m. p. 249° [*methiodide*, m. p. 233—234° (decomp.)], and *methylamide*, m. p. 176° [*methiodide*, m. p. 238—239° (decomp.)]; from 2-methylquinoline-4-carboxylic acid (A., 1898, i, 207), the amide, m. p. 226—227° (decomp.), *methylamide*, m. p. 152—153° [*methiodide*, m. p. 227—228° (decomp.)], and *ethylamide*, m. p. 125° [*methiodide*, m. p. 112—113°]; from Et 2-methylquinoline-3-carboxylate (A., 1883, 1148), the *methiodide*, m. p. 210—211° (decomp.); from acetoacetamide and *o*-aminobenzaldehyde, 2-methylquinoline-3-carboxylamide, m. p. 199—201° [*methiodide*, m. p. 246—247° (decomp.)], and from 2-methylquinoline-8-carboxylic acid, the amide, m. p. 170—171° (*methiodide*, decomp. 245—255°). From the above were prepared the following derivatives of both 2-(*p*-dimethylaminoanil)quinoline and 2-(*p*-dimethylamino-styryl)quinoline: -6-carboxylamide (*methiodides* and *methochlorides*); -6-carboxy-methyl- (anil derivative as *methiodide* and *methochloride*, styryl as *methosulphate*); and -ethyl-amide (*methiodides* and *methochlorides*); -5-carboxylamide (*methiodides*); -5-carboxy-methylamide (*methiodides* and *methochlorides*); -4-carboxylamide (anil derivative as *methiodide* and *methochloride*, styryl as *methiodide*); -4-carboxy-methyl-

(methiodides and methochlorides) and -ethyl-amide (methiodides); -3-carboxylic Et ester-(methiodides, anil derivative as methochloride). 2-(p-Dimethylamino-styryl)quinoline-8-carboxylamide methochloride (methiodide) were also prepared. The trypanocidal properties of the above compounds are most marked in those with the CO-NH₂ group in the 6 position, the styryls being slightly more active than the anil analogues. No powerful antiseptic action is exhibited by any member of the series. F. O. HOWITT.

Quinoline derivatives. XXXVI. Derivatives of 3:4-dihydro-1:2-naphthacridine-14-carboxylic acid. XXXVII. 14-Amino-3:4-dihydro-1:2-naphthacridine. H. JOHN (J. pr. Chem., 1932, [ii], 133, 177—186, 187—194; cf. this vol., 403).—XXXVI. 3:4-Dihydro-1:2-naphthacridine-14-carboxylic acid (modified prep.) (20 inorg. salts described) and SOCl₂ at 100° give the acid chloride, m. p. 230—234° (decomp.), from which the following derivatives were prepared: (a) esters: Me, m. p. 99°; β-chloroethyl, m. p. 73°; Pr^a, m. p. 43°; Pr^B, m. p. 83°; Bu^B, m. p. 68°; αα-dimethylpropyl, m. p. 111°; CH₂Ph, m. p. 107°; (b) amide, m. p. 224°; ethylamide, m. p. 182°; β-hydroxyethylamide, m. p. 184°; urethane, m. p. 115°; diethylamide, m. p. 126°; isoamylamide, m. p. 158°; diisoamylamide, m. p. 83°; NN'-bis-(3:4-dihydro-1:2-naphthacridine-14-carbonyl)ethylenediamine, m. p. above 300°. Numerous salts and complex salts of the amides are described.

XXXVII. 3:4-Dihydro-1:2-naphthacridine-14-carboxyl chloride and N₂H₄.H₂O in abs. Et₂O give the hydrazide, m. p. 232° [hydrochloride, m. p. 286°; picrate, m. p. 183°; isopropylidene (m. p. 131°), benzylidene (m. p. 222°), methylbenzylidene (m. p. 185°), and ethylbenzylidene (m. p. 200°) derivatives], which affords the 3-methylpyrazolone (by boiling Et acetoacetate), m. p. above 300°, and the azide (by HNO₂ below -6°, unstable. The azide with boiling C₆H₆ gives the cyanate (I), m. p. 248° (decomp.), with boiling H₂O the s-carbamido-derivative, m. p. above 300° (picrate, m. p. 276°), and with boiling abs. EtOH the urethane, m. p. 179° (picrate), which with boiling conc. HCl affords 14-amino-3:4-dihydro-1:2-naphthacridine [also obtained from (I) and 30% abs.-alcoholic KOH], m. p. 143° (hydrochloride, m. p. above 300°; picrate; Ac and Ac₂ derivatives, m. p. 264° and 285°, respectively; ethiodide, m. p. 230°; methiodide, m. p. 252°). R. S. CAHN.

3:5-Diketopyrazolidine derivatives. II. T. TSUMAKI (Bull. Chem. Soc. Japan, 1932, 7, 45—50).—By condensation of 3:5-diketo-1:2-diphenylpyrazolidine with the appropriate aldehyde are obtained: 4-p-methyl-, m. p. 175°; -p-methoxy-, m. p. 199°; -p-dimethylamino-, m. p. 256° (decomp.); -p-, m. p. 231—232°; -m-, m. p. 194°, and -o-, m. p. 193°; -hydroxy-, -p-, m. p. 243°, -m-, m. p. 185°, and -o-, m. p. 174—176°, -nitro-, -3':4'-dihydroxy-, m. p. 255° (decomp.); and -4'-hydroxy-3-methoxy-, m. p. 156—157°; -benzylidene: 4-piperonylidene-, m. p. 234—235°; and 4-propylidene, m. p. 260° (decomp.), derivatives. J. W. BAKER.

Derivative of picrolonic acid suitable for analysis; m-bromopicrolonic acid. W. ZIM-

MERMANN and D. P. CUTHBERTSON (Z. physiol. Chem., 1932, 205, 38—46).—m-Bromophenylhydrazine and CH₂Ac.CO₂Et yield 1-m-bromophenyl-3-methylpyrazolone, m. p. 134°, which with HNO₃ gives 4-nitro-1-m-bromo-p-nitrophenyl-3-methylpyrazolone nitrate, decomp. 116°, then m. p. 175°. The nitrate affords m-bromopicrolonic acid, decomp. 128—130°, which is proposed as precipitant for bases as yielding more definite analytical figures than picrolonic acid. Cryst. ppts. are given with guanidine (AB), decomp. 285°; creatinol (AB), m. p. 211°; lysine (a mixture of AB and A₂B), decomp. about 200°; histidine (A₂B), decomp. 216—218°; methylarginine (A₂B), sinters 152—160°. J. H. BIRKINSHAW.

Reaction of dibromobarbituric acid with amines. A. C. COPE (J. Amer. Chem. Soc., 1932, 54, 1250—1252).—The products obtained by Nightingale and Schaefer (this vol., 283) from 5:5-dibromobarbituric acid and amines are not 5-bromo-7-alkyluramils but alkylammonium 5-bromobarbiturates.

C. J. WEST (b).

Polymorphism of veronal. R. FISCHER and A. KOFLER (Arch. Pharm., 1932, 270, 205—214).—Crystallographic data are given for three forms (stable trigonal, unstable monoclinic and triclinic) (obtained by sublimation or crystallisation) of veronal (cf. B., 1931, 90). R. S. CAHN.

Pyrimidines. CXXV. Effect of dilute acids and of light energy on thymine glycol [4:5-dihydroxy-4:5-dihydrothymine]. Synthesis of acetylmethylidialuric acid. T. B. JOHNSON, O. BAUDISCH, and A. HOFFMANN (J. Amer. Chem. Soc., 1932, 54, 1106—1113; cf. A., 1925, i, 1100).—The pyrimidine ring of 4:5-dihydroxy-4:5-dihydrothymine (I) is more stable in acid than in alkaline solution (cf. loc. cit.). Irradiation of (I) in acid solution gives an anhydride (II) (constitution unknown), m. p. 345—350°, of (I). Addition of (I) to a liquid culture of *Sulphomonas thio-oxidans* causes the production of a red coloration and (II) is isolated from the medium. (I) in dil. HCl gives the same coloration when kept in the dark; the red colour is destroyed in all cases by the action of daylight. (I) and H₃PO₄ also give (II). (I) is not oxidised by aq. Br; with CrO₃ in H₂SO₄, cyanuric acid results. (I) and HgO in boiling H₂O give a compound, C₅H₆O₄N₂Hg. Successive treatment of 5-bromo-5-methylbarbituric acid with Ag₂CO₃ and H₂S affords a compound, C₅H₄O₂N₂S, m. p. 240—245° (decomp.), whilst with AgOAc, and subsequent acetylation, acetylmethylidialuric acid, m. p. 244—245°, results. C. J. WEST (b).

Azo-derivatives of pyrimidines. M. T. BOGERT and D. DAVIDSON (Proc. Nat. Acad. Sci., 1932, 18, 215—222).—Alloxan-6-phenylhydrazone, m. p. 260° (decomp.), and its Na p-sulphonate are prepared from isobarbituric acid and benzenediazonium and p-sulphobenzenediazonium salts in slightly acidic solution; Na alloxan-5-phenylhydrazone-p-sulphonate is similarly prepared from barbituric acid. The hydrazone structure corresponds with the insolubility of the 1:3-Me₂ compounds in alkali (cf. A., 1892, 442; 1898, i, 695). Azo-compounds are also prepared

from 5-diazouracil and α -naphthol, β -naphthol, m. p. 285° (decomp.), Na β -naphthol-3:6-disulphonate, isobarbituric acid, and barbituric acid in alkaline, and, in the case of the last two, also in acid medium. Interaction of phenylhydrazine hydrochloride (but not the free base) with isodialuric acid gives uracil-5-azobenzene, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{NPh}$, presumably by rearrangement and dehydration of the initially-formed phenylhydrazone; the Na *p*-sulphonate is similarly prepared. H. A. PIGGOTT.

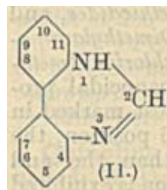
Superfluous isomerides in the chemistry of nitrogen. J. MEISENHEIMER, E. STRATMANN, and W. THEILACKER (Ber., 1932, 65, [B], 418—424).—Ethylenedipiperidine and trimethylene bromide react vigorously, yielding ethylenetrimethylenedipiperidinium bromide, decomp. 327—331° after darkening at 300° [iodide, m. p. 300° (decomp.); picrate, m. p. 249—250° (decomp.)]. Identical products are obtained from trimethylenedipiperidine and $\text{C}_2\text{H}_4\text{Br}_2$, but reaction is slow, incomplete, and accompanied by the production of much difficultly-separable ethylenedipiperidinium dibromide. The "isomerides" of Aschan (A., 1904, i, 350) do not exist. Ethyleneisopropylenedipiperidinium dibromide, decomp. 329—331° after darkening at 299° (picrate, decomp. 289—290°), is derived in slow reaction from ethylene- or isopropylene-dipiperidine and the requisite bromide.

Only the β -form, m. p. 246°, of *m*-xylylene-*p*-xylylenedipiperidinium bromide (corresponding picrate, decomp. 270—280° after darkening above 220°) could be caused to crystallise; the structure of the α -variety could not be investigated (cf. Scholtz, A., 1911, i, 326). *Di-m-xylylenedipiperidinium bromide*, m. p. 236° [picrate, m. p. 165—167° (decomp.)], has been prepared.

The isomerism of the *o*-xylylene-6-phenyl-2-methylpiperidinium bromides is due, not to the N atom, but to their derivation from stereoisomeric 6-phenyl-2-methylpiperidines (due to the presence of two asymmetric C atoms). Dry distillation of cinnamylideneacetoneoxime, m. p. 159°, affords 6-phenyl-2-methylpyridine, b. p. 138—139°/10 mm. (yield 37%), reduced by Na and EtOH to a mixture of 6-phenyl-2-methylpiperidines. The mixture is treated with HCl in Et_2O and subsequently with COMe_2 , thereby yielding a hydrochloride, m. p. 225°. The base derived from this when treated with *o*-xylylene bromide gives the β -*o*-xylylene-6-phenyl-2-methylpiperidinium bromide, m. p. 226—227° (chloroplatinate, m. p. 257°), of Scholtz; 6-phenyl-1-*o*-ethoxymethylbenzyl-2-methylpiperidine, m. p. 72°, is formed as by-product. The α -isomeride of Scholtz is derived from the 6-phenyl-2-methylpiperidinium chloride, sol. in COMe_2 . H. WREN.

Formation of cyclic compounds from diphenyl derivatives containing amino-groups in the 2:2'-positions. S. SAKO (Mem. Coll. Eng. Kyushu, 1932, 6, 263—306).—The diformyl derivative of 2:2'-diaminodiphenyl (I) is converted by dry HCl in boiling xylene into the hydrochloride, decomp. 245—246°, of the viscous diphenimidine (II) [picrate,

m. p. about 235—237° (decomp.)]. (I) and Ac_2O in Et_2O give 2-amino-2'-acetamidodiphenyl, m. p. 89—90° (hydrochloride), converted by HNO_2 into a little 2-methyldiphenimidine (III), m. p. 228° [hydrochloride, m. p. 202—203°; hydriodide (IV)], and (mainly) *N*-acetylcarbazole. (III) is also obtained from the Ac or Ac_2 derivatives of (I) and PCl_3 at 130—140° or 110—120°, respectively. (I) and Bz_2O in C_6H_6 at 100° (bath) give 2-amino-2'-benzamidodiphenyl, m. p. 158—160° [and a little Bz_2 derivative, m. p. 190—191° (lit. 184°)], converted by PCl_3 at 120—130° into 2-phenyldiphenimidine, m. p. 165—166° [hydrochloride; d-tartrate, m. p. 232° (decomp.) (softens at 227°); d-camphorsulphonate, m. p. 260—261°], which could not be resolved. (III) and MeI in MeOH at 65° give the hydriodide (V), decomp. 235°, of 2-methylamino-2'-methylethylaminodiphenyl, m. p. 72—72.5°, and (IV) (mainly); in presence of K_2CO_3 , (V) and 2-amino-2'-*N*-methylacetamidodiphenyl, m. p. 107—108°, result. The Bz_2 , m. p. 182.5°, and the crude Bz derivatives of dl-6:6'-diamino-2:2'-ditolyl (VI) are converted by PCl_3 at 120—125° into dl-2-phenyl-7:8-dimethyldiphenimidine, m. p. 207—208° (hydrochloride; d-camphorsulphonate, m. p. 190—191°), which could not be resolved. l-6:6'-diamino-2:2'-ditolyl (VII) (Bz_2 derivative, m. p. 172—173°, $[\alpha]_D -264.4^\circ$ in EtOH) is similarly converted through its crude Bz derivative into l-2-phenyl-7:8-dimethyldiphenimidine, m. p. 240°, $[\alpha]_D -986.3^\circ$ in C_6H_6 (hydrochloride), hydrolysed by HCl (without racemisation) to (VII). 2:7:8-Trimethyldiphenimidine could not be obtained from the Ac derivative, b. p. 194°/4 mm., of (VI). Carbamide and (VI) heated to 210° give 2-keto-7:8-dimethyl-2:3-dihydrophenimidine (NN'-carbonyl-6:6'-diamino-2:2'-ditolyl), m. p. 332° (decomp.); the l-form, m. p. 332° (decomp.), $[\alpha]_D -67.2^\circ$ in pyridine, is prepared similarly from (VII). H. BURTON.



Anomalous decomposition of the tetrazo-derivative of 2:2'-diamino-1:1'-dinaphthyl. A. CORBELLINI and L. BARBARO (Atti R. Accad. Lincei, 1931, [vi], 14, 341—347).—1-Phenyl- β -naphthisoindazole-2'-aldehyde (A., 1931, 966) gives an anilino-derivative, m. p. 224—225°, which when treated with malonic acid in amyl alcohol suspension, yields [4:5-(naphtho-1':2')-pyrazole(3)]-*o*-cinnamic acid [1-phenyl- β -naphthisoindazole-2'-acrylic acid] (loc. cit.). Oxidation of the latter gives, besides the above aldehyde, 1-phenyl- β -naphthisoindazole-2'-carboxylic acid, m. p. 268—269° (uncorr.). T. H. POPE.

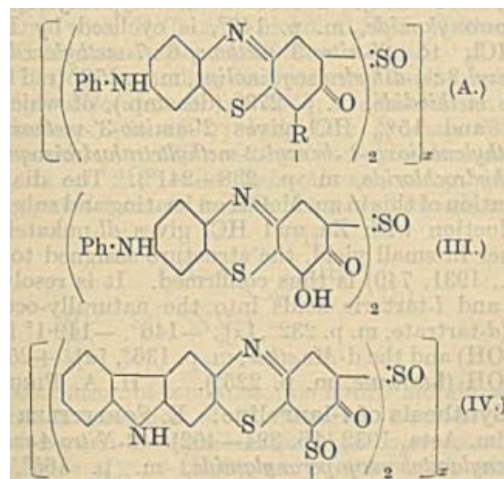
***N*-Diethylamide of tetrazole-5-carboxylic acid.** E. GRYSZKIEWICZ-TROCHIMOWSKI (Rocz. Chem., 1932, 12, 173—176).—The *N*-diethylamide of tetrazole-5-carboxylic acid, m. p. 80—81° (3-Me derivative, an oil) is prepared from N_3H and diethyloxamonitrile. R. TRUSZKOWSKI.

NN'-Substituted pyrimidine and purine derivatives. II. Methylated 3-phenylxanthine. B. HEPNER and S. FRENKENBERG (Helv. Chim. Acta, 1932, 15, 350—356; cf. this vol., 283).—Modifications are introduced into the Traube synthesis of purine derivatives. *s*-Phenylmethylcarbamide with

$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ in warm Ac_2O or with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$, AcOH , Ac_2O , and POCl_3 gives *N*-cyanoacetyl-*N'*-phenyl-*N*-methylcarbamide, m. p. 172° , transformed by 30% aq. NaOH into 4-imino-3-phenyl-1-methylbarbituric acid (I), m. p. about 276° , which with HNO_2 forms 4-imino-3-phenyl-1-methylviolic acid (II), reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in conc. aq. NH_3 to 4:5-diamino-2:6-diketo-3-phenyl-1-methylpyrimidine, m. p. 270° (decomp.). The 5-formyl derivative (III), m. p. 252° (decomp.), of this, obtained by boiling with HCO_2H or by treating (II) with Zn dust in HCO_2H , passes at 260° into 3-phenyl-1-methylxanthine, m. p. above 310° , yielding with Me_2SO_4 and NaOH 3-phenyl-1:7-dimethylxanthine, m. p. $305\text{--}310^\circ$. 4-Imino-3-phenylviolic acid (IV) with $\text{Na}_2\text{S}_2\text{O}_4$ and conc. aq. NH_3 gives 4:5-diamino-2:6-diketo-3-phenylpyrimidine, m. p. 222° (decomp. from 206°), the 5-formyl derivative, decomp. above 255° , of which [obtained from (IV) by Zn dust and HCO_2H] gives (III) with Me_2SO_4 and NaOH , whilst 4-imino-3-phenylbarbituric acid similarly yields (I). The constitution of the products is thus proved.

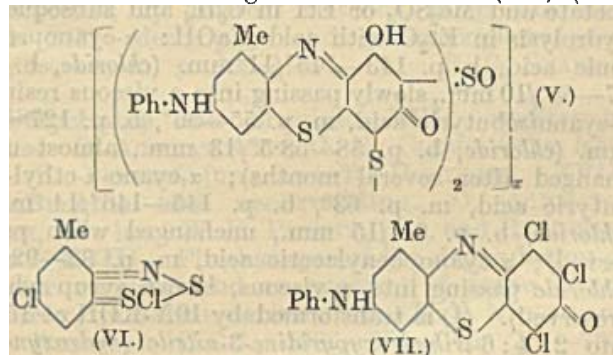
R. S. CAHN.

Blue sulphur dyes. E. BERNASCONI (Helv. Chim. Acta, 1932, 15, 287—314).—Purification of "Pyrogenindigo," taken directly from the melt, by H_2O , KOH , HCl , EtOH , and Et_2O removes sulphates, thiosulphates, Fe salts, and intermediate products (including a thiazine), and yields the pure dye (I) (A; $\text{R}=\text{S}$), $\text{C}_{36}\text{H}_{20}\text{O}_3\text{N}_4\text{S}_5$. Similar treatment of "Pyrogenindigo (Ciba)," purified commercially, gives a pure dye (II) (A; $\text{R}=\text{SO}$), $\text{C}_{36}\text{H}_{20}\text{O}_5\text{N}_4\text{S}_5$. "Immedialindon JBN" contains more alkali-sol. impurity and yields a dye (III), $\text{C}_{36}\text{H}_{22}\text{O}_5\text{N}_4\text{S}_3$, whilst "Hydronblau R konz." gives a dye (IV), $\text{C}_{36}\text{H}_{16}\text{O}_5\text{N}_4\text{S}_5$. The formulæ are based partly on known facts and partly



on the following evidence. (I), (II), and (IV) in H_2SO_4 give with ClSO_3H at $90\text{--}95^\circ$ (not at $80\text{--}90^\circ$ with ClSO_3H alone) H_2O -sol. substances; titration of the product from (I) with TiCl_3 shows 2 thiazine rings per mol., whilst with (II) and (IV) a slight excess (up to 30%) of TiCl_3 is required owing to further reduction. S dyes give yellow vats in alkali, both thiazine and groupings being reduced; aeration oxidises the thiazine groups only, giving stable blue solutions.

When the alkaline vats are boiled, or when the blue solutions are acidified in the cold, oxidation to the insol. disulphide dyes occurs. Unless pptd. from conc. H_2SO_4 , the pure dyes form vats more slowly than the commercial products, owing to the smaller degree of dispersion of the former. Heating the pure dyes with alcoholic KOH gives similar blue solutions, probably owing to reduction of the $\cdot\text{S}\cdot\text{S}\cdot$ groups. The leuco-compounds produced from (I), (II), and (III) by glucose and boiling aq. NaOH condense with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ to yield unstable products, which are sol. in NaOH even after pptn. by acid; Na salts can be isolated, and the product, $\text{C}_{40}\text{H}_{26}\text{O}_6\text{N}_4\text{S}_5$, from (I) was obtained nearly pure. The presence of $\cdot\text{S}\cdot\text{S}\cdot$ groups in (I) and (IV) is thus proved. (III) is more difficult to reduce, and the leuco-substance does not condense with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$. The dye (V), which is synthesised, is similar to (I) in properties. *o*-Toluidine hydrochloride with S_2Cl_2 gives 5-chloro-3-methyl-2:1-phenylenethiazthionium chloride (VI) (hydrolyses in air), which with NH_2Ph in AcOH yields 5-anilino-3-methyl-2:1-phenylenethiazthionium chloride, reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in aq.-alcoholic NaOH at 40° to 2-amino-5-anilino-3-methylthiophenol, the Zn salt of which with chloranil in EtOH gives the substance (VII) (ab-



sorption max. at $627\cdot6$ and secondary at $577\cdot5$). This with Na_2S and S under certain conditions forms (V). The absorption spectra of the dyes in conc. H_2SO_4 or $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, or of the derived mercaptans in dil. alkali, are not characteristic, but when boiled for a short time in PhNO_2 the pure dyes give stable red solutions, showing the following reproducible absorption max., the secondaries (in parentheses) being specially characteristic: (I) $560\cdot3$ ($620\cdot4$); (II) $562\cdot0$ ($617\cdot0$); (III) $560\cdot8$ ($626\cdot4$); (IV) $550\cdot0$ ($604\cdot5$); (V) $561\cdot5$ ($634\cdot5$). S in commercial products in excess of that required by the above formulæ is considered to be present in polysulphide groups or as colloidal S, and may during purification be removed as S or H_2SO_4 ; thus, commercial (IV) contains free H_2SO_4 .

R. S. CAHN.

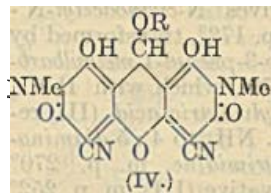
Microchemical reactions of mescaline. E. H. DUCLOUX (Rev. Farm., Buenos Aires, 1931, 74, 87—99).—Mescaline, from *Echinocactus Williamsii*, m. p. $150\text{--}160^\circ$, gives colour reactions with the following reagents: Erdmann, deep red; Bouchardat, bluish ppt.; Dragendorff, red ppt.; Mayer, white ppt.; Millon, yellow ppt.; picric acid, yellow ppt.; Tanret, white ppt.; Schlagdenhaufen, green becoming grey and reddish; FeCl_3 , reddish-yellow ppt.; Jarowski, white ppt.; Fröhde, yellowish-green; Buckingham,

greenish-yellow; HClO_4 , colourless crystals; Mandelin, green; H_2CrO_4 , grey ppt.; HAuCl_4 , H_2PtCl_6 , yellow crystals; H_3PO_4 , slowly developing white crystals.

CHEMICAL ABSTRACTS.

Spontaneous polymerisation of cyanoacetyl chloride and simple synthesis of the alkaloid ricinine. G. SCHROETER, C. SEIDLER, M. SULZBACHER, and R. KANITZ (Ber., 1932, 65, [B], 432—445).—Spontaneous polymerisation of $\text{CN}\cdot\text{CH}_2\cdot\text{COCl}$ at 5—8° affords mainly 6-chloro-2:4-dihydroxypyridine-3-nitrile (chloronor-ricinine) (I), an isomeride, decomp. 263°, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{CH}_2(\text{CO}_2\text{H})_2$; the Na (+5 H_2O), NH_4 , NH_4H , Ca (+6 H_2O), Ag, Ag₂, Pb, and Ba salts of (I) are described. (I) is reduced by Zn dust and 2N- H_2SO_4 to 2:4-dihydroxypyridine-3-nitrile (nor-ricinine) (II), decomp. 307°, converted by conc. H_2SO_4 and NaNO_2 into 2:4-dihydroxypyridine-3-carboxylic acid, m. p. 182° (decomp.), and m. p. about 245° after re-solidification, which yields 2:4-dihydroxypyridine, m. p. 265° (decomp.), when boiled with conc. HCl. In the formation of (I) from $\text{CN}\cdot\text{CH}_2\cdot\text{COCl}$ the intermediate production of cyanoketen and malonimide chloride is postulated. The following acids are prepared from Et sodiocyanoacetate and Me_2SO_4 or EtI in C_6H_6 and subsequent hydrolysis in Et_2O with cold NaOH: α -cyanopropionic acid, b. p. 143—145°/11 mm. (chloride, b. p. 67—68°/10 mm., slowly passing into a viscous resin); α -cyanoisobutyric acid, m. p. 55—56°, b. p. 127°/11 mm. (chloride, b. p. 58—58.5°/13 mm., almost unchanged after several months); α -cyano- α -ethyl-n-butyric acid, m. p. 63°, b. p. 145—146°/14 mm. (chloride, b. p. 81°/15 mm., unchanged when preserved); α -cyanophenylacetic acid, m. p. 92—92.5° (chloride passing into a viscous, brown syrup when preserved). (I) is transformed by 10N-KOH at 150° into 2:4:6-trihydroxypyridine-3-nitrile (hydroxynor-ricinine) (salts, $\text{C}_6\text{H}_4\text{O}_3\text{N}_2$, $\text{C}_6\text{H}_3\text{O}_3\text{N}_2\text{K}$, 4 H_2O , and $\text{C}_{12}\text{H}_7\text{O}_6\text{N}_4\text{Ag}$, 6 H_2O) converted in boiling conc. HCl into 2:4:6-trihydroxypyridine, m. p. 218° (decomp.). (I) and NH_2Ph in boiling AcOH afford anilinonor-ricinine, m. p. 265° (decomp.), transformed by NH_2Ph at 150—160° into the substance $\text{C}_6\text{HN}_2\text{O}(\text{NHPh})_2\cdot\text{H}_2\text{O}$, m. p. 244.5°, also obtained from (I). Piperidinonor-ricinine, decomp. 280°, is described. The Na₂ salt of (I) is converted by Me_2SO_4 into chlororicinine acid, reduced by Zn dust and 2N- H_2SO_4 to ricinic acid, m. p. 293—294° [Na salt (+3 H_2O)], obtained also from (II), Me_2SO_4 , and 2N-NaOH. Na chlororicininate and Me_2SO_4 in $\text{C}_6\text{H}_5\text{Me}_2$ yield chlororicinine, m. p. 239—240°, converted by 2N-NaOH into hydroxyricinine, decomp. 236—238°, by NaOMe into methoxyricinine, decomp. 270° (formerly incorrectly described as trimethoxynicotinonitrile), and by Zn dust and 2N- H_2SO_4 into ricinine, m. p. 199—201° (decomp.), also derived from Na ricinate and MeBr at 100° or Me_2SO_4 in $\text{C}_6\text{H}_5\text{Me}_2$. The following ricinic acid ethers are described: Et, m. p. 138—139° (HgCl_2 compound, m. p. 173—174°); Prⁿ, m. p. 123—124° (HgCl_2 compound, m. p. 129—130°); Prⁱ, m. p. 134—135°; Bu, m. p. 112—113° (HgCl_2 compound); amyl, m. p. 130—131°. Hydroxyricinic acid (III), m. p. 262—263° (decomp.), is derived from (I) and 14% NaOH or boiling AcOH and NH_4 biace-

tate. (III) and boiling HCO_2H yield fluoricinine acid (IV; R=H) [Na (+3 H_2O) and Na_2 (+ H_2O) salts; formyl derivative (IV; R=CHO) and its Na and Na_2 (+3 H_2O) salts; Ac derivative (IV; R=Ac), decomp., 268—270°]. Na chlororicininate and Na_2S afford thiolricinic acid, decomp. 280°,



converted by NaOH and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ into thiolricineacetic acid, $\text{CN}\cdot\text{C}_6\text{HON}(\text{Me})(\text{OH})\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, decomp. 250° (Na salt; Et ester, m. p. 195—196°). Selenoricinine acid (Ba salt) similarly yields selenoricinineacetic acid (Na salt), oxidised by KMnO_4 or H_2O_2 to diselenoricinine acid, $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_4\text{Se}$. 2:4:6-Trichloronicotinonitrile from (I) and PCl_5 at 120—130° has m. p. 112—113°.

H. WREN.

Anonaine. A. C. SANTOS (Philippine J. Sci., 1932, 47, 357).—Anonaine is $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$ (cf. A., 1931, 242).

R. S. CAHN.

Alkaloids of ergot. III. Ergine, a new base obtained by the degradation of ergototoxine and ergotinine. S. SMITH and G. M. TIMMIS (J.C.S., 1932, 763—766).—The action of EtOH-KOH on ergototoxine and ergotinine gives NH_3 and ergine, $\text{C}_{17}\text{H}_{21}\text{ON}_3$ (+1MeOH), decomp. 135°, (+2 H_2O), decomp. 115°, [α]_D²⁰ +51.4° in COMe_2 (hydrochloride, decomp. 255—260°; hydrobromide, decomp. 260°; nitrate, decomp. 225—230°; picrolonate, decomp. 215°; perchlorate, decomp. 225°). The base represents about $\frac{1}{2}$ of the ergototoxine mol., and gives the colour reactions of indole. It contains one NMe group.

F. R. SHAW.

Synthesis of l-puketaine methyl ether. G. BARGER and E. SCHLITTLER (Helv. Chim. Acta, 1932, 15, 381—394).—2'-Nitro-3'-methoxyphenylacetohomopiperonylamine, m. p. 143°, is cyclised by PCl_5 in CHCl_3 to 2'-nitro-3'-methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisquinoline, m. p. 176° (red liquid), the methiodide, m. p. 273° (decomp.), of which with Zn and 15% HCl gives 2'-amino-3'-methoxy-6:7-methylenedioxy-1-benzyl-2-methyltetrahydroisquinoline (dihydrochloride, m. p. 238—241°). The diazotised solution of this in aq. MeOH on heating and subsequent reduction with Zn and HCl gives dl-puketaine Me ether in small yield, the structure assigned to which (A., 1931, 749) is thus confirmed. It is resolved by d- and l-tartaric acids into the naturally-occurring l- (d-tartrate, m. p. 232°, [α]_D -146°, -149.1° in 25% EtOH) and the d-Me ether, m. p. 136°, [α]_D +256.4° in EtOH (l-tartrate, m. p. 225°).

H. A. PIGGOTT.

Synthesis of l-laureline. E. SCHLITTLER (Helv. Chim. Acta, 1932, 15, 394—402).—2-Nitro-4-methoxyphenylacetohomopiperonylamine, m. p. 165°, gives with P_2O_5 in toluene 2'-nitro-4'-methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisquinoline, m. p. 139°, the methiodide, m. p. 224° (decomp.), of which is reduced by Zn and HCl to 2'-amino-4'-methoxy-6:7-methylenedioxy-1-benzyl-2-methyltetrahydroisquinoline (dihydrochloride, m. p. 225—228°). Thermal decomp. and subsequent reduction (Zn and HCl) of the diazonium salt of this gives dl-laureline, resolved by tartaric acid into l- (identical with the natural product) and d-laureline, m. p. 114°, [α]_D +97.6°

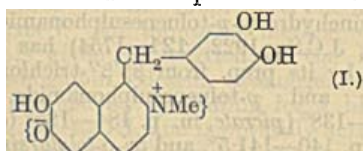
[l-tartrate, m. p. 210° (decomp.)]. The synthetic and the natural products give identical products as a result of Hofmann degradation (cf. A., 1931, 749).

H. A. PIGGOTT.

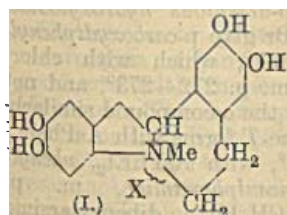
Photochemical reaction between quinine and dichromic acid. I. Quantum yields. G. S. FORBES, L. J. HEIDT, and C. G. BOISSONNAS.—See this vol., 480.

Alkaloids of *Phaeanthus ebracteolatus* (Presl), Merrill. II. Pheanthine. A. C. SANTOS (Ber., 1932, 65, [B], 472—474).—The optically inactive methine base A, m. p. 173°, obtained by the Hofmann degradation of pheanthine, is slowly oxidised by KMnO_4 in COMe_2 to 2-methoxy-1:1'-diphenyl ether 4:5'-dicarboxylic acid, m. p. 313°, also obtained by oxidising pheanthine successively in acid and alkaline solution. The alkaloid appears therefore to have the composition $\text{C}_{37}\text{H}_{38}\text{O}_6\text{N}_2$. H. WREN.

Preliminary synthetic experiments in the morphine group. III. Some derivatives of papaveroline and laudanosoline. Z. KITASATO and R. ROBINSON. **IV. Dehydro-derivative of laudanosoline hydrochloride and its constitution.** R. ROBINSON and S. SUGASAWA (J.C.S., 1932, 785—789, 789—805).—III. *Papaveroline hydriodide*, m. p. 230° (decomp.), is converted by I into an iodo-derivative, m. p. about 202° (decomp.), and the *hydrochloride*, m. p. about 250° (decomp.), on treatment with BzCl in $\text{C}_5\text{H}_5\text{N}$ gives *O-tetrabenzoylpapaveroline*, m. p. 148°. *N-Methylpapaverolinium chloride*, m. p. 264° (decomp.) (lit. 235°), prepared from the iodide, m. p. 208° (decomp.) (lit. 77°), when heated in $\text{C}_5\text{H}_5\text{N}$ gives *anhydro-N-methylpapaverolinium hydroxide*, m. p. above 300° [picrate, m. p. 210° (decomp.)], with BzCl and anhyd. $\text{C}_5\text{H}_5\text{N}$ affords *anhydro-N-methyl-O-tribenzoylpapaverolinium hydroxide* (I), m. p. about 217°, and with BzCl and moist $\text{C}_5\text{H}_5\text{N}$ yields *N-methyl-O-tetrabenzoylpapaverolinium chloride*, m. p. 180°. The corresponding derivatives of laudanosoline are: *hydrochloride*, m. p. 244°; *sulphate*, m. p. 267° (decomp.) (lit. 230°); *hydriodide*, decomp. 239°; *hydrobromide*, m. p. 230°; *O-tetrabenzoyl-laudanosoline picrate*, m. p. 212°, and *hydrochloride*, m. p. 190°. The suggested formula for the phenol-betaine (I) is:



IV. Oxidation of laudanosoline hydrochloride with chloranil in presence of KOAc gives 2:3:11:12-tetrahydroxy-8-methylidibenzotetrahydropyrrocolinium hydrochloride (I), (+1H₂O), m. p. 303—305°, which on acetylation affords a mixture of 2:3:11:12-tetraacetoxydibenzo-tetrahydro-pyrrocoline (II), m. p. 148°, and -dihydropyrrocoline (III), m. p. 215°, (II) being converted by dehydrogenation into (III). (III) gives the typical colour reactions of an indole. Methylation of (I) yields



2:3:11:12-tetramethoxy-8-methylidibenzotetrahydropyrrocolinium iodide (IV), m. p. 242—243° (decomp.) (from the methosulphate, m. p. 222—226°), and from the chloride, m. p. 225° (decomp.), 2:3:11:12-tetramethoxydibenzodihydropyrrocoline, m. p. 201—203°, is obtained. The methosulphate of (IV) gives by either the Hofmann or Emde degradation, 5:6-dimethoxy-2-(3':4'-dimethoxy-6'-vinylphenyl)-1-methyldihydroindole, m. p. 126—127°, hydrogenated to the corresponding (-ethylphenyl) derivative (V), m. p. 92—93°, and in the next stage of the Hofmann degradation affords 6-dimethylamino-3:4:3':4'-tetramethoxy-6'-vinylstilbene (VI), m. p. 109—110° (reduced to -ethylstilbene, m. p. 123—124°). 6-Dimethylamino-3:4:3':4'-tetramethoxy-6'-ethyl-αβ-diphenylethane (VII), m. p. 65°, may be obtained either from (V) by the Emde degradation or by catalytic reduction of (VI). Further degradation of (VII) through the methosulphate gives 3:4:3':4'-tetramethoxy-6'-ethyl-αβ-diphenylethane, m. p. 78° (chloroaurate, m. p. 248—250°), confirmed by its formation by catalytic hydrogenation of the final exhaustive methylation degradation product of laudanosine. The prep. is described of the following: 3:4-dihydropapaverine methiodide, m. p. 191—193°; dl-tetrahydropalmatine methiodide, by different methods, m. p. 215° and 261—263° (decomp.); and penta-acetyltetrahydropapaverine, m. p. 109—110°. F. R. SHAW.

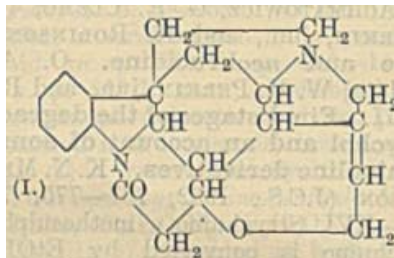
Strychnine and brucine. XVI. neoStrychnine. O. ACHMATOWICZ, G. R. CLEMO, (the late) W. H. PERKIN, jun., and R. ROBINSON. **XVII. neoBrucine and neobrucidine.** O. ACHMATOWICZ, (the late) W. H. PERKIN, jun., and R. ROBINSON. **XVIII. Final stages of the degradation of dinitrostrychol and an account of some nitrohydroxyquinoline derivatives.** K. N. MENON and R. ROBINSON (J.C.S., 1932, 767—775, 775—780, 780—784).—XVI. Strychnine methosulphate or methylstrychnine is converted by EtOH-NaOEt into *ethoxy-*, m. p. 158—159°, and by MeOH-NaOMe into *methoxy-methylidihydroneostrychnine* (I), m. p. 141—143°, and in each case neostrychnine has also been isolated as *methylneostrychninium iodide*, m. p. 325° (decomp.) [prepared from (I) and MeI]. (I) is reduced by H_2 in presence of PdCl_2 to *dihydromethoxy-methylidihydroneostrychnine*, m. p. 174°, and at a Pb cathode to *methoxymethyltetrahydrostrychnidine* (cf. A., 1927, 888). *Methylneostrychninium chloride* (+1MeOH), m. p. 289—290°, prepared from the corresponding iodide or from the base and HCl , forms on careful heating *neostrychnine*, m. p. 228—229°, which gives with H_2O_2 *neostrychnine N-oxide* (+3H₂O), m. p. 179—180°. *neoStrychnine* is hydrogenated similarly to, but less easily than, strychnine to dihydrostrychnine, and reduced electrolytically to *neostrychnidine*, *tetrahydroneostrychnine*, m. p. 167—168°, and *hexahydrostrychnine*, indicating that the double linkings in *neo-strychnine* and *-strychnidine* are situated in like positions and the movement of the unsaturated linking is not influenced by the lactam-CO of strychnine (in confirmation, *neostrychnine* and PhCHO give *benzylideneneostrychnine*, m. p. 158—159°). *Benzylstrychninium chloride* has m. p. 303—305° and *benzylstrychnine* (+9½H₂O), m. p.

270°. *neo*-Strychnine and -strychnidine possess the physiological properties of strychnine.

XVII. Brucidine and CH_2PhCl afford *benzylbrucidinium chloride*, m. p. 305—307° (decomp.), converted by MeOH-KOMe into *methoxybenzyl-dihydrobrucidine* (I), m. p. 159—160° (methiodide (?), m. p. 249—250°), and *neobrucidine*, identical with methyl- ψ -brucidine (cf. A., 1927, 889). Electrolytic reduction of (I) gives *methoxybenzyltetrahydrobrucidine*, m. p. 107—108°. *Benzylneobrucidinium iodide*, m. p. 260—261° (decomp.), obtained from the sulphate, yields the corresponding chloride, which on heating gives CH_2PhCl and *neobrucidine*. This can be reduced as for *neostrychnidine* to give *dihydrobrucidine* ($+\text{COMe}_2$), m. p. 172—173°, which is not identical with methyl- ψ -dihydrobrucidine.

Benzylbrucinium chloride ($+2\frac{1}{2}\text{H}_2\text{O}$), m. p. 275—280° (decomp.), gives with KOH *benzylbrucine* ($+1\frac{1}{2}\text{H}_2\text{O}$), m. p. 195—196°. *Methoxymethyl-dihydro-neobrucine*, m. p. 204—205°, from methylbrucine and MeOH-NaOMe , is converted successively into the sulphate, *methylneobrucinium iodide* ($+1\text{MeOH}$), m. p. 302—306° (decomp.), and the *chloride*, m. p. 255—260° (decomp.), which loses MeCl on heating to give *neobrucine*, m. p. 225—226°, catalytically reduced to dihydrobrucine.

XVIII. 5:7-Dinitro-2-indolylurethane (A., 1931, 750) is hydrolysed to *-2-aminoinsole*, m. p. 265°, which in acid solution with NaNO_2 affords *-isatin-3-oxime*, m. p. 252° (also obtained from dinitroisatin



and NH_2OH). The suggested formula for strychnine on the indole basis is (I)

Carbostyryl-3-carboxylic acid is nitrated to the 6:8-dinitro-derivative, m. p. 240°, of which the *Et* ester, m. p. 210°, is converted into the hydrazide, m. p. 255°, and the azide, m. p. 95° (decomp.), from which 6:8-dinitro-2-hydroxyquinolyl-3-urethane, m. p. 239°, is obtained, converted by NaOH into 6:8-dinitro-3-amino-2-hydroxyquinoline, m. p. 239°. 3-Nitroindole-2-carboxylic acid, m. p. 232°, prepared by nitration of the corresponding acid, cannot be further nitrated and 6-nitro-2-hydroxy-4-ethoxyquinoline-3-carboxylic acid, m. p. 285° (decomp.), behaves similarly. *Et* 2:3-dihydroxyquinoline-4-carboxylate is nitrated to the 6-nitro-acid, m. p. 212° (decomp.), which cannot be further nitrated. 6-Nitrocoumarin-3-carboxylic acid, m. p. 234° (decomp. at 260°), is also described.

F. R. SHAW.

Organic compounds of arsenic. XVI. Fission of dihalides of cyclic arsenic and antimony derivatives. W. STEINKOFF, I. SCHUBART, and J. ROCH (Ber., 1932, 65, [B], 409—412).—Methylcyclopentamethylenearsine is converted by Cl_2 in light petroleum into the *dichloride*, m. p. above 120°, which decomposes

at about 166° into *As cyclopentamethylene chloride*, b. p. 84—86°/13 mm. *As cyclopentamethylenethiocyanate*, from the chloride and NaCNS in COMe_2 , has b. p. 144—146°/11 mm. The Grignard compound of α -dibromopentane and AsMeCl_2 afford *methylcyclopentamethylenearsine*, converted into the *dichloride*, m. p. 112—115°, which decomposes at about 135° into *As cyclopentamethylene chloride*, b. p. 77°/18 mm. α -Tetramethyldiarsinopentane, from the Grignard derivative of α -dichloropentane and AsMe_2Cl in Et_2O , has b. p. 125—130°/14 mm. CNBr and SbPhMe_2 in anhyd. Et_2O afford *Sb Ph Me}_2* *cyano-bromide*, m. p. 135°, yielding at 150° MeBr and *Sb Me Ph cyanide*, b. p. 115—120°/high vac. SbPhMe_2 and Cl_2 in CCl_4 give the corresponding *dichloride*, passing at 210° into SbMe_2Cl and SbPh_2Cl . $(\text{SbPh}_2)_2\text{O}$ is converted by conc. HCl and anhyd. HCN , respectively, into the corresponding chloride, m. p. 67—68°, and *cyanide*, m. p. 115—116°. The Grignard compound from α -dichloropentane and SbMeCl_2 in anhyd. Et_2O afford *methylcyclopentamethylenestibine*, b. p. 73—73.5°/17 mm.; the corresponding *dichloride* suffers decomp. at 160—185° into MeCl and *Sb cyclopentamethylene chloride*, b. p. 110—111°/13 mm.

H. WREN.

Arsenical derivatives of phenols. F. L. VODRET *Annali Chim. Appl.*, 1932, 22, 49—59).—1:3-Dihydroxybenzene-6-azo-*p*-phenylarsinic acid (*K*, *Pb*, and *Ag* salts) (cf. Berlingozzi and Liguori, A., 1931, 105) may be obtained by mixing alkaline solutions of nitrosoresorcinol and *p*-aminophenylarsinic acid. *Thymol-6-azo-*p*-phenylarsinic acid*, $\text{O}:\text{As}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_2\text{MePr}^s\cdot\text{OH}$ (*K*, *Pb*, and *Ag* salts), is obtained from either thymol and diazotised *p*-aminophenylarsinic acid or nitrosothymol and *p*-aminophenylarsinic acid. *Carvacrol-6-azo-*p*-phenylarsinic acid* (*K*, NH_4 , and *Pb* salts) is also obtainable by both methods. *Eugenol-* (*K*, NH_4 , *Ag*, and *Pb* salts) and *isoeugenol-6-azo-*p*-phenylarsinic acid* (*K*, NH_4 , *Ag*, and *Pb* salts) are also obtainable by both methods.

T. H. POPE.

Polarity of the co-ordinate linking. I. Constitution of the arsinimines. F. G. MANN (J.C.S., 1932, 958—972).—The constitution of $\beta\beta'\beta''$ -trichlorotrivinylarsinehydroxy-*p*-toluenesulphonamide (Mann and Pope, J.C.S., 1922, 121, 1754) has now been confirmed by its prep. from $\beta\beta'\beta''$ -trichlorotrivinylarsenoxide and *p*-toluenesulphonamide. *Tri-*p**, m. p. 137—138° [*picrate*, m. p. 184—185° (decomp.)], *tri-m*, m. p. 140—141.5°, and *tri-o*-tolylarsinehydroxy-*p*-toluenesulphonamide, m. p. 98—104°, have also been prepared by the two methods and behave as salts. *p*-Carboxyphenylmethylidoarsine, m. p. 173—175° (decomp.), prepared from *benz-p*-arsinic acid, m. p. above 300° (*benz-p*-arsenious hydroxyiodide, m. p. 92—94°), and MgPhBr give *p*-carboxyphenylmethylarsine, m. p. 155—157°, which with chloramine-*T* yields the *oxide*, m. p. 272—273°, and not the hydroxysulphonamide; the *o*-compound similarly gives the *oxide*. Chloramine-*T* forms with AsPhMe_2 the *oxide*, m. p. 159—161°, with AsPhEt_2 *phenyl-diethylarsinehydroxy-*p*-toluenesulphonamide*, m. p. 100—103°, and with $\text{As}(\text{CH}_2\text{Ph})_3$ *dibenzylarsinic acid* and the *oxide*, m. p. 228—230° (lit. 219—220°).

The compound obtained by Mann and Pope (*loc. cit.*) by the action of chloramine-*T* on AsPh_3 is probably $(\text{C}_6\text{H}_7\text{SO}_2\text{NH}\cdot\text{AsPh}_3)_2\text{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_7$. *Triphenylarsine-hydroxybenzenesulphonamide*, m. p. 151–153°, has also been prepared. The constitution of the above compounds is discussed.

Thiodiglycol and chloramine-*T* afford $\beta\beta'$ -*dihydroxy-diethylsulphine-p-toluenesulphonylimine*, m. p. 86–88°, $(\text{C}_2\text{H}_4\cdot\text{OH})_2\text{S}\rightarrow\text{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{H}_2\text{O}$, since it cannot be prepared from $\beta\beta'$ -*dihydroxydiethyl sulphoxide*, m. p. 110–111°, and *p*-toluenesulphonamide. Thiodiglycol is oxidised to the sulphoxide by benzene-sulphonchlorosodioamide, which can, however, give a sulphilimine, forming *diethyl*, m. p. 114–116°, and *methyl-ethyl-sulphinebenzenesulphonylimine*, m. p. 92–94°.

F. R. SHAW.

Gliadin. K. FELIX and H. REINDL (*Z. physiol. Chem.*, 1932, 205, 11–19).—If moisture is rigidly excluded, gliadin can be esterified with MeOH and HCl without decomp. The OMe content of the ester may be used to characterise the protein. The free carboxyl of gliadin (from the OMe content) amounts to 19.54×10^2 equiv. per 100 g. of protein, the acid-binding basic groups (from the Cl content of the ester hydrochloride) to 12.3×10^{-2} equiv.

J. H. BIRKINSHAW.

Clupein. III. K. DIRR and K. FELIX (*Z. physiol. Chem.*, 1932, 205, 83–92; cf. A., 1931, 245).—Benzoylation of clupein ester hydrochloride at p_H 8–9 yields *benzoylclupein B* (I), decomp. about 240° (anhyd.), containing probably 12 Bz groups per min. mol. wt. corresponding with the monoamino-acid and arginine content. A portion of the Bz is attached to the guanidine groups, the rest is probably linked to O. On warming with Ac_2O , (I) yields *benzoylacetylclupein* (containing 8 Ac groups) which on acid hydrolysis affords ornithine, indicating that the free CO_2H is attached to an arginine mol. Chlorobenzoyl chloride and clupein gave a *chloro*-derivative of (I).

J. H. BIRKINSHAW.

Place of histidine in the protein molecule. G. J. BOONE (*Med. Bull. Univ. Cincinnati*, 1931, 6, 193–205).—An improved electrodialysis apparatus and a method for the prep. of cryst. haemoglobin are described. An improved method of isolating histidine is given. A portion of the histidine in cryst. haemoglobin, edestin, caseinogen, and Witte's peptone is removed by boiling for 1 hr. with 5% NaOH in abs. EtOH, and is optically active. Hence it probably occupies a terminal position in the protein mol. with its carboxyl group free. Subsequent acid hydrolysis of the hydrolysate from the alkaline digestion gave a larger yield of largely racemised histidine.

CHEMICAL ABSTRACTS.

Structure of proteins. XI. Degradation of caseinogen in [hot] resorcinol. Identity of the products with those obtained by heating with glycerol. The conception of acropeptides. A. FODOR and S. KUK (*Biochem. Z.*, 1932, 245, 350–361; A., 1931, 1436).—When caseinogen is heated in resorcinol at 130–150° for 3–6 hr. various polypeptides having different mol. wt. but otherwise chemically identical can be isolated. Such poly-

peptides may be called *acropeptides*. One of them is identical with the substance $\text{C}_{41}\text{H}_{67}\text{O}_{12}\text{N}_9$ previously obtained in the glycerol method. Evidence indicating that gelatin also may contain acropeptides is available. The probable constitutional formula of an acropeptide is given.

W. McCARTNEY.

Constitution of the keratin molecule. C. RIMINGTON (*Nature*, 1932, 129, 580–581).—A discussion (cf. this vol., 184).

L. S. THEOBALD.

Detection of oxygen in liquid organic compounds. H. WUSTNER (*Z. anal. Chem.*, 1932, 87, 114–116).—When I is dissolved in an anhyd. org. liquid the solution is brown if the mol. contains O and violet if O is absent. The violet solution of I in CHCl_3 gradually turns brown with progressive addition of PhOH, showing that I has a greater affinity for substances containing O than for those free from O.

A. R. POWELL.

Micro-analytical identification of organic substances. V. STANÉK and T. NEMES (*Chem. Ztg.*, 1932, 56, 285–287).—The compound is decomposed with KIO_3 and H_2SO_4 and the KIO_3 remaining after complete combustion is determined with $\text{Na}_2\text{S}_2\text{O}_3$. The theoretical oxidation val. can be calc. from the supposed formula. The method is rapid, accurate, and particularly useful in differentiating between substances having only small differences in composition. N is quantitatively converted into NH_3 and S into H_2SO_4 .

E. H. SHARPLES.

Determination of chlorine and bromine in organic compounds acidimetrically. I. Micro-analysis. F. VIEBOCK (*Ber.*, 1932, 65, [B], 493–501).—The substance (=1.5–3 mg. Cl or 5 mg. Br) is gently heated with $\text{K}_2\text{Cr}_2\text{O}_7$ (0.5–1 g.) and a solution of Ag_2SO_4 in conc. H_2SO_4 (10 g. in 400 g.). The gases ($\text{Cl}_2 + \text{ClO}_2$ or Br) are driven by a current of air into about 3% H_2O_2 neutralised to Me-red. Reaction occurs: $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^-$ and $\text{HClO} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Cl}^- + \text{H}_2\text{O} + \text{O}_2$ or $2\text{ClO}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{HClO}_2 + \text{O}_2$; $\text{HClO}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Cl}^- + 2\text{H}_2\text{O} + \text{O}_2$. The liberated HCl (HBr) is titrated with 0.01N-NaOH. As control, CO_2 -free H_2O , equal to the vol. of the titrated liquid, is mixed with 10 c.c. of $\text{Hg}(\text{CN})(\text{OH})$ solution and as much 0.01N-HCl as 0.01N-alkali was used in the titration. The liquid is mixed with 10 c.c. of $\text{Hg}(\text{CN})(\text{OH})$ solution and titrated with 0.01N- H_2SO_4 until both solutions have the same tint with equal amounts of indicator. The reaction is $2\text{Hg}(\text{CN})(\text{OH}) + 2\text{NaCl} \rightarrow \text{Hg}(\text{CN})_2\cdot\text{HgCl}_2 + 2\text{NaOH}$. For the determination of Br the use of a comparison solution is unnecessary.

H. WREN.

Volumetric determination of reducing sugar. E. HADDON (*Rev. agric. Maurice*, 1931, 181).—The clarified, but not deleaded, solution (100 c.c.) is treated with 4 drops of 1% methylene-blue solution; Fehling's solution (5 or 10 c.c.) is treated with 10% $\text{K}_2\text{Fe}(\text{CN})_6$ solution (2 or 4 c.c.) and titrated hot with the sugar solution until the blue colour disappears.

CHEMICAL ABSTRACTS.

Identification of acids. I. Phenacyl esters. K. CHEN. II. *p*-Bromophenacyl esters. K. CHEN and C. SHIH (*Trans. Science Soc. China*, 1931,

7, 73—80, 81—87).—I. Phenacyl esters of 26 aromatic acids have been prepared. Phenacyl 3:5-dinitrosalicylate is a powerful explosive. *p*-Nitrophenoxyacetic acid is a sensitive indicator, changing from yellow (alkali) to colourless (acid) at p_H 7.2.

II. 16 esters were studied. Bromophenacyl bromide is recommended for the identification of acids.

CHEMICAL ABSTRACTS.

Microchemical reactions of vanillin and piperonal. M. WAGENAAR (Pharm. Weekblad, 1932, 69, 190—193).—Characteristic reactions suitable for micro-manipulation are described. S. I. LEVY.

New colour test for cysteine. E. DYER and O. BAUDISCH (J. Biol. Chem., 1932, 95, 483—489).—

Cysteine, in concns. of more than 10 p.p.m., may be detected in the presence of cystine, glutathione, and many other S- and N-containing substances by shaking its slightly acid solution with a CHCl_3 solution of *o*-benzoquinone for 2 min., when a deep red colour is developed in the CHCl_3 layer.

H. DAVSON.

Volumetric analysis of mercaptobenzthiazole and its derivatives. K. KOJIMA, I. AOE, and I. NAGAI (J. Rubber Soc. Japan, 1931, 3, 331—339).—Direct titration in EtOH with NaOH is satisfactory; the iodometric method gives results varying between 99.36 and 107.8%. Both methods can be applied to NH_4 and metallic derivatives except Pb and Zn salts.

CHEMICAL ABSTRACTS.

Biochemistry.

Manometric analysis of gas mixtures. III. Determination of carbon dioxide tension and [plasma] p_H of blood. D. D. VAN SLYKE, J. SENDROY, jun., and S. H. LIU (J. Biol. Chem., 1932, 95, 547—568).—The CO_2 pressure in blood is determined by equilibrating, in a special tonometer, a bubble of gas containing CO_2 and O_2 at pressures approx. the same as in venous or arterial blood. The bubble is then analysed for CO_2 (cf. this vol., 488). The max. error is ± 2.5 mm. CO_2 . The plasma- CO_2 content of the same sample is determined, and using previously determined consts. (A., 1928, 1150, 1268), the plasma- p_H is calc. The val. obtained agrees with electrometric determination to within ± 0.04 p_H .

J. B. BATEMAN.

Effect of the breathing of carbon dioxide on the gas metabolism of diseased, healthy, and trained persons. H. HERXHEIMER and R. KOST (Arch. exp. Path. Pharm., 1932, 165, 101—110).—In normals breathing air containing about 2.5—4% CO_2 , little rise in the O_2 consumption accompanied the increased depth and rate of breathing, but a marked retention of CO_2 took place so that the R.Q. fell. In trained persons the degree of retention was less, whilst in diseased considerable variation was observed, retention being particularly marked in decompensated heart disease. W. O. KERMAK.

Purification of benzidine, and an improved reagent for hæmoglobin determination. F. C. BING (J. Biol. Chem., 1932, 95, 387—388).—Benzidine, used in the determination of hæmoglobin (A., 1931, 1175), is purified by dissolving in EtOH, filtering, and treating with charcoal at 40—60° until colourless. The solution is diluted with H_2O to 60 wt.-% EtOH and cooled until the benzidine crystallises. The reagent used in hæmoglobin determinations is made by dissolving 1 g. of the purified benzidine in 20 c.c. of glacial AcOH and adding 30 c.c. of H_2O and 50 c.c. of 95% EtOH. It is tested by mixing 2 c.c. with 1 c.c. of H_2O and 1 c.c. of 0.6% H_2O_2 . After 2 hr. dilution to 25 c.c. with 20% AcOH should produce a colourless solution. The previous technique is followed except that 2 hr. are allowed for full colour development.

H. DAVSON.

Oxygenation and physico-chemical properties of hæmocyanin of the snail. J. ROCHE (Compt. rend., 1932, 194, 1105—1106).—The p_H for oxy-hæmocyanin is 7.05 and for hæmocyanin 7.60.

P. G. MARSHALL.

Isoelectric point of fibrinogen. F. MAINZER (Biochem. Z., 1932, 246, 164—181).—The isoelectric point of human fibrinogen in solutions containing 0.1% of protein and 1% NaCl determined by cataphoresis is at p_H 5.5 and the centre of the zone of min. stability at p_H 4.36. This min. is determined by the protein:neutral salt ratio, decrease of protein or increase of neutral salt causing a displacement to the acid side. In unbuffered solutions, the isoelectric point is at p_H 5.43 and the zone of min. stability at p_H 4.9. Electrometric titration is not suited to determination of the isoelectric point of lyophobic protein which is pptd. at that p_H .

P. W. CLUTTERBUCK.

Isoelectric point of denatured fibrinogen. F. MAINZER (Biochem. Z., 1932, 246, 182—190).—The isoelectric point of human fibrinogen denatured with EtOH was in phthalate buffer at p_H 5.0 and in unbuffered solution at p_H 5.5, the centre of the instability zone being at p_H 4.0 and 5.5, respectively.

P. W. CLUTTERBUCK.

Determination of blood-catalase; catalase value and catalase index of normal human blood. W. MASCH (Z. ges. exp. Med., 1931, 77, 273—288; Chem. Zentr., 1931, ii, 2890).—Back and Zubkova's method is modified. H_2O_2 (perhydrol, 1.5%) is added immediately to the freshly prepared blood solution. Titration is carried out after 2 hr. The optimal temp. is 19—21°. The catalase val. (mg. H_2O_2 decomposed by 1 c.c. of blood) is: man 18.7—30.6 (average 24.9); woman 15.3—29.6 (average 21.8).

A. A. ELDRIDGE.

Blood-glycolysis. I. Effect of arsenate. S. MORGULIS and S. PRATO (J. Biol. Chem., 1932, 95, 621—631).—Sugar and lactic acid determinations show that in rabbit-blood glycolysis is increased, in dog-blood decreased, by arsenate. In both cases, however, arsenate causes an increase of inorg. $\text{PO}_4^{'''}$ by stimulation of blood-phosphatases.

J. B. BATEMAN.

Adenosinephosphoric acid (adenine-nucleotide) in blood and bile. Origin of endogenous uric acid in man. H. ROTHMANN (Z. ges. exp. Med., 1931, 77, 22—57; Chem. Zentr., 1931, ii, 2898).—The average amount of adenine-nucleotide in human blood is 15—18 mg. per 100 c.c., with limits of 10—28 mg. The val. is increased by administration of yeast-nucleic acid and decreased by that of fat. Low vals. are obtained in gout. There is probably a connexion with the endogenous uric acid val. Experiments on the administration of adenosinephosphoric acid suggest that a large part of the endogenous uric acid is derived from the degradation of adenosinephosphoric acid. Noteworthy quantities of this substance were found in bile.

A. A. ELDRIDGE.

Identification of glutathione in blood and tissue. C. MONCORPS and R. SCHMID (Z. physiol. Chem., 1932, 205, 141—153).—Of the iodometric methods for glutathione determination that of Gabbe (A., 1930, 1307) gives the most trustworthy results, but the King-Baumgartner-Page method (A., 1930, 493), which ordinarily gives high vals., can be made satisfactory by a strict control of the $\text{CCl}_3\text{-CO}_2\text{H}$ concn. employed. A final concn. of 6.5% is suitable. A control method depends on elimination of S by 30% NaOH in presence of Pb(OAc)_2 and spongy Pt. The PbS yields H_2S which is oxidised by H_2O_2 and determined as BaSO_4 .

J. H. BIRKINSHAW.

Extraction of the lipins of serum by ether-alcohol mixtures. A. MACHEBEUF and G. SANDOR (Compt. rend., 1932, 194, 1102—1104).—There is a definite optimum concn. (about 12%) of EtOH in $\text{Et}_2\text{O-EtOH}$ mixtures for extraction of the lipins of horse serum. Opalescence of the serum occurs with a concn. of 6% and again at >14%, the latter being due to denaturation of the proteins.

P. G. MARSHALL.

Rôle of strongly unsaturated fatty acids in the organism. N. BEREND (Biochem. Z., 1932, 246, 117—123).—The amount of strongly unsaturated acids, calc. as triarachidonate, in normal dog's blood is 18 mg. per 100 c.c. or 3.5—4% of the total fat. Of this arachidonate, 57% is present in the serum and the rest in the corpuscles. During starvation the vals. fall by 25% and at the height of fat resorption are increased by 25%. Milk contains 30—50 mg. per 100 c.c. of strongly unsaturated acids corresponding with 1—2% of the total fat. In pancreatic diabetes, the amount of triarachidonate decreases and of fat increases and large doses of insulin cause the vals. to return to normal.

P. W. CLUTTERBUCK.

Micro-determination of urea in animal fluids, particularly blood. B. MATSUMOTO (Biochem. Z., 1932, 246, 383—400).—In normal blood about half, and in the blood of rabbits poisoned with U 80% or more, of the residual N is present as urea. This can be determined (in 0.1 c.c.) by the method described. The deproteinised fluid is shaken in a vac. with alkaline aq. NaOBr and the vol. of N_2 liberated is measured.

W. MCCARTNEY.

Distillation of ammonia in the Folin and Wu method for the determination of urea in blood. R. C. LEWIS (Amer. J. Clin. Path., 1931, 1, 227—229).

—To avoid losses of NH_3 the lower end of the receiving tube should be kept cool. Paraffin prevents frothing.

CHEMICAL ABSTRACTS.

Determination of blood-chlorides using palladous nitrate as indicator. R. C. LEWIS and N. L. BRINKLEY (Amer. J. Clin. Path., 1931, 1, 231—235).—Sulphosalicylic acid is used as the protein precipitant and $\text{Pd(NO}_3)_2$ as the indicator in titrating excess of AgNO_3 with KI.

CHEMICAL ABSTRACTS.

Calcium content of human blood-corpuscles. M. R. RYMER and R. C. LEWIS (J. Biol. Chem., 1932, 95, 441—449).—From determinations of the whole blood- and plasma-Ca contents of normal and psychopathic individuals an average of 0.53 mg. of Ca per 100 c.c. of blood was found in the corpuscles.

H. DAVSON.

Micro-determination of calcium in blood. R. NORDBÖ (Biochem. Z., 1932, 246, 460—462).—The Ca in 0.2—0.3 c.c. of blood is pptd. with saturated aq. NH_4 oxalate, the dried ppt. is converted into carbonate by heating, first at 200—250° and then at 400—450°, the carbonate is dissolved in excess of 0.01N-HCl, and the excess is titrated with 0.01N-NaOH. 0.01 mg. of Ca can be determined with a max. error of 3%.

W. MCCARTNEY.

Determination of magnesium in blood-serum. N. V. KURILOVA and N. K. BOGOMAZ (Ukrain. Chem. J., 1931, 6, [Sci.], 207—211).—Ca is determined in 1 c.c. of serum by deWard's method, and the centrifugate and washings from the CaC_2O_4 are concd. to 2 c.c. in a centrifuge tube, to which 1 c.c. of 0.1% NH_4Cl and 2 c.c. of saturated Na phosphate previously made acid with HCl are added, and the solution is boiled. 5 c.c. of 2% NH_3 are added drop by drop to the hot solution, with stirring, when MgNH_4PO_4 ppts. 1 c.c. of conc. aq. NH_3 is then added, and the solution is left overnight for complete pptn., and centrifuged. The residue is washed twice with 2.5% aq. NH_3 and twice with 30% EtOH , and residual EtOH is removed by heating at 100°. The dry residue is dissolved in 2 c.c. of 0.001N- H_2SO_4 , 3 drops of cochineal extract are added, and excess of H_2SO_4 is titrated with 0.01N-alkali to a rose-red coloration, 1 c.c. of excess H_2SO_4 corresponding with 0.121 mg. of Mg. This method gives an error >2—3%.

R. TRUSZKOWSKI.

Micro-colorimetry. III. Determination of organically bound phosphorus. Analysis of phosphorus compounds in the blood. T. KUTNER and L. LICHTENSTEIN (J. Biol. Chem., 1932, 95, 661—670).—An aq. solution of the substance (equiv. to 0.01—0.04 mg. P) is digested with conc. H_2SO_4 with addition of H_2O_2 . The digest is cooled, diluted with H_2O , boiled to remove H_2O_2 , and the blue colour developed on addition of Na_2MoO_4 and SnCl_2 is compared with suitable standards. The application of the method to lipin-P in $\text{EtOH-Et}_2\text{O}$ or COMe_2 extracts of tissue and, together with the method for inorg. P (A., 1930, 725), to the complete analysis of the blood-P is described.

F. O. HOWITT.

Crystalline urease. II. Haemagglutinating properties of urease. M. HOTCHKISS and H. TAUBER (J. Immunol., 1931, 24, 287—292).—Solutions of cryst. urease produced agglutination of rabbit or

mouse, but not of sheep, erythrocytes, and remained active after the agglutination.

CHEMICAL ABSTRACTS.

Cold-hæmotoxin. IV. Cold, non-complementary hæmolysis caused by heated serum of cold-blooded animals. V. Cold, non-complementary hæmolysis by heated body fluids. K. TOSHIMA (J. Biochem., Japan, 1931, 14, 1—7, 9—23).—IV. Of the sera of cold-blooded animals studied, only that of the frog contains the substance responsible for the cold hæmolysis when the serum has been heated to a suitable temp. The cold-hæmotoxin of heated frog serum is strongest for horse, and weakest for pig or chicken, erythrocytes.

V. Human milk, urine, pleural exudate, and fluid from ovarian cysts are free from the substance causing cold-hæmolysis; heated human peritoneal exudate or transudate causes cold-hæmolysis of chicken, horse, and pig erythrocytes. Human or rabbit's saliva contains the cold-hæmolysis substance for horse and pig corpuscles, whilst rabbit's aq. humour and cerebrospinal fluid are active only for horse cells. Heated rabbit's pleural or peritoneal exudate causes strong, and pericardial exudate weak, cold-hæmolysis.

CHEMICAL ABSTRACTS.

Mechanism of blood-clotting. L. J. DEL BAERE (Biochem. Z., 1932, 246, 38—45).—By cataphoresis, thrombin is shown to have a positive and prothrombin a negative charge. Clotting is regarded as a pptn. of the negatively-charged fibrinogen with the positively-charged thrombin. By osmotic measurements it is shown that although the pptn. of serum-proteins under the action of thrombin does not, union between these substances does, occur.

P. W. CLUTTERBUCK.

Prevention of blood coagulation by cysteine. J. H. MUELLER and S. STURGIS (Science, 1932, 75, 140).—0.5 g. of cysteine hydrochloride prevents the coagulation of 2 c.c. of blood. Aeration of the blood containing cysteine eventually results in coagulation.

L. S. THEOBALD.

Preservation of paraffin sections of amphibian eggs stained by Bismarck brown and Nile-blue sulphate. P. WINTREBERT (Compt. rend., 1932, 194, 1013—1015).—An effective fixative is saturated picric acid containing 5% of HgCl_2 and 2% of phosphomolybdic acid. After immersion for 1 hr. the stains are rendered insol. in saturated picric acid containing 1.0—1.5% of phosphomolybdic acid. Subsequent dehydration and paraffin embedding must be rapidly performed. P. G. MARSHALL.

Conchiolin of shells. F. FRIZA (Biochem. Z., 1932, 246, 29—37).—The shell-conchiolin of *Mytilus edulis* and of the inner and outer layers of *Anodonta cygnea* contain, respectively, total N, 16.66, 15.41, 15.29; total S, 0.61, 0.75 (both layers); tyrosine 3.57, 3.33, 1.46; tryptophan 2.62, 2.62, 2.78; arginine, 5.28, 5.53, 5.31%. For *Pinna nobilis* the tryptophan content is 2.62%.

P. W. CLUTTERBUCK.

Quantitative composition of cartilagenous tissue. W. WINTER (Biochem. Z., 1932, 246, 10—28).—Pure nasal cartilage of the pig consists of glutin (42%), chondroitinsulphuric acid (41.23%),

ash (9.76%), and an unknown constituent (albuminoid 7.01%). Levene's view that chondroitinsulphuric acid consists of 2 mols. glycuronic acid + 2 mols. H_2SO_4 + 2 mols. $\text{AcOH} - 7\text{H}_2\text{O}$ is confirmed and the view that it consists of lutidinecarboxylic acid and chitose is rejected. Chitose arises by secondary reactions from glucosamine. P. W. CLUTTERBUCK.

Determination of the thiol group in tissues. J. D. GUTHRIE and F. WILCOXON (Contr. Boyce Thompson Inst., 1932, 4, 99—106).—The tissue is killed by boiling H_2O and is extracted with aq. EtOH. The extract is treated with S-saturated abs. EtOH in presence of a phosphate buffer solution (p_{H} 6.8). The H_2S produced is determined by aeration, the gas being trapped in $\text{Zn}(\text{OAc})_2$ solution, which is subsequently treated with *p*-aminodimethylaniline and FeCl_3 to produce methylene-blue. The latter is determined colorimetrically. The reducing power of tissue extracts as recorded by I titration was greater than that indicated by H_2S formation except in the case of yeast. The presence of reducing substances other than SH-compounds is presumed.

A. G. POLLARD.

Phosphagens and the origin of vertebrates. D. M. NEEDHAM, J. NEEDHAM, E. BALDWIN, and J. YUDKIN (Proc. Roy. Soc., 1932, B, 110, 260—294).—The occurrence and body-distribution of arginine- and creatine-phosphoric acids in invertebrates were investigated. Argininephosphate is found in all phyla. The functional significance of the phosphagen in *Nereis* is shown by its decrease with heat rigor or on electrical stimulation. Argininephosphate is associated with ciliary as well as with muscular activity. Creatinephosphate is not confined to the vertebrates but is also found in certain invertebrates, e.g., *Strongylocentrotus* and *Balanoglossus*. F. O. HOWITT.

Anserine in mammalian skeletal muscle. W. A. WOLFF and D. W. WILSON (J. Biol. Chem., 1932, 95, 495—504).—Anserine is present in the muscles of the dog, cat, rabbit, and white rat and absent from horse muscle. H. DAVSON.

Mendel and Goldscheider's method for the determination of lactic acid in muscle. A. HANSEN and O. RIESSER (Biochem. Z., 1932, 246, 471—481; cf. Mendel and Goldscheider, A., 1926, 212).—The criticism of Matakas (A., 1931, 1320) notwithstanding, the method of Mendel and Goldscheider is to be preferred to others provided that the quality of the standard solutions and particularly of the conc. H_2SO_4 used is controlled.

W. MCCARTNEY.

Oil from the giant lizard (*Varanus salvator*, Laur.). L. VAN ITALLIE, W. J. VAN EERDE, and A. HARMSMA (Pharm. Weekblad, 1932, 69, 271—276).—The properties, consts., and colour reactions are recorded. The oil consists chiefly of the glycerides of oleic, palmitic, and stearic acids. Esters of formic, acetic, octoic, and a higher highly-unsaturated acid are also present. S. I. LEVY.

Cephalin. I—IV. K. NAKAMURA (Med. Bull. Univ. Cincinnati, 1931, 6, 158—183; Sei-i-kwai Med. J., 1927, 46, No. 491, 1—49).—I. A nephelo-

metric method for the determination of cephalin in the Et_2O extract of blood or plasma is described.

II. Normal cephalin contents of blood and plasma, respectively (mg. per 100 c.c.), are: rabbit 68—94, 60—70; man 90—110, 65—75. The cephalin content is temporarily increased after meals.

III. Whole blood-cephalin is independent of -urea. The ratio plasma: whole blood-cephalin is greater in nephritis than in cardiac cases.

IV. Blood-cephalin is high in cardiac diseases and nearly normal or lower in nephritis; when both kidneys and heart are affected intermediate vals. are obtained.

CHEMICAL ABSTRACTS.

Cephalin. IV. Fatty acids of cephalin from human brain. I. H. PAGE and H. RUDY (*Z. physiol. Chem.*, 1932, 205, 115—125; cf. this vol., 415).—Brain-cephalin was hydrolysed and the acids were examined. 30% of the total fatty acids was present as stearic acid. The unsaturated acids were separated by fractionation of the bromides. The highly-unsaturated C_{22} acids (22%) probably have 4 or 5 double linkings; they give docosoic acid on hydrogenation. The C_{18} acids (about 22%) were not further characterised. A C_{20} acid may be present.

J. H. BIRKINSHAW.

Use of the spark and arc in histospectrography. A. POLICARD and A. MOREL (*Compt. rend.*, 1932, 194, 1015—1017).—More rapid and complete results are obtained by the use of an arc. The distinction is useful in determining the degree of firmness with which an element is bound; the spark reveals the presence of Fe in liver tissue, but not in blood, whilst the arc indicates its occurrence in both.

P. G. MARSHALL.

Micro-determination of silica in tissues. J. C. MORGAN and E. J. KING (*J. Biol. Chem.*, 1932, 95, 613—620).—The tissue is ashed, the SiO_2 dehydrated by heating with 70% HClO_4 , and the pure SiO_2 collected. The SiO_2 residue and crucible are weighed after heating with H_2SO_4 , the SiO_2 is volatilised with HF, and the wt. of the crucible determined. Determinations of SiO_2 in cow and rabbit lung and in silicotic lung are given.

J. B. BATEMAN.

Tyrosine content of cocoons of various moths. A. K. SILBERMAN and H. B. LEWIS (*J. Biol. Chem.*, 1932, 95, 491—494).—The cocoons examined fell into two classes, those with a tyrosine content of 9—11%, characteristic of silk fibroin, and those with a low tyrosine content, characteristic of many common proteins.

H. DAYSON.

F. p. of milk and its relation to protein coagulation by lactic acid and by rennin. M. SAITO (*Bull. Miyazaki Coll. Agric.*, 1931, 3, 9—20).—Milk of Holstein cows had average f. p. -0.555° ; that of Japanese cows had f. p. -0.551° . Milk of acidity $>0.18\%$ shows a depression of f. p. approx. proportional to the increase in acidity. Lactic acid is not the only factor governing the depression. Coagulation of milk by rennin causes a slight elevation of f. p.; heating at $95-100^\circ$ for 2 hr. has no effect.

CHEMICAL ABSTRACTS.

Dialysable nitrogenous constituents of fresh milk. M. SAITO (*Bull. Miyazaki Coll. Agric.*, 1931,

3, 1—7).—A nitrogenous substance in the residue from the dialysis of milk was pptd. with phosphotungstic acid and gave a ninhydrin reaction, but not the biuret or other protein reactions. The N content (20% $\text{NH}_3\text{-N}$) was 2.3—2.8% of the total N of fresh milk. Boiling milk increased the $\text{NH}_3\text{-N}$; lactic fermentation increased $\text{NH}_3\text{-}$ and $\text{NH}_4\text{-N}$ in the dialysed residue, whilst ultra-violet irradiation was without influence. Coagulation of milk decreased the diffusible N-substance.

CHEMICAL ABSTRACTS.

Phosphorus content of caseinogen. R. E. L. BERGGREN (*J. Biol. Chem.*, 1932, 95, 451—460).—Milk is dialysed against H_2O for varying periods and the P:N ratios of the milk are plotted against time of dialysis and the P:N ratio of the caseinogen pptd. from it. The lowering of the P:N ratio on dialysis depends on the of the milk and is due to the loss of phosphates, showing that the P in caseinogen is loosely bound. The results cast doubts on the homogeneity of caseinogen.

H. DAVSON.

Application of the Fiske-Subbarow colorimetric method to determination of phosphorus in caseinogen. R. E. L. BERGGREN (*J. Biol. Chem.*, 1932, 95, 461—464).—To 1.5 g. caseinogen, 30 c.c. of 0.1N-NaOH are added, and the solution is made up to 100 c.c. 1 c.c. is evaporated to dryness and heated. A few drops of H_2O and one drop of saturated $\text{Mg}(\text{NO}_3)_2$ solution are added and the solution is evaporated to dryness and the residue heated until white. Nitrites are removed by washing with 2 c.c. of H_2O , adding one drop of conc. HCl to the residue, warming, and rinsing with H_2O . To the washings are added 2.5 c.c. of a 2.5% solution of NH_4 molybdate in 5N- H_2SO_4 , and 1 c.c. of aminonaphtholsulphonic acid reagent. The solution is made up to 25 c.c. and compared with a standard.

H. DAVSON.

Factors influencing the changes in oxidation-reduction potential on the reduction of methylene-blue in milk. A. C. FAY and G. A. AIKINS (*J. Agric. Res.*, 1932, 44, 71—83).—Methylene-blue in milk is reduced when a certain potential zone is reached. The blue colour and the initial potential are restored by shaking or by aspirating with air.

W. G. EGGLETON.

Effect of light on the reduction of methylene-blue in milk. G. A. AIKINS and A. C. FAY (*J. Agric. Res.*, 1932, 44, 85—95).—Reduction of methylene-blue by light is a reaction distinct from that induced by bacteria.

W. G. EGGLETON.

Stability of calcium in saliva and blood. M. FETTERLY and G. H. MAUGHAN (*Amer. J. Hyg.*, 1931, 14, 723—725).—Irradiation did not affect salivary Ca. A winter decrease in serum-, but not in salivary, Ca is indicated; the decrease is unaffected by irradiation. Salivary- is unrelated to serum-Ca.

CHEMICAL ABSTRACTS.

Inorganic composition of the parotid saliva of the dog and its relation to the composition of the serum. E. J. DE BEER and D. W. WILSON (*J. Biol. Chem.*, 1932, 95, 671—685).—The composition of saliva from the parotid glands of anæsthetised dogs following administration of pilocarpine and that

of blood taken simultaneously from the external jugular veins were determined. The concns. of CO_2 , Ca, and K in the saliva were higher and those of Na and Cl lower than in the serum. Intravenous injection of CaCl_2 or Na_2CO_3 produced an increase in the levels of the respective ions in both blood and saliva, and whereas injections of NaCl, KCl, or K_2CO_3 did not materially affect the composition of the saliva, those of HCl or Na_2CO_3 resulted in an increase of its p_{H} . Thus saliva is not a simple transudate or dialysate, nor is there any equality between the osmotic pressures of the serum and saliva.

F. O. HOWITT.

Pharmacology of bile secretion. IV. Excretion of substances in the bile. E. STRANSKY (Z. ges. exp. Med., 1931, 77, 807—841; Chem. Zentr., 1931, ii, 3353).—Parenteral administration of K, Na, Ca, Mg, Fe, NH_3 , Cl, SO_4 , HPO_4 , or urea leads to little or no increase in excretion in the bile; excretion of HCO_3' is, however, increased. Normally PhOH , $\text{H}_2\text{C}_2\text{O}_4$, and COMe_2 are present in traces; on administration they are excreted in noteworthy quantities. No definite rule governs the excretion of substances not present normally in the body. The bile is insignificant as a mode of excretion, but the hepatic secretion is important in mineral economy. The excretion of all the ions and of urea was increased by chologogues.

A. A. ELDRIDGE.

Secretory function of the liver. IV. J. G. VALDECASAS (Pfluger's Archiv, 1931, 228, 310—321; Chem. Zentr., 1931, ii, 3010).—Sulphonic acid dyes and raffinose solutions, when injected into the blood of rabbits, are eliminated more conc. in the bile; sucrose, cyclic sulphonic acids, Mg and I salts were not conc. The mol. wt. appears to be important in the secretory concentrating power.

A. A. ELDRIDGE.

Formation of bile acids. IV. Okara from soya beans and the secretion of bile acids. S. HIGASHI (Arb. med. Univ. Okayama, 1931, 2, 396—404).—A substance which produces in dogs an increase in the secretion of bile and in the quantity of bile acids appears to be a sterol similar to ergosterol, and to be converted into bile acids in the body.

CHEMICAL ABSTRACTS.

Urobilin-substances. VI. Significance of blood-pigment in the metabolism of urobilin substances. M. OSHIMA (Japan. J. Gastro-enterol., 1931, 3, 207—209).—After hæmoglobin is set free in the blood the bile urobilin substances and bilirubin increase. Urobilin is considered to be formed in the liver without previous intestinal reduction of bilirubin.

CHEMICAL ABSTRACTS.

Fate of bilirubin introduced into the blood vessels. V. Change of bilirubin concentration in the blood vessels when the bile duct is ligated. VI. Transmission of bilirubin into cerebrospinal fluid from blood vessels. VII. Excretion of bilirubin from the kidneys. VIII. Relationship between liver and kidneys with regard to the excretion of bilirubin. S. SAIKI (Japan. J. Gastro-enterol., 1931, 3, 192—194, 195—196, 197—201, 202—206).—V. Bilirubin injected intravenously into rabbits disappears more slowly after ligation of

the common bile duct and still more slowly after additional ligation of the cystic duct.

VI. Injury of the spinal membrane of dogs suffering from obstructive jaundice caused an increase in the bilirubin concn. of the cerebrospinal fluid.

VII. The passage of bilirubin through the kidneys is inhibited by CrO_4'' , U, or cantharidin injury.

VIII. The liver and kidneys have a compensatory function in the excretion of bilirubin.

CHEMICAL ABSTRACTS.

Cholesterol function of the gall-bladder. R. ELMAN and J. B. TAUSSIG (J. Exp. Med., 1931, 54, 775—787).—Cholesterol is present in greater concn. in gall-bladder than in hepatic bile; the gall-bladder has the power of excreting cholesterol into its lumen. The excretion may be accelerated by infection.

CHEMICAL ABSTRACTS.

Gastric secretion. I. Influence of acids and bases. II. Influence of poisoning and electrical excitation of the vegetative nervous system. III. Process of intragastric appearance of pigments introduced into the blood. IV. Chlorine in the gastric juice. Y. MARUNO (Japan. J. Gastro-enterol., 1931, 3, 210—219, 220—225, 226—240, 241—249).—I. Acids, particularly HCl, accelerate the secretion of HCl in the rabbit's stomach; bases inhibit the secretion. Differences in the degree of stimulation depend on the entire mol., and not only on the p_{H} . AcOH and lactic acid stimulate pepsin secretion, whilst bases inhibit it.

II. HCl secretion is stimulated by adrenaline, but is unaffected by pilocarpine or atropine.

III. The secretion of neutral-red (intravenous) is parallel with that of HCl.

IV. HCl-Cl and chloride-Cl show parallel changes when the stomach is filled with normal saline solution.

CHEMICAL ABSTRACTS.

Normal range of gastric acidity from youth to old age. F. R. VANZANT, W. E. ALVAREZ, G. B. EUSTERMAN, H. L. DUNN, and J. BERKSON (Arch. Int. Med., 1932, 49, 345—359).—A study of the data on titration figures of gastric acidity from 3746 human cases. Free gastric acidity increases from childhood, attaining at puberty adult vals. which are markedly higher in the male than in the female. With increasing age achlorhydria becomes more common.

F. O. HOWITT.

Hormone secretion of the stomach. C. E. JOHNSON (Pfluger's Archiv, 1931, 228, 258—266; Chem. Zentr., 1931, ii, 3010).—Meat- and bread-extracts, when introduced into the *cul de sac* of a dog's stomach, stimulated gastric secretion. Gastric mucous membrane (frozen), when treated with Ringer's solution, affords an extract which, on intravenous injection, stimulates gastric secretion. Ringer's solution containing meat- or bread-extract, but not the solution alone, extracts on perfusion a secretory hormone from the stomach.

A. A. ELDRIDGE.

Excretion of dyes by the gastric mucous membrane. Microscopic observations on living animals. N. HENNING (Arch. exp. Path. Pharm., 1932, 165, 191—207).—In frogs, only acid dyes forming highly disperse solutions are secreted by the stomach. The secretory glands of the fundus are the

active agents and the excretion of the dye corresponds with the secretory activity of the glands. Observations with neutral-red demonstrate that the actual glands are alkaline in reaction, the acid reaction developing only at the surface epithelium.

W. O. KERMACK.

Gastric erosion of metal. F. HOELZEL (Science, 1932, 75, 311—312).—Losses in wt. of pieces of Al, Fe, and steel administered to rats are recorded.

L. S. THEOBALD.

Suitability of Wulf's indicator-paper method for the determination of urinary acidity with attention to CO₂ error. K. SCHNEIDER (Arch. exp. Path. Pharm., 1932, 164, 565—569).—The method applied to urine has an accuracy of 0.1—0.2 p_H , and the results are as satisfactory as those obtained with Michaelis' method. The change in reaction due to loss of CO₂ during the measurement is less than 0.2 p_H .

W. O. KERMACK.

Modification of the Lange acetone test. E. RANTZMAN (J. Lab. Clin. Med., 1931, 16, 1217—1218).—For the detection of COME₂ in urine a stable reagent containing 35.5% of NH₄NO₃ and 2.5% of Na nitroprusside is used instead of a fresh solution of the latter. A purple ring appears when 3 c.c. of the urine and 1 c.c. of the reagent are covered with conc. NH₃ solution.

CHEMICAL ABSTRACTS.

Determination of urea in urine. M. J. BREUER (J. Lab. Clin. Med., 1931, 16, 1221—1222).—Folin and Youngburg's method is simplified.

CHEMICAL ABSTRACTS.

Effect of urea ingestion on the nitrogen partition of urine at endogenous nitrogen level. R. A. KOCHER and H. C. TORBERT (J. Biol. Chem., 1932, 95, 427—439).—The total N, total S, and N partition of the urine, the blood non-protein-N and urea, the basal metabolic rate and the faeces-N of normal individuals fed on an almost N-free diet, before and after the administration of 30—50 g. of urea, are determined. The urea was completely recovered in the urine, delayed excretion being parallel with an increased blood-urea; S excretion was unaffected, whilst the basal metabolic rate decreased. The results of Moore, Laviates, Wakeman, and Peters (A., 1931, 762) are brought into agreement with these findings.

H. DAVSON.

Physiology of glands. CXXXVI. Excretion of creatinine and dyes in diuresis. L. ASHER and E. DESCOMBES (Biochem. Z., 1932, 246, 59—86).—Isotonic solutions of creatinine with indigo-carmin and creatinine with cyanol were placed in the peritoneal cavity and the rate of excretion was followed under the influence of a sp. diuretic. With both solutions, but more particularly with the former, the course of the concn. curves of the two substances is approx. the same. The results confirm the view that creatinine is separated by filtration at the glomeruli and is concn. in the tubules by reabsorption of H₂O and salts, creatinine itself not being reabsorbed.

P. W. CLUTTERBUCK.

Guaiacol determination in urine. R. SCHMID (Z. physiol. Chem., 1932, 205, 213—218).—Guaiacol may be separated from other phenols in urine by distillation and hydrolysis with HI to pyrocatechol

followed by treatment with excess of aq. Br which ppts. the phenols. The pyrocatechol is then determined colorimetrically with phosphotungstic-phosphomolybdic acid reagent in aq. Na₂CO₃.

J. H. BIRKINSHAW.

Determination of iodine in urine by X-rays. S. CODINO (Semana méd., 1932, ii, 1074—1076).—Absorption of X-rays is proportional to the I content; comparative measurements are made photographically or photo-electrically.

CHEMICAL ABSTRACTS.

Blood-lipins in health and disease. W. B. S. BISHOP (J. Cancer. Res. Comm. Univ. Sydney, 1932, 3, 223—231).—A review.

Proteolytic enzymes of the human spleen and their alterations during various diseases. Autolysis of spleen tissue. G. BORGER (Arch. exp. Path. Pharm., 1932, 164, 469—500).—Glycerol extracts of human spleens exert proteolytic action on gelatin as well as on spleen-protein with max. in both cases at p_H 4.0 and 8.0, whilst with *dl*-leucylglycine as substrate, there is only one max. at p_H 8.0. Two enzymes are present, a proteolytic enzyme (cathepsin) and a dipeptidase. The action of cathepsin is increased and that of the dipeptidase inhibited by addition of HCN and by reduced glutathione. Glycerol extracts made at p_H about 5.0 are more active than those made at approx. neutral reaction. Extracts made from spleens taken from persons suffering from various diseases show widely differing degrees of activity.

W. O. KERMACK.

Catalase in adrenalectomised guinea-pigs and Addison's disease. II. A new test of impaired adrenal function. F. OEFELIN and H. TRAUTWEIN (Arch. exp. Path. Pharm., 1932, 165, 131—137).—In adrenalectomised guinea-pigs the blood-catalase activity relative to no. of erythrocytes rises steadily after the operation and at death may be more than twice the original val. The catalase index of patients suffering from Addison's disease is also above normal.

W. O. KERMACK.

Adrenalectomised guinea-pigs. III. F. OEFELIN and H. TRAUTWEIN (Arch. exp. Path. Pharm., 1932, 165, 138—144).—In adrenalectomised guinea-pigs the respiration rate gradually rises after the operation to a max. of two or three times the normal rate at 6—7 days after the operation, that is shortly before the death of the animal. The outputs of CO₂ and of H₂O in the expired air also increase to about three times the normal amount. Shortly before death the residual N and globulin of the blood increase.

W. O. KERMACK.

Acidosis. I. Experimental acidosis and protein metabolism. II. Relation of acidosis to inflammatory reaction. W. LAUBENDER (Arch. exp. Path. Pharm., 1932, 165, 5—33, 34—52).—Oral administration to rabbits of 0.154N-NaCl causes hydraemia and chloraemia which partly subsides within 24 hr. Oral administration of 0.154N-HCl leads to a loss of H₂O from the blood and hyperchloraemia. In animals on a mixed diet 8.2 millimols. of HCl per kg. body-wt. cause a fall of p_H of about 0.2 in the carotid blood which lasts for several days. In the animal after administration of HCl the alteration in

p_{H} is partly compensated through the respiration (loss of CO_2). As the addition of acid to blood *in vitro* causes the same fall in p_{H} as when administered proportionally *in vivo*, it seems that the tissues of the animal play an equal part with the blood in neutralising the acid. When the rabbits inhale air containing 6–8% of CO_2 , the blood p_{H} quickly falls by 0.2–0.3, but returns rapidly to normal when ordinary air is again breathed. Neither the total N in the 24-hr. urine nor the residual N in blood, liver, or kidney is increased after oral administration of 0.154N-HCl (20.6 millimols. per kg. body-wt.), but the % residual N (after deduction of urea- and NH_3 -N) in the 24-hr. urine is increased.

II. In rabbits neither the inflammatory action of thiocarbamide nor the vaccine lymph reaction is inhibited by oral administration of 0.3 g. of HCl per kg. body-wt. nor by the breathing of air containing 6–8% of CO_2 in spite of the general acidosis produced. The inhibiting action of CaCl_2 administration on inflammation is not due to the acidosis which is produced. Inhibition of the thiocarbamide reaction is produced by the oral administration of 1.0 g. of NaCl per kg. body-wt. if administered in aq. solution in sufficiently high concn. W. O. KERMACK.

Cancer-producing substances. A. O. ROBSON (J. Cancer Res. Comm. Univ. Sydney, 1932, 3, 242).—Published methods for preparing 1 : 2 : 5 : 6-dibenzanthracene are outlined.

Blood chemistry in neoplastic diseases. W. MANKIN (J. Cancer Res. Comm. Univ. Sydney, 1932, 3, 232–241).—A review.

Biochemical activity of minced Rous sarcoma after filtration. K. VIETORISZ (Biochem. Z., 1932, 246, 217–218).—The protoplasm of the tissue of Rous sarcoma is retained by filters to the same extent as with other tumour tissues, and the activity of the filtrate cannot be due to a greater filtrability of the protoplasm. P. W. CLUTTERBUCK.

Composition of gall-stones and their solubility in dog bile. M. PICKENS, G. O. SPANNER, and L. BAUMAN (J. Biol. Chem., 1932, 95, 505–507).—The average cholesterol content of human gall-stones is 94%; no bile salts and only traces of fatty acids are found. Determination of the contents of dog bile before and after saturation with cholesterol shows that the solubility of human gall-stones in dog bile is due to the low initial cholesterol content of the latter. H. DAVSON.

Urinary excretion of iodine by goitrous and non-goitrous persons in Gilgit. II. R. MCCARRISON and G. SANKARAN (Indian J. Med. Res., 1931, 19, 67–70).—No significant difference was observed. CHEMICAL ABSTRACTS.

Detection of bile pigments in tissue of icterous animals. O. MARTIN (Z. Fleisch-Milch-hyg., 1931, 41, 497–499; Chem. Zentr., 1931, ii, 2945).—The fat (20–25 g.) or connective tissue is extracted for 30–120 min. with 96% EtOH, and 5–8 c.c. of the filtrate are boiled with 5–10 drops of H_2SO_4 ; in presence of bile pigments a green to blue coloration appears. A. A. ELDRIDGE.

Bile in various affections of the liver. O. SCHULTZ-BRAUNS (Verh. deut. path. Ges., 1929, 24, 336–342; Chem. Zentr., 1931, ii, 3112).—Gall-bladder bile is more strongly buffered and more strongly acid than liver bile. Since carbonates and phosphates are resorbed by the mucous membrane, the reaction and degree of buffering must depend on the bile acids and partly on the bilirubin. In cirrhosis and obstructive atrophy too little of the bile appears to be secreted. A. A. ELDRIDGE.

Quantity of lactic acid in blood, bile, and urine during the disturbance of hepatic functions. I. Liver disease. II. Experimental disturbance. H. MIZUNO (Japan. J. Gastro-enterol., 1931, 3, 175–183, 184–191).—I. Normal human blood contains 5.5–8.5 mg. of lactic acid per 100 c.c. Pathological interference with hepatic function increases the blood-lactic acid.

II. Rabbit's blood contains 13–24 mg. of lactic acid per 100 c.c. Liver injury by ligature of the bile duct, X-irradiation, hepatotoxin, P, CHCl_3 , or CCl_4 increases the val. CHEMICAL ABSTRACTS.

Content of reduced glutathione in organ tissues of rabbits with experimentally disturbed liver function. R. SATO (Sei-i-kwai Med. J., 1930, 49, No. 10, 81–87).—Male rabbits contained: liver 0.2588, adrenals 0.0126, kidney 0.0934, lung 0.0746, heart 0.0399, spleen 0.01047, testicles 0.0630, muscle 0.0185% of glutathione. In experimental icterus or P poisoning the liver- and kidney-glutathione is decreased, but otherwise the glutathione content increases. Starvation decreases the liver-, kidney-, lung-, and spleen-, but increases the heart-, testicle-, and muscle-glutathione. CHEMICAL ABSTRACTS.

Proteolytic enzymes of lymphocytes. H. A. OELKERS (Klin. Woch., 1931, 10, 1459–1460; Chem. Zentr., 1931, ii, 2625).—In lymphatic leucæmia the lymphocytes contained dipeptidase, tryptase, and cathepsin. A. A. ELDRIDGE.

Mastitis and carbohydrate deficiency. F. WIEDMANN (Z. Unters. Lebensm., 1932, 63, 113–129).—In general, inflammation of the udder is accompanied by decreases in the lactose, P, and K contents of the milk, and increases in Na and Cl. Cows given 4 kg. of wheat-grist yielded, after 4 weeks, milk in which the Cl had fallen by at least 20–45 mg.-% and the lactose had increased by 0.6–0.9 g. per litre. Removal of the wheat from the diet then caused a definite carbohydrate deficiency. A low Cl content indicates a low probability of infection, and therefore a sound milk. J. GRANT.

Detection of the antidiuretic component of the posterior pituitary hormone and a pressor substance in blood in nephropathy and eclampsia of pregnancy. K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1931, 10, 1438–1441; Chem. Zentr., 1931, ii, 2750).—The ultrafiltrate contains a substance similar in antidiuretic action and properties to the posterior pituitary hormone. The blood of such patients also contains a substance corresponding with the vasopressor substance of the posterior pituitary, but differing from it in that the former is active when administered subcutaneously. A. A. ELDRIDGE.

Behaviour of serum-calcium and -phosphorus in pregnancy and in osteomalacia under the action of "vigantol." O. TIMPE (Arch. Gynakol., 1931, 146, 240—247; Chem. Zentr., 1931, ii, 3356).—In a no. of cases administration of vigantol increased the total and dialysable Ca and decreased the acid-insol. P.

A. A. ELDRIDGE.

Bence-Jones protein. I. Isoelectric point of Bence-Jones protein in buffer solutions. II. Isoelectric point of Bence-Jones protein in strong acids and bases. III. Isoelectric point of denatured Bence-Jones protein. F. MAINZER (Biochem. Z., 1932, 246, 134—148, 149—155, 156—163).—I. Partial denaturation of Bence-Jones protein occurs on keeping in aq. solution and on pptn. with either $(\text{NH}_4)_2\text{SO}_4$ or EtOH. The isoelectric point determined by cataphoresis in PO_4''' and glycine buffer solution is at p_H 6.70. The zone of min. stability is at p_H 8.0—9.2. The buffer anion also affects stability.

II. The isoelectric point in unbuffered solutions is at p_H 6.59. In HCl solutions (with EtOH addition) a zone of min. stability is obtained, the centre at p_H 4.84. Bence-Jones proteins from different sources are different in constitution.

III. By heating, Bence-Jones protein gives a denatured product which in phthalate buffer shows an isoelectric point at p_H 4.9. The same product is obtained on denaturing with EtOH or $(\text{NH}_4)_2\text{SO}_4$, or on keeping in aq. solution. P. W. CLUTTERBUCK.

Rickets. III. Phosphorus metabolic disturbances in experimental thallium rickets. E. ROMINGER, H. MEYER, and C. BOMSKOV (Z. ges. exp. Med., 1931, 78, 272—286; Chem. Zentr., 1931, ii, 2632; cf. A., 1931, 511).—In rats suffering from rickets induced by injections of Tl acetate, the retention of P_2O_5 is impaired very shortly after the injections commence. A significant inability to retain CaO occurs only when the retention of P_2O_5 has been impaired for some time and when deposition of CaO in the bones begins to be defective. Rickets of different origins always commences with a disturbance of the P-economy. L. S. THEOBALD.

Experimental rickets in rats. V. Toxicity of irradiated ergosterol preparations. P. GYORGY and G. POPOVICU (Jahrb. Kinderheilk., 1931, 82, 34—74; Chem. Zentr., 1931, ii, 2896).—By irradiation of ergosterol a highly antirachitic but non-toxic prep. has not yet been obtained. A. A. ELDRIDGE.

Treatment of rickets without the use of irradiated ergosterol preparations. B. BLEYER and F. FISCHLER (Deut. med. Woch., 1931, 57, 1741—1743; Chem. Zentr., 1931, ii, 2896).—A study of vitophos and its effect on the mineral portion of the skeleton. The synergism between plant-vitamins and Ca Mg inositolphosphates is discussed.

A. A. ELDRIDGE.

Egg-yolk extract preparation; composition, antirachitic activity, and effect on the calcium-phosphorus metabolism. E. KOMM (Klin. Woch., 1931, 10, 1581—1584; Chem. Zentr., 1931, ii, 3012).—"Helioctin" with rachitic rats produced no change in total P. The total Ca was increased.

A. A. ELDRIDGE.

Specific characteristics of syphilitic blood-proteins. I. Surface tension and solubility. S. T. WALTON (J. Exp. Med., 1931, 54, 859—873).—When normal blood is kept for 1 hr. the surface tension is considerably lowered; the greatest time-drop recorded is with serum diluted approx. 10^4 times in fresh serum and 5×10^4 times in heated serum. Immune serum is not affected in the same manner by heat as is normal serum. Syphilitic serum and anti-sheep-cell rabbit serum behave similarly in this respect. Serum-albumin is much more readily sol. than globulin in alkaline buffer solutions, and globulin from normal serum ionises more than that from syphilitic serum. CHEMICAL ABSTRACTS.

Co-enzymes, hydrogen donors, and arsenic poisoning of cell respiration. I. BANGA and A. SZENT-GYORGYI (Biochem. Z., 1932, 246, 203—214).—In the respiration of minced heart-muscle a co-enzyme takes part which assists in the oxidation (dehydrogenation) of lactic acid and zymophosphate, the action being poisoned by As_2O_3 . Oxidations insensitive to As play a greater role in the respiration of washed muscle reactivated with boiled muscle-juice than in unwashed muscle. Adenylic and adenylypyrophosphoric acids and zymophosphate all play a part in the As-insensitive type of oxidation.

P. W. CLUTTERBUCK.

Effect of acidosis and alkalosis on body work. H. DENNIG, K. PETERS, and O. SCHNEIKERT (Arch. exp. Path. Pharm., 1932, 165, 161—168).—The power of healthy humans to perform work is decreased by acidosis and increased by alkalosis produced by administration of NH_4Cl and NaHCO_3 , respectively. The onset of fatigue is largely determined by changes in the blood- p_H , the important factor being not the abs. val., but the rate of fall with time. W. O. KERMACK.

Metabolism during work of carbohydrate-poor muscles of cold-blooded animals. C. L. GEMMILL (Biochem. Z., 1932, 246, 319—331; cf. Hill and Kupalov, Proc. Roy. Soc., 1929, B, 105, 313).—The isomeric coeff. of anaerobic lactic acid production in working frog muscle (sartorius and gastrocnemius) the carbohydrate content of which has been reduced by administration of sufficient insulin to cause convulsions is not much greater than in muscle rich in carbohydrate. When the carbohydrate content is very low, however, work sometimes seems to be performed without corresponding production of lactic acid and apparently also without decomp. of phosphagen, so that some source of energy other than carbohydrate may then be involved. The R.Q. of the working muscle with low carbohydrate content is not appreciably lower than that of normal muscle. W. MCCARTNEY.

Recovery process after exercise in the mammal. II. Conversion of infused d -lactic acid into muscle-glycogen. C. N. H. LONG and F. L. HORSEFALL, jun. (J. Biol. Chem., 1932, 95, 715—733).—No deposition of muscle-glycogen occurs when d -lactic acid is diffused into the eviscerated decapitated cat which utilises 0.2 g. per kg. per hr. Considerable deposition occurs, however, in presence of glucose and, to a greater extent, of glucose and

insulin. Carbohydrate metabolism alone appears to supply the energy necessary for glycogen synthesis from *D*-lactic acid, the recovery process in the intact animal being a function of the whole organism rather than one of the muscles alone. F. O. HOWITT.

Glycogenesis from glucose administered to the fasting dog. M. DANN and W. H. CHAMBERS (J. Biol. Chem., 1932, 95, 413—426).—Administration of glucose to dogs starved for 3 weeks shows no impairment of the process of glycogenesis, as at least 35% of the glucose absorbed was deposited as glycogen in the liver and muscles; an increase of 1 g. per 100 g. of muscle and 3 g. per 100 g. of liver was noted. The blood-sugar curve attains its max. 2 hr. after glucose ingestion. Heart-glycogen is unusually high. H. DAVSON.

Significance of liver-glycogen in liver function. III. 2. Glucose test when glycogen is increased. IV. Lævulose test when glycogen is (1) diminished, (2) increased. V. Adrenaline hyperglycæmia when glycogen is (1) diminished, (2) increased. T. IKUSHIMA (Japan. J. Gastroenterol., 1931, 3, 250—252, 253—256, 257—259, 260—262, 263—265).—III. Administration of lactose or galactose produces smaller increases in liver-glycogen than glucose, fructose, sucrose, or maltose. Any sugar which increases the liver-glycogen promotes glucose tolerance.

IV. (1) When liver-glycogen is diminished the fructose tolerance falls. (2) Increased tolerance in high liver-glycogen is due to inhibition of the glycolytic process by the injected fructose.

V. (1) In diminished liver-glycogen the time taken to attain max. adrenaline hyperglycæmia is delayed and the max. blood-sugar vals. are lower, probably owing to transformation of other glycogen stores. (2) Adrenaline hyperglycæmia is very marked after liver-glycogen has been increased by ingestion of mono- or di-saccharides. CHEMICAL ABSTRACTS.

Importance of the carbohydrates, especially sugar, for human nutrition. B. SUSSKIND (Z. Ver. deut. Zucker-Ind., 1932, 82, 159—176).—Since 1923 the author has studied the effects of variations in his own diet. For the first 9 months health and wt. were maintained on a diet, largely fruit, containing 35 g. of protein (including 1 egg), 63 g. of fat, and 342 g. of carbohydrates per diem. Restriction of protein to 30 g., from vegetable sources alone, for 16 months produced weakness and other symptoms of increasing severity bordering on collapse. Later observations appear to indicate that 1 g. of protein per kg. of body-wt. is sufficient for an adult provided 70% of the protein is of high nutritive val., e.g., from eggs or milk. The author could not maintain complete health on less carbohydrate than 300—400 g. per day. Susceptibility to colds and infection was greatly reduced by taking a large proportion of the carbohydrates in the form of sugar, but polysaccharides could not be entirely excluded without ill effects. Herrmannsdorfer's modified Gerson diet for tuberculosis of the skin, viz., 90 g. of protein, 164 g. of fat, and 244 g. of carbohydrate, was found deficient in carbohydrate for long-con-

tinued use. Fats, even in large excess, cannot reduce the carbohydrate requirements of the body.

J. H. LANE.

Fat as nutriment for growth. Natural, artificial, and centrifuged milk. H. ISAACHSEN (Milch. Zentr., 1932, 61, 1—4, 17—20, 29—30, 45—48, 57—61).—The nutritive val. of fats, carbohydrates, and proteins for the growth of young pigs and calves is discussed. The feeding of such animals with diets containing various types of milk with added milk-fat, cod-liver oil, or peanut oil indicates that rearing may be achieved without impairment of final body-wt. or health when the total fat in the diet is considerably decreased. Fat thus removed, however, must be replaced by an appropriate amount of carbohydrate, whilst for the first 3 months of life the fat should be in the same proportion as that of the corresponding natural milk. The fat of artificial milk, i.e., centrifuged milk containing finely-dispersed plant-fat and cod-liver oil, does not exert such a favourable influence on the course of digestion as whole milk.

F. O. HOWITT.

Diet and blood-lipins. W. R. BLOOR (J. Biol. Chem., 1932, 95, 633—644).—Changes in the fat content of the diets result in corresponding changes in the phospholipin and cholesterol levels of the blood-plasma of the dog and, to a greater extent, of the rabbit. The significance of these changes *per se* and the difference between the two species are discussed with reference to the metabolism of fat and carbohydrate in these two animals.

F. O. HOWITT.

Metabolism of phospholipins. IV. Rate of phospholipin metabolism with reference to their role in fat metabolism. R. G. SINCLAIR (J. Biol. Chem., 1932, 95, 393—408; cf. A., 1930, 809, 1471; 1931, 1183).—By measuring the degree of saturation of the phospholipins of the carcasses of rats the rate of change of their constituent fatty acids, due to changing the diet from a fat-free one to one containing cod-liver oil, is obtained and is more rapid than could be accounted for by protoplasmic wear and tear. It is, however, independent of fat metabolism, since the change is independent of the temp. at which the rats are kept. Feeding rats on a 1% cod-liver oil diet produces a high degree of unsaturation of the phospholipins, which decreases slowly during subsequent starvation, showing that the tissue-phospholipins have a marked tendency to attain and maintain a high degree of unsaturation. The function of phospholipins is not that of an intermediary in fat metabolism.

H. DAVSON.

Effect on the carbon and oxidation quotients of the urine of enteral administration of amino-acids. T. OSUKA (Biochem. Z., 1932, 246, 104—116).—Tables show the variation in quotient when the diet protein of rats is partly or completely replaced with various NH_2 -acids of the same N content. In physiological and pathological urines, the variations of the O : N ratio are always greater than those of the C : N ratio.

P. W. CLUTTERBUCK.

Chemistry of the conjugation of benzoic acid. A. J. QUICK (J. Biol. Chem., 1932, 95, 189—196).—The synthesis of hippuric acid and benzoylglycuronic acid from BzOH and glycine and glycuronic acid,

respectively, has been studied from the viewpoint of the law of mass action. The elimination of the conjugated products from the dog depends on the factors which influence a reversible reaction. The conjugation of $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ has been similarly studied.

F. R. SHAW.

Metabolism and energy exchange in growing pigs. G. FINGERLING (Landw. Versuchs-Stat., 1932, 113, 273—318).—Results of calorimeter and digestibility trials are recorded.

A. G. POLLARD.

Metabolism of artificially perfused organs. T. KOSUGI and C. H. KIM (Keijo J. Med., 1931, 2, 551—565).—The organs of the toad were perfused for 30 to 60 min. with oxygenated Locke's solution introduced through the abdominal vein and followed by dil. Indian ink or oil emulsions. Histological comparison of the liver, kidney, and alimentary canal with those from control animals in which the ink or emulsion had been administered intravenously into the lymph-sacs, or direct into the lumen of the intestine, indicated that the true physiological functioning of these organs is not retained following perfusion.

F. O. HOWITT.

Perfusion of the thyroid. S. DIETRICH and H. SCHWIEGK (Arch. exp. Path. Pharm., 1932, 165, 53—83).—The rate of perfusion of the intact thyroid in the fasting dog, under light chloralose anaesthesia and normal temp., is 3.2 c.c. per min. per g. thyroid, and the O_2 consumption is 2.7 cm. per mg. thyroid per hr. Both these figures are decreased by warming and increased by cooling either the whole animal or the blood in the carotid vein. During fever produced by injection of bacterial toxin the rate of perfusion is not increased, but is markedly increased when the fever is produced by tetrahydro- β -naphthylamine. Adrenaline, sympatol, ergotamine, and hypophysin decrease the rate of perfusion, whilst histamine, pilocarpine, and peptone increase it.

W. O. KERMAK.

Diffusion-capacity of living cells. S. HOZAWA (Z. Biol., 1932, 92, 373—383).—On the grounds of a mathematical analysis in combination with the theory of electrolytic processes at the cell phase-boundaries, the diffusion-capacity is considered as the degree of permeability for electrolytes.

H. DAVSON.

Water content of white and yolk of hens' eggs during the development of the embryo. A. ORRÛ (Atti R. Accad. Lincei, 1931, [vi], 14, 523—527).—During incubation, the H_2O content of the albumin falls until the 12th—13th day and afterwards increases to almost its original val. That of the yolk rises until the 12th day and then falls, but never to the val. it has in the yolk of the quiescent egg.

T. H. POPE.

Calcium:phosphorus ratio in the nutrition of the growing chick. R. M. BETHKE, D. C. KENNARD, C. H. KICK, and Z. ZINZALIAN (Poultry Sci., 1929, 8, 257—265).—The optimal Ca:P ratio is 3—4:1. Within certain limits of concn. the ratio is of greater significance in calcification and growth than are the abs. amounts. The addition of vitamin D permits greater variation in the ratio and concn. P may be as much a limiting factor as is Ca in growth and bone formation.

CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism of the growing chick. G. D. BUCKNER and J. H. MARTIN (Poultry Sci., 1929, 8, 284—289).— $\text{Ca}_3(\text{PO}_4)_2$, alone or with CaSO_4 or CaCO_3 , causes increased growth and leg-bone development, although it does not materially influence the percentage of ash in the bones or the percentages of Ca and P in the ash. CaCO_3 , CaSO_4 , and $\text{Ca}_3(\text{PO}_4)_2$ are equally satisfactory sources of Ca; $\text{Ca}_3(\text{PO}_4)_2$ also supplies the required P.

CHEMICAL ABSTRACTS.

Age and anti-fixators of calcium. G. MOURIQUAND, A. LEULIER, and WEILL (Compt. rend., 1932, 194, 1029—1031).—Young and adolescent rats are very sensitive to the antifixative action of SrCO_3 when fed on a rachitic diet. Adult animals are but little affected.

P. G. MARSHALL.

Modification of the Osborne-Mendel salt mixture containing only inorganic constituents. L. G. WESSON (Science, 1932, 75, 339—340).

L. S. THEOBALD.

Influence of pyocyanin on the respiration of normal tissues and tumours. E. A. H. FRIEDHEIM (Naturwiss., 1932, 20, 171—172).—Pyocyanin increases the respiration of animal tissues in the presence of glucose.

W. R. ANGUS.

Odour. E. M. VON HORNBOSEL (Pflüger's Archiv, 1931, 227, 517—538; Chem. Zentr., 1931, ii, 3014).—"Clarity" of odour is discussed. The "clarity" increases with increase in the no. of C atoms, decreases on introduction of double or triple linkings, halogen atoms, or CO, NO_2 , or OH groups, or on ring closure, and increases when several electrically similar groups (OH, CO, NH_2 , Et) are adjacent in the mol. The function is correlated with the frequency of the optical absorption bands.

A. A. ELDRIDGE.

Stimulation of the Nervus accelerans by hydrogen ions and capillary-active substances. B. HOFFER (Biochem. Z., 1932, 246, 46—58).—The excitability of the nerve is increased by a small decrease in p_{H} and is either unaffected or slightly decreased by a small rise in p_{H} . The nerve rendered inexcitable by ergotamine becomes excitable again on treatment with capillary-active material (octyl alcohol). Atropine, which normally inhibits the vagus, accelerates it after treatment with octyl alcohol.

P. W. CLUTTERBUCK.

Osmotic pressure. I. Depression of f. p. of various physiological salt and narcotic Ringer solutions. T. SUZUKI (Sei-i-kwai Med. J., 1930, 49, no. 11, 1—9).—217 solutions were examined.

CHEMICAL ABSTRACTS.

Claude Bernard's theory of narcosis. V. E. HENDERSON and G. H. W. LUCAS (J. Pharm. Exp. Ther., 1932, 44, 253—267).—The evidence adduced by Bancroft from the literature in support of the Bernard reversible coagulation theory of narcosis is criticised and shown, in many cases, to be valueless. The theory that thiocyanates will act as peptising agents to the colloids of the nervous tissues and so have an anti-narcotic effect is disproved by experiments on anaesthetised rabbits, the experimental results of Bancroft on the same animals being inadequate. (Cf. A., 1931, 1088.)

H. DAVSON.

Blood-alcohol and its relation to intoxication. R. G. TURNER (J. Pharm. Exp. Ther., 1932, 44, 305—324).—EtOH in blood may be determined by a modification of the method of Nicloux with an average error of 5.1%. Dogs to which various quantities of EtOH have been administered show definite signs of intoxication when the concn. of EtOH in the blood is almost 0.25% and develop alcoholic stupor when it is 0.4—0.5%. EtOH given after or during a meal produces a smaller rise in blood-EtOH and less marked signs of intoxication than a similar amount of EtOH given to the fasting animal. Destruction of EtOH is abnormally rapid in an animal accustomed to EtOH. W. O. KERMACK.

Determination of the relative toxicities and efficiencies of local anaesthetics. I. A. D. MACDONALD and M. C. G. ISRAELS (J. Pharm. Exp. Ther., 1932, 44, 359—368).—The relative toxicities of local anaesthetics may be determined by finding the dose required to paralyse respiration when a solution of the drug is slowly infused intravenously into an anaesthetised cat, and from the data so obtained together with the relative efficacies (ratios of the concns. which achieve adequate anaesthesia for any purpose), a useful estimate may be derived of the relative efficiencies of the drug.

W. O. KERMACK.

Duration of action of the barbituric acid hypnotics as a basis of classification. R. H. FITCH and A. L. TATUM (J. Pharm. Exp. Ther., 1932, 44, 325—335).—The toxicities of a no. of barbituric acid derivatives have been determined when these are administered orally or intraperitoneally to rats or orally to rabbits. The various derivatives are characterised by the duration of the anaesthesia produced by the administration of 60% of the M.L.D., but the results depend to some extent on the animal and the route of administration.

W. O. KERMACK.

Picrotoxin as an antidote in acute poisoning by the longer-acting barbiturates. A. H. MALONEY and A. L. TATUM (J. Pharm. Exp. Ther., 1932, 44, 337—352).—Picrotoxin acts as an antidote to the poisoning of rabbits by barbituric acid hypnotics.

W. O. KERMACK.

Role of chemical structure of cocaine in the cocaine sensitisation-desensitisation phenomena. S. K. WIRT and M. L. TAINTER (J. Pharm. Exp. Ther., 1932, 44, 299—303).—The peculiar relation of cocaine to the sympathomimetic amines (sensitising action with adrenaline, desensitising action with other amines) is not shown either by compounds closely related to cocaine (benzoylecgonine, ecgonine, methyl-ecgonine) or by other local anaesthetics, "nupercaine" or "tutocaine." AcOMe and CH₂Ph.OH were also inactive.

W. O. KERMACK.

Action of ephedrine on the breathing of healthy persons under basal conditions and the effect of carbon dioxide. Action of morphine on the respiration of humans, healthy and suffering from heart disease, under basal conditions and during carbon dioxide breathing. H. HERXHEIMER and R. KOST (Arch. exp. Path. Pharm., 1932, 165, 111—113, 114—119).—Administration of ephedrine to humans increases the O₂ consumption and the CO₂ output.

tonine to humans increases the O₂ consumption and the CO₂ output.

In healthy humans and in patients suffering from heart disease morphine lowered the rate of respiration, the O₂ intake, and the CO₂ output, the effect being most marked on the last-named. These results are obtained both under normal conditions and during CO₂ breathing.

W. O. KERMACK.

Is the action of papaverine due to the benzyl group? H. KREITMAIR (Arch. exp. Path. Pharm., 1932, 164, 509—517).—Comparison of the action of several isoquinoline derivatives on the isolated rabbit's intestine as well as *in vivo* shows that the characteristic paralyzing action of papaverine is not dependent on the presence of a CH₂Ph group. 6:7-Methylene-dioxy-1-phenylethyl-3-methyltetrahydroisoquinoline has a stimulating instead of a paralyzing action on the rabbit's intestine.

W. O. KERMACK.

Effect of ultra-violet irradiation on the toxicity of pure nicotine. G. WAKEHAM and G. P. TRACY (J. Pharm. Exp. Ther., 1932, 44, 295—298).—Irradiation of nicotine by ultra-violet light from a Hg-vapour lamp results in a decrease in its toxicity to albino rats (cf. Pacini and McGuigan, A., 1930, 1063). Under particular conditions the toxicity may be reduced to 25—30% of its original val. in 1 hr., after which time it increases with further irradiation to almost its original val.

W. O. KERMACK.

Colloidal osmotic (oncotic) pressure. XX. Effect of caffeine and euphyllin on the colloidal osmotic pressure of the blood in nephrectomised rabbits. E. KYLIN (Arch. exp. Path. Pharm., 1932, 164, 621—625).—The administration of caffeine to nephrectomised rabbits brings about a decrease of the venous colloidal osmotic pressure as in the case of intact animals (cf. this vol., 301). The rise in colloidal osmotic pressure observed with intact rabbits after the administration of euphyllin is also observed in the case of nephrectomised animals. It follows that this effect of euphyllin cannot, as previously suggested, be of renal origin.

W. O. KERMACK.

Behaviour of histone in biological experiments. E. ANNAU (Z. physiol. Chem., 1932, 205, 154—156).—Many properties of histone, and probably in part of protamines, particularly the action on frog preps., are due to their guanidine groups, whereby these proteins behave as colloidal guanidine salts.

J. H. BIRKINSHAW.

Synthalin. III. Effect of synthalin on the formation of lactic acid in the isolated frog muscle. O. GESSNER (Arch. exp. Path. Pharm., 1932, 165, 177—184).—In the isolated, rhythmically stimulated, isotonic contracting, oxygenated frog's muscle, synthalin increases the production of lactic acid by 20% when present in concns. between 1/100,000 and 1/20,000 and by more than 70% at a concn. of 1/10,000.

W. O. KERMACK.

[Pharmacology of] thio- and thiomethyl-ammonium compounds. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1932, 44, 151—169).—The substitution of the O atom in the OEt group of choline by S greatly increases the curare-like and

"paralysing-nicotine" actions, diminishes the muscarine, and abolishes the "stimulating-nicotine" actions of the drug, whilst in the ethers of formocholine the substitution diminishes the toxicity and increases the muscarine and "stimulating-nicotine" effects. The addition of O_2 to the S atom in the thiomethyl ethers to form sulphonyl compounds greatly reduces their toxicity and muscarine action. H. DAVSON.

Chinese anti-diabetic drugs. IX. Blood-sugar-lowering action of *Rehmannia lutea*. N. SUGIHARA and K. KIN (Keijo J. Med., 1931, 2, 594—605).—Aq. or EtOH extracts of *R. lutea* contain a substance which lowers the blood-sugar of rabbits and inhibits the hyperglycaemia due to NH_4Cl or $NaCl$, but not that due to adrenaline. The active principle is pptd. by addition of Et_2O to the EtOH extract and purified by continuously re-dissolving in abs. MeOH followed by pptn. with Et_2O . The white, amorphous material thus obtained is named "rehmannin."

F. O. HOWITT.

Are saponins in foodstuffs harmful to health? L. KOFLER (Z. Unters. Lebensm., 1932, 63, 154—166).—Examples are cited from the literature indicating that small amounts of saponin in fruit juices and other foods are not harmful, and may even serve a useful purpose, e.g., stimulation of digestive juices and of resorption.

J. GRANT.

Physiological properties of nerein and other principles of *Nerium oleander*. H. SIMONNET and G. TANRET (Compt. rend., 1932, 194, 1099—1101).—Nerein is toxic to the frog in a dose of 20 mg. and to mice in a dose of 90—100 mg. per kg. Intravenous injection of 0.85 mg. per kg. in dogs causes death. Large doses normally cause fibrillation, which, however, does not occur when the vagus is cut. Moderate doses cause a slowing of respiration which is not observed in atropinised animals. Marked diuresis occurs following injection of 0.25 mg. per kg. Other glucosides present in the plant or obtained from nerein exhibit similar physiological properties.

P. G. MARSHALL.

Pharmacological and toxicological studies of digitalis leaves and their effective components. S. AOKI (Sei-i-kwai Med. J., 1930, 49, No. 9, 1—49).—Digitalis leaves increase their toxicity by hydrolysis proportionally to the amount of acid used (p_H 1.2—2.3). Pepsin does not alter the toxicity of the leaves. Digitoxin, digitalin, and digitalein become more toxic if hydrolysed to a certain point. Digitoxigenin is more, and isodigitoxigenin less, toxic than digitoxin; anhydrodigitoxigenin is not toxic. The cardiac stimulating power of digitalis leaves, digitoxin, digitalin, and digitalein is increased by hydrolysis. Parallelism is observed between the cardiac stimulating power and toxicity of digitoxin, digitoxigenin, isodigitoxigenin, and anhydrodigitoxigenin, but not of digitalin and digitalein.

CHEMICAL ABSTRACTS.

Cardiac glucosides of *Cheiranthus cheiri* and related species. R. JARETZKY and M. WILCKE (Arch. Pharm., 1932, 270, 81—94).—The S-free glucoside cheiranthin (modified prep.) (cf. A., 1899, 1, 378) is similar to, but more active than, digitalis glucosides, the min. lethal dose for the frog being

2.2×10^{-7} g. per g. It is contained mostly in the seeds and leaves of *C. cheiri*; the amount in the leaves is greatest between noon and 3 p.m., and in the seeds in September. The activity of the drug decreases on keeping or on drying (least between 40° and 60°). Various species of *Erysimum* contain similar substances.

R. S. CAHN.

Pharmacological action of flavone compounds. T. FUKUDA (Arch. exp. Path. Pharm., 1932, 164, 685—694).—Kämpferol and its glucosides have a purgative action and form the active constituents of the seeds of *Rhamnus japonica* and other Japanese purgatives. All flavonols and flavonol glucosides tested have a diuretic action, a stimulating action on the heart, and they raise the blood-pressure. The flavonols are well absorbed from the intestinal tract and rapidly excreted in the urine and they are also found in the bile.

W. O. KERMACK.

Toxicological investigation of phenol and iodine. L. W. RISING and E. V. LYNN (J. Amer. Pharm. Assoc., 1932, 21, 138—141).—EtOH is the best preservative for samples of viscera containing PhOH. A specimen so preserved after 7 months yielded 90% of the PhOH present in the tissue at death. $HgCl_2$ and As_2O_3 under similar conditions gave 80%, whilst CH_2O and embalmer's fluid had no effect in the preservation of the PhOH in the organs. In the case of I, using EtOH, after 1, 3, and 7 months the amounts of I recovered from the tissues were 38, 34, and 29%, respectively. With the other preservatives the major portion of the I was lost immediately by combination either with the tissue or preservative and the I recovered remained const. after the first large decrease over the period of examination, 7 months.

E. H. SHARPLES.

Actions of various metallic salts on the central nervous system of the rabbit. A. PENTSCHKEV and H. KASSOVITZ (Arch. exp. Path. Pharm. 1932, 164, 667—684).—The actions of a large no. of salts, chiefly chlorides, have been observed after the suboccipital injection of their solutions. All the metals with the exception of Na are more or less toxic when the quantities administered are sufficiently great. Cu and U are the most toxic, whilst Th is only slightly so. Peculiar and characteristic reactions are observed in the case of Hg and Pb.

W. O. KERMACK.

Pharmacology of water-soluble bismuth. I. Distribution of bismuth in the organs of animals.

II. Bismuth content of blood and accompanying appearance of calcium in blood. K. HAMAYA (Sei-i-kwai Med. J., 1930, 49, No. 10, 44—51, 52—56).—I. After injection of Na Bi citrate (82 mg. of Bi per kg.) into a rabbit, Bi was detected in the blood, liver, and kidney (30 min.), lung and spleen (2 hr.); the small intestine contains a little. After 24 hr. the muscle contains the largest amount. The brain is reached in 48 hr. and the spinal cord in 5—7 days.

II. The blood-Bi is max. in 30—60 min. after injection and is const. for 3—48 hr.; the Ca is max. (15.6—17.9 mg. per 100 c.c.) in 1—2 hr. and is normal after 5 hr. In 24—72 hr. the serum-globulin and -albumin contain about the same amount of Bi.

CHEMICAL ABSTRACTS.

Secondary poisoning of birds and mammals. F. E. CARLOUGH and J. C. WARD (Science, 1932, 75, 335—337).—Experiments with hawks fed on rats poisoned by As, Tl, and strychnine show that large amounts of these substances are required to produce death and that the danger of secondary poisoning from them is small. L. S. THEOBALD.

Quantitative distribution of an arsenical antigen in the organism. F. HAUROWITZ and F. BREINL (Z. physiol. Chem., 1932, 205, 259—270).—The As content of various tissues and organs was determined after intravenous injection of an antigen (obtained by coupling diazotised arsanilic acid with protein) into the rabbit. The As content of the blood reaches the normal val. after 24 hr. The highest As content was found in the liver and marrow bones. The spleen was relatively high in As. The brain, skin, and muscle showed only a slight increase over normal. The kidneys contained much As probably in the form of excretable fission products of the antigen, since $\frac{1}{3}$ of the total As is excreted in 24 hr. Similar effects were observed on injection of immunised animals. J. H. BIRKINSHAW.

Pharmacology of lead. VI. Determination of small quantities of lead. B. BEHRENS and H. O. BEHRENS (Arch. exp. Path. Pharm., 1932, 164, 501—508).—Minute quantities of Pb ($1-10 \times 10^{-6}$ g.) may be determined by adding a suitable quantity of radioactive Pb, pptg. the total Pb as chromate, and measuring the proportion of radioactive Pb which remains unpptd. As the solubility of PbCrO_4 is approx. const. under the conditions employed, and the proportion of active and inactive Pb remaining in solution is equal to the proportions in which they are pptd., the original Pb present can be calc. W. O. KERMACK.

Porphyrin in the urine in lead poisoning. W. GROTEPASS (Z. physiol. Chem., 1932, 205, 193—197).—From the urine of a case of Pb poisoning there was isolated, as the Me ester, coproporphyrin derived from aetioporphyrin III. Uroporphyrin was absent. J. H. BIRKINSHAW.

Toxicity of distilled water. V. SACERDOTI (Arch. Farm. sperim., 1931, 53, 241—254).—With rabbits, intravenous doses of 120 c.c. and upwards of distilled H_2O per kg. of body-wt. disturb the renal functions and doses of 220—240 c.c. cause rapid death. T. H. POPE.

Action of ultra-short electromagnetic waves on silkworms' eggs irradiated prior to incubation. G. MEZZADROLI (Atti R. Accad. Lincei, 1931, [vi], 14, 441—443).—Exposure of silkworms' eggs for 30 min. to these radiations ($\lambda=2-3$ m.) accelerates hatching, growth, and spinning, and produces an increased yield. The effects are greater with "late" than with "early" varieties. T. H. POPE.

Biological effect of X-rays. I. Effect on blood constituents of splanchnicotomised or vagotomised dogs. II. Mechanism of decreased blood-sugar caused by X-rays. S. KIKUCHI (Tohoku J. Exp. Med., 1931, 17, 545—570, 571—578).—X-Irradiation of dogs increases the blood-sugar (25—50%), the max. being reached in

3—7 hr.; the site and dose are comparatively unimportant. The serum-protein and total N are increased initially. Irradiation of the liver area causes a large increase in total N and non-protein-N. The serum-Cl decreases; an initial decrease in inorg. P is followed by an increase. Ketonic substances increase only when the liver area is irradiated. A slight increase in lactic acid is followed by a decrease. Following splanchnicotomy, irradiation decreases the blood-sugar and does not affect lactic acid or total ketonic substances. Vagotomy does not appreciably change the effects of irradiation.

II. Lymph from the thoracic duct of irradiated dogs (unless subjected to splanchnicotomy before irradiation), when injected into rabbits, does not affect the blood-sugar. CHEMICAL ABSTRACTS.

General action of Röntgen rays. III. E. WOENCKHAUS and W. MÜNZEL (Arch. exp. Path. Pharm., 1932, 165, 145—160).—The irradiation of guinea-pigs with X-rays produces characteristic changes in the nos. of white blood-cells. Similar changes are produced in a rabbit into which blood has been transfused from another rabbit strongly irradiated by X-rays. In this case, besides the changes in the white blood-cells, hyperglycemia lasting for several days occurs. Defibrinated dog's blood irradiated *in vitro* and reintroduced into the animal causes characteristic changes in the nos. of leucocytes and lymphocytes. W. O. KERMACK.

Biological activity of visible monochromatic light. E. KEESER (Arch. exp. Path. Pharm., 1932, 164, 626—634).—Lecithin is decomposed by visible light and most rapidly by that of λ 580—630 m μ . The activity of certain enzymes is increased when the reaction mixture is irradiated with visible light, the most effective wave-lengths being, for blood catalase 660—730 m μ ; trypsin acting on gelatin, 510—580 m μ ; trypsin acting on caseinogen max. in violet; pepsin on ovalbumin 580—630 m μ ; pepsin on gelatin 430—470 m μ ; lipase on Et butyrate 430—470 m μ , secondary max. at 660—730 m μ . W. O. KERMACK.

Dehydrogenation in muscle. A. HAHN (Z. Biol., 1932, 92, 355—365).—Pyruvic acid is produced by the dehydrogenation of succinic, fumaric, citric, lactic, and hexosediphosphoric acids, and from lact-acidogen; it is probable that decomp. never goes farther than the 3-C-atom skeleton. In the intact muscle the nature of the end-products is unknown.

Natural acceptors" exist in muscle which play the same part as methylene-blue in the process. H. DAVSON.

Effect of p_{H} on the inactivation temperature of fruit oxidase. Y. WONG (Trans. Sci. Soc. China, 1931, 7, 88—94).—Resistance to heat was greatest at p_{H} 5—7; at p_{H} 2 or 12 the peroxidase was inactivated at room temp. in 24 hr. or less. CHEMICAL ABSTRACTS.

Isolation from erythrocytes of the enzyme which produces lactic acid. O. MEYERHOF (Biochem. Z., 1932, 246, 249—284).—Extracts of erythrocytes (man, rabbit, ox, horse, and, especially, goose and rat), having a glycolytic power greatly exceeding that of the intact cells, are prepared. The glycolysis is accompanied by production of hexosephosphoric

esters and requires the presence of the co-enzyme system necessary for the corresponding action of muscle extracts although the preformed co-enzyme of the blood-cells may not be identical with that of muscle. Hexokinase must also be present. The behaviour of the extracts of the erythrocytes is very similar to that of the corresponding muscle extracts, but the erythrocyte extracts do not hydrolyse glycogen. W. MCCARTNEY.

Antiglyoxalase of the pancreas. L. VON VARGHA (Biochem. Z., 1932, 246, 215—216).—The inhibition of lactic acid formation by glyoxalase on adding pancreatic extract is due not to the presence of antiglyoxalase, but to the union of the glyoxal with proteins and other substances.

P. W. CLUTTERBUCK.

Starch hydrolysis as affected by light. II. A. E. NAVEZ and B. B. RUBENSTEIN (J. Biol. Chem., 1932, 95, 645—660; cf. A., 1929, 216).—The hydrolysis of starch by a diastase prep. purified in the dark or under very dim red light and in presence of certain dyes of the fluorescein series is accelerated by sp. zones of light-waves to a greater extent than that occurring in absence of these dyes. This photosensitisation is a max. at the limit of the regions between max. fluorescence and max. absorption for the dye used. Both ordinary and plane-polarised light have the same effect, which is due to removal of an inhibitory substance attached to the diastase complex by the peroxide action of a photosensitive complex between enzyme and dye.

F. O. HOWITT.

α -Glucosidase and disaccharide fission. K. MYRBACK (Z. physiol. Chem., 1932, 205, 248—250).—The enzymes of *Aspergillus Wentii* and taka-diastase hydrolyse maltose but not α -methylglucoside, contrary to Weidenhagen's hypothesis (A., 1930, 499).

J. H. BIRKINSHAW.

Enzymic fission of inulin. R. WEIDENHAGEN (Naturwiss., 1932, 20, 254).— β -*h*-Fructosidase, a typical enzyme for the fission of sucrose, converts non-reducing inulin into fructose quantitatively; the reaction velocities for the conversion of sucrose and inulin are in the ratio of 7500 : 1, the low rate of the inulin reaction being due either to the colloidal form of the polysaccharide or the method of union of its fructose residues. Simple glucosidases are capable of splitting the polysaccharides. H. DAVSON.

Emulsin. V. B. HELFERICH, R. GOOTZ, and G. SPARMBERG (Z. physiol. Chem., 1932, 205, 201—212; cf. A., 1931, 873).—The activity of emulsin on the β -*d*-glucosides of MeOH, glucose (cellobiose), PhOH, and saligenin (salicin) was compared with that on the corresponding β -*d*-galactosides. The activity ratio glucoside/galactoside was const. for each type of substrate, using different enzyme preps., indicating that β -glucosidase and β -galactosidase are identical.

J. H. BIRKINSHAW.

Emulsin. VI. B. HELFERICH and H. APPEL (Z. physiol. Chem., 1932, 205, 231—247).—The following substrates and precursors were prepared: β -ethyl-*l*-arabinoside, (I) m. p. 136—137°, $[\alpha]_D^{25} +9.28^\circ$, triacetyl- α -ethyl-*l*-arabinoside, m. p. 72.5°, $[\alpha]_D^{25} +8.1^\circ$ (in CHCl_3), α -ethyl-*l*-arabinoside (II), m. p. 124—126°, $[\alpha]_D^{25} +14.4^\circ$, β -phenyl-*d*-xyloside (III), m. p. 178—179.5°, $[\alpha]_D^{25} -47.0^\circ$, α -phenyl-*d*-galactoside (IV), m. p. 143—145°, $[\alpha]_D^{25} -217^\circ$, triacetyl- β -phenyl-*d*-glucoside 6-bromohydrin, m. p. 134—136°, $[\alpha]_D^{25} -27.6^\circ$, β -phenyl-*d*-glucoside 6-bromohydrin (V), m. p. 162.5—164°, $[\alpha]_D^{25} -95.4^\circ$ (all m. p. corr.). The substrates salicin, β -phenyl-*d*-glucoside, β -methyl-*d*-glucoside, β -phenyl-*d*-galactoside, (IV), (III), (V), (II), trehalose, α -methyl-*d*-mannoside, (I), β -methyl-*d*-xyloside, α -phenyl-*d*-glucoside are hydrolysed by emulsin at rates varying from 0.72 min. to 1000 days for 50% fission in the order given. It is suggested that all the activities of emulsin are due to a single enzyme.

J. H. BIRKINSHAW.

Structure of organic compounds and their inhibiting effect on liver-esterase. Resemblance to a lyotropic series of anions. D. GLICK and C. G. KING (J. Biol. Chem., 1932, 95, 477—482; cf. this vol., 193).—Measurement of the inhibiting effect of CN, I, NO₃, SH, OH, Cl, CO, CO-NH₂, and NH₂ groups, attached to an amyl radical, on liver-esterase gives a series similar to the lyotropic series of analogous ions in their effect on protein dispersion in aq. solution. Substitution of a Ph group for the amyl group has little effect on the series; unsaturation and increasing size of the hydrocarbon ring increase the inhibition. Hexylresorcinol produced the greatest inhibiting effect. H. DAVSON.

Activity-*p*_s curves in enzymic resolution of racemates. H. FISCHGOLD and R. ANMON (Biochem. Z., 1932, 246, 463—470).—A method by which the difficulties encountered by the authors (A., 1931, 874) in obtaining satisfactory activity-*p*_s curves can be overcome is described and applied to the hydrolysis of Me *dl*-mandelate by esterase from human liver with and without the addition of strychnine. The equation and curve for a racemate have the typical form of those of a residual dissociation curve. The equation showing the relation between the apparent dissociation const. of the racemate and those of the optically active modifications and also the equation for the hydrolysis const. of the racemate are given.

W. MCCARTNEY.

Formation of acetaldehyde in pancreatic digestion and on irradiation of proteins. A. HOFFMEISTER (Z. physiol. Chem., 1932, 205, 183—192).—In pancreatic digestion of fibrin, ovalbumin, and caseinogen in 0.5% NaHCO₃, MeCHO is produced. In peptic digestion in 0.25% HCl no MeCHO is formed. Ultra-violet irradiation of peptone and blood-albumin also yields MeCHO.

J. H. BIRKINSHAW.

Aminopolypeptidase. A. K. BALLS and F. KOHLER (Z. physiol. Chem., 1932, 205, 157—170).—By Fe(OH)₃ adsorption and COMe₂ pptn. a prep. of aminopolypeptidase is obtained having 145 times the original activity. It contains P and N (as protein); S, As, carbohydrates, tryptophan, and tyrosine are absent. The COMe₂ preps. are not so stable as those obtained by simple Fe adsorption. On keeping they lose activity, the loss being proportional to the increase in conductivity. On dialysis of a purified prep. the enzymic activity and the P content decrease to the same extent. The ratio of P content

to enzymic concn. is const. for the same prep., but varies from prep. to prep. J. H. BIRKINSHAW.

Urea formation in the animal body. V. A. 3. Formation in surviving organs and in their press-juice. S. SALASKIN and L. SOLOVIEV (*Z. physiol. Chem.*, 1932, 205, 171—182; cf. A., 1931, 1332).—In autolysis of buffered liver tissue or press-juice, O_2 inhibits urea formation and lowers the active arginase content. CO_2 scarcely affects the urea and increases the active arginase in the liver tissue experiment only. An arginase solution is practically unchanged after $3\frac{1}{2}$ hr. at 38° , but O_2 decreases the active arginase, CO_2 only slightly. In solutions previously treated with O_2 , CO_2 and H_2 decrease, and in solutions pretreated with CO_2 , O_2 decreases, the arginase. Cysteine increases the arginase after depression by gas treatment. Cystine had no action. J. H. BIRKINSHAW.

Chemical nature of urease. J. B. SUMNER and J. S. KIRK (*Z. physiol. Chem.*, 1932, 205, 219—230).—2% gum arabic is a better "protector" for urease than caseinogen digest with additions of alanine and cysteine. When large amounts of urease are treated with trypsin the remaining protein precipitable by sulphosalicylic acid is practically equiv. to the remaining urease activity after correcting for the protein of the trypsin. With small amounts of urease, trypsin causes no diminution in the ppt. with anti-urease serum, except that due to auto-inactivation. Dil. HCl completely destroys the activity of urease and its precipitability by immune serum. The inactivated product is quickly digested by trypsin. A method of purification of anti-urease is described. J. H. BIRKINSHAW.

Cell-nuclei. I. O. FURTH. Yeast nucleic acid. Its alkaloid salts, purification, and purine content. T. LEIPERT and T. KUROKAWA (*Biochem. Z.*, 1932, 246, 1—9).—Alkaloidal salts are prepared containing with each mol. of yeast nucleic acids, 2 mols. of quinine, 2 mols. of quinidine, 4 mols. of brucine, and 4 mols. of strychnine, respectively. Purification of the nucleic acid, by way of the brucine salt and by pptn. of its solution in conc. H_3PO_4 with $AcOH-EtOH$, is described. Purified preps. contain 9.06% P and 16.01% N, and give on hydrolysis 95.4—101.7% (mean 99.5%) of the theoretical amount of purine base-N. P. W. CLUTTERBUCK.

Significance of oxygen in yeast metabolism. F. WINDISCH (*Biochem. Z.*, 1932, 246, 332—382; cf. A., 1931, 101).—An apparatus in which respiration and fermentation can be studied under aerobic, semi-anaerobic, and wholly anaerobic conditions is described. The fermenting power of cultivated yeasts (25 species tested) is increased by anaerobic propagation which, at the same time, produces characteristic morphological changes in them and also results in stimulation of their metabolic activity as indicated by increased respiration. O_2 stimulates the fermenting power of yeasts which have ceased to grow, although it has an inhibiting effect on growing yeasts and on their respiration. Wild yeast (*Torula utilis*) behaves like cultivated species. With yeasts grown aerobically the rate of fermentation and of respiration decreases with age, but nevertheless those

grown anaerobically, after passing through several generations in the absence of O_2 , cease to propagate unless O_2 is admitted. Rise of temp. acts like O_2 on yeasts, increasing propagation and diminishing metabolic activity. In all cases increase (or decrease) in the degree of fermenting power is accompanied by corresponding increase (or decrease) in respiratory activity. W. MCCARTNEY.

Prolonged action of potassium chloride on the optimum growth temperature of yeasts. E. BACHRACH and J. ROCHE (*Compt. rend.*, 1932, 194, 1023—1024).—The rise in optimum growth temp. of *Saccharomyces* produced by KCl in a concn. of 10% is a function of the duration of such action. P. G. MARSHALL.

Conditions of activation of washed zymoin. III. A. A. STHEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1931, 34, 1347—1350; cf. A., 1929, 1107).—Euler's principle is unable to reactivate an inactivated zymase system unless a suitable H-acceptor is simultaneously present. Methylene-blue, $MeCHO$, boiled yeast-juice, the boiled washings, or a protein solution free from Euler's principle can act in this way. Auhagen's "co-zymase II" (A., 1931, 1457) is a H-acceptor naturally present in yeast. E. S. HEDGES.

Activation of zymase with rubidium chloride. M. GIORDANI (*Annali Chim. Appl.*, 1932, 22, 153—156).—Rb may replace K in the activation of zymase, but large doses are toxic. O. F. LUBATTI.

Phosphorylation of galactose. M. GIORDANI (*Annali Chim. Appl.*, 1932, 22, 148—153).—Bottom yeast (Zürich) is superior to pure cultures of *Saccharomyces cerevisiae* in the fermentation of mixtures of galactose containing fructose. O. F. LUBATTI.

Mitogenetic spectral analysis. IV. Mitogenetic spectrum for the hydrolysis of nucleic acid. A. GURWITSCH and L. GURWITSCH (*Biochem. Z.*, 1932, 246, 124—126).—The detection of mitogenetic radiation during the hydrolysis of thymus nucleic acid with the tissue pulp of mouse adenocarcinoma is described. Spectral analysis of the radiation gave typical results readily distinguished from the similar spectra for glycolysis and oxidation. P. W. CLUTTERBUCK.

Transmission of mitogenetic effects in solution and the relationship between enzymic power and irradiation. A. GURWITSCH and L. GURWITSCH (*Biochem. Z.*, 1932, 246, 127—133).—The process described in the preceding abstract is further analysed. P. W. CLUTTERBUCK.

Theory of mitogenetic radiation. G. FRANK and S. SALKIND (*Biochem. Z.*, 1932, 246, 247—248).—A reply to the criticisms of Moissejeva (this vol., 201). P. W. CLUTTERBUCK.

Fermentation products of moulds. IX. Y. SUMIKI (*J. Agric. Chem. Soc. Japan*, 1931, 7, 819—826).—2-Hydroxymethylfuran-5-carboxylic acid was produced by *Aspergillus clavatus*, *A. niger*, *A. oryzae*, *A. Wentii*, and *A. glaucus*; *A. clavatus* produced mannitol, whilst others produced only $EtOH$, $MeCHO$, succinic, oxalic, fumaric, gluconic, and acetic acids. CHEMICAL ABSTRACTS.

Action of moulds on solutions of aldoses. III. Formation of *d*-gluconic acid by *Penicillium crustaceum* (L.), Fries. A. ANGELETTI (Annali Chim. Appl., 1932, 22, 59—62).—This pathogenic mould gives a 12.2% yield (on the sugar) of *d*-gluconic acid when grown on *d*-glucose solutions (cf. this vol., 145). T. H. POPE.

Growth and sterol content of moulds. L. M. PRUESS, H. J. GORCICA, H. C. GREENE, and W. H. PETERSON (Biochem. Z., 1932, 246, 401—413; cf. A., 1931, 531).—Factors which favour the growth of *Aspergillus* (30 species tested), *Penicillium* (20 species tested), and other (15 species tested) moulds grown on inorg. and org. media (both containing glucose) also favour, to a greater extent, the production of sterols in the moulds. Acidity of the medium is detrimental to the growth. W. MCCARTNEY.

Mycological methods in the identification of sugars and other carbon compounds. A. CASTELLANI (J. State Med., 1931, 39, 621—639).—Of 27 carbohydrates tested, rhamnose was the only one fermented by *B. rhamnose-fermentans*.

CHEMICAL ABSTRACTS.

Decomposition of lactic and pyruvic acids by acetic bacteria. S. HERMANN and P. NEUSCHUL (Biochem. Z., 1932, 246, 446—459; cf. A., 1931, 769).—Of 13 species of acetic bacteria all except *B. gluconicum* convert Na lactate and Na pyruvate first into acetoin, which is then oxidised to AcOH (occasionally then to CO₂), NaHCO₃ being also produced. *B. gluconicum* also converts the salts into AcOH, but not by the same route.

W. MCCARTNEY.

Growth of micro-organisms (*B. coli*). M. FAGUET (Compt. rend., 1932, 194, 1027).—The opacity of bouillon inoculated with *B. coli* is taken as an indication of the growth. A pencil of rays from a monochromatic source of light passes through the medium (at 37°) and impinges on a photo-electric cell connected with a galvanometer and an automatic continuous recording apparatus.

P. G. MARSHALL.

Proteases of "acidoproteolytes." C. GORINI, W. GRASSMANN, and H. SCHLEICH (Z. physiol. Chem., 1932, 205, 133—136).—The acidity produced in milk cultures of acidoproteolytes corresponds with a *p_H* of 4—5. The enzyme excreted is not of the true papain type. It has optimum *p_H* 7.0 for gelatin (6.0 for skim-milk) and is inhibited by HCN. Peptidases are present in the bacterial cells, but are not excreted into the medium. J. H. BIRKINSHAW.

Fission of arcaine by micro-organisms. III. Biological degradation of agmatine to carbamylputrescine. F. LINNEWEH (Z. physiol. Chem., 1932, 205, 126—132; cf. this vol., 94).—By the action of putrefactive organisms agmatine affords carbamylputrescine (I) (dipicrate, m. p. 164—165°; hydrochloride, m. p. 185°). (I) was synthesised from putrescine monosulphate and BaCNO. Putrescine disulphate similarly yields dicarbamylputrescine, m. p. 225° (dipicrate, m. p. 168—169°). The conversion of guanidino- into carbamyl derivatives is a widespread biological reaction. J. H. BIRKINSHAW.

Microbiology of soil. VI. Synthesis of ammonia by *Azotobacter*. S. VINOGRADSKI (Ann. Inst. Pasteur, 1932, 48, 269—300; cf. this vol., 437).—The primary product of N fixation by *Azotobacter* is NH₃, which is subsequently assimilated by the organism. In certain circumstances assimilation may be arrested, but NH₃ production continues and NH₃ appears in the media. Liberation of NH₃ from *Azotobacter* cells continues after their death, and may be entirely a post-mortem process. *Azotobacter* utilises the decomp. products of vegetable tissues as a source of energy. A. G. POLLARD.

Serological study of the polysaccharides of meningococcus, *B. anthracis*, *Proteus vulgaris*, *B. subtilis*, and *B. mesentericus*. J. ZOZAYA (J. Exp. Med., 1931, 54, 725—732).

CHEMICAL ABSTRACTS.

Pneumococcus. I. Specific antigenic carbohydrate of type-I pneumococcus. II. Ether-soluble fraction of type-I pneumococcus. A. WADSWORTH and R. BROWN (J. Immunol., 1931, 21, 245, 255).—I. Shiemann's sp. precipitable substance and Enders' A substance appear to be identical.

II. The Et₂O-sol. fraction, low in N and P, failed to give protein, sterol, glycerol, or carbohydrate reactions.

CHEMICAL ABSTRACTS.

Electrophoresis experiments with the virus and protective bodies of yellow fever. M. FROBISHER (J. Exp. Med., 1931, 54, 733—745).

CHEMICAL ABSTRACTS.

Properties of the bacteriophage. K. MURAMATSU (Japan. J. Exp. Med., 1931, 9, 333—342).—The bacteriophage is inactivated at *p_H* <4 or >11; the optimum is *p_H* 5—9. It is electronegative. An attempt to determine the size of the mol. is described.

CHEMICAL ABSTRACTS.

Heat-inactivation of antistaphylococcus bacteriophage. A. P. KRUEGER (J. Gen. Physiol., 1932, 15, 363—368).—The heat-inactivation of antistaphylococcus bacteriophage suspended in broth of *p_H* 7.6 at temp. between 51° and 62° proceeds as a unimol. reaction, and the crit. thermal increment for the inactivation is 101,000. This val., being the same as that determined by other workers for the denaturation of protein, would indicate that such a reaction is involved in the heat-inactivation of the bacteriophage. A. LAWSON.

Antiseptic and trypanocidal action of certain styryl- and anil-quinolinecarboxylamides. C. H. BROWNING, J. B. COHEN, J. N. ASHLEY, and R. GULBRANSEN.—See this vol., 522.

Bactericidal properties of mono-ethers of dihydric phenols. III. Mono-ethers of pyrocatechol. Comparative notes on the three series of mono-ethers. E. KLARMANN, L. W. GATES, and V. A. SHTERNOV (J. Amer. Chem. Soc., 1932, 54, 1204—1211; cf. this vol., 308).—The following mono-ethers of pyrocatechol (I) are prepared: *Et*, b. p. 74—76°/4 mm.; *Pr*, b. p. 80—83°/4 mm.; *Bu*, b. p. 93—96°/5 mm.; *amyl*, b. p. 104—106°/4 mm.; *sec.-amyl*, b. p. 102—104°/5 mm.; *hexyl*, b. p. 114—116°/3.5 mm.; *heptyl*, b. p. 125—127°/4 mm.; *Ph*, m. p. 104°; *benzyl*, b. p. 157°/6 mm.; *CH₂Ph-CH₂*,

m. p. 48°; $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2$, m. p. 51°. These ethers are bactericidal agents of varying potency, depending on the mol. wt. and structure of the substituting radical. (I) is less effective than, but guaiacol has approx. the same activity as, PhOH . The activity of the ethers towards *B. typhosus* reaches a max. at C_5 and then decreases. With *S. aureus*, it increases with length of the C chain. The sec.-amyl ether is less effective in both cases than the n-ether. Of the aromatic ethers, the $\text{CH}_3\text{Ph}\cdot\text{CH}_2$ ether is most effective in both cases. The quinol ethers (*loc. cit.*) are (with certain exceptions) more effective than the above series. The higher mono-alkyl ethers of (I) have not the high activity towards *S. aureus* of the corresponding resorcinol and quinol ethers. The max. effect on *B. typhosus* is shown by the amyl ethers of quinol and pyrocatechol, and by the hexyl ether of resorcinol. The activities of the mono-ethers of the three dihydric phenols towards *B. coli* and *B. pyocyaneus* are similar to those with *B. typhosus*. The results with *Streptococcus haemolyticus* resemble closely those with *S. aureus*. *Vibrio cholerae* is very susceptible to the action of certain of the compounds studied. The three hydroxydiphenyl sulphides are more active towards *B. typhosus* than the hydroxydiphenyl ethers. \

C. J. WEST (b).

Bactericidal action of metallic silver. P. LASSEUR, M. PIERRET, A. DUPAIX, and C. MAGUITOT (*Compt. rend.*, 1932, 194, 1024—1026).—With suspensions of *B. coli*, *B. chlororaphis*, *B. prodigiosus*, and *B. caryocaneus* the efficiency of the bactericidal action is dependent on the disposition of the metallic wire.

P. G. MARSHALL.

Influence of the blood constituents on the bactericidal power of colloidal silver. S. UEGAKI (*Japan. J. Exp. Med.*, 1930, 8, 573—613).—Blood-serum decreases the effect in proportion to its protein content. Glucose inhibits and lactic acid promotes the bactericidal power.

CHEMICAL ABSTRACTS.

Adrenals and the carbohydrate metabolism of the musculature. H. F. ROESE (*Z. ges. exp. Med.*, 1931, 78, 426—437; *Chem. Zentr.*, 1931, ii, 3354).—Experiments on the perfusion of extremities in the presence or absence of the adrenals are recorded. The results are similar to those obtained by Cori with adrenaline.

A. A. ELDRIDGE.

Function of the adrenal medulla. J. L. SVIRBELY and A. SZENT-GYORGYI (*Nature*, 1932, 129, 541—542).—Adrenaline appears to be a decomp. product of the substance primarily produced by the adrenal gland. When post-mortem enzymic reactions are minimised by rapid excision and cooling of the glands, careful extraction with 0.5% $\text{CCl}_3\text{CO}_2\text{H}$ gives a new substance, called "novadrenaline," which has a physiological action different from that of adrenaline. For large doses the rise in blood pressure produced is higher than that produced by corresponding amounts of adrenaline. Novadrenaline appears to be an ester of adrenaline with the esterifying radical attached to the alcoholic OH of the side chain.

L. S. THEOBALD.

Adrenaline hyperglycaemia. I. Effect of thyroxine. II. Effect of posterior pituitary

substances. S. SILVER and E. MISLOWITZER (*Z. ges. exp. Med.*, 1931, 78, 733—740, 741—748; *Chem. Zentr.*, 1931, ii, 2629).—I. Adrenaline causes less marked hyperglycaemia in thyreotoxic than in normal animals owing to the liver being poor in glycogen.

II. Orasthin and tonephin similarly diminish adrenaline hyperglycaemia.

A. A. ELDRIDGE.

Effect of adrenaline on the free muscle-sugar and total carbohydrate. F. BISCHOFF and M. L. LONG (*J. Biol. Chem.*, 1932, 95, 743—754).—In adrenalinised (0.5 mg. per kg.) rabbits under amylal anaesthesia the fermentable muscle-sugar was significantly lower than that of controls. Examination of the muscle-carbohydrate distribution indicated a depletion by adrenaline of a carbohydrate reserve of unknown constitution as well as of glycogen. No marked changes occurred in the urinary N or in the muscle-fat. The possibility of conversion of carbohydrate into fat is discussed.

F. O. HOWITT.

Action of insulin inhalation with an atmosphere containing carbon dioxide. K. WILKOWITZ and H. SCHIEBE (*Z. ges. exp. Med.*, 1931, 78, 757—763; *Chem. Zentr.*, 1931, ii, 2630).—Repeated inhalations of insulin at short time intervals using an air stream containing 6% CO_2 produce a decrease in blood-sugar; 4—6 times the effective subcutaneous dose is necessary to produce an equal effect.

L. S. THEOBALD.

Effect of treatment with glucose and insulin under reduced atmospheric pressure. F. HELMANN (*Z. ges. exp. Med.*, 1931, 78, 223—228; *Chem. Zentr.*, 1931, ii, 2750).—In rats and rabbits kept under 310—430 mm. pressure fatty degeneration of the liver and disappearance of liver-glycogen take place; in animals receiving insulin and glucose the liver-glycogen is always higher.

A. A. ELDRIDGE.

Effect of extracts of endocrine organs on carbohydrate metabolism of normal and hypophysectomised dogs. K. KOBAYASHI (*Sci-i-kwai Med. J.*, 1930, 49, no. 12, 71—114).—Blood-sugar is 0.102, 0.07%, and -inorg. P 4.2, 3.2 mg. per 100 c.c., respectively. Pituitrin and pituglandol increase the blood-sugar and decrease the -inorg. P; antuitrin decreases both, whilst thyroprotein decreases the blood-inorg. P but does not affect the -sugar. The lowering of inorg. P by injection of insulin is more marked in the normal animal; the increase in blood-sugar and decrease in inorg. P due to adrenaline are less in the hypophysectomised dog. Injection of oophormin causes a slight transient rise in the blood-sugar in such animals.

CHEMICAL ABSTRACTS.

Growth-promoting hormone of the pituitary. A. SIMON and L. BINDER (*Arch. exp. Path. Pharm.*, 1932, 165, 120—127).—The method of Van Dyke and Wallen-Lawrence (*J. Pharm. Exp. Ther.*, 1930, 38, 349) for the testing of the growth-promoting principle of the anterior lobe of the pituitary is satisfactory, negative results being obtained with thymocrescin, extracted from the thymus gland. It is better to use female than male rats for this method.

W. O. KERNACK.

Effect of di-iodotyrosine on abnormal thyroid metabolism. B. KOMMERELL (*Arch. exp. Path.*

Pharm., 1932, 165, 169—176).—The effect of the subcutaneous administration of thyroxine on the basal metabolism, calc. per unit surface area, is the same for parathyroidectomised as for normal dogs. Di-iodotyrosine (0.1—0.5 g.) administered by mouth does not affect the basal metabolism.

W. O. KERMACK.

Vagus substance. G. VIALE (Rev. sudamer. endocrinol., 1931, 14, 583—590).—The vagus substance is thermostable; its action, which largely resembles that of acetylcholine, is inhibited by atropine. The substance is probably not necessary for the vagus function. CHEMICAL ABSTRACTS.

Callicrein. VII. H. KRAUT, E. K. FREY, E. BAUER, and F. SCHULTZ (Z. physiol. Chem., 1932, 205, 99—114; cf. A., 1930, 1624).—Adsorption of callicrein on $\text{Al}(\text{OH})_3$ or BzOH gives an activity of 1 unit per 0.3 mg. Further purification by adsorption on charcoal, Pb phosphate, or $\text{Al}(\text{OH})_3$ yields still impure preps. containing 1 unit per 0.1 mg. From one or other of these preps. the following groups are absent: nuclein bases, pentoses, H_3PO_4 , and the Millon, ninhydrin, and biuret reactions are negative. The Pauly diazo-reaction is positive but no relationship is shown between its intensity and callicrein activity.

J. H. BIRKINSHAW.

Effect of the spleen hormone "prospen" on blood-sugar. O. HEPPE and E. SCHLIEPHAKE (Z. ges. exp. Med., 1931, 78, 209—222; Chem. Zentr., 1931, ii, 2630).—Injection of prospen into rabbits causes irregular hypoglycæmia. Choline differs from prospen-hypoglycæmia.

A. A. ELDRIDGE.

Thelykinin and androkinin, the female and male sexual hormones, in [the urine of] women. H. SIEBKE (Arch. Gynakol., 1931, 146, 417—462; Chem. Zentr., 1931, ii, 2628).—Further thelykinin analyses of the urine of women have been made and are discussed in relation to hormone therapy. In menstruation and pregnancy and in cases of cancer the androkinin content reaches high vals. Androkinin could not be detected in the carcinoma itself.

L. S. THEOBALD.

Crystalline sex hormones from the urine of pregnant mares. A. GIRARD, G. SANDULESCO, A. FRIDENSON, C. GAUDEFRY, and I. J. J. RUTGERS (Compt. rend., 1932, 194, 1020—1022).—A crystallographic description of equilin (cf. this vol., 433) is given. It occurs only in the orthorhombic form, whilst folliculin occurs in monoclinic form and is transformed into the orthorhombic form on fusion or sublimation. Both hormones are levorotatory, and the absorption spectra are analogous. Equilin (semicarbazone, m. p. 265—267°; orime, m. p. 221—223°; Bz derivative, m. p. 197—198°) sublimes easily in a vac. at 170—200°; its oestrogenic activity is only $\frac{1}{3}$ that of folliculin. From the most sol. fractions a third hormone, *hippulin*, has been isolated (m. p. 233°; $[\alpha]_D +128^\circ$ in 1% solution in dioxan); it sublimes unchanged, has approx. the same oestrogenic activity as equilin, and is isomeric with it.

P. G. MARSHALL.

Biological test for the corpus luteum hormone. H. KNAUS (Klin. Woch., 1931, 10, 742—743; Chem.

Zentr., 1931, ii, 3353).—Polemical, in support of the specificity of the author's test. A. A. ELDRIDGE.

Hormone action in plants and increase in hormone [content] by red light. H. KUSTNER (Klin. Woch., 1931, 10, 1585; Chem. Zentr., 1931, ii, 2892).—Urine of pregnancy stimulates the germination of barley in red light more than an equal quantity of normal female urine of the same N content.

A. A. ELDRIDGE.

Biological detection of vitamins. I, II. H. SEEL (Chem.-Ztg., 1932, 56, 245—247, 266—267).—A summary of existing knowledge on the occurrence, properties, and biological determination of vitamin-A, -B, -C, and -D.

F. O. HOWITT.

Vitamin-A, -B₁, -B₂, and -C content of Sultanina and Malaga grapes and two brands of commercial grape juice. E. P. DANIEL and H. E. MUNSELL (J. Agric. Res., 1932, 44, 59—70).—Both varieties of grape contained fair amounts of vitamin-B₁ and small amounts of -A. The amount of -C present was insufficient to prevent scurvy in guinea-pigs. Vitamin-B₂ was present in min. quantity in Sultanina and lacking in Malaga grapes. One commercial juice (from Concord grapes) contained a small quantity of -B₁, but was lacking in -A, -C, and -B₂. No vitamins could be detected in the other juice (mixture of juices from Flame Tokay and Zinfandel varieties).

W. G. EGGLETON.

Vitamin-A and the iodine-fat balance. F. E. CHIDESTER (Science, 1932, 75, 286—287).—The significance of carotene in the formation of vitamin-A in animals is discussed in relation to the I-fat balance.

L. S. THEOBALD.

Carr-Price reaction with carotenoids. B. VON EULER and P. KARRER (Helv. Chim. Acta, 1932, 15, 496—502).—The Carr-Price reaction depends on the reaction time, mode of mixing, and to some extent on the quality of light used in its observation. The method is suitable for determination of cod-liver oil val. when the max. blue coloration is reached within 3 min.; the accuracy is estimated at 10%.

H. A. PIGGOTT.

Preparation of crystalline anti-beriberi vitamin from yeast. R. TSCHESCHE (Chem.-Ztg., 1932, 56, 166—167).—A review and summary (cf. this vol., 310). The cryst. hydrochloride is identical with the prep. of Jansen and Donath, which likewise contains S.

R. K. CALLOW.

Avitaminosis-B and the role of the factors and B₆ in cell oxidation. O. K. COSLA, O. VASILCO, and S. OERIU (Arch. exp. Path. Pharm., 1932, 164, 608—620).—A dog on diet of high calorific val. but free from vitamin-B exhibits certain abnormal features of metabolism including an abnormally high urinary C/N ratio and the excretion of lactic acid and MeCHO in the urine. These symptoms are removed by the administration of fresh brewers' yeast or of insulin. Yeast washed with distilled H₂O is without effect, the active factor being the H₂O-sol. vitamin-B₁.

W. O. KERMACK.

Avitaminosis. IV. Effect of a deficiency of vitamin-B complex on lipin metabolism and glycogen content of the liver of the albino rat.

B. SURE and M. E. SMITH. V. Specific effect of vitamin-B₁ deficiency on the differential count of the albino rat. B. SURE and D. J. WALKER (Arch. Int. Med., 1932, 49, 397—404, 405—408).—IV. B-Avitaminosis is characterised by a marked reduction in the liver-glycogen and by a lipæmia indicated by an increase in fatty acids and their I val., cholesterol, and lecithin.

V. The deficiency results in a decrease of lymphocytes and a corresponding increase of polymorphonuclear leucocytes in the blood. F. O. HOWITT.

Hexuronic acid as the antiscorbutic factor. J. L. SVIRBELY and A. SZENT-GYÖRGYI (Nature, 1932, 129, 576).—Guinea-pigs receiving daily 1 mg. of cryst. hexuronic acid, prepared from ox suprarenal glands, showed no signs of scurvy, whilst controls receiving an amount (1 c.c.) of lemon juice less than the min. protective dose showed mild symptoms of scurvy. Negative controls receiving only the basal diet survived for an average period of 26 days and showed severe symptoms. L. S. THEOBALD.

Hexuronic acid as the antiscorbutic factor. W. N. HAWORTH (Nature, 1932, 129, 576).—The hexuronic acid (cf. preceding abstract) is probably the 6-carboxylic acid of a keto-hexose, which does not appear to be related to *d*-fructose or to the ketose corresponding with *d*-galactose. L. S. THEOBALD.

Hexuronic acid as the antiscorbutic factor. E. L. HIRST and R. J. W. REYNOLDS (Nature, 1932, 129, 576—577).—Hexuronic acid (cf. preceding abstracts), m. p. 184—187° (decomp.), gives irregular aggregates of almost colourless crystals, composition C 41.0, H 4.7% (N and OMe absent), $[\alpha]_D^{20} +23^\circ$ increasing to $+31^\circ$ in 3 days, and decreasing to zero in 11 days. Fehling's solution, AgNO₃, and KMnO₄ are reduced in the cold, the Molisch test and orcinol reaction are positive, but the naphthoresorcinol test for glycuronic acid is negative. Oxidation by atm. O₂ in alkaline solution with Cu as catalyst introduces CO₂H in place of a primary alcohol group: the product reduces Fehling's solution. Neutral, acid, or slightly alkaline KMnO₄ rapidly oxidises hexuronic acid to the same stage and then adds a further atom of O per mol. more slowly to give a non-reducing product. NHPH·NH₂ in dil. AcOH gives dark-coloured, amorphous, impure products, whilst *p*-bromophenyldiazine in dil. AcOH and Ba hexuronate yield dark-red micro-crystals, m. p. 230—235° (decomp.), of the *p*-bromophenylosazone of a hexose-uronic acid, with a formula C₁₈H₁₈O₅N₄Br₂. A basis for the above reactions is outlined.

L. S. THEOBALD.

Biological evaluation of vitamin-D preparations. F. HOLTZ, F. LAQUER, H. KREITMAIR, and T. MOEL (Münch. med. Woch., 1931, 78, 1688—1689; Chem. Zentr., 1931, ii, 3355).—A discussion.

A. A. ELDRIDGE.

Irradiated milk: amount of vitamin-D and its rate of formation. G. C. SUPPLEE, Z. M. HANFORD, M. J. DORCAS, and H. H. BECK (J. Biol. Chem., 1932, 95, 687—697; cf. this vol., 312).—The degree of antirachitic potency imparted to milk by ultra-violet irradiation bears a direct relationship to the amount of energy applied up to certain limits beyond

which additional energy does not increase the content of vitamin-D proportionately. This irradiation, the efficiency of which is greatest during the first few sec. of exposure, produces a max. concn. of vitamin (0.0025 mg. per litre) when approx. 2.5×10^6 ergs per c.c. have been applied. The total energy emission is a more important factor in the irradiation of milk than is the spectral energy distribution.

F. O. HOWITT.

Separation of the reactions in photosynthesis by means of intermittent light. R. EMERSON and W. ARNOLD (J. Gen. Physiol., 1932, 15, 391—420).—With *Chlorella pyrenoidosa* photosynthesis involves a light reaction taking place in about 10^{-5} sec., unaffected by temp., and a dark reaction taking place in about 0.04 sec. at 25°, and 0.4 sec. at 1.1°. The light reaction is dependent on CO₂ concn. and is inhibited by narcotics, the dark reaction being unaffected by either of these factors, but inhibited by CN'. *Chlorella vulgaris* and *Zostera marina* gave parallel results. A. LAWSON.

Biochemical study of maize grains. M. I. SMIRNOVA (Bull. Appl. Bot., Russia, 1931, 25, 329—343).—The hydrolysis of starch by diastase is about twice as rapid in "sweet" maize grain as in "flint" or "soft" grain. The catalase content of the grains at the base of the cob is 4—5 times as great as of those at the top, probably owing to difference in maturity. About 95% of the fat, 80% of the sugar, and nearly all the oil are conc. in the embryo.

CHEMICAL ABSTRACTS.

Estimation of the quality of seeds by their enzyme content. M. I. LISHKEVITSCH (Bull. Appl. Bot., Russia, 1931, 25, 103—126).—A high catalase and amylase activity is found in the grain of barley and wheat which, because grown in higher latitudes, never reached full maturity. In ripe grains the starch is less digestible by amylase than in unripe ones. The activity of lipase in oleiferous plants is less affected by conditions of ripening, but that of protease varies inversely with the degree of maturity.

CHEMICAL ABSTRACTS.

Changes in leaves during the night. F. E. DENNY (Contr. Boyce Thompson Inst., 1932, 4, 65—83).—In many plants there occurred an increase in the fresh wt. of leaves during the night. The dry wt. decreased markedly in many cases (mainly herbaceous plants), but was only slightly affected in others (mainly woody plants). Changes in the N content were small. During artificially prolonged darkness there was a transition of insol. to sol. N, but no translocation of N from the leaves occurred. Considerable changes in carbohydrate contents are recorded. In some species more than half of the total carbohydrate disappeared during the night, starch being notably affected. A. G. POLLARD.

Significance of activators and paralyzers in plant protein metabolism. T. SCHULZE (Planta [Z. wiss. Biol.], 1932, 16, 116—173).—The protein balance in isolated leaves tends to reach an equilibrium characterised by a "stability val." of protein per unit dry wt. or per unit leaf surface. The stability val. declines with age. Protein decomp. and synthesis occur both in old and young leaves to maintain the

stability val. HCN from cyanogenetic glucosides activates protein exchange. COME, extracts of leaves contain a substance resembling cystine in its action on the proteolytic system, *i.e.*, activating during the flowering period and inhibiting during fruit formation. Activation by this "mutator" is associated with the presence of oxidising substances and inhibition with that of reducing substances. Control of the protein metabolism of leaves is thereby explained. A. G. POLLARD.

Dynamics of carbohydrates in wheat. I. Effect of water supply on transformation of carbohydrates. I. M. VASSILIEV (Pflanzenbau, 1931, 7, 126—146; Chem. Zentr., 1931, ii, 3350—3351).—With progressively increasing lack of H₂O the monose and sucrose content of the leaves is at first diminished owing to diminished photosynthesis; thereafter increased hydrolysis of insol. carbohydrates leads to a transient increase in sugar. Monoses and sucrose disappear shortly before the death of the plant. A. A. ELDRIDGE.

Transformation of sugars in mandarins during the process of ripening and in storage. M. A. KUDRYAVZEVA (Bull. Appl. Bot., Russia, 1931, 25, 305—326).—During maturation the monosaccharide content was practically const., whilst the sucrose content increased. In the last two months the p_H changed from 2.8 to 3.6. CHEMICAL ABSTRACTS.

Chemical equivalent base-exchange reactions in plants. W. T. McGEORGE (Plant Physiol., 1932, 7, 119—124).—Air-dried lucerne tissue exhibits typical base-exchanging properties which may be operative in controlling the permeability of plant tissues to cations. Diffusion of bases through tissues may also be facilitated by the chemical combination of cations with a relatively insol. anion, *e.g.*, that of lignin, or by the formation of an adsorption complex with other electro-negative colloids of the cell contents. A. G. POLLARD.

Mineral composition of pasture grasses. B. SJOLLEMA (Bied. Zentr., 1932, B, 3, 507—519).—Pastures on which grass tetany occurred have, in general, low Ca and Na, normal PO₄^{'''}, normal to high Mg, and high K contents. The K:Na ratio is very wide (50:1) and the K:Ca ratio considerably wider than normal. The S content was proportional to that of protein. All samples had an excess of bases over acids. A. G. POLLARD.

Lime and phosphoric acid content of lucerne as influenced by the application of superphosphate. A. A. RAMSAY and E. L. GRIFFITHS (Agric. Gaz. New South Wales, 1931, 42, 855—863).—The % of Ca and PO₄^{'''} in lucerne varies considerably not only in different districts but in successive cuttings in one district. Superphosphate increases the Ca and PO₄^{'''} contents to slight but similar extents. A. G. POLLARD.

Aluminium content of plants, especially of vegetables. G. BERTRAND and G. LEVY (Ann. Agron., 1932, 2, 1—9; cf. A., 1931, 662).—The rate of intake of Al varied widely with different crops, but, in general, was greatest in the earlier stages of development. Al is probably concerned in plant metabolism. A. G. POLLARD.

Cobalt in plant ash. E. R. BISHOP and M. LAWRENZ (Science, 1932, 75, 264—265).—Co is present in vegetables which give a green or blue ash but not in those giving a white or brown ash. Fe, Cr, Mn, and Cu are always present, but Ni is absent.

L. S. THEOBALD.

Changes in the biochemical processes of soil under the influence of clover culture. N. N. SUSKINA (Bull. Acad. Sci. U.R.S.S., 1931, 1219—1252).—The chernozems in the region of the Nosovka Agricultural Experiment Station were at one time salinised and subsequently underwent a process of desalinisation, during which the soils were deprived of org. matter necessary for the life of plants and bacteria and thus became relatively infertile. Introduction of a clover crop into the rotation is followed by improvement in the physical properties and acceleration of the microbiological activity of the soil, by increased rate of growth of plants, and by augmented crops. T. H. POPE.

Synthesis of a humus-nucleus, an important constituent of humus in soils, peats, and composts. S. A. WAKSMAN and K. R. N. IYER (J. Wash. Acad. Sci., 1932, 22, 41—50).—By bacterial decomp. of a mixture of protein and lignin in a solution containing Ca, Mg, and Fe, of p_H about 7.0, "humus-nucleus," which has the properties of humic acid, has been obtained. The mechanism of the formation of humus-nucleus in the soil is discussed. C. W. GIBBY.

Growth inhibition of potato sprouts by the volatile products of apples. O. H. ELMER (Science, 1932, 75, 193).—Volatile products from ripe apples, and in one case from ripe pears, inhibited the normal development of potato sprouts. The effect is transitory and normal growth takes place after removal of the inhibitor. *iso*Amyl valerate and the volatile substances from immature or decayed apples, from oranges, and bananas have no effect. L. S. THEOBALD.

Hardiness of plants by measurements of electrical conductivity. S. T. DEXTER, W. E. TOTTINGHAM, and L. F. GRABER (Plant Physiol., 1932, 7, 63—78).—Hardiness is measured by the rate of exosmosis of electrolytes from suitably frozen tissue, the latter being determined conductometrically in H₂O extracts of tissue, or in the tissue itself. A. G. POLLARD.

Rapidity of response of spinach to change in photo-period. J. E. KNOTT (Plant Physiol., 1932, 7, 125—130).—The catalase activity of fresh apical bud tissue of spinach increases under the stimulus of exposure to a lengthened photo-period. A. G. POLLARD.

Effect of hot-water treatment on the carbohydrate changes in narcissus bulbs during storage. H. HASSELBRING (Plant Physiol., 1932, 7, 145—154).—Normal changes in stored bulbs, *viz.*, decline of starch and increase in sucrose contents, and also the temporary increase in reducing sugars in the early period of storage, are all accentuated by the customary hot-water treatment (43.5° for 4 hr.). A. G. POLLARD.

Growth hormone of plants. I. H. E. DOLK and K. V. THIMANN (Proc. Nat. Acad. Sci., 1932, 18,

30—46).—Methods are described for obtaining from cultures of *Rhizopus suinus* a solution containing the substance which promotes the elongation of plant cells and for measuring the concn. of the substance in arbitrary units by means of its effect on the coleoptiles of *Avena*. By the determination of its partition coeff. between Et_2O and H_2O at various p_{H} vals. the substance is shown to be an acid with dissociation const. 1.8×10^{-5} . It is very readily destroyed by oxidation. Considerable purification may be effected by means of fractional extraction with Et_2O at different p_{H} .

W. O. KERMAK.

Water-soluble growth factors. H. VON EULER and T. PHILIPSON (Biochem. Z., 1932, 245, 418—430).—The tip of the coleoptile of *Avena* produces a substance which promotes the growth of yeast (*Saccharomyces cerevisiae*) and this substance is also synthesised by the detached tip, but it does not contain the Z-factor which promotes fermentation. The growth-promoting factor also occurs in *Rhizopus tritici*, *R. nigricans*, *Aspergillus Wentii*, and *Penicillium*. To name growth-promoting substances the letter *B* (alone) should be used, whilst *B*₁, etc. should be applied to *B*-vitamins and *BP* (with the name of the plant affected or a number, if desired) to factors which promote growth in plants. W. MCCARTNEY.

Evolution of barley mutants. H. VON EULER, D. BURSTROM, and H. HELLSTRÖM (Svensk Kem. Tidskr., 1932, 44, 23—28; cf. A., 1930, 382, 1318).—The catalase activities of germinating barley grains separated from the endosperm, of those from which the radical had been removed, and of the cotyledons were determined both for hetero- and homo-zygotes. Unlike the whole grain, the cotyledons exhibited an activity which was not markedly greater in the chlorophyll-normal than in the chlorophyll-defective varieties. Spectroscopic investigation indicated that the cotyledons of the normal varieties contained xanthophyll on the third day of germination. Cotyledons of a heterozygote contained both cozymase and "factor-Z," the principle transitional between the carbohydrate activator and the growth-promoting substance which is allied to vitamin-B. This factor-Z occurs in the husk. F. O. HOWITT.

Catalase content of different barley varieties. G. AUFHAMMER and H. WEINMANN (Woch. Brau., 1932, 49, 57—59, 68—70).—The catalase contents of 29 commercial varieties of barley grown during several seasons were higher when grown at Halle than at Munich. The catalase activity falls sharply during ripening, hence is high in early harvested barley; it also falls slightly during storage. There is no definite relationship between the catalase content of a variety and its early or late ripening property, nor do winter and spring barleys differ in this respect.

F. E. DAY.

Catalase activity in tomato fruits at different stages of development. F. G. GUSTAFSON, I. CLARK, D. A. SHAW, and E. WARWEG (Plant Physiol., 1932, 7, 155—160).—Relationships between changes of catalase activity and rates of growth are examined.

A. G. POLLARD.

Plasmolysis with potassium thiocyanate. S. STRUGGER (Ber. deut. bot. Ges., 1932, 50, 24—31).—Epidermal cells of *Allium cepa* are impermeable to KCNS in hypotonic and permeable in hypertonic (plasmolysing) solutions. The amount of KCNS entering the cell is indicated by its effect on microscopic structure of the nucleus. J. B. BATEMAN.

Irritability and anaesthesia in plants. W. D. BANCROFT and J. E. RUTZLER, jun. (J. Physical Chem., 1932, 36, 273—285; cf. A., 1931, 1328).—Na salicylate and NaCNS peptise, whilst Na citrate, Na amytal, and Et_2O coagulate, the colloids of plants. The tomato plant is killed by over-exposure to Et_2O , but this effect is greatly retarded by treatment with NaCNS, whilst the stimulating action of C_2H_4 is counteracted by NaCNS. NaCNS breaks the dormant period of potato tubers, probably by peptising the colloids. C. T. SNELL (b).

Thallium poisoning and soil fertility. S. C. BROOKS (Science, 1932, 75, 105—106).—Continued use of Ti_2SO_4 for vermin control will lead to denudation of small areas of pasture land and general toxicity or complete sterility of cultivated land.

L. S. THEOBALD.

Sections from frozen paraffin blocks. R. VON VEH (Ber. deut. bot. Ges., 1932, 50, 42—44).

J. B. BATEMAN.

Analysis of sections of small and medium-sized Philippine bagtikan trees, *Parashorea malaanonan* (Blanco), Merrill. F. M. YENKO, L. BAENS, and A. P. WEST (Philippine J. Sci., 1932, 47, 281—285).

Gasometric determinations with a ureometer of calcimeter type. G. D'ESTE (Boll. chim.-farm., 1932, 71, 87—94).—An apparatus for determination of evolved gases is described. R. K. CALLOW.

Electrometric measurement of true acidity in cells and tissues with an iridium hydrogen electrode. T. VON LANZ (Z. wiss. Mikros., 1931, 48, 1—8; Chem. Zentr., 1931, ii, 2487).—Lenz and Malyoth's apparatus has been adapted to micro-determinations. A. A. ELDRIDGE.

Electrophoresis of biological media. P. GIRARD and L. GUASTALLA (Compt. rend., 1932, 194, 747—749).—Experiments fail to substantiate a modification of the Lamb-Helmholtz formula which requires constancy of p_{H} . Acid and alkaline zones occur and are easily demonstrated by addition of suitable indicators to the colloid medium.

P. G. MARSHALL.

Determination of carbon in biological fluids. T. OSUKA (Biochem. Z., 1932, 244, 284—293).—The C content of biological fluids can be determined with sufficient accuracy on the semimicro-scale by a modification of the method of Nicloux (A., 1929, 204).

W. MCCARTNEY.

Ashing plant materials to determine total phosphorus. B. W. HOWK [with E. E. DE TURE] (Ind. Eng. Chem. [Anal.], 1932, 4, 111—112).—The plant material is ignited with CaCO_3 in a Ni crucible. The residue is dissolved in dil. HNO_3 and PO_4 is determined in the solution. E. S. HEDGES.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1932.

General, Physical, and Inorganic Chemistry.

Magnitude of spectral lines of stellar hydrogen. P. ROSSIER (*Arch. Sci. phys. nat.*, 1932, 14, 5—23).—Using a spectrocomparator, the relative and abs. magnitudes of the lines of stellar H_2 as a function of the length of the spectrogram are plotted and interpreted from an examination of more than 400 spectrograms relating to a similar number of stars.

N. M. BLIGH.

Lower energy levels of the carbon atom. N. F. BEARDSLEY (*Physical Rev.*, 1932, [ii], 39, 913—921).—Mathematical. Approx. calculations are compared with experimental data.

N. M. BLIGH.

Mechanism of the positive column in monatomic gases. II. R. SEELIGER (*Physikal. Z.*, 1932, 33, 313—327).

A. J. MEE.

Energy balance in the positive column in rare gases. K. SOMMERMEYER (*Ann. Physik*, 1932, [v], 13, 315—336).

A. J. MEE.

Luminosity of a flame containing sodium vapour. T. W. BONNER (*Physical Rev.*, 1932, [ii], 40, 105—111).—The luminosity of a flame into which a Na salt is sprayed is a function of the product of the thickness of the flame and the concn. of the Na in it (cf. A., 1928, 449; 1931, 1210).

N. M. BLIGH.

Arc spectrum of phosphorus. C. C. KIESS (*Bur. Stand. J. Res.*, 1932, 8, 393—401).—Using infra-red sensitised plates, the P arc spectrum has been photographed in the near infra-red region, and about 400 wave-lengths have been measured over the range 9100—10,800 Å. These have been classified as combinations between quadruplet and doublet terms, all required theoretically for the P atom. From the series-forming terms the val. of the lowest term $4S_{11}^0$ is 90,000 cm^{-1} ; ionisation potential 11.11 volts.

J. W. SMITH.

Arc discharge not obtained in pure argon. G. E. DOAN and J. L. MYER (*Physical Rev.*, 1932, [ii], 40, 36—39).—In highly-purified A an arc could not be struck between pure Fe electrodes. Explanations of the apparent dependence of the normal arc discharge on the presence of chemically active atoms or mols. are discussed.

N. M. BLIGH.

Zeeman effect of the K II spectrum. A. E. WHITFORD (*Physical Rev.*, 1932, [ii], 39, 898—904).—Anomalies of classification are investigated and explained. A special press for feeding an arc with K metal is described.

N. M. BLIGH.

Band spectra of calcium hydride. II. B. GRUNDSTROM (*Z. Physik*, 1932, 75, 302—312).—

The energy of dissociation of the 2Π state is approx. 15,000 cm^{-1} .

A. B. D. CASSIE.

Nuclear moment of gallium. D. A. JACKSON (*Z. Physik*, 1932, 75, 229—230).—Both Ga isotopes have nuclear moment $3/2$.

A. B. D. CASSIE.

Nuclear spin of arsenic. S. TOLANSKY (*Nature*, 1932, 129, 652).—The fine structures now observed in the lines of the As Π spectrum (6400—4300 Å.) involve transitions between $4p5s$ and $4p5p$ electron configurations. The nuclear spin is $3/2$.

L. S. THEOBALD.

Resonance spectrum of selenium vapour. W. KESSEL (*Bull. Acad. Polonaise*, 1931, A, 196—200).—The resonance series of Se excited by the mercury 4047 Å. line is most intense at about 600° , and that excited by the 4358.5 Å. line at 750° . The wave-lengths are given in tabular form. The lines form two series of doublets with $\Delta\nu=34.7$ and 29 cm^{-1} , respectively.

J. W. SMITH.

Temperature shift of the transmission band of silver. J. V. PENNINGTON (*Physical Rev.*, 1932, [ii], 39, 953—956).—The shift of the frequency at which max. transmission is found for Ag when the temp. is varied is explained by Kronig's quantum theory of dispersion in metals (cf. A., 1931, 1209). The calc. rate of shift is in fair agreement with experiment.

N. M. BLIGH.

Emission and absorption of radiation by metallic silver. F. L. MOHLER (*Bur. Stand. J. Res.*, 1932, 8, 357—364; cf. A., 1931, 781; this vol., 4).—The spectrum emitted by Ag bombarded by 100-volt electrons in a high vac. is similar to that emitted from an Ag probe surface by 7-volt electrons in a Cs discharge, being characterised by a high intensity from the visible to 3600 Å., and decreasing to a very low val. beyond 3200 Å.

J. W. SMITH.

Fluorescence of diatomic tellurium vapour excited by the cadmium arc. J. PIÉRARD and M. MIGEOTTE (*Bull. Acad. roy. Belg.*, 1932, [v], 18, 246—255; cf. this vol., 439).—Observed and calc. vals. of the frequencies, wave-lengths, and term differences of three new series excited by the 4415.68, 4678.15, and 4799.91 Å. arc lines of Cd are tabulated. The series are contrasted with those excited by the Cd spark.

N. M. BLIGH.

Absorption bands of iodine and tellurium. E. HIRSCHLAFF (*Z. Physik*, 1932, 75, 315—324).—Predissociation was observed in the spectrum of Te_2 at 3895 Å. 50 band edges were measured between 7000 and 9000 Å. in the I_2 spectrum.

A. B. D. CASSIE.

Resonance spectra of iodine vapour at high temperatures. E. HIRSCHLAFF (Z. Physik, 1932, 75, 325—337).—A resonance spectrum was observed between 2400 and 4800 Å. on exciting I vapour at 600° with Hg line 2537 Å.; He did not change the bands. A. B. D. CASSIE.

Anti-Stokes terms in the fluorescence spectrum of I_2 . J. J. AGARBICEANU (Compt. rend., 1932, 194, 1338—1340; cf. A., 1922, ii, 177; 1931, 7, 667).—The fluorescence spectrum of I_2 excited by the Hg line 5461 Å. is shown to contain in addition to terms of order (0), (1), (3), and (5), the anti-Stokes terms (−1) and (−2). Hence the quantum no. v'' (=0) cannot be ascribed to the final level of vibration of order (0) ($\lambda=5461$). C. A. SILBERRAD.

Separation of the 2F levels of Ce IV. R. BRUNETTI and Z. OLLANO (Z. Physik, 1932, 75, 415—416).—Raman photographs of conc. solutions of $CeCl_3$ and $Ce(NO_3)_3$ gave the displacements 1640 and 1473 cm^{-1} , respectively, probably due to electronic transitions between the 2F levels of the Ce^{+3} ion. A. B. D. CASSIE.

Transparency of thin platinum sheets in the wave-length range 0.25—2.5 μ . E. SCHUCH (Ann. Physik, 1932, [v], 13, 297—314).—For thinnest sheets there is an increase of transparency with increasing wave-length. There is a thickness at which the effect over a wave-length range of 0.25—1.0 μ is the same. Reflexion determinations in the visible range were carried out. A. J. MEE.

Supposed proof of a nuclear moment for the even isotope of Hg, 198. L. A. SOMMER (Z. Physik, 1932, 75, 134—136).—Polemical, against Schuler (this vol., 4). The isotope 198 has no nuclear moment. A. B. D. CASSIE.

Fluorescent excitation of mercury by the resonance frequency and by lower frequencies. III. (LORD) RAYLEIGH (Proc. Roy. Soc., 1932, A, 135, 617—627).—A method is devised for studying the band spectrum of Hg produced by absorption of the at. resonance line (core excitation) over a range of temp. at one photographic exposure. At 20 mm. pressure the max. 3300 Å. is greatly enhanced by heating, and the wing series bands come into view. At 2 mm. the max. 3300 Å. is diminished by heating. Wood's bands, 2345, 2338, 2334, 2330 Å., come out conspicuously in core excitation. The "forbidden" line 2270 Å. is recorded in fluorescence for the first time. L. L. BIRCUMSHAW.

Hyperfine structure of mercury. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 97—100; cf. this vol., 315).—Using a Geissler discharge and Aron's lamp the structure of the zero lines of $\lambda\lambda$ 5461, 4358, and 4077 was obtained. Intensities and separations of the components of λ 3984 and λ 6123 are tabulated. N. M. BLIGH.

Fluted band at 3900 Å. in the spectrum of mercury. J. OKUBO and E. MATUYAMA (Nature, 1932, 129, 653). L. S. THEOBALD.

Hyperfine structure of the thallium arc lines. D. A. JACKSON (Z. Physik, 1932, 75, 223—228).—

Observed hyperfine structure agrees with two TI isotopes of nuclear moment 1/2. A. B. D. CASSIE.

Nuclear moment of three lead isotopes. H. KOPFERMANN (Z. Physik, 1932, 75, 363—379).—The Pb isotopes 206 and 208 have probably nuclear moment zero, and 207 has 1/2. A. B. D. CASSIE.

Positive column in diatomic gases. R. HOLM (Z. Physik, 1932, 75, 171—190).—Potential gradients in the positive column of diat. gases agree with Schottky's theory (*ibid.*, 1924, 25, 637), and indicate the presence of negative ions. A. B. D. CASSIE.

Light-intense excitation of spectra in the electric vacuum furnace by electron collisions of small energy. R. RITSCHL (Ann. Physik, 1932, [v], 13, 337—357).—The apparatus is described. The arc spectra of Cu, Au, Be, and Al were investigated. A. J. MEE.

Coupling broadening and collision damping. V. WEISSKOPF (Z. Physik, 1932, 75, 287—301).—Theoretical. A. B. D. CASSIE.

Uniqueness of the decomposition of an intensity curve into its components. E. LONN (Z. Physik, 1932, 75, 348—349). A. B. D. CASSIE.

Excitation of some nebular lines by disruptive discharge. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1932, 8, 78).— H_2 lines of nebular spectra are reproducible in the laboratory, whilst lines of N_2 and O_2 are difficult to obtain. A disruptive discharge method is described. W. R. ANGUS.

Infra-red lines in the spectrum of the aurora. L. VEGARD (Naturwiss., 1932, 20, 268—269).—Neither the anticipated O_2 triplets nor the lines of the second positive group of N_2 have been observed in the near infra-red spectrum of the aurora. The strongest band head corresponds with the $1 \rightarrow 0$ transition of the first positive group of N_2 . J. W. SMITH.

Spectrum of solar corona. T. L. DE BRUIN (Naturwiss., 1932, 20, 269).—New terms have been discovered in the neutral O_2 spectrum enabling several strong lines in the solar spectrum to be interpreted. J. W. SMITH.

Red oxygen radiation in the night sky. L. A. SOMMER (Naturwiss., 1932, 20, 330—331).—A reply to Grotrian (this vol., 441). W. R. ANGUS.

[Red oxygen radiation in the night sky.] W. GROTRIAN (Naturwiss., 1932, 20, 331).—A rejoinder (cf. preceding abstract). W. R. ANGUS.

Spectra of light zones at the cathode of glow discharges. A. GUNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 75, 105—110). A. B. D. CASSIE.

Scattering of fast cathode rays in single crystals. F. KIRCHNER (Ann. Physik, 1932, [v], 13, 38—58). W. R. ANGUS.

Atom factors for X-rays in the region of anomalous dispersion. D. COSTER and K. S. KNOL (Z. Physik, 1932, 75, 340—347).—A theoretical discussion indicates that the influence of anomalous dispersion on atom factors, near a K -absorption edge, increases with the angle of reflexion: this agrees with experimental results obtained for Zn crystals. A. B. D. CASSIE.

Continuous and continuous-discrete X-ray spectrum. A. W. MAUE (Ann. Physik, 1932, [v], 13, 161—190).—The retardation of electrons at nuclei gives rise to a continuous and a discrete spectrum. A. J. MEE.

Absolute measurements of X-rays with an electron counter. A. HUPPERTSBERG (Z. Physik, 1932, 75, 231—248).—Electrons ejected from the walls of an electron counter by X-rays may be used as a measure of the intensity of the beam; the counter gave ionisation proportional to the irradiated surface and to the intensity of the beam.

A. B. D. CASSIE.

Dependence of the ratio of intensity of secondary X-ray lines on the wave-length of the exciting radiation. E. ALEXANDER (Z. Physik, 1932, 75, 391—394).—The intensity ratio $Ag\ L\beta_2 : L\beta_3$ changes from 4 : 1 to 1.33 : 1 when the exciting wave-length is changed from 2.6 to 1.3 Å., and the absorption ratio changes in agreement with Sommerfeld and Schur's theory (A., 1930, 391). A. B. D. CASSIE.

Reflexion and absorption of long-wave X-rays. E. DERSHEM and M. SCHEIN (Z. Physik, 1932, 75, 395—414).—Absorption coeffs. were determined for He, Ne, A, Kr, N₂, O₂, CO₂, and air at the wave-length 44.6 Å. A. B. D. CASSIE.

Fine structure of X-ray absorption edges. II, III. R. DE L. KRONIG (Z. Physik, 1932, 75, 191—210, 468—475; cf. A., 1931, 993).

A. B. D. CASSIE.

Spectrography of X-rays by transmission of non-canalised rays across a curved crystal. (MILLER) Y. CAUCHOIS (Compt. rend., 1932, 194, 1479—1482; cf. this vol., 246). C. A. SILBERRAD.

Intensity ratio of fluorescent X-ray lines. H. R. ROBINSON (Nature, 1932, 129, 618).

L. S. THEOBALD.

Dependence of the X-ray excited K-spectrum of sulphur on chemical combination. A. FAESSLER (Z. Physik, 1932, 75, 424; cf. A., 1931, 670).—Attention is directed to similar work by Lindh (*ibid.*, 1925, 31, 218).

A. B. D. CASSIE.

Appearance of continuous spectra during cathode-ray bombardment. VI. Vapours and gases. W. M. COHN (Z. Physik, 1932, 75, 544—554).—A tube with a Lenard window was used to obtain these continuous spectra outside the discharge tube. The spectrum observed was independent of the window material, was always continuous with a max. at 4500 Å., and in no case extended below 3000 Å.

A. B. D. CASSIE.

Ionisation of argon and neon by neutral argon beams. O. BEECK (Proc. Nat. Acad. Sci., 1932, 18, 311—313).—The production of neutral A atoms is described; a qual. study of intensity of ionisation and atom speed was made, and possible ionisation mechanisms are discussed.

N. M. BLIGH.

Ionisation in gases by ions and atoms. F. ZWICKY (Proc. Nat. Acad. Sci., 1932, 18, 314—318).—The quant. relations governing ionisation are interpreted, and predictions therefrom relative to ionisation by neutral atoms are discussed (cf. preceding abstract).

N. M. BLIGH.

Dependence of the photo-emission from potassium on the arrangement of atomic hydrogen and potassium layers on its surface. P. I. LUKIRSKY and S. RIJANOV (Z. Physik, 1932, 75, 249—257).—Experiments showed that two equal quantities of at. H are adsorbed on a K surface; the first forms a monat. layer below a monat. layer of K and increases the photo-emission, whilst the second is above the K and diminishes the emission. A. B. D. CASSIE.

Photo-ionisation probabilities of atomic potassium. (MISS) M. PHILLIPS (Physical Rev., 1932, [ii], 39, 905—912; cf. Lawrence, A., 1929, 1356).—Mathematical. N. M. BLIGH.

Photo-electric absorption in hydrogen-like atoms. P. A. M. DIRAC and J. W. HARDING (Proc. Camb. Phil. Soc., 1932, 28, 209—218).—Mathematical. N. M. BLIGH.

Secondary electron emission from nickel and ferromagnetism. P. TARTAKOVSKI and V. KUDR-JAVZEVA (Z. Physik, 1932, 75, 137—142).—At the Curie point secondary electron emission changes discontinuously. The secondary electrons are thus associated with ferromagnetism, and if they are identical with conductivity electrons, ferromagnetism is due to conductivity electrons. A. B. D. CASSIE.

Emission of radiation by the retardation of protons and rapid electrons. O. SCHERZER (Ann. Physik, 1932, [v], 13, 137—160).—Theoretical.

A. J. MEE.

Polarisation of electrons by crystal reflexion. J. THIBAUD, J. J. TRILLAT, and T. VON HIRSCH (Compt. rend., 1932, 194, 1223—1225).—No definite evidence of such polarisation could be found, confirming Thomson's result (cf. A., 1931, 12), but in opposition to that of Rupp (cf. A., 1930, 392).

C. A. SILBERRAD.

Surface electrons. J. E. NYROP (Physical Rev., 1932, [ii], 39, 967—976).—The theory of surface electrons covering the surface of a conductor is applied to the ordinary and selective photo-effect and the evaporation from heated metals. The absorption and catalytic effect of metallic surfaces and the potential barrier which accounts for the work function can be calc. N. M. BLIGH.

Diffraction of electrons by thin films of paraffin. J. HENGSTENBERG and J. GARRIDO (Anal. Fis. Quim., 1932, 30, 175—181).—Thin films of paraffin (m. p. 40—45°) on collodion, prepared by evaporation of a dil. solution in C₆H₆, have been examined by determination of the electron diffraction diagram. The *c* axes are perpendicular to the plane of the film, and hexagonal orientation is apparent in the *ab* plane. The results indicate that the films consist of thin laminar crystals, and not of crystals having a 3-dimensional lattice. H. F. GILLBE.

Diffraction of electrons in pure and passive iron. W. BOAS and E. RUPP (Ann. Physik, 1932, [v], 13, 1—8).

W. R. ANGUS.

Scattering of slow electrons by neutral atoms. E. FEENBERG (Physical Rev., 1932, [ii], 40, 40—54).—Mathematical. N. M. BLIGH.

Secondary electron emission from metals. H. FROHLICH (Ann. Physik, 1932, [v], 13, 229—248).—Theoretical. For the liberation of secondary electrons there is a lower limit to the primary energy of about 10 volts. The secondary electrons have a velocity below 25 volts, independent of the primary energy.

A. J. MEE.

Free electrons of ionised gases in a magnetic field. T. V. IONESCU and C. MIHUL (Compt. rend., 1932, 194, 1330—1332; cf. this vol., 209).

C. A. SILBERRAD.

Method of observing the scattering of slow electrons. A. BUHL (Naturwiss., 1932, 20, 317).

W. R. ANGUS.

Collisional friction on electrons moving in gases. E. C. CHILDS (Phil. Mag., 1932, [vii], 13, 873—887).—The frictional coeff. in air is of the same order as the val. calc. from kinetic theory.

H. J. EMELEUS.

Molecular dissociation by electron impact. F. L. ARNOT (Nature, 1932, 129, 617—618).—Attention is directed to the neglect of radial potential gradients in determining the energies of the dissociation products of N_2 and CO formed by electron impact (cf. this vol., 321).

L. S. THEOBALD.

Photo-dissociation of atomic molecules into ions. A. TEREININ and B. PAPOV (Z. Physik, 1932, 75, 338—339).—The photo-currents observed in TII and TIBr vapours (cf. A., 1930, 1238) were shown by mol. ray methods to be due to dissociation into Ti^+ and (halogen $^-$), and not to the liberation of electrons. If the electron affinities of I and Br be 3.16 and 3.4 volts, the energies of dissociation of TII and TIBr into ions are 5.5 and 5.9 volts.

A. B. D. CASSIE.

Production of high-speed light ions without the use of high voltages. E. O. LAWRENCE and M. S. LIVINGSTON (Physical Rev., 1932, [ii], 40, 19—35).—A method of multiple acceleration of ions to high speeds is described. A current of 10^{-9} amp. of 1,220,000 volt-protons for a max. applied voltage of 4000 has been obtained.

N. M. BLIGH.

Recombination of ions in gases at high pressures. W. R. HARPER (Proc. Camb. Phil. Soc., 1932, 28, 219—233).—Previous theories of the recombination of ions in gases are inapplicable to high pressures; taking into account the effect of thermal agitation and mutual attraction, a theory, in agreement with experimental data, is developed.

N. M. BLIGH.

Conditions of operation of an expansion chamber for H-rays. S. GORODETZKY (J. Chim. phys., 1932, 29, 63—66).—A Wilson expansion chamber provides a convenient method of studying H-rays. The curve relating the range to the frequency of occurrence of the range shows a pronounced min. at about 7.5 cm.

J. W. SMITH.

Observation of neutral H_3 in canal rays. R. CONRAD (Z. Physik, 1932, 75, 504—511).—A method, that reveals whether or not charged particles are neutral over part of their range, showed the existence of H_3 with a half-val. period of 3×10^{-8} sec.

A. B. D. CASSIE.

Charge cross-section of hydrogen mols. in relation to slow protons. N. BARTELS (Ann. Physik, 1932, [v], 13, 373—376).—There is a max. cross-section at about 7 kv.

A. J. MEE.

Report of the Atomic Weight Commission of the International Union for Chemistry. G. P. BAXTER, M. CURIE, O. HONIGSCHMID, P. LEBEAU, and R. J. MEYER (Ber., 1932, 65, [A], 33—42).—The report follows the usual lines. The following changes are adopted. Kr 83.7 and X 131.3, instead of 82.9 and 130.2, respectively. In agreement with Aston, the Commission considers a change from the accepted bases of chemical at. wts., O=16.0000, to be undesirable.

H. WREN.

At. wt. of fluorine. E. MOLES (J. Chim. phys., 1932, 29, 53—62).—A crit. survey of recent determinations of the at. wt. of F indicates a probable val. of 19.000. There is no experimental evidence for the existence of a heavier isotope of F in any large quantity.

J. W. SMITH.

Distribution of elements in nature, and the atomic volume curve. I. I. ZASLAVSKI (J. Gen. Chem. Russ., 1931, 1, 1080—1082).—The most widely-distributed elements are those at the minima of the at. vol.-at. no. curve.

R. TRUSZKOWSKI.

Hydrogen isotope of mass 2 and its concentration. H. C. UREY, F. G. BRICKWEDDE, and G. M. MURPHY (Physical Rev., 1932, [ii], 40, 1—15).—Samples of H_2 from the last few c.c. of large quantities evaporated at atm. pressure and at a few mm. above the triple point were investigated for the visible at. Balmer series of H^2 and H^3 from a H discharge tube. With a time of exposure increased 4000 times very faint lines at the calc. positions for H^2 appeared as broad doublets. The $H^2\alpha$ line was resolved into a close doublet with separation agreeing with that for $H^2\alpha$. Estimated relative abundances of H^2 and H^1 in natural H_2 are 1 : 4000, agreeing with that required for an explanation of the discrepancy between the at. wts. of H as determined chemically and by the mass spectrograph.

N. M. BLIGH.

Measurements of the intensity ratio of the neon isotopes, Ne^{20} and Ne^{22} . L. S. ORNSTEIN and J. A. VREESWIJK, jun. (Z. Physik, 1932, 75, 109—110).—This isotope ratio is 10 : 1, giving an at. wt. of 20.18 for atm. Ne.

A. B. D. CASSIE.

Regularities in the structure of isotopes. A. CARRELLI (Z. Physik, 1932, 75, 111—114).—Nuclei of the type $4N_a+1$, $4N_a+2$, and $4N_a+3$ are associated with those of type $4N_a$.

A. B. D. CASSIE.

Copper isotopes. (Miss) E. R. BISHOP (Physical Rev., 1932, [ii], 40, 16—18).—A magneto-optic method shows that Cu has an isotope of at. wt. <63, less abundant than Cu^{63} and Cu^{65} .

N. M. BLIGH.

Isotopic constitution of lead from different sources. F. W. ASTON (Nature, 1932, 129, 649).—Isotopic analyses of Pb from four different sources have been amplified, and several rare isotopes previously suspected in ordinary Pb (A., 1927, 806) have been confirmed. Data for ordinary Pb, Pb from Katanga pitchblende, Wilberforce uraninite, and Norwegian thorite are recorded. The quantities of

Pb²⁰⁶ and Pb²⁰⁷ in the last-named do not correspond with those expected from ordinary Pb as impurity.

L. S. THEOBALD.

Periodical properties of atomic nuclei. G. I. POKROVSKI (Science, 1932, 75, 443—444).—The no. of isotopes having the same at. wt. is a function of this at. wt., and the curve obtained by plotting these nos. against at. wts. resembles the at. vol.-at. wt. curve. The no. of isotopes having the same at. wt. is determined by the properties of the nuclei, the at. vol. by the properties of the electron sheaths of the atom, and since both cases show the same periodicity there must be a connexion between the outer electrons and the protons and electrons in the nucleus.

L. S. THEOBALD.

Mobility of radioactive atoms on the surface of solid bodies. H. JEDRZEJOWSKI (Compt. rend., 1932, 194, 1340—1343).—A patch of Po on Pt foil heated in a quartz tube to 600—637° spreads increasingly over the whole surface of the foil, only about 1/10th being evaporated and found on the quartz. On Au at 1000° there is very little spreading, evaporation predominating, and on mica at 440° almost exclusively evaporation. It is suggested that the Po diffuses along the surface of the Pt (cf. A., 1926, 467; 1929, 737).

C. A. SILBERRAD.

Radioactivity of potassium. P. AUGER (Compt. rend., 1932, 194, 1346—1347; cf. Perrin, this vol., 556).—Assuming K⁴¹ to consist of 10 helions, 1 neutron, and 1 electron, the emission of the neutron and electron would leave ordinary Ca⁴⁰, thus explaining the absence of the isotope Ca⁴¹ (cf. A., 1928, 1169). A similar explanation applies to Rb and Sr.

C. A. SILBERRAD.

Half-value period of uranium-X₁. E. WALLING (Z. Physik, 1932, 75, 432—433).—The half-val. period of U-X₁ is 24.5 days.

A. B. D. CASSIE.

Fine structure of α -radiation of radiothorium. S. ROSENBLUM and (MME.) C. CHAMIE (Compt. rend., 1932, 194, 1154—1155; cf. A., 1931, 280).—The α -magnetic spectrum of Rd-Th (prepared from BaCl₂ containing Ms-Th) contains (figures denote velocities in cm. $\times 10^{-9}$ /sec.) Rd-Th α_1 1.612(4), strong; Rd-Th α_2 1.600(3), medium; and a very weak ray α_x 1.594(2) of uncertain origin; and (from an older prep.) Th-A 1.802(3); Th 1.736(0), and Th-X 1.650(8).

C. A. SILBERRAD.

Fluctuations of the rate of emission of α -particles for weak sources and large solid angles. L. F. CURTISS (Bur. Stand. J. Res., 1932, 8, 339—346).

Penetrating radiation excited in light nuclei by α -particles. (MME.) I. CURIE and F. JOLIOU (Compt. rend., 1932, 194, 1229—1232).—From a consideration of the absorption of the radiation from Po+Be (cf. this vol., 318) in Pb, and the dissymmetry of the radiation emission as a function of the thickness of Pb interposed between the source and the ionisation chamber (containing successively A, N₂, and He), it is concluded that Be thus irradiated emits a complex radiation in which are recognisable (1) a γ -radiation absorbed by a Compton effect on the electrons, emitted approx. equally in all directions, and of energy up to 4×10^6 electron-volts; and (2) a very penetrating radiation absorbed by projection of nuclei,

and emitted dissymmetrically relatively to the direction of the incident α -particles. C. A. SILBERRAD.

Fine structure of α -magnetic spectrum of radioactinium. (MME.) P. CURIE and S. ROSENBLUM (Compt. rend., 1932, 194, 1232—1235).—The α -magnetic spectrum of Rd-Ac, prepared by Curie's method (cf. A., 1931, 783), contains (figures indicate velocities in 10^{-9} cm./sec.): α_1 1.703, strong; α_2 1.700, feeble; α_3 1.695, very strong; ? (1.683), feeble; α_4 1.676, feeble; α_5 1.662, strong; and α_6 1.656, very strong. Energy differences correspond to a certain extent with the γ -rays due to Rd-Ac (cf. A., 1926, 105). Other rays found as the preps. aged were: Ac-A 1.883; Au 1.810; Ac-C α 1.783; Ac-C α_1 1.734; Ac-X α_1 1.640, strong; and Ac-X α_2 1.631, feeble.

C. A. SILBERRAD.

Decrease in velocity of α -particles from thorium-C' in air. G. MANO (Compt. rend., 1932, 194, 1235—1237).—If v_0 is the initial velocity of an α -particle and v its velocity after passing through p cm. of air, the deviation from Geiger's law is expressed by $\epsilon = v/v_0 - (1 - p/\pi)^{1/3}$, where $\pi = 8.54$ cm., the mean free path of the α -particles. Results agree with other determinations (cf. A., 1931, 1349; this vol., 442).

C. A. SILBERRAD.

Artificial disintegration of certain elements by the α -rays of polonium. M. C. PAVLOVSKI (J. Phys. Radium, 1932, [vii], 3, 116—126).—The disintegration of elements by bombardment with the α -rays of Po has been studied by determining the no. of particles emitted in a direction making an angle of 130° with the direction of the incident radiation. H-Radiation has been obtained in the case of C, Mg, Al, Si, and S, confirming the results of other investigators that it is possible to disintegrate elements of an at. wt. which is a multiple of 4. The extent of disintegration obtained agrees most closely with that observed by Bothe and Franz (A., 1928, 810). No disintegration was obtained in the case of Fe, Zn, Ag, and Pb.

M. S. BURR.

Permanent magnet for β -ray spectroscopy. J. D. COCKCROFT, C. D. ELLIS, and H. KERSHAW (Proc. Roy. Soc., 1932, A, 135, 628—636).—The construction and use of a large permanent magnet, by means of which a max. field of 2300 gauss is obtainable, are described.

L. L. BIRCHUMSHAW.

Diffusion of β -radiation by the support carrying the radioactive material. Importance of this effect in determination of these materials. (MME.) A. POMPEI (J. Chim. phys., 1932, 29, 77—80).—The intensity of the β -radiation from a radioactive deposit increases with the at. wt. of the supporting material, a Pb support leading to 50% greater intensity than an Al support. This should be taken into account when determining radioactive materials by their β -radiation.

J. W. SMITH.

β - and γ -radiation of uranium-Z. The branching ratio of uranium-Z to the principal branch of the uranium series. E. WALLING (Z. Physik, 1932, 75, 425—431).—Studies of the absorption of radiation emitted by U-Z showed these to consist of two penetrating β -rays and a penetrating γ -ray. 3% of U-X₁ disintegrates into U-Z. A. B. D. CASSIE.

Absolute energies of the lines in β -ray spectra. C. D. ELLIS (Nature, 1932, 129, 691).—Published vals. of the energies of the lines in the Th-B+C and in the Ra-B+C spectra may be high. L. S. THEOBALD.

Spectrum of γ -rays from derivatives of radiothorium. D. SKOBELZYN (Compt. rend., 1932, 194, 1486—1488; cf. A., 1927, 710; 1930, 8).—Using the method described previously, the γ -spectrum of Ra-Th (rays filtered through 30 mm. of Pb, angle of emission $>10^\circ$) has been examined and the energy of the secondary Compton electrons determined. In addition to the chief max. for 2650 kv. (due to Th-C''), smaller max. occur for 2000 and 1650 kv. Ms-Th+Ra-Th shows a similar distribution with a still smaller max. for about 1550 kv. C. A. SILBERRAD.

Homogeneity of filtered γ -rays of thorium-C'' and the verification of the Klein-Nishina formula. D. SKOBELZYN (Compt. rend., 1932, 194, 1568—1571; cf. preceding abstract).—The bearing of the softer rays found by the author on the verification of the Klein-Nishina formula as regards γ -rays from Th-C'' (cf. A., 1931, 142, 281, 995) is discussed. σ_r (for Al) and the effective wave-lengths (in X.) of the principal ray and of rays after filtration through 3 and 4 cm. of Pb, respectively, are 0.098, 4.7; 0.105, 5.3; and 0.103, 5.1, correct to ± 0.001 . C. A. SILBERRAD.

Penetrating beryllium radiation. F. RASETTI (Naturwiss., 1932, 20, 252—253; cf. this vol., 443).—The behaviour of Be radiation, produced by the action of α -rays from Po on Be, suggests that it is a mixture of neutrons and γ -rays. Using an ionisation chamber, the data obtained are primarily due to the neutrons, and substances containing H appear to absorb the radiation abnormally, whereas with a counter γ -rays are detected and the absorption of paraffin etc. appears to be normal. J. W. SMITH.

Existence of neutrons and constitution of light atomic nuclei. F. PERRIN (Compt. rend., 1932, 194, 1343—1346).—The possibility of the very penetrating radiation emitted by Be under the influence of Po (cf. this vol., 555) consisting of neutrons is deduced from Fournier's theories (cf. A., 1930, 269), which are extended to suggest constitutions for several elements of helions (α -particles), protons, and neutrons, and also the radiation emitted or emissible by each. C. A. SILBERRAD.

Constitution of atomic nuclei. G. FOURNIER (Compt. rend., 1932, 194, 1482—1483; cf. A., 1930, 1087, and preceding abstract).—Theoretical. Atoms are built up of neutrons, demi-helions (consisting of two protons and one electron—the nucleus of H^2), and helions, and disintegrate by loss of a helion, demi-helion, neutron, or an electron. C. A. SILBERRAD.

Passage of neutrons through matter: a correction. H. S. W. MASSEY (Nature, 1932, 129, 691; cf. this vol., 443). L. S. THEOBALD.

Disintegration of lithium by swift protons. J. D. COCKROFT and E. T. S. WALTON (Nature, 1932, 129, 649).—Bombardment of Li by protons moving under an accelerating potential of 125 kv. produces scintillations which increase rapidly with an increase in voltage up to 400 kv. The range of the particles

is approx. 8 cm. in air and does not vary greatly with voltage. The brightness of the scintillations and the density of the tracks observed in an expansion chamber indicate that the particles are normal α -particles; at 250 kv., 1 particle per 10^9 protons is estimated to be produced. Li^7 may occasionally capture a proton and the resulting nucleus of mass 8 may break into 2 α -particles, mass 4, and each with an energy of approx. 8×10^6 electron volts. L. S. THEOBALD.

Ionisation by penetrating radiation as a function of pressure and temperature. A. H. COMPTON, R. D. BENNETT, and J. C. STEARNS (Physical Rev., 1932, [ii], 39, 873—882).—The approach to a limiting val. at high pressures of the ionisation of a gas by γ - or cosmic rays is explained by ionic reunion. Relations between saturation ionisation current and pressure are obtained. N. M. BLIGH.

Disintegration of lead by cosmic radiation. E. G. STEINKE and H. SCHINDLER (Z. Physik, 1932, 75, 115—118).—Cosmic radiation apparently ejects H nuclei, with a range of 10 cm. in Pb, from the Pb shields of ionisation chambers; the frequency of this ejection disagrees with the hypothesis that cosmic radiation consists of electrons. A. B. D. CASSE.

Cosmic-ray particles. G. L. LOCHER (Physical Rev., 1932, [ii], 39, 883—888; cf. this vol., 5).—Sp. ionisation along the tracks previously found has been determined. Explanations of group phenomena in the tracks are discussed. N. M. BLIGH.

Tables of the ionisation in the upper atmosphere. E. O. HULBURT (Physical Rev., 1932, [ii], 39, 977—992; cf. A., 1930, 392). N. M. BLIGH.

Hydrogen nucleus of mass 2 (isohydrogen nucleus p_2e) as a unit in atom building. W. D. HARKINS (J. Amer. Chem. Soc., 1932, 54, 1254—1256). C. J. WEST.

Structure of atomic nuclei. C. D. ELLIS (Nature, 1932, 129, 674—676).—A report of a discussion of the recent work (cf. this vol., 443). L. S. THEOBALD.

Pauli's principle and the structure of the atomic nucleus. II. E. N. GAPON (J. Gen. Chem. Russ., 1931, 1, 1089—1094).—The at. wt. of isotopes of elements of the H—Cu series can be derived from Aston's and Pauli's principles, and from the principle of increasing complexity of the nucleus. R. TRUSZKOWSKI.

Electronic radius. M. BORN (Naturwiss., 1932, 20, 269).—It is suggested that the electronic radius should be defined as the effective radius with respect to photon collision, in which case it is expressed by $r = \frac{1}{3} \sqrt{8 \times e^2 / m_0 c^2}$. J. W. SMITH.

Calculation of the atomic constants, e , h , and N , from Rydberg number, specific electronic charge, and measurement of short-wave limit of the Röntgen spectrum. F. KIRCHNER (Ann. Physik, 1932, [v], 13, 59—62).—Using the measurements of the short-wave limit of the Röntgen spectrum of Duane (I) and of Feder (II) together with the val. for $h/e^{5/3}$ ($= 2.2494 \times 10^{-11}$) obtained from the Rydberg formula, the following vals. are obtained: from (I) $e = 4.798 \pm 0.006 \times 10^{-10}$, $h = 6.615 \pm 0.012 \times 10^{-27}$, $N = 6.029 \pm 0.008 \times 10^{23}$; and from (II) $e = 4.782 \pm 0.006 \times$

10^{-10} , $h=6.577 \pm 0.012 \times 10^{-27}$, $N=6.049 \pm 0.008 \times 10^{23}$. The vals. of the reciprocal of the fine structure const. are (I) 137.09 and (II) 137.25. W. R. ANGUS.

Mass of the electron. W. DUANE (Proc. Nat. Acad. Sci., 1932, 18, 319—322).—From the val. of m_0 calc. from experimental data, without using vals. of e and h , vals. of these const. from available measurements of e/m_0 by various methods are compared. N. M. BLIGH.

Precision measurements of the crystal parameters of some of the elements. E. A. OWEN and J. IBALL (Phil. Mag., 1932, [vii], 13, 1020—1028).—Parameters of the following elements, showing cubic symmetry, were measured: Ag 4.0773, Al 4.0406, Cu 3.6076 Å. (all ± 0.0003 Å.); Au 4.071, Ir 3.831, Mo 3.140, Ni 3.517, Pb 4.939, Pd 3.885, Rh 3.795, Ta 3.311, W 3.159 Å. (all ± 0.001 Å.).

H. J. EMELEUS.

Natural colours of various glasses and colours produced by radiation and fluorescence. J. HOFFMANN (Z. anorg. Chem., 1932, 205, 193—204; cf. A., 1931, 579).—Very small proportions of alkali sulphate change the brown radiation colour due to Na atoms into greenish-yellow. The coloration of 12 glasses containing Mn and Mn with Fe by ultra-violet light and by β - and γ -rays has been examined. It is considered that violet radiation colours are due to Mn^{+++} and Mn^{++} ions, and blue to manganomanganic ions. The colour of amethyst is not due to alkali-metal atoms. F. L. USHER.

Action of a transverse electrostatic field on flames. J. K. MCNEELY and E. W. SCHILLING (Iowa State Coll. J. Sci., 1931, 6, 1—9).

CHEMICAL ABSTRACTS.

Interpretation of spectrograms. A. H. TAYLOR and T. KNOWLES (J. Opt. Soc. Amer., 1932, 22, 229—235).—The use of diffusing quartz over the slit of the spectrograph is recommended to secure even illumination. Other precautions in the making and interpretation of spectrograms are detailed.

J. LEWKOWITZ.

Line reflexion spectra of solids. F. H. SPEDING and R. S. BEAR (Physical Rev., 1932, [ii], 39, 948—952).—A new interpretation of reflexion spectra in solids, particularly $SmCl_3 \cdot 6H_2O$, is proposed. The difference in spectrum of a conglomerate compared with that of a single crystal is attributed to increased path length through the crystal rather than to surface atoms. A new phenomenon of reversal of lines from absorption in a single crystal to emission in a conglomerate is described for a multiplet of the $GdCl_3 \cdot 6H_2O$ spectrum (cf. A., 1929, 1362).

N. M. BLIGH.

Light from solidified gases. Relations between electronic levels and phosphorescence of gaseous nitrogen. L. VEGARD (Z. Physik, 1932, 75, 30—62).—By means of a new phosphoroscope the phosphorescent radiation emitted by solid N_2 and NO under bombardment of cathode rays of up to 6000 volts was analysed as far as 1600 Å. Positive and negative N_2 bands were not observed, showing them peculiar to the gaseous phase; NO with 1% of A gave N_2 bands. The ϵ -system was analysed, and its end level has an energy of dissociation of 11.5

volts. A new scheme for the A, B, C, and D electronic levels leads to possible new explanations of active N_2 . A. B. D. CASSIE.

Emission and absorption spectra of BaF. F. A. JENKINS and A. HARVEY (Physical Rev., 1932, [ii], 39, 922—931).—Electronic terms and vibration frequencies are tabulated for BaF, LaO, SrF, YO, CaF, and ScO and classified for BaF. Existing data are revised and corrected. N. M. BLIGH.

Absorption of water in the visible spectral region. B. LANGE and C. SCHUSTERIUS (Z. physikal. Chem., 1932, 159, 303—305).—Determination of the absorption coeff. between 400 and 800 m μ by a photoelectric method has revealed absorption maxima at 600, 660, and 750 m μ . The absorption of the shorter wave-lengths is quite small, but is considerably increased by the presence of impurities.

R. CUTHILL.

Absorption of light by aqueous potassium permanganate solutions. B. LANGE and C. SCHUSTERIUS (Z. physikal. Chem., 1932, 159, 295—302).—Determination of the absorption curve of 0.01N- $KMnO_4$ by means of unidirectional photo-cells has shown that between 450 and 700 m μ there are absorption maxima at 490, 508.4, 526.5, 546.5, and 566 m μ only. On dilution to $10^{-5}M$ the bands are not displaced; Beer's law holds.

R. CUTHILL.

Absorption spectra of the rare earths. II. Y. UZUMASA (Bull. Chem. Soc. Japan., 1932, 7, 85—91).—The spectra of $NdCl_3$ and $Nd(NO_3)_3$ in H_2O , glycerol, MeOH, EtOH, and $COMe_2$ have been compared. The effect of Et_2O , C_6H_6 , CCl_4 , and $CHCl_3$ on the spectrum of $Nd(NO_3)_3$ in EtOH has been examined. The position of the Nd bands varies slightly according to the concn., anion, and solvent, displacement being due to deformation of the electron shell of the Nd^{+++} ion by the anion and by solvation. D. R. DUNCAN.

New band system of beryllium oxide. L. HERZBERG (Nature, 1932, 129, 653—654).

L. S. THEOBALD.

Chromium oxide and vanadium oxide band spectra. W. F. C. FERGUSON (Bur. Stand. J. Res., 1932, 8, 381—384).—Measurements have been made of the band heads due to CrO and to VO, and vibrational analyses made of these spectra.

J. W. SMITH.

Relations between the structure of organic molecules and their absorption spectra in the ultra-violet. (MME.) P. RAMART-LUCAS (Bull. Soc. chim., 1932, [iv], 51, 289—338).—A lecture.

Structure and ultra-violet absorption of organic molecules. (MME.) RAMART-LUCAS and J. HOCH (Ann. Chim., 1932, [x], 17, 207—253).—The ultra-violet absorption of the members of the homologous series $Ph[CH_2]_nR$, where R is CO_2H , CO_2Et , CN, $CO \cdot NH_2$, $CH(CO_2H)_2$, or Ph, shows that when n is 1 the chromophores Ph and R may have a marked influence on one another. This influence practically disappears for $n=3$ and the ultra-violet absorption spectrum of the mol. is then practically the same as for a mixture of PhEt and MeR. When the chromophores are separated by 5C the reciprocal influence again becomes manifest, indicating proximity

in space and hence a curvature of the mol. chain. If the chain is sufficiently long, *i.e.*, when n is 6 for acids and 4 for hydrocarbons, the absorption spectrum of the mol. in EtOH solution becomes the same as that of a mixture of PhEt and MeR in C_6H_{14} , but not in EtOH. The result is as if the mol. chain curved around the chromophores and thus prevented the action of the solvent EtOH. M. S. BURR.

Autoxidation. IV. Absorption spectrum of aqueous solutions of sulphurous acid in relation to their autoxidation. H. W. ALBU and P. GOLDFINGER (Z. physikal. Chem., 1932, B, 16, 338—350; cf. A., 1931, 1252).—The absorption of the solutions between 1950 and 5000 Å. depends only on the p_H and concn., and, provided that autoxidation is prevented, not on the age or mode of prep. The spectrum of SO_3'' , which is structureless and regarded as an electron affinity spectrum, is observed with solutions of $p_H > 6$ and has the long-wave limit of 2660 Å., whilst the absorption of undissociated dissolved SO_2 ($p_H \leq 4$) starts at 3270 and has a max. at 2800 Å. Franck and Haber's theory (*ibid.*, 917) indicates that an electron affinity spectrum of HSO_3' will be 1.5—2 volts nearer the ultra-violet than that of SO_3'' , and in agreement with this there is no evidence of absorption by HSO_3' at wave-lengths > 2250 Å. The long-wave limits of the absorption of S_2O_8'' and S_2O_6'' are 2700 and 2600 Å., respectively. No absorption by SO_4'' was detected. R. CUTHILL.

Absorption spectrum of cyanogen gas in the ultra-violet. S. C. WOO and R. M. BADGER (Physical Rev., 1932, [ii], 39, 932—937).—Data for more than 100 bands in the region λ 2300—1820, with probable origin at $44,900\text{ cm}^{-1}$, are tabulated, and relations with the infra-red absorption and Raman spectra are discussed. N. M. BLIGH.

Predissociation of the benzene molecule in the electronic ground state. F. ALMASY (Naturwiss., 1932, 20, 296—297).—The monochromatically excited fluorescence spectrum of C_6H_6 vapour at pressures < 2 mm. has been examined with large dispersion and the results are discussed. W. R. ANGUS.

Spectrographic study of some heterocyclic compounds. M. MILONE (Gazzetta, 1932, 62, 154—158).—A study of the absorption spectra of various compounds of the furazan, azoxime, and oxadiazole types shows that the selective absorption depends more on the nature of the side-chain than on the position of the atoms in the C_2N_2O ring. O. J. WALKER.

Lignin. V. R. O. HERZOG and A. HILLMER (Papier-Fabr., 1932, 30, 205—209; cf. A., 1931, 942).—In the spectrographic examination of phenolic and other substances related to the primary components of lignin it is found that the introduction of phenolic OH groups into the C_6H_6 nucleus causes intensification of the absorption and displacement of the absorption bands towards the region of longer wave-length. The presence of a saturated side-chain, or one containing a double linking in the $\beta\gamma$ position or a carbonyl or OH group in the β position causes no important change in the spectrum. On the other hand, a conjugated double linking in the $\alpha\beta$ position, or a carbonyl group

in the α position, alters the spectrum. The members of a homologous series in which the repeating groups of atoms have a characteristic spectrum show one and the same spectrum. The spectrum of a mixture of substances that do not react with one another is additive. B. P. RIDGE.

Influence of substitution on the natural frequencies of organic compounds. G. ALLARD (Compt. rend., 1932, 194, 1495—1498).—If ν , $\nu + \delta\nu$, and ν_0 are respectively the frequencies of absorption bands of mols. AB and AC and the group A, $h\delta\nu$ should equal the difference between the energies of perturbation of group A by B and by C (cf. A., 1931, 978, this vol., 7). C. A. SILBERRAD.

Rotation-vibration bands of water vapour between 0.9 and 6.5 μ . P. LUEG and K. HEDFELD (Z. Physik, 1932, 75, 512—520).—The bands at 9050, 9400, and 11,300 Å. were photographed under high dispersion, and an analysis of the bands up to 6.5 μ gives the moments of inertia as 6.70, 2.13, and 0.97×10^{-40} g. cm^2 . A. B. D. CASSIE.

Parallel type absorption bands of ammonia. D. M. DENNISON and J. D. HARDY (Physical Rev., 1932, [ii], 39, 938—947).—The predicted doubling of the 3.0 μ band is confirmed experimentally. Calc. intensities of the 3.0 and 10.5 μ bands are in good agreement with experiment. N. M. BLIGH.

Infra-red absorption spectra of the oxides of chlorine. C. R. BAILEY and A. B. D. CASSIE (Nature, 1932, 129, 652—653).—Details are given for Cl_2O and ClO_2 . A determination of mol. consts. makes it probable that both SO_2 and ClO_2 are equilateral triangles with sides 1.37 Å. in length, with a single linking between each O and the central atom. The mol. of Cl_2O is triangular with a vertical angle of approx. 90° and with single linkings between the Cl and O atoms. There is a large repulsive force between the two Cl atoms, since the force const. for the particles at the base of the triangle increases from 1.7×10^5 dynes per cm. for SO_2 and ClO_2 to 5×10^5 dynes per cm. for Cl_2O . L. S. THEOBALD.

Absorption by formaldehyde vapour in the infra-red. J. R. PATTY and H. H. NIELSEN (Physical Rev., 1932, [ii], 39, 957—966).—Bands at 3.5, 1.8, 1.4, 1.25, and a new band at 4.8 μ were observed. The region of intense absorption at 3.5 μ consisted of three partly overlapping bands with centres near 3.4, 3.5, and 3.6 μ . The 4.8 μ band, resolved under high dispersion, showed similar structure. N. M. BLIGH.

Infra-red spectra and structure of tautomeric compounds. C. E. H. BAWN (J.C.S., 1932, 1189—1198).—The infra-red spectra of acetyl- and benzoyl-acetone, Et acetoacetate and methylacetoacetate have been investigated between 2.8 and 6.3 μ . The spectra show no band characteristic of an O-H linking, as would have been expected for enolised tautomers. The absorption spectra of acids do not show O-H bands, although the C=O bands are found. The absence of bands due to O-H linkings may be due either to no O-H group in the enolic tautomeride or to a displacement of the characteristic band due to the influence of the neighbouring $\cdot C \cdot C \cdot$ group or to

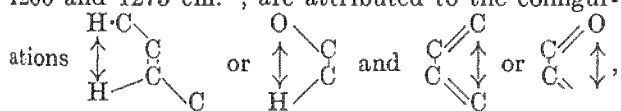
an abnormal vibration of the H atom in the OH group. W. R. ANGUS.

Infra-red absorption spectra of ethylenic and aromatic derivatives. R. FREYMAN (Compt. rend., 1932, 194, 1471—1474; cf. this vol., 6).—The absorption spectra between 0.84 and 1.16 μ of 10 ethylenic and 27 aromatic liquids have been determined: OH, NH₂, CH not attached to C by double linking, CH thus attached, and C=C are characterised respectively by bands at 0.96, 1.03, 0.9 and 1.0, 0.87, and 1.14, and (probably) 1.10 and 1.12 μ . Results indicate identity of effect of double linkings in ethylenic and aromatic compounds. In the latter an electronegative group is accompanied by a shift towards shorter wave-length, a positive group the reverse. C. A. SILBERRAD.

Molecular light scattering by solids. V. Theory of light scattering. M. LEONTOVITSCH and S. MANDELSTAM, jun. (Z. Physik, 1932, 75, 350—351).—A formula is deduced for the intensity of light scattered by rock-salt and other isotropic solids. A. B. D. CASSIE.

Raman effect. G. ELSÉN (Chem. Weekblad, 1932, 29, 183—188, 194—200).—A review of the theory and of some of the more important results which have been obtained. H. F. GILLBE.

Interpretation of certain Raman frequencies of the carbon double linking. G. ELSÉN (Ber., 1932, 65, [B], 525—534).—The Raman lines, ν = about 1200 and 1275 cm.⁻¹, are attributed to the configurations



respectively, present in a variety of aliphatic and aromatic substances. The frequencies are probably simple vibrations, although the possibility of rotations in which valency electrons can participate is not excluded. The theoretical consequences are discussed at length. H. WREN.

Light absorption, the Raman effect, and the motions of electrons in gases. V. A. BAILEY (Phil. Mag., 1932, [vii], 13, 993—1000).—The relation between the energy transferred from a slow electron to a mol. and the energy transferred from radiation to a mol. during absorption or scattering is discussed.

H. J. EMELEUS.
Raman spectrum of water. H. HULUBEI (Compt. rend., 1932, 194, 1474—1477).—The Raman spectrum of H₂O, using the line 2536.52 Å. (cf. A., 1931, 892), shows a double band with max. at 3233 and 3443 cm.⁻¹, but with no trace of a third band (cf. A., 1930, 662); ten other bands (6747—10,944) were also measured, most of which disappear on adding a salt. C. A. SILBERRAD.

Raman effect of salt solutions. A. SILVEIRA (Compt. rend., 1932, 194, 1336—1338).—Using Hg light filtered through quinine sulphate and solutions of MgCl₂, Mg(NO₃)₂, and Mg(ClO₄)₂ about 5.5M, optically purified by ultra-filtration, the Raman spectra include lines at 1652 and 1655 cm.⁻¹ in the chloride and nitrate, respectively, and 376 (feeble) in both, but in the chlorate only doubtfully at 376. It

is inferred that these are due to hydrated Mg⁺⁺ ions, and that the structure of the chlorate solution is essentially different. C. A. SILBERRAD.

Valency- and deformation-oscillations of simple molecules. I. General theory. II. Triatomic molecules. R. MECKE (Z. physikal. Chem., 1932, B, 16, 409—420, 421—437).—I. The theory of the subdivision of the characteristic frequencies of a polyat. mol. into valency- and deformation-oscillations (cf. A., 1930, 1236) is described.

II. Interpretation of the Raman and infra-red spectra of triat. mols. by means of the theory shows that the three atoms lie in the one straight line only if, as in CO₂, CS₂, N₂O, and HCN, a triple linking is present. In such mols. the mutual interaction of the linkings is only 3—6% of the strength of the linking, so that the deformation oscillation is small. With non-linear mols., such as H₂O, H₂S, —CH₂, SO₂, —NO₂, —CCl₂, —CBr₂, and —Cl₂, the mutual interaction is about 30%, and results in stable valency flexure. R. CUTHILL.

Raman spectra of mono-, di-, and tri-saccharides. W. KUTZNER (Naturwiss., 1932, 20, 331—332).—Aldoses are characterised by a Raman displacement of 1140 cm.⁻¹; ketoses by a displacement of 1180 cm.⁻¹. Glucose gives two other displacements of 513 and 454 cm.⁻¹. Maltose shows only the characteristic aldose displacement, whereas sucrose gives a broad band (1130—1188 cm.⁻¹) embracing the characteristic displacements of an aldose and a ketose. The spectrum of raffinose, 1150 cm.⁻¹, is diffuse and weaker than the spectra of other sugars.

W. R. ANGUS.
Raman spectra of cyclanes. E. CANALS, M. GODCHOT, and (MLLE.) G. CAUQUIL (Compt. rend., 1932, 194, 1574—1577).—Raman spectra of cyclopropane, -pentane, -hexane, -heptane, and -octane and their Me derivatives show great similarity; lines characteristic of C—H, e.g., that near 800 cm.⁻¹, decline in frequency as the ring enlarges; 1440, characteristic of —CH₂, is almost const.; introduction of Me causes a general lowering of frequency, less as the ring enlarges. Comparison with the corresponding paraffins shows that a line near 1200 characterises the cyclanes (cf. this vol., 109, 213).

C. A. SILBERRAD.
Raman spectrum and constitution of substances of high mol. wt. R. SIGNER and J. WEILER (Helv. Chim. Acta, 1932, 15, 649—657).—The Raman spectra of styrene, PhEt, and polystyrene (in the solid state and in CCl₄) are closely similar, but styrene alone shows the lines associated with the ethylenic linking. The results strongly support Staudinger's structure for polystyrene (A., 1929, 305). The continuous background is attributed to fluorescence, due to impurities, or to the end-groups of the polystyrene chain. Venkateswaran's explanation (A., 1928, 1170) is rejected. D. R. DUNCAN.

Luminescent compounds. II. A. SCHLOEMER (J. pr. Chem., 1932, [ii], 133, 257—258; cf. this vol., 352).—ThO₂, moistened with CeO₂ (best 0.9%), dried, and strongly heated, is luminescent in a conc. stream of cathode rays (70 kv.). Luminescence reaches a

max. after 0.5 sec. and rapidly fades on cessation of the excitation.

R. S. CAHN.

Phosphorescent sulphides: intervention of collisions of the second kind. M. CURIE (Compt. rend., 1932, 194, 1566—1568).—The *d*-process absorption bands are due to absorption by mols. of diluent near a light-forming centre, bringing them into an excited state, followed by collisions of the second kind with electrons previously detached from such centre. Such collisions remove the electrons from the influence of the centre and so prolong the fluorescence. Similar collisions explain the max. of *d*-process phosphorescence for certain wave-lengths (cf. A., 1910, ii, 369; 1931, 894).

C. A. SILBERRAD.

Analysis of ultra-violet emission of alkaline-earth phosphors. O. SCHELLENBERG (Ann. Physik, 1932, [v], 13, 249—264).

A. J. MEE.

Electrolytic valve action. A. GÜNTHER-SCHULZE (Z. Physik, 1932, 75, 143).—Polemical against Müller (this vol., 214).

A. B. D. CASSIE.

Nature of the unidirectional layer in cuprous oxide rectifiers. F. WAIBEL and W. SCHOTTKY (Naturwiss., 1932, 20, 297—298).

W. R. ANGUS.

Structure experiments with the cuprous oxide rectifier. K. SCHARF and O. WEINBAUM (Physikal. Z., 1932, 33, 336—341).—A microscopical investigation of the cryst. structure of a Cu_2O rectifier has been made.

A. J. MEE.

Constitution of the oxide of copper oxide rectifiers and of cuprous oxide photo-electric cells. L. DUBAR (Compt. rend., 1932, 194, 1332—1334; cf. A., 1931, 409).— Cu_2O is probably a perfect insulator. The substance causing conductivity in "semi-conducting Cu oxide" is present in very small amount, $> 1.5\%$, disseminated in intercryst. spaces of Cu_2O ; it is possibly CuO in solid or colloidal solution.

C. A. SILBERRAD.

Internal photo-effect and photo-electric cells. I. I. V. KURTSCHATOV and C. D. SINELNIKOV. II. I. KURTSCHATOV, C. SINELNIKOV, and M. BORISSOV (Physikal. Z. Soviet Union, 1932, 1, 23—41, 42—59).—I. The spectral sensitivity, influence of temp. and of electrode material have been investigated for cells with Cu_2O and Cu_2S between metal electrodes. The origin of the e.m.f. is discussed.

II. Results similar to those for Cu_2O were obtained with Se in the cell.

H. J. EMELÉUS.

Catalysis and photo-conductors. [Selenium.] F. H. CONSTABLE and A. F. H. WARD (Trans. Faraday Soc., 1932, 28, 497—508).—Small quantities of Ag, Bi, Pb, Hg, Zn, Cu, and Fe were incorporated in amorphous red Se and thin films of the mixture were annealed at temp. between 170° and 215° . Phase data are given. The effects of illumination are characterised by the light ratios, *L* (current in light/current in dark, at const. applied p.d.) obtained from data at various stages during illumination and subsequent darkness. The "dark resistance," *R*, and vals. of *L* are diminished by Fe, only slightly affected by Zn and Pb, but are increased by Bi, Cu, Hg, Ag, and especially by Tl, at the same annealing temp.

Vals. of *L* are higher at the lower annealing temp. for Se alone and with the added metals. In general, the addition of the metals does not increase median vals. of *L*, for a given resistance, to a higher val. than would correspond with that of a film of pure Se with the same val. of *R*, but distortion of the annealing temp.—*L* curve may occur. The metals, therefore, have little effect on the liberation of electrons by light, but greatly influence the chemical constitution of the cryst. mass.

J. G. A. GRIFFITHS.

Spectral distribution of the depolarisation current due to the photo-electric conductivity of X-rayed rock-salt. N. KALABUCHOV and B. FISCHER (Z. Physik, 1932, 75, 282—286).

A. B. D. CASSIE.

Anomalous variation of the electrical conductivity of quartz with temperature. S. SHIMIZU (Phil. Mag., 1932, [vii], 13, 907—934).—The conductivity increases linearly with rise of temp. up to the transition point at 573° , where a discontinuity occurs. At higher temp. the temp. coeff. is greater, and the conductivity increases with the measuring potential.

H. J. EMELÉUS.

[Two different liquid states.] L. MEYER (Z. Physik, 1932, 75, 421—423).—The hypothesis of two mol. forms (Wolfke and Mazur, this vol., 329) is probably incorrect: the observed change in dielectric const. with temp. is more probably associated with some phenomenon analogous to change from vibration to rotation within the liquid.

A. B. D. CASSIE.

Electrical properties of mixed crystals from sodium potassium tartrate. B. KURTSCHATOV and M. EREMEJEV (Physikal. Z. Soviet Union, 1932, 1, 140—154).—Isomorphous mixed crystals of Na K tartrate and K NH_4 tartrate give anomalous high vals. of the dielectric const. from -107° to -190° . In this range they resemble ferro-magnetic substances.

H. J. EMELÉUS.

Dielectric constants of some oxides. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 75, 78—83).—Dielectric consts. were determined for oxides of Mg, Ba, Al, Ce, Zr, Th, Ta, Sb, Bi, and Cr.

A. B. D. CASSIE.

Measurements of the dielectric constants of salts. P. SCHUPP (Z. Physik, 1932, 75, 84—104).—Dielectric consts. were measured for the carbonates and nitrates of the alkali and alkaline-earth metals, and for the alkali chlorides; the relation of the results to the periodic table and refractive indices is discussed.

A. B. D. CASSIE.

Dipole moments of the naphthols. M. PUCHALIK (Physikal. Z., 1932, 33, 341—345).—The resonance method was used to find the dipole moments of α - and β -naphthol. The β -derivative has a higher moment than the α , and the moment of α -naphthol is lower than that of PhOH , whilst that of β -naphthol is lower than that of EtOH .

A. J. MEE.

Determination of the dielectric constant of liquid dielectrics, using the heterodyne method. K. HRYNAKOWSKI and S. KALINOWSKI (Rocz. Chem., 1932, 12, 225—231).—A description of apparatus for approx. determination of the dielectric const. of liquids.

R. TRUSZKOWSKI.

Determination of dielectric constants by the oscillatory circuit method. G. MÖNCH (Z. physikal. Chem., 1932, B, 16, 438—442).—In determining the dielectric const. of a gas or liquid with high-frequency oscillations a calibrated variable condenser is required to determine the change in capacity of a condenser when the dielectric is replaced by the substance under examination. This condenser may be calibrated in arbitrary units if the abs. val. of one const. is determined. R. CUTHILL.

Dielectric measurements with organic dipole-free substances. G. BRIEGLEB (Z. physikal. Chem., 1932, B, 16, 276—283).—The dielectric const. and n of binary mixtures of C_6H_6 , CS_2 , CCl_4 , and heptane have been determined. The vals. for the two components of the displacement polarisation of the pure substances calc. by applying the mixture rule to the mixtures vary with concn., indicating that the electron frequencies and rotation-vibration frequencies are influenced by intermol. forces. C_6H_6 , CS_2 , $C_{10}H_8$, Ph_2 , phenanthrene, *p*-dichlorobenzene, and *p*-xylene have zero dipole moment. R. CUTHILL.

Dipole moment of *n*-propyl ether. L. MEYER and A. BÜCHNER (Physikal. Z., 1932, 33, 390—391).—The val. obtained is $1.16 \pm 0.05 \times 10^{-18}$ e.s.u.

A. J. MEE.
Association in dipole liquids. J. MALSCH (Physikal. Z., 1932, 33, 383—390).—The dependence of the dielectric const. of some highly-associated liquids ($BuOH$, $EtOH$, $PrOH$, H_2O) on temp., field strength, and frequency is discussed. It is possible to calculate the deviations from the normal as regards high-frequency effects due to association.

A. J. MEE.
Dielectric constant and power factor of some solid dielectrics at radio frequencies. W. ANDERSON (Phil. Mag., 1932, [vii], 13, 986—993).—Frequencies between 150 and 1500 kilocycles were used.

H. J. EMELÉUS.
Influence of substitution in naphthalene derivatives on, and comparison of dispersion of, magnetic rotation and birefringence. C. SALCEANU (Compt. rend., 1932, 194, 1227—1229).—The magnetic rotation at 150° compared with that of H_2O at 20° , and the magnetic birefringence compared with that of $PhNO_2$, both at 20° , have been determined for $C_{10}H_8$ and 10 derivatives. The influence of the substituents Me, Cl, Br, OH, NO_2 , NH_2 , and CN is similar to their effect in C_6H_6 (cf. A., 1907, ii, 727; J.C.S., 1896, 69, 1025), save as regards Me in $1-C_{10}H_7Me$, where it is opposite. The dispersion of the rotation and birefringence between the green, yellow, and indigo lines of Hg for $PhNO_2$, $2-C_{10}H_7Me$, and phenanthrene are approx. the same.

C. A. SILBERRAD.
Variation of the temperature constant and of Havelock's constant of magnetic birefringence for some fused organic substances. C. SALCEANU (Compt. rend., 1932, 194, 863—865).—Assuming that the optical magnetic anisotropies are independent of (a) temp, (b) λ , expressions are deduced (a) for the temp. const., holding only near the m. p., for $C_{10}H_8$, $-C_{10}H_7Me$, and phenanthrene; and (b) for Havelock's

const., decreasing with decrease in λ , for $2-C_{10}H_7Me$ and phenanthrene (cf. A., 1910, ii, 368; 1923, ii, 707).

C. A. SILBERRAD.
Rotatory dispersion of benzene solutions of α - and β -pinenes. J. RABINOVITCH (Compt. rend., 1932, 194, 1474; cf. this vol., 448).—The calculation of the amount of the third constituent has been corrected.

C. A. SILBERRAD.
Effect of solvents and temperature on the optical rotation of esters of menthyl and bornyl hydrogen xanthates and on menthyl and bornyl dixanthides. (MISS) I. M. McALPINE (J.C.S., 1932, 1016—1022).—Menthyl Me, menthyl Pr^3 , menthyl CH_3Ph , menthyl *p*-nitrobenzyl, and bornyl Me xanthates and the menthyl and bornyl dixanthides were examined in 7 solvents; all showed strong anomalous rotation dispersion between 6716 and 4358 Å.

W. R. ANGUS.
Theory of anisotropic liquids. XV. Geometrical optics of nematic substances. C. W. OSEEN (Ark. Matemat. Astron. Fysik., 1931, A, 22, 1—23; Chem. Zentr., 1931, ii, 3185—3186).—The path of the rays in the neighbourhood of a rectilinear thread of a nematic substance has been investigated.

L. S. THEOBALD.
Optical properties of mixed crystals; sodium ammonium and sodium rubidium tartrates. S. KOZIK (Bull. Acad. Polonaise, 1931, A, 247—266).—The properties of the double Na K, Na Rb, and Na NH_4 tartrates are tabulated. The refractive indices and mol. vols. increase slightly in the order given. The geometric properties of mixed crystals of Na tartrate with K, Rb, and NH_4 tartrates are similar to those of the pure tartrates. Refractive indices and densities are additive properties of the components.

J. W. SMITH.
Calculation of the refractive power of mixed immersion liquids. A. MAYRHOFER and F. WRATSKO (Pharm. Presse, 1931, 33—35; Chem. Zentr., 1931, ii, 3232).—When no change in mol. condition occurs on mixing, $n = (V_1n_1 + V_2n_2)/(V_1 + V_2)$ as in the case of paraffin oil and $1-C_{10}H_7Br$. In other cases n depends on the type of solution formed, and ultimately on the indices and densities of the components.

L. S. THEOBALD.
Variations in the optical constants of copper. H. LOWERY and R. L. MOORE (Phil. Mag., 1932, [vii], 13, 938—952).—Methods of measuring the optical consts. of polished metals are described and discussed.

H. J. EMELÉUS.
Physics of the nitrobenzene Kerr cell. V. Determination of electro-optical Kerr constant of nitrobenzene ($\lambda = 5461$ Å.). F. HEHLGANS (Physikal. Z., 1932, 33, 378—382; cf. A., 1931, 1220, 1355).—An interference method of determining the Kerr const. gives good agreement with others, the val. found being 3.86×10^{-5} e.s.u.

A. J. MEE.
Nature of the chemical linking. III. Transition from one extreme type of linking to another. L. PAULING (J. Amer. Chem. Soc., 1932, 54, 988—1003; cf. A., 1931, 1356).—The ionic and electron-pair linkings are discussed as examples of extreme types of linkings. As the parameters determining the nature of the atoms are changed, transitions from one type

to the other will take place continuously if the two possible electronic states are nearly degenerate and have the same multiplicity. If the multiplicities are different and the spin-orbit interaction of the electrons is negligible, the normal state may show a discontinuity at the crossing of two non-combining levels. The linking type may be determined from a consideration of electronic energy curves. The normal alkali halide mols. are essentially ionic; HF is largely ionic, and HCl, HBr, and HI have electron-pair linkings. The normal state of CO is a combination of a doubly- and a triply-linked structure, the latter being the more important. The types of linking formed by metals of the transition groups are also discussed.

G. M. MURPHY (c).

Electronic structures of polyatomic molecules and valency. R. S. MULLIKEN (Physical Rev., 1932, [ii], 40, 55—62).—The electronic structures of H_2O , NH_3 , CH_4 , CF_4 , Cl_4 , ClO_4' , SO_4'' , ClO_3' , SO_3'' , and CO_2 are briefly described in terms of one-electron wave functions.

N. M. BLIGH.

Interatomic distances in covalent molecules and resonance between two or more Lewis electronic structures. L. PAULING (Proc. Nat. Acad. Sci., 1932, 18, 293—297).—Tables of radii for non-metallic atoms in covalent mols., and radius sums and observed interat. distances from band spectra data for ICl , HCl , HBr , HI , H_2O , NH_3 , CH_4 , MeF , O_2 , CH_2O , N_2 , HCN , CN , and C_2H_2 are given. The effect of resonance among several equiv. structures is examined for N_2O , CO_2 , graphite, C_6H_6 , CO_3^- , NO_3^- , and the chemical properties of several org. mols.

N. M. BLIGH.

Quantum theory of the transference of energy of activation between molecules of the same kind. Fluorescent solutions. F. PERRIN (Ann. Physique, 1932, [x], 17, 283—314).—Mathematical. The interaction between a normal and an active atom is investigated and interpreted; the probable at. energy varies continuously, the energy transfer is discontinuous. The theory is extended to dissolved mols. and the action of the solvent.

N. M. BLIGH.

Structure of the isomeric diamminoplatinous chlorides. Discovery of a third isomeride. H. D. K. DREW, F. W. PINKARD, W. WARDLAW, and (in part) E. G. COX (J.C.S., 1932, 988—1004).—In place of Werner's *cis*- and *trans*-planar isomerides of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, there are recognised 3 isomerides, which probably differ structurally. The reaction with phenoxtellurine dibisulphate shows that only the β -isomeride is a compound of bivalent Pt. The α -isomeride has 4 groups arranged round the Pt atom, but there is at present no evidence to show whether the distribution is tetrahedral or planar. The reactions with moist Ag_2O or aq. NaOH show that, whilst the β -isomeride gives a corresponding base, the α -isomeride gives a base which with HCl yields a β -isomeride, which can be transformed into the α -isomeride. The isomerides differ in colour, solubility, min. n , and X-ray diagrams. Formulæ have been assigned, and a mechanism is suggested for the transformation α -dichloride $\rightarrow \beta$ -base is borne out by comparison with the behaviour of the corresponding α - and β -dipyridino-dichlorides, containing tert.

N. The α - and β -isomerides of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ are also shown to be structural and not stereo-isomerides.

E. S. HEDGES.

Structure of simple and mixed tetramminoplatinous dihalides. H. D. K. DREW, F. W. PINKARD, W. WARDLAW, and (in part) E. G. COX (J.C.S., 1932, 1004—1016).—There is no definite evidence to show that the isomeric mixed tetrammines $\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$ are *cis*- and *trans*-planar isomerides, as supposed by Werner. A study of their reactions indicates that the isomerism can be explained by assuming that the co-ordinate linkings between the NH_3 groups and Pt are paired. A tetrahedral arrangement is considered more probable.

E. S. HEDGES.

Connexion between chemical constitution and X-ray λ absorption spectra. X. X-Ray spectroscopic investigation of structure of chemical complexes. II. O. STELLING (Z. physikal. Chem., 1932, B, 16, 303—337; cf. A., 1930, 671).—It is found experimentally that if a solid chloride of the first order exhibits two absorption edges in the Cl absorption spectrum, those of its complex compounds which contain non-ionisable Cl have edges at similar wave-lengths, whereas those compounds containing only ionisable Cl have only one edge. It has thus been possible to determine the structure of complex compounds of Fe^{II} , Co^{II} , Ni , Cu^{II} , and Cd chlorides. The harder edge is assumed to correspond with the ejection of a K electron from the Cl atom, and the softer with the transfer of an electron from the K to the M level. The difference between the two wave-lengths is a linear function of the at. no. of the metal for MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 , and CuCl_2 , although each wave-length rises to a max. and falls again as the at. no. increases. For geometrical isomerides with 2 Cl atoms in the complex, the soft edge corresponds with a longer wave-length for the *trans* form than for the *cis* form. The experimental conditions under which satisfactory K -absorption spectra may be obtained are examined. The most essential is suitable thickness of the absorbing material; with too thick layers structural details in the spectrum are obscured, and misleading simplicity results.

R. CUTHILL.

Magnetic resolution and nuclear moment of rhenium. P. ZEEMAN, J. H. GISOLF, and T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 2—9).—A detailed account of work already noted (A., 1931, 1345).

Magnetisation of ferromagnetic powders. R. CHEVALLIER (Compt. rend., 1932, 194, 1327—1329).—The magnetic behaviour of a medium, e.g., basalt, in which ferromagnetic material is dispersed, in a weak field depends mainly on the form and dispersion of the particles of that material, in a strong one on the susceptibility of the non-ferromagnetic portion.

C. A. SILBERRAD.

Curie point of ferro-cerium. G. RASSAT (Compt. rend., 1932, 194, 1153).—Ferro-cerium containing 27.5% Fe loses its magnetism at about 40° ; samples containing about 32% Fe do not cease completely to be magnetic up to the temp. of ignition, indicating the presence of more than one substance.

C. A. SILBERRAD.

Variability of magnetic ionic moment of some elements of the iron series. H. FAHLENBRACH (Ann. Physik, 1932, [v], 13, 265—296).—The susceptibilities of aq. solutions of NiCl_2 , CoCl_2 , and FeCl_3 , and of solutions of CoCl_2 in $\text{C}_5\text{H}_5\text{N}$ and EtOH , and their dependence on temp. and concn. were determined, and the variation of susceptibility with temp. of H_2O , EtOH , COMe_2 , and $\text{C}_5\text{H}_5\text{N}$. The relationship of susceptibility to temp. for COMe_2 and EtOH is linear; for $\text{C}_5\text{H}_5\text{N}$ it is independent of temp. There is no simple connexion between paramagnetism and colour. The dependence of magnetic ionic moment on concn. is investigated. A. J. MEE.

Mechanism of intermolecular forces in organic compounds. II. G. BRIEGLER (Z. physikal. Chem., 1932, B, 16, 249—275; cf. A., 1931, 1214).—The equations for the Kerr const. deduced by Langevin and Born's theory and by Gans may be applied to liquids if the polarisability anisotropies of the mol. in the gaseous state are replaced by the vals. for the condensed state. Kerr consts. of various org. compounds dissolved in non-polar solvents have been determined. The consts. deduced from the mol. Kerr consts. at infinite dilution are all less than those for the gaseous state, which is attributed to the presence in the solutions of "swarms" of solvent and solute mols. more or less oriented in relation to each other. From the variation with concn. of the mol. Kerr const., K , of non-polar substances without polar groups dissolved in an indifferent solvent, it appears that the orientation of these mols. relative to each other in the condensed state is determined by the polarisability anisotropy, as well as by the mean polarisability itself; the greater is the abs. anisotropy, the more pronounced is the orientation. From the variation with concn. of K and the mol. polarisation the relative orientations in associated complexes of mols. containing a single polar group may be deduced. With mols. containing several polar groups, the association will be such that the max. possible no. of polar groups saturate each other, or the groups with the largest moments are brought into proximity. The types of linkings effective in mol. compounds are analysed. R. CUTHILL.

Weiss' molecular field. K. HONDA (Z. Physik, 1932, 75, 352—362).—Weiss' hypothesis of an intense mol. field, magnetising to saturation the elementary regions of a ferromagnetic substance, is incompatible with experimental facts. A. B. D. CASSIE.

Tetrahedral field of force of atoms. R. REINICKE (Ann. Guébbard-Severine, 1930, 6, 141—150).—A theory of mol. structure on the basis of regular tetrahedral atoms is advanced. J. W. SMITH.

Collision areas and shapes of carbon chain molecules in gaseous state: n -heptane, n -octane, and n -nonane. R. M. MELAVEN and E. MACK, jun. (J. Amer. Chem. Soc., 1932, 54, 888—904).—From viscosity measurements at 100—250° with n -heptane, n -octane, and n -nonane the collision areas are calc. to be 26.7, 34.9, and 42.5 Å.², respectively. The shadowgraphic collision areas of various mol. models agree well with the calc. vals. if C chain compounds are assumed to coil into helical shapes. Vogel's empirical equation $c=1.47T_b$ is not valid for large mols. E. J. ROSENBAUM (c).

Quantum-theoretical calculation of molecular linking energies. II. H. WEYL (Nachr. Ges. Wiss. Gottingen, 1931, 33—39; Chem. Zentr., 1932, i, 173).

X-Ray reflexion from inhomogenously strained quartz. C. S. BARRETT and C. E. HOWE (Physical Rev., 1932, [ii], 39, 889—897). N. M. BUGH.

Chemical reactions between metal sulphides and anticathode metals observed in photographs of the $K\beta$ spectrum of sulphur. B. SVENSSON (Z. Physik, 1932, 75, 120—128).—The S of metal sulphides deposited on anticathodes may form sulphides with the metals of the anticathode; the transition of S from one metal to another is revealed by changes in the $K\beta$ spectrum of S, and this gives a measure of the relative affinity of the two metals for S. Anticathodes used were Cu, Ag, Fe, and Al.

A. B. D. CASSIE.

Affinity. LVII. Diagram of state of pyrites, magnetic pyrites, troilite, and sulphur vapour, judged by vapour pressures, X-ray diagrams, densities, and magnetic measurements. R. JUZA and W. BILTZ (Z. anorg. Chem., 1932, 205, 273—286; cf. this vol., 239).—V. p.-composition curves have been determined at temp. from 629° to 1055°, the constitution of the solid phase being ascertained by X-ray analysis. The diagram consists chiefly of a two-phase region (saturated solution of FeS in FeS_2 + magnetic pyrites) in which the v. p. is nearly const., bounded on one side by a pyrites phase ($\text{FeS}_{2.04}$ — $\text{FeS}_{1.94}$), and on the other by a "troilite" phase ($\text{FeS}_{1.12}$ — $\text{FeS}_{1.02}$). Densities and magnetic susceptibilities were also determined. The latter increases linearly with composition from zero at $\text{FeS}_{1.94}$ to a max. (magnetic pyrites) at $\text{FeS}_{1.12}$, any further loss of S causing it to fall abruptly. This composition falls between the extreme compositions of the naturally occurring substance. No evidence of the existence of Fe_2S_3 or Fe_3S_4 was obtained. F. L. USHER.

Cry of tin. B. CHALMERS (Nature, 1932, 129, 650—651).—When single-crystal wires of Sn or Cd are stretched no sound is produced during the gliding stage of extension, but the twinning which succeeds is accompanied by the characteristic "cry." The same sound also occurs when such wires are bent or violently twisted. The cry also occurs with polycryst. cast Sn or Cd, but drawn wires of small diameter do not give it unless annealed; the production of sound apparently depends on the size of the crystallites being greater than a min. Thermal measurements indicate that some of the mechanical energy supplied to the lattice to cause twinning is afterwards liberated as heat and, in some cases, as sound energy. A "cry" can be produced from Zn which twins readily, but no sound has been produced from metals which show no twinning. L. S. THEOBALD.

Cry of tin. E. N. DA C. ANDRADE (Nature, 1932, 129, 651).—A discussion (cf. preceding abstract).

L. S. THEOBALD.

Fatigue of single crystals of pure metals. H. J. GOUGH (Erste Mitt. neuen Int. Verband. Materialprüf., 1930, A, 133—144; Chem. Zentr., 1932, i, 177—178).

Sudden translation of zinc crystals. E. SCHMID and M. A. VALOUCH (Z. Physik, 1932, 75, 531—538).—After slight extension a sudden translation occurs within the Zn crystals, probably due to a relaxation effect. A. B. D. CASSIE.

Grating theory of ionic crystals. M. BORN and J. E. MAYER (Z. Physik, 1932, 75, 1—18).—The power law of repulsive potential is replaced by an exponential law, which, together with the attractive dynamic polarisability forces, explains the difference in stability of the NaCl and CsCl types. A. B. D. CASSIE.

Grating energy of the alkali halides and the electron affinity of the halogens. J. E. MAYER and L. HELMHOLTZ (Z. Physik, 1932, 75, 19—29).—The method of the preceding abstract is applied to the alkali halides. Calc. electron affinities are: F 95.3, Cl 86.5, Br 81.5, and I 74.2; an accuracy of 2% is claimed. A. B. D. CASSIE.

Growth-forms of metal crystals. G. TAMMANN and K. L. DREYER (Z. anorg. Chem., 1932, 205, 77—80).—Cu separates from a dil. solution in Bi in angular crystals, but from a conc. solution in rounded ones. From a 25% solution rounded crystals are formed by slow (1° per min.), and angular by rapid (40° per min.), cooling. Similar differences were noted with Ag in Pb, and with Zn in Sn, Pb, or Cd, the behaviour in the case of Zn being independent of the solvent. F. L. USHER.

Arrangements of the micro-crystals in copper and gold deposited by electrolysis. H. HIRATA and Y. TANAKA (Mem. Coll. Sci., Kyoto, 1932, 15, 9—22).—The deposits were examined by X-rays by the "transmission" method. Micro-crystals of Au are not deposited with any regularity. W. R. ANGUS.

Secondary structure and mosaic structure of crystals. F. ZWICKY (Physical Rev., 1932, [ii], 40, 63—77; cf. this vol., 12).—The relation of the mosaic to the secondary structure, and factors affecting the formation of thermally stable configurations, are discussed. N. M. BLIGH.

Determination of the parameter of calcite by the temperature effect. E. FUKUSIMA (J. Sci. Hiroshima Univ., 1931, A, 1, 195—201).—Laue photographs at 16°, 300°, and 600° confirm Tsuboi's results (A., 1927, 400). C. W. DAVIES.

Solid solutions [obtained] by precipitation and isomorphism between complexes of platinum and of quadrivalent tellurium. I. Structure of the chloroplatinates of caesium and of rubidium. G. NATTA and R. PIRANI (Atti R. Accad. Lincei, 1932, [vi], 15, 92—99).—An X-ray investigation of Cs₂PtCl₆ and of Rb₂PtCl₆ shows that both compounds are cubic, with 4 mols. in unit cell. Data: Cs₂PtCl₆, a 10.15 ± 0.01 Å., v 1045.7 × 10⁻²⁴ c.c., d 4.25; Rb₂PtCl₆, a 9.83 ± 0.01 Å., v 949.85 × 10⁻²⁴ c.c., d 4.04. Both compounds belong to the space group O_h^5 , and have the same type of structure as K₂PtCl₆. The val. of the parameter u which defines the position of the Cl ions is about 0.23—0.24 in the case of the Cs compound. O. J. WALKER.

Organic molecular compound with a small unit cell. K. SCHNEIDER (Z. physikal. Chem., 1932,

B, 16, 460—464).—The unit cell of the compound of acenaphthene and styphnic acid has I_a 9.05, I_b 14.8, and I_c 6.8 Å., and contains 2 mols. The mols. cannot be arranged according to the three-dimensional alternation principle. R. CUTHILL.

Rotational motion of chain molecules in normal paraffins in the neighbourhood of their melting points. A. MULLER (Naturwiss., 1932, 20, 282—283).—Near their m. p. mols. of normal paraffins show considerable vibration and rotation; the phenomena are discussed. W. R. ANGUS.

X-Ray diagram of "hendecamethyltriase" from cellulose. C. TROGUS (Naturwiss., 1932, 20, 317).—X-Ray measurements are given for the compound of which osmotic pressure was measured previously (cf. *ibid.*, 316). W. R. ANGUS.

Plasticity of micellar systems, especially of cellulose. H. MARK (Papier-Fabr., 1932, 30, 197—205).—The plastic behaviour of cryst., amorphous, and micellar systems is discussed, and the changes in the typical X-ray diagrams of cellulose and cellulose derivatives produced as a result of plastic flow and orientation of the micelles are described. The effect of swelling, temp., H₂O content, etc. on the behaviour of filaments or strips of cellulose acetate and nitrate during stretching, and the significance of the usual load-extension diagrams given by these and other cellulose materials are also discussed. Approx. formulæ give quant. expression to the stress-strain curves. B. P. RIDGE.

Crystal structure and molecular configuration of simple derivatives of tetramethylmethane. I. Tetrachloro-, tetrabromo-, and tetra-iodohydrins of pentaerythritol. G. WAGNER and G. DENGEL (Z. physikal. Chem., 1932, B, 16, 382—396).—The crystals belong to the class C_{2h} , the vals. of I_{100} , I_{010} , and I_{001} being: C(CH₂Cl)₄, 6.91, 6.28, 5.49; C(CH₂Br)₄, 7.19, 6.32, 5.71; C(CH₂I)₄, 7.55, 6.43, 6.07 Å. The space-group is C_{2h} and the unit cells contain 1 mol. From the small vols. of the unit cells, the packing of the atoms in the mols. is closer than is compatible with a tetrahedral structure. It is probable that the 4 halogen atoms lie in a plane which intersects the plane containing the 4 C atoms in the two-fold axis, at the intersection of which with the planes of symmetry lies the central C atom. R. CUTHILL.

Cristobalite structures. I. High-cristobalite. T. W. BARTH (Amer. J. Sci., 1932, [v], 23, 350—356).—Contrary to previous work (A., 1925, ii, 638) high-cristobalite has the space-group $P2_13$ (T^4). The unit cube has 8 mols. of SiO₂. N. H. HARTSHORNE.

Artificial spherulites and related aggregates. H. W. MORSE, C. H. WARREN, and J. D. H. DONNAY (Amer. J. Sci., 1932, [v], 23, 421—432).—Many inorg. substances have been obtained in the form of spherulites by pptn. in jellies. Their optical characteristics are described. C. W. GIBBY.

Spherulite optics. H. W. MORSE and J. D. H. DONNAY (Amer. J. Sci., 1932, [v], 23, 440—461).—Theoretical. C. W. GIBBY.

Electrostriction of benzene. M. PAUTHENIER and O. DELAHAYE (Compt. rend., 1932, 194, 1465—1466). C. A. SILBERRAD.

Hall effect in gold-silver alloys. E. VAN AUBEL (Z. Physik, 1932, 75, 119; cf. Ornstein and Geel, this vol., 12).—Attention is directed to the relation of the Hall effect to Ettinghausen and thermoelectric effects. A. B. D. CASSIE.

Mechanism of electrical discharge in solid insulators. III. Electric strength and crystal structure. A. VON HIPPEL (Z. Physik, 1932, 75, 145—170).—The electrical strength of 11 NaCl type crystals was determined by a method that eliminates boundary effects; this method showed the strengths to be greater than present available vals. Dependence on orientation was also studied, and rules are given for relating strength to size, charge, and polarisability of the constituent ions, and to the hardness of the crystal. A. B. D. CASSIE.

Magnetic properties of iron and its most important alloys. O. VON AUWERS (Naturwiss., 1932, 20, 257—264).—Magnetisation curves for different forms of Fe and its alloys are illustrated and discussed. J. W. SMITH.

Magnetic properties of matter in strong magnetic fields. III. Magnetostriction. IV. Method of measuring magnetostriction in strong magnetic fields. V. Magnetostriction in dia- and para-magnetic substances. P. KAPITZA (Proc. Roy. Soc., 1932, A, 135, 537—555, 556—567, 568—600).—III. The general theory of magnetostriction is revised, mainly from the point of view of the thermodynamic relations and the requirements of crystal symmetry. There are three types of magnetostriction, the classical, at., and thermal, due respectively to the stress of magnetic lines of force, to the disturbance of the magnetic properties of the substance produced by the magnetic field, and to change of temp. The last-named type appears only in adiabatic magnetisation. Moduli or consts. of different orders for adiabatic and isothermal magnetostriction are defined.

IV. An extensometer is described for measuring changes of length down to 10^{-7} cm. in a short interval of time. The accuracy of the measurements and the possible stray effects when the apparatus is applied to the measurement of magnetostriction in strong magnetic fields are discussed.

V. Experiments on Bi crystals are described. In weak magnetic fields at all temp. and for all orientations of the crystal the magnetostriction follows the square law, having a positive sign along the trigonal axis and a negative sign perpendicularly. In strong fields at low temp. a saturation effect is observed. The influence of crystal orientation, impurities, and stress is discussed. An at. magnetostriction is also found in Sb, Ga, graphite, and probably Sn and W; and the limits of a possible magnetostriction are established for Be, Mg, and rock-salt. In general, the most marked effect occurs in those diamagnetic substances having a crystal lattice of low symmetry which change their resistance considerably in magnetic fields. The difficulty of applying the modern theory

of diamagnetism to account for the observed phenomena is discussed, and certain new hypotheses are suggested to explain the results.

L. L. BIRCUMSHAW.

Magnetic transformation of ferromagnetic metals. R. RUER (Z. anorg. Chem., 1932, 205, 230—234; cf. A., 1927, 925).—Heating and cooling curves have been redetermined with very pure Fe, and earlier results confirmed. The arrest on the heating curve is, however, 2° higher than that on the cooling curve. F. L. USHER.

Influence of adsorbed surface films on the strength of fine quartz fibres. S. SCHURKOV (Physikal. Z. Soviet Union, 1932, 1, 123—131).—The strength per unit cross-section increases with decreasing cross-section, and is lowered by adsorbed vapours.

H. J. EMELÉUS.

Influence of foreign particles on cohesion limits and ultramicroscopic sol formation of synthetic rock-salt crystals. II. Single and mixed states of alkaline-earth chlorides. H. SCHONFELD (Z. Physik, 1932, 75, 442—467).—Large increases of the cohesion limits appear when CaCl_2 and SrCl_2 disperse as mols. throughout the crystal; the chlorides (MgCl_2 , BaCl_2) that form ultramicroscopic particles have little or no effect. Elastic limits, and stresses at breaking point were studied.

A. B. D. CASSIE.

Evaporation of incandescent wires in vacuum. II. L. PRÁSNÍK (Z. Physik, 1932, 75, 417—420; cf. A., 1931, 1106).—Numerical applications of the theory are made for W. A. B. D. CASSIE.

Determination of mol. wt. by Horstmann's combination of vapour-pressure measurements. II. Vapour pressures and vapour densities of aluminium halides. W. FISCHER and O. RAHLFS [with B. BENZE] (Z. anorg. Chem., 1932, 205, 1—41; cf. A., 1930, 142).—Densities of unsaturated and saturated vapours of AlCl_3 , AlBr_3 , and AlI_3 have been determined, and v. p. of the same substances have been obtained between 10 and 700 mm. by four different methods. Heats of evaporation and sublimation are calc. The only mol. species present in the vapours are AlX_3 and Al_2X_6 . Cryst. AlCl_3 possesses a constitution different from that of the other two solids. Details of technique generally suitable for substances sensitive to traces of moisture or air are described. F. L. USHER.

Relations between fundamental physical constants. R. T. BIRGE (Science, 1932, 75, 383).—A crit. discussion (cf. this vol., 444). L. S. THEOBALD.

Thermal properties of tantalum. C. L. UTTERBACK and L. A. SANDERMAN (Physical Rev., 1932, [ii], 39, 1008—1011; cf. A., 1929, 1212).—The total radiation from very pure Ta was measured from 1000° to 2220° abs. A spectral temp. scale, $\lambda = 0.667 \mu$, is given up to 2100° abs. The variation of resistance was measured up to 2600° , and the thermoelectric power with Pt up to 692° abs. N. M. BLIGH.

Superconductivity. K. CLUSIUS (Z. Elektrochem., 1932, 38, 312—326).—A review.

Measurements with liquid helium. XVI. Superconductivity of carbides, nitrides, borides,

and silicides. W. MEISSNER, H. FRANZ, and H. WESTERHOFF (Z. Physik, 1932, 75, 521—530).—Resistance down to 1.2° abs. was determined for Ti, Zr, Hf, Ta, and Fe carbides, Ti and Zr nitrides, Hf, Ti, and Zr borides, and for Ta silicide and the mixed crystals Fe-Si and Ni-Si. Carbides, nitrides, borides, and silicides of the heavier metals become superconductive, but transition temp. are lower for the last two. A. B. D. CASSIE.

Energy exchanges between molecules. P. S. H. HENRY (Proc. Camb. Phil. Soc., 1932, 28, 249—255).—An explanation of the discrepancy between the sp. heats at high temp. of the diat. gases as found by sound velocity measurements and by calculation is examined on the evidence of a shorter period of relaxation for the vibrational energy than the previously accepted val. N. M. BLIGH.

Accurate determination of physico-chemical constants at very high temperature. F. M. JAEGER (Bull. Soc. chim. Belg. 1932, 41, 30—52).—A lecture, dealing especially with the determination of the sp. heats of solids at temp. up to 1625° , and of the surface tension and electrical conductivity of liquids up to 1650° . The significance of the variation with temp. of the sp. heats of the metals is reviewed. H. F. GILLBE.

Vapour-pressure constant of ammonia, entropy of crystalline ammonia, and the reaction $N_2 + 3H_2 \rightarrow 2NH_3$. T. E. STERNE (Physical Rev., 1932, [ii], 39, 993—1007; cf. A., 1931, 1222).—Mathematical. An expression for the v.-p. const. of an NH_3 mol. is calc. by statistical quantum mechanics, and evaluated for ordinary temps. as -1.55 . For the reaction $2NH_3 \rightarrow N_2 + 3H_2$ between the cryst. phases at abs. zero there is an increase in entropy of $(9R/4) \log 3$. N. M. BLIGH.

Density of carbon monoxide. At. wt. of carbon. E. MOLES and M. T. SALAZAR (Anal. Fis. Quím., 1932, 30, 182—199).—The mean normal density of CO, prepared from HCO_2Na , HCO_2H , and from $K_4Fe(CN)_6$ is 1.25010 g. per litre; the at. wt. of C is thus 12.006, in conformity with the suggestion that there exists an isotope of C of at. wt. 13. H. F. GILLBE.

Specific volume of water between 20° and 650° and of ethyl ether and ethyl alcohol between 20° and 400° , at pressures of 1—2500 kg. per sq. cm. G. TAMMANN and A. RUHENBECK (Ann. Physik, 1932, [v], 13, 63—79).—Vol. and dilatation isotherms and isobars are given. The max. and min. dilatation above and below the crit. temp. are considered. W. R. ANGUS.

Pressure variation of the heat function as a direct measure of the van der Waals forces. F. G. KEYES and S. C. COLLINS (Proc. Nat. Acad. Sci., 1932, 18, 328—333).—A direct method of measuring the change of thermodynamic potential with pressure at const. temp. and results for CO_2 and NH_3 are given. Good agreement with vals. calc. from the equation of state is obtained. N. M. BLIGH.

Heat of vaporisation of water at 50° , 70° , and 90° . E. F. FLOCK and D. C. GINNINGS (Bur. Stand. J. Res., 1932, 8, 321—324).—The latent heat at 50° ,

70° , and 90° is 2381.6, 2333.6, and 2283.4 international joules per g., respectively. These agree with the vals. obtained by extrapolating the data for temp. $>100^\circ$. J. W. SMITH.

Collision area of the gaseous carbon tetrachloride molecule. E. H. SPERRY and E. MACK, jun. (J. Amer. Chem. Soc., 1932, 54, 904—907).—From viscosity data for CCl_4 between 50° and 250° , the Sutherland const. was calc. to be 335 and the collision area 22.0 sq. \AA . The radius of the Cl atom domain is estimated to be 1.2 \AA . E. J. ROSENBAUM (c).

Fluidity method for the determination of association. I. E. C. BINGHAM and L. W. SPOONER (J. Rheology, 1932, 3, 221—244).—The fluidities and α of the following compounds have been measured at 0° , 10° , 20° , 30° , 40° , 60° , 80° , and 100° : *n*-amyl ether, isoamyl ether, Bu^a_2O , $(CH_2Ph)_2O$, tri-*n*-amylamine, triisoamylamine, NBu^a_3 , *m*- $NH_2 \cdot C_6H_4Me$, and eugenol. Published data have been used for a revision of the at. temp. const. for H, O, Cl, Br, I, S, N, and CH_3 . Tables are given, from which it is possible to find the abs. temp. required to give any compound made up of these atoms any desired fluidity. E. S. HEDGES.

The α and β solid solutions of copper-zinc alloys and corresponding liquid solutions in equilibrium with them examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1932, 28, 452—455).—Existing equilibrium data suggest that the α and β solid phases are solutions of $CuZn_4$ and $CuZn_2$, respectively, in monat. Cu, in equilibrium with a liquid solution of $CuZn_4$ in monat. Cu. The conclusions are discussed in relation to the X-ray data for the Cu-Sn system (A., 1929, 987; 1931, 418). J. G. A. GRIFFITHS.

Constitution of liquid and solid alloys of the copper-gold system examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1932, 28, 455—457).—The co-existing liquid and solid alloys consist of monat. Cu and monat. Au. J. G. A. GRIFFITHS.

Silver-copper alloys. W. BRONIEWSKI and S. KOSLACZ (Compt. rend., 1932, 194, 973—975).—Curves are given to show the relation between the composition of alloys annealed at 650° and fusibility, conductivity, temp. coeff. of resistance, thermoelectric power and its variation with temp., electrode potential in aq. $CuSO_4$ (cf. A., 1898, ii, 582), and various mechanical properties. The eutectic, m. p. 779° , contains 71% Ag; the max. solubility of Ag is 7%, of Cu 6% (cf. A., 1931, 556); when slowly cooled 1% of either remains in solution. Annealing improves all the alloys, which if prepared in a reducing atm. are malleable, but if fused in an oxidising atm. are affected by Cu_2O . C. A. SILBERRAD.

System gold-mercury. I. N. PLAKSIN (Arb. Staats-Univ. Fernen Ostens, 1929, 7, (13); Z. Metallk., 1932, 24, 89).—The system contains two compounds, Au_2Hg and $AuHg_2$. The latter decomposes at 310° into Au_2Hg and liquid; $AuHg_2$ is stable up to 420° and undergoes a polymorphic transformation at 402° in alloys with 51—84 at.-% Au. A second transformation occurs in alloys with 1.3—37 at.-% Au at 12°

with a max. heat effect at 32.5–36.1 at.-% Au, and a third transformation at -36° in alloys with up to 66.6 at.-% Au. The eutectic lies at -38.89° and <0.1% Au. When the alloy corresponding with AuHg₂ is melted and allowed to solidify the lower layers have a higher Au content than the upper (40 against 33 at.-%), but small crystals of AuHg₂ may be isolated from the upper layers. A. R. POWELL.

Lattice spacings of iron-aluminium alloys. A. J. BRADLEY and A. H. JAY (Iron and Steel Inst., May, 1932, advance copy).—The lattice spacings of Fe-Al alloys between 0 and 33% Al have been determined by an improved powder method. Although all the alloys lie within the Fe-rich α -solid solution field in the diagram of Gwyer and Phillips, the lattice spacings agree with Vegard's law only when Al < 10%. Between 10 and 17% Al, annealed alloys have const. lattice spacings and a lattice arrangement which is based on the compound Fe₃Al. Between 17 and 20% Al, annealed alloys show a slight decrease in lattice spacing and the structure tends towards the FeAl type. Quenched alloys up to 14% Al have random lattice structure with increasing lattice spacing, but at this point there is a sudden fall in lattice spacing corresponding with the formation of the FeAl type of structure. The spacing between 14 and 20% Al in quenched alloys is somewhat variable. Alloys with >20% Al, whatever the heat treatment, contain the FeAl type of lattice with increasing lattice spacing as the Al content rises. E. H. BUCKNALL.

X-Ray investigation of bismuth-antimony alloys. E. G. BOWEN and W. M. JONES (Phil. Mag., 1932, [vii], 13, 1029–1032).—Bi-Sb alloys maintained above the m. p. of Bi, and cooled slowly, become homogeneous, and show an "almost linear change of lattice edge with composition over the whole range of compositions. H. J. EMELEUS.

Effect of hot rolling on mechanical properties of yttrium alloy. T. WATASE (Suiyokai-Shi, 1931, 6, 631–638).—Yt alloy should be hot-worked to one third of the original section to obtain a strength of 40 kg. per sq. mm. and elongation more than 15%. Mg (0.5–1.0%) has less effect on the mechanical properties, but addition of Si up to 0.67% lowers the ductility and caused cracking on rolling.

CHEMICAL ABSTRACTS.

[Spontaneously] hardening alloys of lead, nickel, and cadmium. B. GARRE and A. MÜLLER (Z. anorg. Chem., 1932, 205, 42; cf. A., 1931, 900).—When quenched from 220° alloys of Pb, Ni, and Cd behave similarly to those of Pb, Sb, and Cd previously described. The hardening effect increases with duration of heating. Pb alloyed with NiCd₄ is less resistant to conc. H₂SO₄, but more resistant to 10% acid, than pure Pb. F. L. USHER.

Silumin containing copper. N. KAWASHIMA (Suiyokai-Shi, 1931, 6, 585–592).—The hardness and tensile strength of silumin increase and the elongation decreases with increase in Cu content up to 4%. Salt-water corrosion is diminished.

CHEMICAL ABSTRACTS.

Equilibrium diagram of the aluminium-rich aluminium-tin-nickel system. S. KATO (Suiyokai-Shi, 1931, 6, 529–533).

—Alloys containing up to 5% Sn and 10% Ni were studied; a binary eutectic line liquid \rightleftharpoons Al + Al₃Ni and a ternary eutectic point liquid \rightleftharpoons Sn + Al + Al₃Ni were found at 270° at the Sn corner of the equilibrium diagram.

CHEMICAL ABSTRACTS.

Conditions of applicability of Trouton's rule to liquid mixtures and solutions. A. KIREEV (J. Gen. Chem. Russ., 1931, 1, 1057–1061).—Trouton's rule is applicable to normal liquid mixtures for which the ratio of the partial pressure of a component to its mol. concn. is const. The formation of compounds leads to an increase in the val. of Trouton's coeff., K_s , when the concn. of the component in question is diminished. Dissociation of a component leads to opposite effects. In mixtures of associated liquids the val. of K_s may remain const. or may vary, according to the nature of the given mixture.

R. TRUSZKOWSKI.

Composition of vapours from boiling binary solutions. D. F. OTHMER (Ind. Eng. Chem. [Anal.], 1932, 4, 232–234).—An improved method (cf. A., 1928, 943) and apparatus for determining vapour composition curves and the elevation of the b. p. of solutions are described. Results are given for C₆H₆-AcOH, H₂O-HCO₂H, and AcOH-Ac₂O. The C₆H₆-AcOH mixture has an azeotropic composition at 98.5% of C₆H₆.

E. S. HEDGES.

Measurement of the diffusion constant. Y. NISIZAWA (Bull. Chem. Soc. Japan, 1932, 7, 72–84).—When a solid or conc. solution is placed at the bottom of a vertical column of solvent and allowed to diffuse upwards for a time t , it may be shown that $\log c_1/c_2 = (x_1^2 - x_2^2)/4Dt$, where c_1 and c_2 are the concns. at heights x_1 and x_2 , respectively, and D is the diffusion const. By this method, D has been determined for KI, BaCl₂, CaCl₂, EtOH, CMe₂, carbamide, glycerol, pepsin, and various org. acids, dyes, sugars, soaps, and cellulose derivatives, the changes in concn. being followed by means of sp. gr. beads. Irradiation and preliminary heating cause an increase in the rate of diffusion of cellulose nitrate, indicating an increase in the degree of dispersion.

D. R. DUNCAN.

Influence of magnetic field on crystallisation. D. SAMURACAS (Compt. rend., 1932, 194, 1225–1227).—The crystallisation of solutions of FeSO₄, NiSO₄, CoCl₂, CuSO₄, and MgSO₄ is accelerated by a magnetic field. C. A. SILBERRAD.

Application of Dühring's relation to solubilities. R. L. HARRIS (Ind. Eng. Chem., 1932, 24, 455–457).—The solubilities of inorg. salts in H₂O are shown to vary with temp. in accordance with an empirical formula which is analogous to Dühring's formula for v.-p. variations. J. G. A. GRIFFITHS.

Solubility in the solid state and atomic dimensions of the oxides of the bivalent, trivalent, and quadrivalent metals. L. PASSERINI (Gazzetta, 1932, 62, 85–101).—The cubic oxides of Ni, Mg, Co, Mn, Cd, and Ca are completely miscible in the solid state only provided that the radius of the larger cation does not exceed that of the smaller one by more than 12%. For differences up to 29% there is only partial miscibility and the max. amount of

dissolved oxide varies inversely as the % difference of the radii of the two cations. For differences of 30% and upwards miscibility in the solid state is no longer possible. Analogous relations are found when the miscibility is compared with the % difference in the mol. vol. of the two oxides. The rhombohedral oxides of Al, Fe, and Cr behave similarly both qualitatively and quantitatively, but in the case of the cubic oxides of Th, Co, Hf, and Zn the limits of complete and partial miscibility are about 1–2% higher. The solid solutions were mostly obtained at temp. well below the m. p. or sublimation point of the oxides.

O. J. WALKER.

Behaviour of polonium during crystallisation of metals. G. TAMMANN and A. VON LOWIS OF MENAR (Z. anorg. Chem., 1932, 205, 145–162).—The solubility of Po in Bi, Te, Sn, Sb, or Cd is of the order $5 \times 10^{-10}\%$. Po does not exhibit enhanced solubility in cryst. metal tellurides. During crystallisation Po begins to separate at temp. considerably higher than the m. p. of the poly-eutectic.

F. L. USHER.

Mechanism of dissolution of organic substances in non-aqueous liquids. I. Cellulose nitrate and acetone. C. TROGUS, T. TOMONARI, and K. HESS. II. Formation of celluloid. K. HESS, T. TOMONARI, and C. TROGUS (Z. physikal. Chem., 1932, B, 16, 351–373, 374–381).—I. The dissolution of cellulose nitrate in binary mixtures of COMe_2 with benzene, alcohols, aromatic hydrocarbons, and H_2O has been investigated by X-ray examination of the solid phase and analysis of the liquid phase; two compounds of cellulose nitrate with COMe_2 are formed which lose COMe_2 in air. The amount of COMe_2 taken up by the solid phase for a given equilibrium concn. of COMe_2 falls as the temp. rises. It seems that for any medium to dissolve cellulose or its derivatives it must be able to form a compound with the substance to be dissolved, and also to dissolve this compound.

II. In ligroin solution *d*-camphor and cellulose trinitrate form a compound in which there is at least 1 mol. of camphor per C_6 mol.; this compound is sol. in many org. solvents. Commercial celluloid contains crystallites of camphor and of this compound, the latter being smaller than those formed in the cellulose trinitrate fibre.

R. CUTHILL.

System HIO_3 – HNO_3 – H_2O ; solubilities and viscosities. E. MOLES and A. PÉREZ VITORIA (Anal. Fis. Quím., 1932, 30, 200–207).—The solubility of HIO_3 at 25° in HNO_3 solution rises continuously from about 1% in 65.30% HNO_3 to 10% in 43.32% HNO_3 and to 35.08% in 20.33% HNO_3 . The viscosity ($\text{H}_2\text{O}=1$) of aq. HIO_3 solutions rises at an increasing rate from 1.021 for a 3.2% solution to 1.650 for a 46% solution; there is no evidence of hydrate formation. The viscosity of HNO_3 solution is a max. at about 65.30% HNO_3 . The viscosity-composition diagram of the ternary system exhibits a min. which suggests the formation of a compound $\text{HIO}_3 \cdot 3\text{HNO}_3$.

H. F. GILLBE.

Influence of magnesium salts on the solubility of potassium and sodium chlorides. D. LANGAUER (Rocz. Chem., 1932, 12, 258–269).—The solu-

bility of mixtures of NaCl and KCl at 25 – 105° has been determined in the presence of various concns. of MgCl_2 and MgSO_4 .

R. TRUSZKOWSKI.

Characteristics of vanillin and coumarin. R. M. HITCHENS.—See this vol., 615.

Kinetics and energetics of gas adsorption. H. FREUNDLICH (Trans. Faraday Soc., 1932, 28, 195–201).—A general survey. J. G. A. GRIFFITHS.

Kinetics of adsorption of hydrogen on platinum and nickel. E. B. MAXTED and N. J. HASSID (Trans. Faraday Soc., 1932, 28, 253–261).—The magnitude of the slow process following the initial rapid adsorption increases with rise of the absorption temp. and then decreases to zero at the temp. of outgassing. The adsorptive power at a low temp. is increased by previously raising the temp. to a high val. without degassing. Repetition of the process increases the adsorption at the lower temp. to a const. val. An activation process is probably involved.

J. G. A. GRIFFITHS.

Heats of adsorption and kinetics of adsorption. W. E. GARNER (Trans. Faraday Soc., 1932, 28, 261–269; cf. A., 1931, 1226).—Thermal and velocity data for adsorption processes are discussed (A., 1931, 1365). The equation developed for the diffusion process is of the same form as that for the velocity of activated adsorption, hence Kingman's results (see below) do not prove the absence of diffusion in the system H_2 –C.

J. G. A. GRIFFITHS.

Discontinuities in adsorption processes. A. J. ALLMAND, L. J. BURRAGE, and R. CHAPLIN (Trans. Faraday Soc., 1932, 28, 218–222).—A summary and extension of the authors' recent work with charcoal and SiO_2 gel. With CCl_4 at 25° , the increments between successive breaks in the isotherms are almost const. The adsorption by charcoal of CS_2 – H_2O mixtures and of PhOH from H_2O is discontinuous.

J. G. A. GRIFFITHS.

Possible connexion between activated adsorption and gas displacement effects. A. J. ALLMAND and R. CHAPLIN (Trans. Faraday Soc., 1932, 28, 223–226; cf. this vol., 331).—Existing data and fresh results with charcoal degassed at various temp. are in accord with the view that in many cases of adsorption the process requiring activation is the displacement of traces of residual gas from the adsorbing surface by the freshly-adsorbed mols. Examples of "activated adsorption" may well be cases of displacement phenomena.

J. G. A. GRIFFITHS.

Adsorption of hydrogen by charcoal. F. E. T. KINGMAN (Trans. Faraday Soc., 1932, 269–272).—An account of previous work (A., 1931, 677, 1006).

J. G. A. GRIFFITHS.

Sorption of hydrogen by platinised charcoal. R. BURSTEIN and A. FRUMKIN (Trans. Faraday Soc., 1932, 28, 273–275; cf. A., 1929, 640).—The adsorption of H_2 by sugar charcoal outgassed at 900° increases with rise of temp. and is therefore "activated." 0.2% of Pt increases the adsorptive capacity of the C.

J. G. A. GRIFFITHS.

Adsorption and reflexion processes in interaction of hydrogen and metals. K. F. BONHOEFFER and A. FARKAS (Trans. Faraday Soc., 1932, 28, 242–

247; cf. A., 1931, 691; this vol., 28).—In confirmation of theory, the accommodation coeff.-temp. curves for H_2 on the clean and poisoned surfaces of a metal intersect. Corresponding with the discontinuity in the velocity of *para*- H_2 transformation on Ni, a discontinuity occurs in the accommodation curve at a certain density of adsorption. Similar discontinuities occur with Pt and Fe, thus indicating hydride formation. H_2 can be adsorbed on "O₂-covered charcoal" without adjustment of the *ortho*:*para* ratio, thus showing that the H_2 is adsorbed in the "mol." state and not in the "at." state characteristic of adsorption on metals in which the H atoms are more firmly bound to the metal than to each other. J. G. A. GRIFFITHS.

Activated adsorption of hydrogen and the *para*-hydrogen conversion. H. S. TAYLOR and A. SHERMAN (Trans. Faraday Soc., 1932, 28, 247—253; cf. A., 1931, 678).—Data are presented for Ni, ZnO, ZnO-Cr₂O₃, Cd, CdO, MnO-Cr₂O₃, CuO-Cr₂O₃, and Al₂O₃ which show that surfaces at which activated adsorption of H_2 occurs exhibit at the same temp. parallel efficiencies in *ortho-para*- H_2 interconversion. No such parallelism exists between "van der Waals adsorption" and the interconversion process. The decrease of efficiency of the *para* → *ortho* change with rising temp. of charcoal is shown to be due to the bimol. nature of the surface process, the velocity of which decreases owing to increasing bareness of the surface at higher temp. J. G. A. GRIFFITHS.

Adsorption and dissolution of gases by metals. A. F. BENTON (Trans. Faraday Soc., 1932, 28, 202—218; cf. A., 1930, 990; 1931, 902, 1005, 1225).—From existing and new equilibrium and velocity data for the sorption of N₂, H₂, and O₂ by Cu and Fe, and of H₂ by Ni, definite evidence has been obtained in all cases, except those involving N₂, that physical adsorption, activated adsorption, and a third process, probably dissolution, occur, and the contribution of each process to the total sorption has been determined. The differentiation among the three processes and the relation between activated adsorption and compound formation are discussed.

In the system Ag-O₂ between 174° and 200°, oxide formation occurs at sufficiently high pressures of O₂. The above three processes can be distinguished, however, in the sorption of O₂ at pressures below the dissociation pressure of the oxide (cf. A., 1929, 274).

J. G. A. GRIFFITHS.

Adsorption by humic acid. K. KAWAMURA (Utsonomiya Agric. Coll. Bull., 1931, No. 1; Proc. Internat. Soc. Soil Sci., 1932, 7, 14—15).—"Humic acid" obtained from peat by pptn. from alkaline solution and washing with EtOH and Et₂O forms definite "humates" with Ba(OH)₂ and NaOH from solutions >3 milli-equivs. per 100 c.c. Further addition of base is followed by its adsorption. Humus from sucrose behaves similarly. Crude humus both from peat and sugar reacts with AlCl₃ solution with the apparent formation of an Al trihumate. No Cl' is absorbed from the solution. Humic acid after treatment with AlCl₃ exhibits exchange acidity which increases with the amount of AlCl₃ used, reaching a

const. val. corresponding with the formation of a trihumate. A. G. POLLARD.

Rates of condensation and evaporation in intensively dried systems. Effect of intensive drying on accommodation coefficient of liquid and solid surfaces for molecules of their own vapours. F. J. WILKINS (Phil. Mag., 1932, [vii], 13, 1014—1020).—The decrease in the rate of evaporation of NH₄Cl and EtBr on intensive drying, without alteration of the v. p. (cf. A., 1929, 636; this vol., 329), is attributed to a decrease in the accommodation coeff. of solid NH₄Cl and liquid EtBr for their own vapours.

H. J. EMELEUS.

Surface activity and orientation of polar molecules in relation to the nature of the phase boundary. VII. Capillary properties of aromatic amines and their salts. A. B. TAUBMAN (J. Gen. Chem. Russ., 1931, 1, 1039—1056).—The surface activity and adsorption of *p*-toluidine at the phase boundaries of H₂O and C₆H₆ or hexane are in close accordance with Langmuir's law, slight deviations from which are, however, encountered at the aq. solution-air interface. The mol. consts. of *p*-toluidine are the same at all boundaries, the length of the oriented mol. being 6.6×10^{-8} cm. and the area occupied by it at saturation 25.8×10^{-16} sq. cm. A method for the determination of the concn. of surface-active substances in solution is described which depends on the capillo-manometric measurement of surface tension. *p*-Toluidine is present partly as associated mols. in hydrocarbon solution. The above method is applied to determine the solubility of *p*-toluidine and *o*-, *m*-, and *p*-cresol in H₂O. Antonov's law (cf. A., 1907, ii, 606) is not applicable to the above systems. R. TRUSZKOWSKI.

Water-jet affected by tobacco smoke. T. TERADA, S. TANAKA, and K. ITÔ (Nature, 1932, 129, 614—615).—A change produced by tobacco smoke in the shape of a H₂O jet, and explained by a lowering of the surface tension of H₂O, is described.

L. S. THEOBALD.

Accommodation coefficient of hydrogen; a sensitive detector of surface films. (Miss) K. B. BLODGETT and I. LANGMUIR (Physical Rev., 1932, [ii], 40, 78—104; cf. Knudsen, A., 1911, ii, 368).—An equation for the coeff. is derived. The effect on the coeff. of adsorbed films is investigated.

N. M. BLIGH.

Behaviour of picric acid, *p*-nitrophenol, and certain hydroxyanthraquinones towards vacuum-sublimed films of salts. J. H. DE BOER (Z. physikal. Chem., 1932, B, 16, 397—407).—Quinizarin vapour undergoes a surface reaction with a vac.-sublimed film of BaCl₂ on moderate heating similar to that of alizarin (this vol., 223), whereas picric acid vapour forms Ba picrate and displaces HCl, reaction ultimately proceeding through the whole thickness of the film. *p*-Nitrophenol vapour is strongly but reversibly adsorbed by films of BaCl₂ or CaF₂, the absorption spectrum in the adsorbed state being displaced towards longer wave-lengths.

R. CUTHILL.

Osmosis in binary systems in which [there are] two membranes. F. A. H. SCHREINEMAKERS

(Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1380—1387).—The theoretically possible phenomena are discussed. J. W. SMITH.

Abnormal osmosis at non-swelling membranes. III. K. SOLLNER and A. GROLLMANN (Z. Elektrochem., 1932, 38, 274—282; cf. A., 1930, 688).—Abnormal osmosis is not due solely to variations of the sizes of the membrane pores, but may be caused also by other types of heterogeneity of the membrane such as result from a mosaic-like structure and occur frequently in natural membranes. Very great and rapidly established negative osmosis is observed with solutions of Li salts; in accordance with the theory, the effect is smaller with Na salts, whilst with K salts the negative effect reverses on increasing the thickness of the membrane. Details are given of the experimental verification of the theory. H. F. GILLBE.

Hydrogen-ion exchange and its regularities. R. W. BELING (Kolloid-Beih., 1932, 35, 265—330).—The amount of H^+ exchange in H-permutite, humic acid, and MnO_2 with the cations of various salts depends on the amount of the added cation. A connexion with the nature of the cation, particularly its degree of hydration, is apparent only when secondary influences, such as hydrolysis and change in the degree of dispersion of the colloidal substance, are absent. The exchange is increased by rise of temp., but to different extents, depending on the cation; the influence of temp. is particularly strong in the weakly hydrated K^+ and Ba^{++} . By repeated treatment with conc. solutions practically all the H^+ can be exchanged. The process of cation exchange is investigated mathematically. E. S. HEDGES.

Anomalous electrical dispersion of polar solutions. R. GOLDAMMER (Physikal. Z., 1932, 33, 361—367).—The anomalous dispersion due to the mol. polarisation of Bu^oOH , Bu^pOH , and isoamyl alcohol in dil. solution has been investigated (1) for wave-lengths of 0.5—1.4 m. by Drude's second method, and (2) for wave-lengths of 25 and 250 m. by the resonance method. There is good qual. agreement between theory and experiment. A. J. MEE.

Cryoscopic study of ether and acetone in water and solutions of sodium chloride. E. BOURION and E. ROUYER (Compt. rend., 1932, 194, 1240—1242; cf. A., 1931, 910).—F.-p. data are recorded. C. A. SILBERRAD.

Cryoscopy of solutions containing more than one electrolyte. V. K. SEMENTSCHENKO and E. A. ZAVADA (J. Gen. Chem. Russ., 1931, 1, 1114—1124).—For the systems $NaCl-NH_4Cl-H_2O$ and $NaCl-(NH_4)_2Al_2(SO_4)_4-H_2O$ the f.-p. depressions are in accordance with the mixture rule for total concn. of 1.5—2*M*. In the presence of H^+ anomalous results are obtained. For $NaCl-NH_4Cl-HCl-H_2O$ and $NaCl-HCl-H_2O$ the depressions are less than those calc. from the mixture rule. This rule is followed in all cases studied at the van't Hoff point, at which the osmotic coeff. and the activity factor of the solvent are equal to 1. R. TRUSZKOWSKI.

Colloidal properties of charcoal. I. Preparation and properties of the sol. H. LACHS and K. GESTLÓWNA (Rocz. Chem., 1932, 12, 213—224).—

Charcoal hydrosols are obtained by the action of H_2SO_4 on dry sucrose, the reaction mixture being diluted with H_2O after 24 hr., and purified by repeated ultrafiltration. The hydrogel so obtained yields sols in which the particles are negatively charged and consist of roughly spheroidal, amorphous masses containing 53% C. 70% of the particles have a diameter of about 144 $\mu\mu$, 15% about 35 $\mu\mu$, and the remainder about 4.4 $\mu\mu$. R. TRUSZKOWSKI.

Constitution of gold sols. W. PAULI (Oesterr. Chem.-Ztg., 1932, 35, 79—80).—A lecture.

Validity of the Lambert-Beer law for colloids. B. LANGE (Z. physikal. Chem., 1932, 159, 277—294).—Measurements of the absorptive power of sols have been made by a new photo-electric method capable of measuring very small absorptions very accurately. Lambert's law for sols may be deduced from probability considerations, and the validity of the law has been fully confirmed experimentally by observations on Au sols and diluted Indian ink. The deviations reported by Soos (A., 1926, 575) must be ascribed to defective experimental technique. Beer's law has also been shown to be valid for a variety of colloids, and such deviations as occur with other colloids are attributable to variations in the degree of dispersity and similar causes. R. CUTHILL.

Solvation equilibrium in colloidal solutions. G. V. SCHULZ (Z. physikal. Chem., 1932, 159, 374).—A correction (cf. this vol., 225). R. CUTHILL.

Osmosis and solvation of disperse systems. W. OSTWALD (Z. physikal. Chem., 1932, 159, 375—392).—The equation $P = cRT/M + kc^n$, where R and T have their usual significance and k is a const., is suggested for the measured osmotic pressure, P , of a solution, of concn. c , of a substance of mol. wt. M . The first term represents the usual van't Hoff pressure and the second a swelling or solvation pressure, the val. of n usually being about 2 (cf. A., 1918, ii, 391). This equation, which may be deduced both thermodynamically and by mol.-kinetic considerations (cf. A., 1929, 1380; 1931, 1230), agrees well with available data for the osmotic pressure of sols and of mol. dispersions up to the highest concns. For dil. sols the second term becomes zero, whilst for conc. sols the first term is negligible compared with the second (cf. this vol., 225). R. CUTHILL.

Behaviour of disperse systems in filtered ultra-violet light. K. BORGMANN (Süddeut. Apoth.-Ztg., 1931, 71, 70—72; Chem. Zentr., 1932, i, 190).— $BaPt(CN)_4$ does not fluoresce in solution, whilst the fluorescence of a solution of hydrastinine hydrochloride is stronger than that of the solid. The difference is not due to the formation of a colloidal solution. The fluorescence is associated with mol. aggregates. A solution of $BaPt(CN)_4$ and gelatin is strongly fluorescent, even after passing an ultra-filter. A. A. ELDRIDGE.

Centrifuging alkaline solutions of polonium. (MILES.) C. CHAMIE and A. KORVEZEE (Compt. rend., 1932, 194, 1488—1490; cf. A., 1931, 809, 1230; this vol., 236).—The max. proportions of Po centrifuged from solutions in NH_3 (3×10^{-4} to 10*N*) and aq.

NaOH (10^{-4} to $4N$) are 82% and 63%, respectively, for 0.1*N* and 0.007*N*. C. A. SILBERRAD.

Double refraction due to flow. P. BOEDER (Z. Physik, 1932, 75, 258—281).—The orientation of rod-like particles under forces due to Brownian motion and to shear has been examined in relation to the resulting double refraction. A. B. D. CASSIE.

Influence of non-electrolytes on the coagulation of gold hydrosol. H. TSUTSUI (J. Biochem. Japan, 1932, 15, 163—166).—EtOH, MeOH, camphor, thymol, Et urethane, and carbamide exert a sensitising action on the sol as indicated by the stability of the system towards NaCl. Glucose has no marked action, whilst Na glycocholate has a stabilising influence.

F. O. HOWITT.

Coagulation of colloids by electrolytes. XI. Cataphoretic and potentiometric measurements during coagulation of colloidal ferric hydroxide. A. J. RABINOVITSCH and E. FODIMAN (Z. physikal. Chem., 1932, 159, 403—413).—Potentiometric titration of $\text{Fe}(\text{OH})_3$ sols with Na_2SO_4 and measurements of the rate of cataphoresis, v , in presence of varying amounts of Na_2SO_4 have shown that the superequiv. displacement of Cl^- by SO_4^{2-} (A., 1928, 586) does not run parallel with the variation of v , but is favoured by increase in the age of the sol; in some cases it may be absent. With increase in the Na_2SO_4 concn. v increases in all cases. R. CUTHILL.

Influence of concentration of peptiser on velocity of coagulation of hydrosols of chromic and ferric hydroxides. J. LISIECKI (Rocz. Chem., 1932, 12, 241—257).—The velocity of coagulation of the above hydrosols by KCl depends on the concn. of peptising substances (CrCl_3 and FeCl_3).

R. TRUSZKOWSKI.

Photosensitising effect of colourless fluorescent substances on the flocculation of colloidal solutions. J. BOUCHARD (Compt. rend., 1932, 194, 1245—1246; cf. A., 1931, 907).—The action of ultra-violet light on a colloidal solution of As_2S_3 in presence of aesculin or β -naphthol- or β -naphthylamine-sulphonic acid reduces the period of flocculation by KCl from 75 to 60—35 min. C. A. SILBERRAD.

Influence of various substances on the peptisation of ferric arsenate, phosphate, tungstate, and molybdate by ferric chloride. H. P. VARMA and S. PRAKASH (Z. anorg. Chem., 1932, 205, 241—250; cf. A., 1930, 1114).—Positive sols are obtained when Fe^{III} arsenate, phosphate, tungstate, or molybdate is peptised with aq. FeCl_3 , the degree of peptisation decreasing in the order given. Peptisation is promoted by glycerol or glucose and repressed by carbamide or SO_4^{2-} . The relation between peptisation and gelatinisation, and the mechanism of the peptisation process, are discussed. F. L. USHER.

Physico-chemical degradation of starch. R. HEINIGER (Kolloid-Beih., 1932, 35, 331—371).—The changes taking place in amyloamylose and amylopectin when boiled with H_2O have been followed by observing the sp. gr., p_{H} of the sol, reducing properties, surface tension, viscosity, adsorptive power, fluorescence, behaviour on ultrafiltration, and tenacity of

the paste. The results indicate an increase in the ultrafilterable portion at the expense of the colloidal material; this takes place mainly during the first 36 hr., and the concomitant changes in other properties have been examined. The change is due mainly to a physico-chemical disaggregation of the particles.

E. S. HEDGES.

Lyophilic colloids. XI. Electrolyte binding in albumin solutions. H. R. KRUYT and A. B. BOELMAN (Kolloid-Beih., 1932, 35, 165—202).—A method for accurate potential measurements in solutions of high electrical resistance is described and applied to the solutions of gelatin and albumin. The binding of Cl^- in the system albumin-NaCl could not be recognised; it is apparently masked by a hydration effect. In the systems gelatin- AgNO_3 and albumin- AgNO_3 the amount of bound Ag^+ varies exponentially with the equilibrium concn. Experiments with albumin sols of different concn. indicate that the binding of the ions is due to adsorption. The amount bound varies with the treatment of the gelatin and is decreased by any treatment which reduces the sp. surface. Isoelectric gelatin from which mineral matter has been removed by HCl binds more Ag^+ than does gelatin similarly treated with AcOH, but this is partly due to the formation of AgCl .

E. S. HEDGES.

Lyophilic colloids. XII. Character of electrical phenomena. H. R. KRUYT and H. G. B. DE JONG (Kolloid-Beih., 1932, 35, 203—210).—A discussion of the properties of the electrical double layer in hydrophobic and hydrophilic systems.

E. S. HEDGES.

Determination of the isoelectric point of gelatin. G. P. FAERMAN (J. Appl. Chem. Russ., 1931, 4, 321—323).—Shukov and Schukarev's method (A., 1925, ii, 386) is untrustworthy. Determination of the max. turbidity of the gel is preferred.

CHEMICAL ABSTRACTS.

Rhythmic phenomena in gels. J. M. JOHLIN (Science, 1932, 75, 462).—The pitch of the note which precedes the fracture of SiO_2 gels varies with time.

L. S. THEOBALD.

Influence of hydrolysed gelatin on the precipitation of silver chromate. B. N. DESAI and G. M. NABAR (Trans. Faraday Soc., 1932, 28, 449—452; cf. A., 1928, 126).—When approx. 0.01*N*- AgNO_3 is mixed with 0.01*N*- K_2CrO_4 in the presence of partly hydrolysed aq. gelatin the activity of Ag^+ , determined electrometrically, remains const. for a time and independent of the extent of hydrolysis, and then decreases rapidly to a const. val. The first appearance of red colour coincides with the commencement of the fall in the Ag^+ activity. This occurs earlier with more extensive hydrolysis and the final Ag^+ activity is higher. The results support the view that Ag_2CrO_4 is pptd. from true solution and not by coagulation of a colloidal sol, and that hydrolysis of gelatin does not facilitate pptn. by increasing free $[\text{Ag}^+]$.

J. G. A. GRIFFITHS.

Coacervation. R. S. T. MODDERMAN and L. W. J. HOLLEMAN (Nature, 1932, 129, 654).—Coacervation is discussed for the systems H_2O -gelatin-EtOH, H_2O -gelatin- Na_2SO_4 , and H_2O -gelatin-resorcinol.

L. S. THEOBALD.

Gels. III. Vapour pressure of silica gels. D. G. R. BONNELL (Trans. Faraday Soc., 1932, 28, 463—471; cf. this vol., 123).—Sorption isotherms of dialysed and undialysed SiO_2 gels were determined by a static method at 20° . During the first desorption the undialysed gels crumble spontaneously and remain thus during the reverse cycle until the v. p. of H_2O is approached, when the gels prepared with HCl , AcOH , and H_2SO_4 behave differently, but in all cases a clear liquid separates. With these gels the first sorption and desorption isotherms are not connected by part of the second desorption curve, but after the first cycle sorption and desorption of H_2O vapour become reversible. Other differences between undialysed and dialysed gels are noted and an explanation, based on Zsigmondy's theory, is suggested. Determinations of the vol. changes during desiccation support the conclusion that the H_2O sorbed by the gel is in the uncombined state. J. G. A. GRIFFITHS.

Dielectric constants of thixotropic systems and of oriented layers. H. KALLMANN and W. KREIDL (Z. physikal. Chem., 1932, 159, 322—335).—The dielectric const. of a thixotropic V_2O_5 sol measured with a wave-length of about 50 m. was about 7% greater than that of H_2O and diminished by about 6% when the gel was formed. From the smallness of the decrease it seems improbable that the H_2O mols. lose their freedom of motion to any considerable extent when the sol-gel transformation occurs. The decrease is ascribed to loss of the power of free rotation by the rod-shaped V_2O_5 particles. The dielectric const. of a thin layer of palmitic or lauric acid enclosed between parallel metal plates with diminution in thickness of the layer, attaining a limiting val. when the thickness is 10—20 μ . This effect, which is absent with a non-polar substance such as NHPh , is ascribed to the presence of an oriented film of acid mols. on the surface of the layer. R. CUTHILL.

Primary dissociation constants of the methylcyclohexane-1:1-diacetic acids. Anomaly between the physical and chemical tests of the valency-deflexion hypothesis. D. J. G. IVES, R. P. LINSTEAD, and H. L. RILEY (J.C.S., 1932, 1093—1100).—Conductometric measurements of cyclopentane-, cyclohexane-, 2-methylcyclohexane-, and 3-methylcyclohexane-1:1-diacetic acids give the following vals. for the primary dissociation const. $K_1 \times 10^4$ at 25° : 1.76, 3.23, 3.25, and 3.21, respectively. The results are discussed with reference to the valency-deflexion hypothesis. M. S. BURR.

Electrolytic dissociation of acids in salt solutions. IV. Dissociation constants of fatty acids with branched carbon chains, and activity relations of their ions in sodium chloride and potassium chloride solutions. V. Dissociation constants of aliphatic unsaturated acids, and activity relations of their ions in sodium and potassium chloride solutions. E. LARSSON (Z. physikal. Chem., 1932, 159, 306—314, 315—321; cf. this vol., 124).—IV. Extension of previous investigations to other fatty acids has shown that in NaCl and KCl solutions the vals. of $-\log \psi$ and $-\log \phi$ for a fatty acid are influenced only by the no. and nature of the atoms attached to the α -C atom and by branching of

the chain when that occurs at the α -C atom. The vals. for a mono- or tri-alkylacetic acid are practically independent of the constitution of the acid, and vary only with the nature and concn. of the salt which is present. For dialkylacetic acids the vals. at low salt concns. are little higher than for monoalkylacetic acids, but at high salt concns. the difference is greater.

V. Geometric isomerism caused by a C:C linking does not appreciably affect $-\log \phi$ and $-\log \psi$, and tetrolic acid has the same vals. as the crotonic acids. The vals. for an unsaturated acid at high salt concns. are always rather higher than for the corresponding saturated acid if the double linking is between the α - and β -C atoms. Introduction of an unsaturated C linking into a fatty acid affects the vals. only if it occupies the closest possible position to the CO_2H group. R. CUTHILL.

Extremely weak acids. J. B. CONANT and G. W. WHELAND (J. Amer. Chem. Soc., 1932, 54, 1212—1221).—The interaction of extremely weak acids, such as enols, alcohols, and derivatives of NH_3 and phenylated hydrocarbons, with the Na and K compounds of similar acids has been studied in anhyd. Et_2O . From the results, CHPhMe_2 appears to be the weakest acid studied and BzMe the strongest; CPh_2CH , indene, and phenylfluorene are of nearly the same strength. A study of the interaction of $\text{C}_6\text{H}_5\text{Ph}\cdot\text{CHPh}_2$ with CPh_3Na and of xanthane with $\text{C}_6\text{H}_5\text{Ph}\cdot\text{CPh}_2\text{Na}$ at several temp. showed no real parallelism between the rates and acid strength, since the K salt of the weakest acid reacts rapidly with the next four acids in the series. *Diphenyl- α -naphthylacetic acid*, m. p. 240° , its *Me* ester, m. p. 189 — 191° , *diphenyldiphenylacetic acid*, m. p. 220 — 222° , and its *Me* ester, m. p. 170° , have been prepared. C. J. WEST (c).

Acid hydrates and hydroxonium salts. A. HANTZSCH (Z. anorg. Chem., 1932, 205, 163—179).—A general exposition of the author's views regarding the constitution of acids in solution and as cryst. solids. F. L. USHER.

Buffer action of tungstate solutions. W. QVIST and A. LUND (Z. anorg. Chem., 1932, 205, 87—94).—The p_H of solutions of Na_2WO_4 has been studied with respect to the influence of concn., val. of the ratio $\text{WO}_3:\text{Na}_2\text{O}$, and quantity of aq. HCl or H_2SO_4 added. Provided the ratio $\text{WO}_3:\text{Na}_2\text{O}$ does not fall below 1, the p_H is very insensitive to the addition of acids, and the solutions can be used as buffers over the range p_H 7—8. F. L. USHER.

Activity coefficients of the silver ion in aqueous solutions of some strong electrolytes. II. J. B. CHLOUPEK and V. Z. DANEŠ (Coll. Czech. Chem. Comm., 1932, 4, 165—175).—E.m.f. measurements with saturated Ag_2SO_4 solutions containing variable amounts of K_2SO_4 or KNO_3 yield -0.7996 volt for the standard potential of Ag at 25° . The calc. activity coeffs. of the Ag and SO_4 ions are in fair agreement with the Debye-Hückel equation, assuming ionic diameters of 1 and 3 Å., respectively. H. F. GILLBE.

Combinations of thoryl chloride and an alkali chloride. E. CHAUVENET and R. CHAUVENET

(Compt. rend., 1932, 194, 1246—1247).—The heat evolution on mixing solutions of ThOCl_2 and MCl ($\text{M} = \text{Li, Na, K, Rb, Cs, or NH}_4$) suggests the existence of compounds $\text{MCl} \cdot \text{ThOCl}_2$, except when $\text{M} = \text{NH}_4$. $\text{KCl} \cdot \text{ThOCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CsCl} \cdot \text{ThOCl}_2 \cdot 4\text{H}_2\text{O}$ were isolated in cryst. form. C. A. SILBERRAD.

Complex compounds of amino-acids with neutral salts. F. LEUTHARDT (Helv. Chim. Acta, 1932, 15, 540—557).—The depressing action of neutral salts (MgSO_4 , MgBr_2 , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2 , LiCl) on the p_{H} of solutions of NH_2 -acids (glycine, alanine, leucine, aspartic acid, asparagine, glycylglycine, and ovalbumin) has been determined by electrometric titration. MgCl_2 has no effect on the ultra-violet absorption spectrum (220—246 $\text{m}\mu$) of free glycine, but it weakens the absorption in the presence of alkali. The nature of the equilibria is considered in detail. D. R. DUNCAN.

Physico-chemical behaviour of polypeptides composed of *DL*-alanine. E. ABDERHALDEN and J. HEUMANN.—See this vol., 503.

Thermal dissociation of certain oxides and peroxides. IV. Calcium peroxide. M. BLUMENTHAL (Rocz. Chem., 1932, 12, 232—240).— CaO_2 exists in the difficultly dissociable α -form below 220° , and in the readily dissociable β -form above 220° . The temp. coeff. of dissociation of α - CaO_2 is 1.19.

R. TRUSZKOWSKI.

Thermodynamic activities in binary alloys. C. WAGNER and G. ENGELHARDT (Z. physikal. Chem., 1932, 159, 241—267).—From e.m.f. measurements with cells of the type molten alloy of metals 1 and 2 | molten salt of metal 1 | molten metal 1, the activity, a , of the baser constituent in the alloys Pb-Bi , Sn-Bi , Ti-Bi , Mg-Pb , and Ag-Au has been determined over a range of concns. and at either one or two temp., the results being on the whole in agreement with vals. calc. from existing data for distribution ratios and with data for heat of mixing. The variation of a with concn. agrees broadly with equations deduced by applying van der Waals' equation to binary mixtures, but Lorenz' method of finding the consts. in the equation of state must be used with care. The activities of Ag and Cu in solid alloys with Au have been determined at several temp., the measured potentials apparently being equilibrium vals.

R. CUTHILL.

Affinity of metals for sulphur. II. Thermal dissociation equilibria of sulphides of silver, copper, and arsenic. E. V. BRITZKE and A. F. KAPUSTINSKI (Z. anorg. Chem., 1932, 205, 95—112; cf. A., 1931, 169).—The thermal dissociation of Ag_2S has been examined at different temp. by measuring the partial pressure of H_2 in equilibrium with the solid phase. The dissociation pressure (of S_2) varies from 0.033 mm. at 912° to 0.456 mm. at 1067° . The dissociation of As_2S_2 and of As_2S_3 was determined by measuring the v.d., and of Cu_2S by a gas-streaming method. The pressure of S_2 in equilibrium with $\text{Cu}_2\text{S} + \text{Cu}$ at 1000° is about 10^{-10} atm. The following data are recorded: $2\text{As} + 2\text{S}$ (rhombic) $= \text{As}_2\text{S}_2 + 19.2$ kg.-cal., $2\text{Cu} + \text{S}$ (rhombic) $= \text{Cu}_2\text{S} + 20.2$ kg.-cal. Affinities for S : Cu^{I} 45.49 kg.-cal. at 1004° , Ag 23.65 kg.-cal. at 1185° . F. L. USHER.

Vapour pressure of water over aqueous solutions of the chlorides of the alkaline-earth metals. IV. Evaluation of activity coefficients. J. R. I. HEPBURN (J.C.S., 1932, 1284—1292).—The activity coeffs. calc. from v.-p. data at 25° for Ca , Sr , and Ba chlorides in H_2O are in general agreement with those derived from e.m.f. data, passing through min. vals. at approx. the same concn. The results also confirm to a certain extent Allmand's conclusions (A., 1927, 1029) relating to the connexion between v.-p. lowering and activity coeffs. M. S. BURR.

Binary systems: nitrates of metals of group II and water. I. Magnesium nitrate-water. A. SIEVERTS and W. PETZOLD (Z. anorg. Chem., 1932, 205, 113—126).—Solubility data for the above system have been determined. The stable cryohydric temp. is -31.5° . The enneahydrate is stable below -17.1° . The hexahydrate has congruent m. p. 89.3° , and forms a eutectic mixture with the dihydrate at 55.6° . The anhyd. salt (above 128°) could not be obtained owing to decomp. Isothermal dehydration curves and cooling curves establish the existence of a metastable tetrahydrate. F. L. USHER.

Sodium sulphate. T. OKUNO and K. MIYAZAKI (J. Soc. Chem. Ind. Japan, 1932, 35, 97—99b).—The solid phases in the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 25° are Na_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{H}(\text{SO}_4)_2$, $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$, NaHSO_4 , and $\text{NaH}_3(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. The dissociation pressures of NaHSO_4 and $\text{Na}_3\text{H}(\text{SO}_4)_2$ have been measured by means of Wohler's apparatus and with a thermobalance. The velocity of decomp. of NaHSO_4 between 200° and 900° has been followed and changes in constitution during heating observed by X-ray analysis. J. W. SMITH.

Thermodynamic study of potassium hydroxide. F. L. E. SHIBATA, S. ODA, and S. FURUKAWA (J. Sci. Hiroshima Univ., 1932, A, 2, 85—102).— KOH forms three hydrates, $\text{KOH} \cdot 2\text{H}_2\text{O}$, stable below 27.3° , $\text{KOH} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, stable below 33.4° , and $\text{KOH} \cdot \text{H}_2\text{O}$. The dissociation pressures and free energies of hydration are recorded, and the free energy of formation and entropy of KOH at 25° are found to be $-92,950$ g.-cal. and 23.0, respectively.

C. W. DAVIES.

Thermodynamic study of sodium hydroxide. F. L. E. SHIBATA (J. Sci. Hiroshima Univ., 1931, A, 1, 215—228).—Measurements at 25° of the v. p. of NaOH and its saturated solution, and e.m.f. of the cell $\text{Na-Hg}|\text{NaOH} \cdot \text{H}_2\text{O}$ sat., $\text{HgO}|\text{Hg}$ lead to: (1) $\text{NaOH} + \text{H}_2\text{O} = \text{NaOH} \cdot \text{H}_2\text{O}$; $\Delta F = -2835$, $\Delta H = -2900$ g.-cal. (2) $\text{H}_2\text{O} + 0.9496\text{NaOH} \cdot \text{H}_2\text{O} = \text{NaOH}$ sat.; $\Delta F = -1556$, $\Delta H = +633$ g.-cal. (3) $\text{Na} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{NaOH}$; $\Delta F = -90,762$, $\Delta H = -102,401$ g.-cal. (4) The entropy of NaOH is 12.43.

C. W. DAVIES.

Decomposition pressures of crystalline hydroxides [with special reference to those] of aluminium and beryllium. R. FRICKE and H. SEVERIN (Z. anorg. Chem., 1932, 205, 287—308).—Isobaric (100 mm.) dehydration of cryst. diaspore, bohmite (bauxite), bayerite, hydrargillite, and stable and metastable $\text{Be}(\text{OH})_2$ has been carried out in vessels having a very small vol. (<1 c.c.). Although the materials were finely ground, the attainment of equi-

librium required from 1 to 10 weeks. In all cases the observed temp. of decomp. were considerably lower than those given by other workers. X-Ray examination affords evidence that the lattice of all these substances is built up from metal and hydroxyl ions, and dehydration must therefore be preceded by formation of H_2O . The thermal effect calc. from the temp. coeff. of dehydration represents chiefly heat of activation. The following vals. of d^{20} are given: bohmite 3.014, bayerite 2.529, hydrargillite 2.424, metastable $\text{Be}(\text{OH})_2$ 1.920, stable $\text{Be}(\text{OH})_2$ 1.924.

F. L. USHER.

Thermal analysis of the system lithium nitrate-thallos nitrate. H. V. A. BRISCOE, C. EVANS, and P. L. ROBINSON (J.C.S., 1932, 1100—1103).—The equilibrium diagram for LiNO_3 – TlNO_3 is simple and similar to that of NaNO_3 – TlNO_3 . There is no evidence of compound formation or solid solution between 50° and 250° . The single eutectic at 136.5° corresponds with 63.8 mol.-% TlNO_3 . The following consts. were redetermined and differ appreciably in some cases from earlier data: m. p. LiNO_3 , $252.0 \pm 0.2^\circ$; m. p. TlNO_3 , $206.0 \pm 0.2^\circ$; transition $\alpha \rightarrow \beta$ - TlNO_3 , 143.5° ; $\beta \rightarrow \gamma$, 61.0° .

M. S. BURR.

System aniline, ethylaniline, and diethylaniline. T. YAGINUMA and K. HAYAKAWA (J. Soc. Chem. Ind. Japan, 1932, 35, 117—118B).—Phase diagrams are given for the systems NH_2Ph – NHPhEt , NH_2Ph – NPhEt_2 , NHPhEt – NPhEt_2 , and NH_2Ph – NPhEt_2 .

J. W. SMITH.

Thermodynamic study of the system iron-carbon-oxygen. II. H. DUNWALD and C. WAGNER (Z. anorg. Chem., 1932, 205, 205—208; cf. A., 1931, 1128).—Polemical against Krings (this vol., 22).

F. L. USHER.

System calcium-sulphur-oxygen. J. ZAWADSKI (Z. anorg. Chem., 1932, 205, 180—192; cf. A., 1928, 1095).—Equilibrium pressures over CaSO_4 – CaO have been measured at and above 840° . The observed pressures decrease with time and reach a const. val. characteristic of anhydrite. The heat of reaction calc. from these data agrees with the accepted thermochemical val. A qual. and quant. study of the reactions $(4\text{CaSO}_3) \text{CaS} + 3\text{CaSO}_4 \rightarrow 4\text{CaO} + 4\text{SO}_2$ and $\text{CaS} + 2\text{SO}_2 \rightarrow \text{CaSO}_4 + \text{S}_2$ has also been made.

F. L. USHER.

Synthesis of calcium silicates. IV. S. NAGAI and K. AKIYAMA (J. Soc. Chem. Ind. Japan, 1932, 35, 118—122B; cf. this vol., 350, 481).—The systems CaO – SiO_2 – Fe_2O_3 , CaO – SiO_2 – Al_2O_3 , CaO – SiO_2 – Fe_2O_3 – Al_2O_3 have been studied at 1450° .

J. W. SMITH.

System CaO – Na_2O – Al_2O_3 . L. T. BROWN-MILLER and R. H. BOGUE (Bur. Stand. J. Res., 1932, 8, 289—307).—The system contains two ternary compounds, $3\text{CaO}, 2\text{Na}_2\text{O}, 5\text{Al}_2\text{O}_3$, m. p. $>1630^\circ$, and $8\text{CaO}, \text{Na}_2\text{O}, 3\text{Al}_2\text{O}_3$ dissociating at 1508° into CaO and liquid. The first compound forms eutectics with $3\text{CaO}, 5\text{Al}_2\text{O}_3$ (CaO 23, Na_2O 8, Al_2O_3 69%, 1550°), $\text{CaO}, \text{Al}_2\text{O}_3$ (CaO 30.5, Na_2O 5, Al_2O_3 64.5%, 1515°), $5\text{CaO}, 3\text{Al}_2\text{O}_3$ (CaO 40, Na_2O 4.5, Al_2O_3 55.5%, 1450°), and the second ternary compound (CaO 43.2, Na_2O 10.3, Al_2O_3 46.5%, 1465°). CaO and $\text{Na}_2\text{Al}_2\text{O}_4$ form a eutectic with 20% CaO at 1565° .

Ternary eutectics are formed between $3\text{CaO}, 5\text{Al}_2\text{O}_3$, $\text{CaO}, \text{Al}_2\text{O}_3$, and $3\text{CaO}, 2\text{Na}_2\text{O}, 5\text{Al}_2\text{O}_3$ (CaO 27.5, Na_2O 6, Al_2O_3 66.5%, 1465°), $\text{CaO}, \text{Al}_2\text{O}_3$, $5\text{CaO}, 3\text{Al}_2\text{O}_3$, and $3\text{CaO}, 2\text{Na}_2\text{O}, 5\text{Al}_2\text{O}_3$ (CaO 38, Na_2O 4, Al_2O_3 58%, 1430°), and $5\text{CaO}, 3\text{Al}_2\text{O}_3$, $8\text{CaO}, \text{Na}_2\text{O}, 3\text{Al}_2\text{O}_3$, and $3\text{CaO}, 2\text{Na}_2\text{O}, 5\text{Al}_2\text{O}_3$ (CaO 46, Na_2O 5, Al_2O_3 49%, 1420°). Two quadruple points occur with CaO – $3\text{CaO}, \text{Al}_2\text{O}_3$ (57% CaO , 1535°) and with CaO – $8\text{CaO}, \text{Na}_2\text{O}, 3\text{Al}_2\text{O}_3$ (CaO 46.8, Na_2O 9, Al_2O_3 44.2%, 1508°), and three quintuple points between the 5:3 and 3:1 Ca aluminates and the 8:1:3 ternary compound (CaO 46.5, Na_2O 4.5, Al_2O_3 49%, 1423°), CaO , 3:1 Ca aluminate, and the 8:1:3 compound (CaO 50, Na_2O 6, Al_2O_3 44%, 1490°) and CaO , $\text{Na}_2\text{Al}_2\text{O}_4$, and the 8:1:3 and 3:2:5 ternary compounds (CaO 42.5, Na_2O 13, Al_2O_3 44.5%, 1475°). A. R. POWELL.

Phase equilibria in the system SiO_2 – ZnO – Al_2O_3 . E. N. BUNTING (Bur. Stand. J. Res., 1932, 8, 279—287).—In the binary system ZnO – Al_2O_3 the compound $\text{ZnO}, \text{Al}_2\text{O}_3$ (m. p. $1950 \pm 10^\circ$) forms a eutectic with ZnO at 83 mol.-% ZnO and $1720 \pm 10^\circ$. Tridymite, Zn_2SiO_4 , and ZnAl_2O_4 form a eutectic at $1305 \pm 5^\circ$ and SiO_2 52, ZnO 40, and Al_2O_3 8 mol.-%; ZnO , Zn_2SiO_4 , and ZnAl_2O_4 form a second eutectic in the ternary system at $1440 \pm 5^\circ$ and SiO_2 18.5, ZnO 71.3, and Al_2O_3 10.3 mol.-%. The system also contains two quintuple points which are not eutectics, one at $1400 \pm 5^\circ$ and SiO_2 63, ZnO 26, Al_2O_3 11 mol.-% with tridymite, ZnAl_2O_4 , and mullite as the solid phases, and the other at about 1750° and about SiO_2 40, ZnO 23, and Al_2O_3 37 mol.-% with Al_2O_3 , ZnAl_2O_4 , and mullite as the solid phases. The results are discussed with reference to a suitable refractory for retorts for the distillation of Zn ; it would appear that a high- Al_2O_3 mixture, in the neighbourhood of a mullite composition, should have a long life not only on account of its resistance to the slagging action of ZnO , but also because of its high resistance to spalling on rapid changes of temp.

A. R. POWELL.

Heterogeneous equilibrium in the system CdBr_2 – KBr – H_2O . H. HERING (Compt. rend., 1932, 194, 1348—1350).— CdBr_2 crystallises with $4\text{H}_2\text{O}$ below, anhyd. above, 35° (cf. A., 1905, ii, 375). $\text{KBr}, \text{CdBr}_2$ crystallises from H_2O above 57.3° , but is decomposed by H_2O above 102° and on fusion; $\text{KBr}, \text{CdBr}_2, \text{H}_2\text{O}$, stable -9.3° to 57.3° , solubility congruent; $\text{KBr}, 2\text{CdBr}_2, \text{H}_2\text{O}$, exists 52 – 86° , never congruent; $\text{KBr}, 3\text{CdBr}_2, 4\text{H}_2\text{O}$, exists 14.8 – 57.5° , congruent 24 – 48° . $2\text{KBr}, \text{CdBr}_2$ was not obtained (cf. A., 1926, 791).

C. A. SILBERRAD.

Thermal analysis of ternary mixtures of isomeric compounds. T. VAN DER LINDEN (Helv. Chim. Acta, 1932, 15, 591—592).—Wyler's m. p. method for the analysis of mixtures of dinitrobenzenes (this vol., 259) is unsound. The author's method (A., 1913, ii, 106; cf. Kohman and Andrews, A., 1925, ii, 1053) is recommended.

D. R. DUNCAN.

Formation and properties of precipitates. Theory of coprecipitation. I. M. KOLTHOFF (Chem. Weekblad, 1932, 29, 286—291).—Simultaneous pptn. may be due to (a) adsorption of foreign ions during crystal growth, causing irregular crystal formation, (b) surface adsorption after formation, (c) formation

of mixed crystals, and (d) chemical combination. Subsequent pptn., as in the case of MgC_2O_4 and CaC_2O_4 , and ZnS and CuS , is to be distinguished.

S. I. LEVY.

Heats of formation of rhenium oxides. W. A. ROTH and G. BECKER (Z. physikal. Chem., 1932, 159, 415—416; cf. this vol., 469).—Corrected heats of formation are Re_2O_7 , 297.5 ± 2 and ReO_3 , $82.5 \pm 10\%$ kg.-cal.

R. CUTHILL.

Heat of formation of compounds between lanthanum and magnesium and between lanthanum and aluminium. G. CANNERI and A. ROSSI (Gazzetta, 1932, 62, 202—211).—The heats of dissolution of Mg, Al, and La in HCl (1 mol./8.808 mols. H_2O) are 112.8, 125.4, and 172.4 kg.-cal. per g.-atom, respectively; the values for LaMg , LaMg_3 , LaAl_2 , and LaAl_3 are 279.5, 497.9, 387.1, and 631.8 kg.-cal. per mol., respectively. From these vals. the heats of formation of the four compounds are 5.7, 12.9, 36.1, and 42.2 kg.-cal. per mol., respectively.

O. J. WALKER.

Energy differences of different modifications of crystalline beryllium and aluminium hydroxides and heats of formation of crystalline zinc and beryllium hydroxides. R. FRICKE and B. WULLHORST (Z. anorg. Chem., 1932, 205, 127—144).—The heats of formation of cryst. Zn and Be hydroxides from oxide and H_2O have been calc. from heats of dissolution of the respective substances in aq. HF. The vals. found are: ($\text{BeO}, \text{H}_2\text{O}$) 1.87—3.35, ($\text{ZnO}, \text{H}_2\text{O}$) 2.28—3.21 kg.-cal., the val. in each case depending on the character of the oxide and hydroxide used. The energy differences observed indicate an order of stability in agreement with that given by measurements of solubility and v. p. F. L. USHER.

Electrolytic water transport in barium chloride solution. J. BABOROVSKY and O. VIKTORIN (Coll. Czech. Chem. Comm., 1932, 4, 155—164).—The transport nos. of the Ba ion, and the electrolytic transport of H_2O in 0.1—2.0N- BaCl_2 solutions have been determined. Transference is towards the anode at concns. above about 0.2N, and in the reverse direction at lower concns. The quantity of H_2O transferred is a linear function of the dilution.

H. F. GILLBE.

Conductivity of nitric and perchloric acids, and the mobility of the hydrogen ion. M. HŁASKO and W. KLIMOWSKI (Rocz. Chem., 1932, 12, 201—212).—The conductivity coeffs. for HNO_3 and HClO_4 , in concn. $< N/32$, are identical, and are 1% lower than the vals. calc. from Onsager's formula (cf. A., 1927, 517). The limiting mobility of H^+ is 355.1 and 355.0 for the two acids at 25°.

R. TRUSZKOWSKI.

Electrical conductivity of binary aggregates. G. S. SON FREY (Z. Elektrochem., 1932, 38, 260—274).—Theoretical. Lichteneker's equation (cf. A., 1925, ii, 632) is inapplicable for high ratios of the conductivities of the two components. Formulae are derived for different types of binary aggregates for ratios between 1 and ∞ . The calc. relation between composition and conductivity agrees closely with the observed vals. both for alloys and for systems composed of insulating and conducting materials, such as,

e.g., sand saturated with a solution of an electrolyte. The great influence of a poorly conducting metal (e.g., Bi or Pb) on the conductivity of another metal (Ag or Mg), which in some cases has been attributed to mixed crystal formation, is shown to be in accordance with the theory. Application of the formulae to the correction of observed conductivities of substances containing impurities is described.

H. F. GILLBE.

Behaviour of quartz electrodes. II. B. VON LENGYEL and T. MATRAI (Z. physikal. Chem., 1932, 159, 393—402; cf. this vol., 471).—Measurements with quartz electrodes in acid-alkali cells show that the electrode potential passes through a min. in about 1N-acid, then rises and passes through a max. in about 0.01N-alkali. The quartz electrode probably represents a limiting type of glass electrode. Its potential is determined by adsorption effects, whereas the potential of a soft glass electrode is influenced by distribution and diffusion.

R. CUTHILL.

Electrometric titration and certain properties of ferrous sulphate. N. A. SCHISCHAKOV (J. Gen. Chem. Russ., 1931, 1, 1012—1025).—The E_h of a solution containing Fe^{2+} and Fe^{3+} is given by $E_h - 0.380 + 0.058 \log c_3/c_2$, where c_2 and c_3 are the concn. of Fe^{2+} and Fe^{3+} , respectively. Fe^{2+} can be determined potentiometrically by titration with $\text{K}_2\text{Cr}_2\text{O}_7$, the break in the curve obtained being the more marked the greater is the concn. of acid present. FeSO_4 does not undergo oxidation in the presence of atm. O_2 , when its concn. is $> 0.001M$; at higher concn. the velocity of oxidation is proportional to the concn., and is greater in presence of light. The reaction is catalysed by smooth Pt, and more powerfully by platinised Pt. The concn. of Fe^{2+} can be found from the E_h found for solutions for which the ratio c_3/c_2 varies from 5/95 to 95/5, using a rotating Pt electrode for determination of E_h , and extrapolating from the E_h - $\text{K}_2\text{Cr}_2\text{O}_7$ curve.

R. TRUSZKOWSKI.

Electrochemical periodicities. J. A. V. BUTLER and G. ARMSTRONG (Nature, 1932, 129, 613—614).—Marked periodicities occur at small c.d. in the anodic polarisation of Pt electrodes in dil. H_2SO_4 saturated with H_2 . The periodicities are not obtained during the first anodic polarisation of the electrode. A mechanism in which the electrons passing into the metal are derived from absorbed H_2 is discussed.

L. S. THEOBALD.

Reduction of aromatic mono- and poly-nitro-compounds. XIII. K. BRAND and F. STRACHE (J. pr. Chem., 1932, [ii], 133, 355—364; cf. A., 1931, 1151).—When PhNO_2 is reduced with Zn dust and CaCl_2 for 5 min., the solution after filtration and extraction with Et_2O has p_H 11.75. When reduction is continued for 40 min., the p_H is 11.05, rising after 40 min. to 11.3. When NH_4Cl is used instead of CaCl_2 and reduction continued for 40 min., the p_H is 7.9 (max. after 40 min., falling after 60 min. to 7.6); these lower vals. are due to loss of NH_3 during reduction and in the stream of H_2 during the potentiometric measurements. The mechanism of the reduction previously proposed (A., 1928, 1366) is proved experimentally. The alkalinity of the solution is

due to the formation of $\text{Zn}(\text{OH})_2$. Extraction of aq. NaOAc with Et_2O has no effect on its p_H .

R. S. CAHN.

Time factor in anodic passivation of metals. W. J. MÜLLER (Trans. Faraday Soc., 1932, 28, 471—473).—Polemical against Shutt and Stirrup (cf. A., 1930, 1527). Vigorous stirring does not necessarily prevent the formation of salt or surface layers at the anode. The observations of Shutt and Stirrup are consistent with the existence of a surface layer.

J. G. A. GRIFFITHS.

Specific nature of energy exchange in uni-molecular reactions. E. W. R. STEACIE (J. Amer. Chem. Soc., 1932, 54, 1695).— Me_2O and Et_2O decompose in an almost identical way; they have a pronounced resemblance in physical properties and in the manner in which the velocity coeff. decreases with pressure, yet have no activating effect on each other.

C. J. WEST (c).

Chemical kinetics of De Donder and Arrhenius' heat of activation. P. VAN RYSELBERGHE (Bull. Acad. roy. Belg., 1932, [v], 18, 170—179).—Mathematical. A relation between chemical affinity and heat of activation is deduced, and considered in relation to high temp., complete reactions, and photo-chemical reactions.

N. M. BLYTH.

Kinetics of degradation of long-chain molecules. F. KLÄGES (Z. physikal. Chem., 1932, 159, 357—367).—The kinetics of the degradation are worked out theoretically assuming that the velocity coeff. of decomp. is the same for all the linkings in the chain but one. The results agree with existing experimental data (A., 1930, 1025).

R. CUTHILL.

Kinetics of degradation of long-chain molecules. W. KUHN (Z. physikal. Chem., 1932, 159, 368—373).—The kinetics are worked out on the lines followed by Klages (cf. preceding abstract), but in a more exact manner.

R. CUTHILL.

Inflammation of mixtures of hydrogen and oxygen by hydrogen atoms. F. HABER and F. OPPENHEIMER (Z. physikal. Chem., 1932, B, 16, 443—459).—Explosion already occurs at about 300° when H_2 containing about 10⁻⁴% H atoms is mixed with O_2 under 20—150 mm. The H atoms are the cause of explosion, above 80 mm. at any rate, for the ignition temp. of the mixtures without at. H on quartz lie above 500°. Increase in pressure is unfavourable to surface ignition, but promotes the explosive reaction, possibly because the H atom concn. was increased.

R. CUTHILL.

Chemical kinetics in a vessel surrounded by a large thickness of mercury. M. BOLL (Compt. rend., 1932, 194, 1242—1243).—Using the author's electrometric method (cf. A., 1912, ii, 384) the velocity coeff. of the hydrolysis of $\text{H}_2\text{PtCl}_6(\text{OH})_2$ in a tube of diam. 2 cm. placed vertically in a vessel of 20 cm. diam., filled with Hg, was 0.002 c.g.s., compared with 0.0130 when Hg was absent (cf. A., 1919, ii, 256). It is suggested that the difference is due to cosmic rays. No such difference was observed in the inversion of sucrose.

C. A. SILBERRAD.

Deterioration of hypochlorites. R. H. AGUILAR.—See B., 1932, 382.

Rate of hydrolysis of pyrophosphoric acid. J. MUUS (Z. physikal. Chem., 1932, 159, 268—276; cf. A., 1927, 26).—The hydrolysis in $N\text{-KCl}$ at various $[\text{H}^+]$ at 20° and 40° is kinetically unimol., the velocity coeff. being proportional to $[\text{H}^+]$. The reaction apparently consists in the hydrolysis of $\text{H}_3\text{P}_2\text{O}_7$ catalysed by H^+ . From H electrode measurements the second and third dissociation consts. of $\text{H}_4\text{P}_2\text{O}_7$ are found to be 2.7×10^{-2} and 3×10^{-6} , respectively, in the reaction medium.

R. CUTHILL.

Oxidation of sodium sulphide and sodium hydrogen sulphide. S. A. SCHUKAREV and E. M. KIREVA-TUZULACHOVA (J. Gen. Chem. Russ., 1931, 1, 1125—1144).—The products of oxidation of aq. NaHS or Na_2S by atm. O_2 are Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, and Na_2SO_4 ; those of $\text{Na}_2\text{S}_2\text{O}_3$ are S , Na_2SO_3 , and Na_2SO_4 . The reaction of oxidation of NaHS is one of zero order. The velocity of oxidation of Na_2SO_3 is reduced by the presence of $\text{Na}_2\text{S}_2\text{O}_3$, which, however, itself undergoes oxidation in the presence of Na_2SO_3 . The velocity of oxidation of HS^- falls with increase in p_H and with increasing concn. of NaHS or Na_2S . The reaction is represented as $\text{HS}^- \longrightarrow \text{HSO}_3^- \longrightarrow (a)\text{S}_2\text{O}_3^{2-}$, (b) $\text{HSO}_3^- \longrightarrow \text{HSO}_4^-$.

R. TRUSZKOWSKI.

Chemical reactions in concentrated electrolytes. Reduction of vanadic acid by hydrogen bromide and its course in concentrated electrolyte. (In sulphuric acid with constant evolution of bromine.) I. M. BOBTELSKI and S. CZOSNEK (Z. anorg. Chem., 1932, 205, 401—413).—In conc. H_2SO_4 the rate of reduction of V^{V} to V^{IV} by HBr is directly proportional to the concn. of V^{V} , but is proportional to the HBr concn. only in a dil. solution of the latter. For const. HBr and V^{V} , but increasing concn. of H_2SO_4 , no reaction takes place until there are less than 12 mols. of H_2O to 1 mol. of H_2SO_4 . For 10—5 H_2O the reaction velocity is inversely proportional to H_2O . Below 4 H_2O the results are uncertain and only slightly influenced by the amount of H_2O . The influence of increasing HBr depends on the concn. of H_2SO_4 and under certain conditions an optimum concn. of HBr is obtained. The position of this is not changed by temp., but the max. becomes more marked with rising temp.

If the Br formed is not removed the reaction ceases. HCl behaves similarly to H_2SO_4 . If different salt solutions are added to a mixture containing less than the optimum concn. of HBr a definite neutral salt effect is observed and the reaction is considerably accelerated, but there is practically no salt effect above the optimum concn. of HBr . The reverse is the case for Zn salts.

M. S. BURR.

Equilibria and rates of some organic reactions. J. B. CONANT (Ind. Eng. Chem., 1932, 24, 466—472).—The relation between the structure of compounds and the free energy of reaction in the standard states is discussed with reference to the reduction of quinones and the recently investigated equilibria between the keto and enol isomerides of substituted acetoacetic esters in the gas phase. The free energy of enolisation has been calc. and the results for the vapours are closely parallel to those obtained with dil. solutions in C_6H_{14} . The disturbing influence of solvents on many equilibria is emphasised. Reactions are dis-

cussed in which close relationships exist between rates of reaction and equilibria (cf. A., 1930, 322, 711). The rate of formation of the semicarbazones of pyruvic acid, four aldehydes, and three ketones has been investigated in buffer solutions. The reaction takes place between free semicarbazide and the carbonyl compound and is catalysed by acids, but at acidities $> p_H$ 4.9 the acceleration is opposed by a decrease in the concn. of free semicarbazide owing to salt formation. There is no apparent relation between the velocity of formation and the stability of the semicarbazide as measured by the hydrolysis const., but there appears to be a fairly simple relation between structure and the energy relationships of semicarbazone formation, the equilibrium const. being determined by factors similar to those governing the dissociation consts. of acids. J. G. A. GRIFFITHS.

Oxidation velocity of sodium sulphate solution by oxygen in presence of a molecular film of fatty acid. S. MIYAMOTO, T. KAYA, and A. NAKATA (J. Sci. Hiroshima Univ., 1931, A, 1, 203—214).—The max. rate of absorption of O_2 by a Na_2SO_4 solution which is rapidly stirred without breaking the surface is unaffected by addition of stearic acid. This disproves the existence under these conditions of a stationary surface film through which the O_2 must diffuse. C. W. DAVIES.

Influence of certain agents on the velocity of formation and thermal decomposition of some carbonates. J. ZAWADZKI and S. BRETZNAJDER (Compt. rend., 1932, 194, 1160—1162).—The velocity of absorption of CO_2 by CaO or CdO is not in accordance with the equation $v = K(p - P)$, where K is a const., p the actual and P the equilibrium pressure, but increases at first more rapidly, passes through a max., and then declines. Occasionally the reaction stops half completed, but continues after a period of rest. C. A. SILBERRAD.

Carbon dioxide absorption velocity of potassium and sodium hydroxide solutions. K. MASAKI (J. Biochem., Japan, 1932, 15, 29—32).—Following a reconsideration of the data previously obtained (A., 1931, 916) the corrected interpretation is that the CO_2 absorption velocity of $N-KOH$ is 1.14 times that of $N-NaOH$ at any temp. between 11° and 25° . F. O. HOWITT.

Reactions between carbon and certain gases. W. E. J. BROOM and M. W. TRAVERS (Proc. Roy. Soc., 1932, A, 135, 512—537).—Measurements have been made of the ratio $K_t = P_{CO}/P_{CO_2}$, and of the rates of reaction of sugar C and coconut C with CO and CO_2 . The influence of the H_2 present in the C and the presence of O_2 retained on the C on the rate of reduction of CO_2 has been investigated. The reaction between C, CO , and CO_2 is not represented by $C + CO_2 = 2CO$, but takes place in two stages: $CO_2 + C = CO$ gas + C-O complex and $CO + C = C-CO$ complex. L. L. BIRCUMSHAW.

Reduction of cupric oxide by carbon monoxide and hydrogen. A. JULIARD (Bull. Soc. chim. Belg., 1932, 41, 65—84).—A detailed description of an experimental method used to measure the rate of

reduction of CuO by CO or H_2 is given. Results obtained by it are satisfactorily reproducible.

F. L. USHER.

Reduction of cupric oxide by carbon monoxide and hydrogen. A. JULIARD (Bull. Soc. chim. Belg., 1932, 41, 138—151; cf. preceding abstract).—The influence of the vol. and thermal treatment of CuO , the velocity and concn. of CO , and the temp. of reaction (450 — 900°) has been studied. The velocity of reaction depends largely on factors affecting the porosity of the reduced Cu . E. S. HEDGES.

Temperature increment of the velocity of heterogeneous reactions. II. Reduction of silver halides. K. FISCHBECK and K. SCHNAIDT (Z. Elektrochem., 1932, 38, 299—304).—The reduction of $AgCl$ by H_2 proceeds without an induction period, and its velocity at const. temp. is determined only by the available $AgCl$ surface, i.e., diffusion is of no account. The following heats of activation, in $kg.-cal.$, have been determined: $AgCl$ (fused) 61.0; $AgCl$ (pptd.) 20.7; $AgBr$ (pptd.) 22.5. H. F. GILLBE.

Intercrystalline corrosion of duralumin. A. J. SIDERY, K. G. LEWIS, and H. SUTTON.—See B., 1932, 429.

Distribution of corrosion. S. C. BRITTON and U. R. EVANS.—See B., 1932, 429.

Kinetics of a type of heterogeneous reactions. II. Mechanism of combustion of lump fuel. S. P. BURKE and T. E. W. SCHUMANN (Ind. Eng. Chem., 1932, 24, 451—453; cf. A., 1931, 574).—The authors' mathematical treatment is extended to the combustion of a sphere of solid fuel and the theory is confirmed, in general, by the work of Smith and Gudmundsen (B., 1931, 466). The rate of reaction increases with diminution of particle size and with increase of air velocity, but vals. of the surface temp. of C do not accord with the theory. The discrepancies may be related to the effects of H_2O and the formation of CO in the combustion process.

J. G. A. GRIFFITHS.

Role of phosphate in oxidation processes. A. M. MAL'KOV and N. ZVETKOVA (Biochem. Z., 1932, 246, 191—202).—Phosphate inhibits the decomp. of H_2O_2 by $FeSO_4$ and also inhibits the oxidation of various sugars by the system $Fe^{II} + H_2O_2$. The oxidation of sugar by $FeSO_4$ is accelerated by 0.15M-phosphate, but is completely inhibited by higher concns. ($M/1$ — $M/3$). P. W. CLUTTERBUCK.

Constitutional factors controlling prototropic changes in carbonyl compounds. II. Acid and base catalysis in the bromination of halogenated acetones. H. B. WATSON and E. D. YATES (J.C.S., 1932, 1207—1215).—Measurements of the rate of bromination of various halogenated acetones have confirmed the conclusion (cf. this vol., 129) that an electron-attracting substituent reduces the extent to which the ketone co-ordinates with an acid catalyst and increases the ease with which the proton ionises. The influence of the halogen substituent is shown by the change in the ratio k_{acid}/k_{base} , as expressed in the displacement of the point of min. velocity in the direction of higher acid concn. This displacement is

very marked and is continuous as halogen atoms are successively introduced into the mol. of COMe₂.

E. S. HEDGES.

Catalysis by hydrogen chloride in the system acetic acid-ethyl alcohol-ethyl acetate. C. A. DURRUTY (Anal. Assoc. Quím. Argentina, 1931, 19, 227—253).—The equilibrium const. of the esterification is 3.7 at 100°. The net velocity of formation of AcOEt is proportional to the AcOH concn. An expression has been derived for the velocity of the reaction in presence of HCl; at low HCl concns. the velocity is proportional to the concn., and, further, the equilibrium const. increases in an approx. linear manner with increase of the (initial) HCl concn. Equilibrium is attained within 80—90 hr., and the percentage of free HCl at equilibrium is 5—10% of that present initially.

H. F. GILLBE.

Activation of complex salts in aqueous solution. II. P. PFEIFFER and K. QUEHL (Ber., 1932, 65, [B], 560—565; cf. this vol., 30).—Increase in the concn. of the camphorsulphonic ion greatly enhances the activation of the [Zn phen₃]⁺⁺ ion (phen=phenanthroline). The activating effect of α -bromo- π -camphorsulphonic acid on ZnSO₄ and phenanthroline (1:1) is comparatively small. Activation of [Zn phen₃]SO₄ by cinchonine hydrochloride or quinine sulphate is not due to entry of the alkaloid into the Zn complex. Activation is caused by cinchonine mono- but not by di-methochloride. Nicotine is active. The salts [Cd 1:1-dipyridyl]₂X₂ and [Cd phen₃]X₂ in H₂O are similarly activated by optically active acid ions or optically active alkaloids. The compounds [Cd phen₃](NO₃)₂·6H₂O and [Cd phen(OH)₄](NO₃)₂·6H₂O are described.

H. WREN.

Catalysis in an inert solvent. E. A. MOELWYN-HUGHES (Nature, 1932, 129, 316).—For the mutarotation of Be benzoylcamphor in CCl₄ with C₅H₅N or EtOH as catalysts the observed vals. agree with those calc. from Lewis' gas collision formula. This affords another example of a reaction proceeding in solution at the same rate as theory predicts for the gaseous phase (cf. Traill, this vol., 346).

L. S. THEOBALD.

Effect of magnesium hydroxide on the oxidation of quinol. A. SAINT-MAXEN (Compt. rend., 1932, 194, 1583—1585).—The oxidation of quinol (cf. A., 1930, 1128) is not affected by a saturated aq. solution of Mg(OH)₂, or by Mg(OH)₂ pptd. in the hot. A freshly-prepared suspension of Mg(OH)₂ activates the oxidation during 10 min.; in presence of 50% glycerol, the activity is retained for some days. Conductivity measurements indicate the existence of an equimol. compound of Mg(OH)₂ and quinol. An aq. solution of the product obtained when hydrated Mg(OAc)₂ is heated at 110°/30 mm. in N₂ also activates the oxidation; max. action is after about 24 hr., and the activity parallels the viscosity of the reaction mixture.

H. BURTON.

Mechanism of decomposition of esters in presence of feebly alkaline alcohol. E. M. BELLET (Compt. rend., 1932, 194, 1655—1658; cf. this vol., 42).—Displacement of PhOH from PhOAc by EtOH in presence of a little NaOH becomes less rapid as the solution becomes neutral, and is probably due to

addition to the C:O group, which is activated by alkali (or acid).

E. W. WIGNALL.

Desensitisers, antioxygens, and antifuorescents. E. BAUR (Z. physikal. Chem., 1932, B, 16, 465—470).—The variation with concn. of the effect of these substances may be expressed by $v=1/[\alpha+\beta(D)]$, where v is the ratio of the reaction velocity or intensity of fluorescence to that in absence of the added substance, D the concn. of the latter, and β a const. which is a measure of its effectiveness (cf. A., 1929, 892). It is therefore concluded that all three types of inhibition depend on a mol. electrolysis involving the inhibitor and the active mols. of the dark reaction or those created by light absorption (cf. A., 1928, 1338).

R. CUTHILL.

***o*-Quinones as enzyme models. III. Experiments in alkaline media.** B. KISCH and K. SCHUWIRTH (Biochem. Z., 1932, 247, 371—385; cf. this vol., 427).—The optimum reaction for the deamination of glycine (as measured by yield of NH₃) by pyrocatechol derivatives is between p_H 9 and 11 and is dependent on the nature of the catalysts, which themselves are affected, in differing degrees, by the reaction. In consequence of the action of O₂ on the catalysts the optimum lies the more to the alkaline side of neutrality the smaller is the amount of air present. The yield of NH₃ resulting from the action of hydroxyquinol may reach 70% of the theoretical. In the region p_H 6.0—12.0 serine is deaminated by the catalysts almost to the same extent as is glycine. Leucine is deaminated to a much smaller extent, whilst isoleucine, valine, α - and β -aminopropionic acids and α -aminobutyric acid are not appreciably affected.

W. MCCARTNEY.

Catalysts for the production of hydrogen by means of the water-gas reaction. V. Thermal sensitivity of ferric oxide catalyst. VI. Thermal influence on the activity of ferric oxide-chromium sesquioxide catalysts. I. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1932, 35, 85—87B, 87—88B; cf. A., 1931, 1017, 1134; this vol., 235).—V. Fe₂O₃ loses its catalytic effect for CO oxidation when heated in air above 700°. This coincides with the temp. at which a pastille of Fe₂O₃ shows a sharp vol. contraction when heated. There is no abrupt change in the velocity of reaction with SiO₂ at this temp., so it is concluded that there is no allotropic change although there is a magnetic transformation. The effect is attributed to the unsaturated atoms, to which the catalytic activity appears to be due, shifting from the crystal corners and angles to more stable configuration.

VI. The magnetic transformation point of Fe₂O₃ is lowered by addition of Cr₂O₃, but not the temp. at which Fe₂O₃ pastilles contract abruptly.

J. W. SMITH.

Production of hydrogen sulphide by heating paraffin and other hydrocarbon mixtures with sulphur. E. D. SCUDDER and R. E. LYONS (Proc. Indiana Acad. Sci., 1931, 40, 185—188).—Lampblack and anhyd. AlCl₃ are effective catalysts.

CHEMICAL ABSTRACTS.

Sulphuric acid catalysis. V. B. NEUMANN [with K. KNOBLICH] (Z. Elektrochem., 1932, 38, 304—

311).—Catalysis of the reaction $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$ by various oxides and by mixtures of CuO and Cr_2O_3 has been studied. CuO is active only at above 400° , CuSO_4 being the sole intermediate product; conversion is a max. (58.73%) at 700° . At temp. below that at which the dissociation pressure of CuSO_4 is considerable (650°) the catalyst is sluggish. The activity of MnO_2 rises to a max. (18.3%) at 560° , whilst that of the Mn_2O_3 then formed rises from about 12% at 600° to 22% at 700° ; Mn_3O_4 produces about the same percentage conversion as Mn_2O_3 . PbO_2 and Bi_2O_3 are scarcely active, owing to formation of sulphate. The reaction in presence of MoO_3 commences only at the temp. at which the catalyst begins to sublime (600°), and reaches a max. (47%) at 720° ; no apparent change takes place in the MoO_3 . UO_3 is inactive below 700° , when U_3O_8 is formed, but very little conversion takes place and UO_2SO_4 is produced. With CeO_2 13.67% conversion is obtained at 700° . A mixture of CuO with Cr_2O_3 (2 : 1) is slightly more active than is Cr_2O_3 alone, but a 1 : 1 mixture is less active; CuSO_4 is formed, and the activity in time approximates to that of Cr_2O_3 . H. F. GILLBE.

Platinum versus vanadium as catalyst for sulphuric acid. A. P. THOMPSON.—See B., 1932, 381.

Reduction of zinc oxide in presence of metallic copper. V. A. PLOTNIKOV and O. K. KUDRA (J. Gen. Chem. Russ., 1931, 1, 1075—1079).—When mixtures of CO and H_2 are passed over Cu-Zn catalyst at 400° , the particles of Cu become coated with brass, pointing to the formation of a volatile Zn compound, which decomposes on the surface of Cu . The process of synthesis of MeOH is hence explained as follows : $2n\text{ZnH}_2 + \text{Cu}(\text{CO})_n \longrightarrow \text{Cu} + 2n\text{Zn} + n\text{MeOH}$.

R. TRUSZKOWSKI.

Oxidation of phosphorous acid by water in the presence of colloidal metals. A. A. VEDENSKI and A. V. FROST (J. Gen. Chem. Russ., 1931, 1, 1108—1113).—The oxidation of H_3PO_3 by H_2O is catalysed by colloidal Pt , Cu , or Ag . The catalysts are activated by H_3PO_4 in small concn., whilst at higher concn. they are inactivated. R. TRUSZKOWSKI.

Heterogeneous catalysis of binary gas reactions. C. KROGER (Z. anorg. Chem., 1932, 205, 369—397).—Heterogeneous catalysis of binary gas reactions may be physical, whereby the catalysed reaction takes place in an adsorbed layer, or chemical, when the surface of contact undergoes a permanent chemical alteration due to the formation of stable intermediate compounds. There are two kinds of chemical catalysis, the first in which a valency change takes place in the contact metal, and the second kind in which no valency change occurs. The factors determining the two different kinds of chemical catalysis are discussed with reference to particular cases. M. S. BURR.

Oxidation of ethyl alcohol by air in presence of binary or ternary catalysts. MARTINEAU (Compt. rend., 1932, 194, 1350—1353).— C-ZrO_2 and C-ThO_2 catalysts are prepared by treating with aq. NH_3 active C impregnated with the appropriate nitrate and drying at 150° . $\text{Cu-Ce}_2\text{O}_3$ and Cu-ThO_2 mixtures are

obtained by mixing Ce_2O_3 or ThO_2 with Cu carbonate, treating with NH_3 , and reducing with H_2 at 300° . Ternary catalysts, Cu-C -oxide, are prepared by a combination of these methods. The oxidation of EtOH by air at 63° in contact with these catalysts is measured; the max. efficiency is shown by 1C , 1Cu , 1ZrO_2 , and 10C , 2Cu , 1ThO_2 , the latter effecting oxidation at a measurable rate at $15-20^\circ$.

H. A. PIGGOTT.

Preparation of a catalyst (aluminium ethoxide) for the synthesis of ethyl acetate from acetaldehyde. K. SUMIYA, S. YAMADA, and Y. TAJIMA (J. Soc. Chem. Ind. Japan, 1932, 35, 88—91B).—The prep. of $\text{Al}(\text{OEt})_3$ by the action of EtOH on Al in AcOEt solution, using a mixture of I and HgCl_2 as catalyst, is accelerated by the addition of anhyd. FeCl_3 . The catalyst solution thus prepared enables AcOEt to be synthesised from MeCHO with very high yield.

J. W. SMITH.

Dehydration of phenol. Contact catalysis. E. BRINER, (MME.) J. BRON-STALET, and H. PAILLARD (Helv. Chim. Acta, 1932, 15, 619—634).—At 450° in the absence of a catalyst, PhOH is converted slowly but completely into Ph_2O and H_2O . The reaction occurs in the gas phase and is accelerated by increase of pressure. In presence of ThO_2 the reaction is much quicker, but is reversible, only 60—64% of the PhOH being decomposed at 450° , 54% at 500° , and 50.1% at 540° . Pressure has no influence on the velocity, the reaction occurring in an adsorbed phase. The heats of adsorption account for the difference in the equilibrium composition. Equilibrium was reached from both sides, and static and dynamic methods gave approx. the same results. The best catalyst was prepared by pptg. from boiling solutions of $\text{Th}(\text{NO}_3)_4$ and KOH and drying at 250° . With Al_2O_3 a similar equilibrium is established, max. dehydration (72—85%) occurring at 420° , but phenylene oxide is formed simultaneously. β -Naphthol at 450° decomposes completely to β -naphthyl oxide in the absence of a catalyst, whilst the % decomp. at equilibrium with ThO_2 is 58. The heat of combustion of Ph_2O is 1455 kg.-cal. D. R. DUNCAN.

Suitability of cobalt catalysts for benzene synthesis. F. FISCHER and H. KOCH.—See B., 1932, 376.

Use of nickel as a catalyst for hydrogenation. II. L. W. COVERT, R. CONNOR, and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1651—1663; cf. A., 1931, 919).—The amount of Ni held by the support, the proportion of Ni compounds reducible to metal, and the optimum time and temp. for the reduction of Ni oxides to the active catalyst depend on the precipitants and mode of pptn. A method of preparing easily reproducible and very active catalysts is described. Various additional elements incorporated in the catalyst may increase its activity in respect of some hydrogenations and inhibit others. The course of certain hydrogenations is considerably affected by the presence of amino-compounds. The optimum conditions for the hydrogenation of various org. compounds have been established. C. J. WEST (c).

Alkali borides. L. ANDRIEUX and D. BARBETTI (Compt. rend., 1932, 194, 1573—1574; cf. this

vol., 348).—130 g. of $\text{Na}_4\text{B}_2\text{O}_7$ and 30 g. of NaF with varying amounts of CaO (4–12 g.), SrO (5–10 g.), BaO (50–60 g.), CeO_2 (3–20 g.), La_2O_3 (15 g.), Nd_2O_3 (10–12 g.), or ThO_2 (4–15 g.) were electrolysed at 950° . Black crystals of $x\text{MB}_6\cdot y\text{NaB}_6$ ($M=\text{Ca}$, etc.) were obtained. x decreases as the amount of added oxide is less, but below a certain limit, e.g., about 50% for ThB_6 , the mixture is unstable and some impure B is formed. Similar results were obtained with K and Li. C. A. SILBERRAD.

Metallic lanthanum free from iron and silicon. F. TROMBE (Compt. rend., 1932, 194, 1653–1655; cf. A., 1931, 1253).—With the arrangement described for Ce a mixture of LaCl_3 60 parts, KCl 35, and CaF_2 5, electrolysed at 960 – 980° with a current of 12 amp. per 25 g. of LaCl_3 at 7 volts (c.d. 4 amp. per sq. cm.), yields 65% La, free from Ca or Al, and containing 0.005–0.1% Fe, and, if prepared in a fluorite crucible, <0.05% Si; m. p. $885\pm 5^\circ$, Brinell hardness 36, d 6.139. C. A. SILBERRAD.

Preparation of potassium ferricyanide by electrolytic oxidation of potassium ferrocyanide in aqueous solution. (a) V. F. JUFEREV and J. I. BOKINIK, (b) V. F. JUFEREV and L. L. KUGMIN (Bull. Inst. polytech. Ivanovo-Vosniesensk, 1930, 15, 163–179, 181–196).—(a) Grube's results (A., 1914, i, 814) are confirmed; efficient stirring is necessary. The fine crystals (yield 40%) contain 0.1–0.3% of $\text{K}_3\text{Fe}(\text{CN})_6$, larger crystals contain 0.5%, and the mother-liquor 1–1.5%. Recrystallisation was effected with simultaneous oxidation with KMnO_4 in presence of AcOH . Evaporation after oxidation results in decomp. of $\text{K}_3\text{Fe}(\text{CN})_6$ proportionally to the amount of $\text{K}_4\text{Fe}(\text{CN})_6$ and KOH present; the Cu anode requires an alkaline solution. The efficiency of the anode is lowered by deposition of crystals.

(b) Oxidation with a Hg cathode without a diaphragm is not economical. With a diaphragm nearly 100% current efficiency is attained with a c.d. of 0.004–0.005 amp. per sq. cm. The material of the anode does not influence current efficiency. With a Hg cathode and a Ni anode the solution at the anode should be kept alkaline; if the solution is kept neutral, Pt must be substituted for Ni. The final concn. of $\text{K}_3\text{Fe}(\text{CN})_6$ is increased by saturation of the anode solution outside the anodic space.

CHEMICAL ABSTRACTS.

Lead accumulator. I. Changes of resistance at the plates during use. E. DENINA and A. FRATES (Energia Elett., 1931, 8, 8 pp.; Chem. Zentr., 1932, i, 559).—The changes support the theory of double sulphatisation. A. A. ELDRIDGE.

Electrodeposition of ternary alloys of copper, cadmium, and zinc from cyanide baths. R. C. ERNST and C. A. MANN.—See B., 1932, 430.

Electrolytic production of heavy metals from fused electrolytes. III. F. SAUERWALD.—See B., 1932, 430.

[Electrolytic] sodium amalgam formation from sodium chloride solutions. K. S. TESH and H. E. WOODWARD.—See B., 1932, 430.

Action of some organic substances in the electrolytic deposition of zinc. L. CAMBI and G.

DEVOTO (Atti R. Accad. Lincei, 1932, [vi], 15, 27–29).—Addition of pyridine bases to solutions of ZnSO_4 increases the current efficiency for Zn deposition and decreases the deposition potential. Piperidine and analogous bases have no effect. Solutions of NiSO_4 behave similarly in presence of pyridine.

O. J. WALKER.

Deposition of brass from thiocyanate solutions. N. THON and J. PINILLA.—See B., 1932, 387.

Hydrogen peroxide and the Kolbe reaction. S. GLASSTONE and A. HICKLING (Nature, 1932, 129, 616).—Electrolytic oxidation reactions indicate that H_2O_2 plays an important role in certain anodic processes (cf. this vol., 348). L. S. THEOBALD.

Anode phenomena in the electrolysis of potassium acetate. III. Formation of methane. S. N. SHUKLA and O. J. WALKER (Trans. Faraday Soc., 1932, 28, 457–462; cf. A., 1931, 193, 1371).—Electrolysis of KOAc in MeOH , EtOH , and AcOH with low c. d. at a smooth Pt electrode affords results similar to those obtained with aq. KOAc (*loc. cit.*). With aq. KOAc and a Au anode, no hydrocarbons were produced with c. d. between 0.7 and 700 milliamp. per sq. cm., but with Ir and graphite anodes the composition of the evolved gas is similar to that obtained with Pt; the variation of $[\text{AcOH}]$ causes comparatively small changes in the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio.

J. G. A. GRIFFITHS.

Formation of acetylene from methane by the condensed spark at low pressure. R. MONTAGNE (Compt. rend., 1932, 194, 1490–1492; cf. A., 1925, ii, 1194; 1927, 322).—Applying the method previously described to CH_4 at 1–11 mm., the main reaction (to the extent of about 75%) is $2\text{CH}_4=\text{C}_2\text{H}_2+3\text{H}_2$, complicated by subsequent decomp. and condensation of C_2H_2 . The energetic yield is about 15%. The reaction is accelerated and yield, both chemical and energetic, improved by increasing the capacity of the condenser. At the temp. of liquid air up to 10% CH_4 is transformed into saturated or ethylenic hydrocarbons, and the energetic yield is diminished.

C. A. SILBERRAD.

Electric discharges in liquids. I. Arc discharge in water. H. D. CARTER and A. N. CAMPBELL (Trans. Faraday Soc., 1932, 28, 479–496).—The CO_2 , CO , H_2 , saturated hydrocarbons, and O_2 obtained from a specially-designed low-voltage C arc in H_2O were determined. The 1–5% of O_2 is attributed to electrolysis and not to the arcing. The origin of the non-combustible gaseous residue (N_2) was investigated. In addition to particles of C, a solid product similar to “graphitic acid” and a sparingly sol. acid of high m. p. were obtained. With metallic electrodes, hydroxidic substances were produced. The yield of gaseous products increases with rise of temp. of the H_2O , but is independent of pressures as high as 205 lb. per sq. in. The apparent temp. of the C arc, determined by means of an optical pyrometer, is raised from 1300 – 2700° in H_2O at room temp. to 2500 – 3600° with the H_2O at 100° . The mechanism of the process is discussed. In addition to thermal dissociation of H_2O , electrical dissociation of H_2O vapour into H and OH ions is suggested and the form-

ation of solid products is attributed to the reactions of the latter with the electrodes. J. G. A. GRIFFITHS.

Characteristics of polar and non-polar chemical reactions. W. A. WATERS (Proc. Univ. Durham Phil. Soc., 1932, 8, 459—467).—Reactions are classified as non-polar (concerned only with electrically neutral radicals or mols.) and polar (involving the separation of oppositely charged ions). Photochemical activation may be concerned with the former. C. W. GIBBY.

Gaseous photodecomposition of chlorine dioxide. J. W. T. SPINKS (J. Amer. Chem. Soc., 1932, 54, 1689—1690).—The decomp. seems to be a chain reaction. There is an initial decrease in pressure, apparently due to the formation of Cl_2O_6 and its deposition on the walls. The subsequent increase in pressure is probably due to the sensitised decomp. of Cl_2O_6 by Cl atoms. The final rise in pressure closely resembles that observed with a $\text{Cl}_2\text{--O}_3$ mixture.

C. J. WEST (c).

Photodecomposition of chlorine dioxide solutions. E. J. BOWEN and W. M. CHEUNG (J.C.S., 1932, 1200—1207).—The main products of the photochemical decomp. of aq. ClO_2 are HClO_3 and HCl in equimol. proportions. The quantum efficiency rises from 0.2 at 4360 Å. to 1.0 at 3000 Å. In CCl_4 solution the limiting quantum efficiency is about 2. The mechanism of reaction is discussed and the results are explained by making use of the observation that gaseous ClO_2 exhibits the phenomenon of predissociation at 3753 Å. E. S. HEDGES.

Hydrazine formation in the synthesis and decomposition of ammonia. I. Synthesis of hydrazine and ammonia by cathode rays. G. R. GEDYE and T. E. ALLIBONE. II. Photochemical decomposition of ammonia. III. Synthesis of hydrazine at catalytic surfaces. G. R. GEDYE and E. K. RIDEAL (J.C.S., 1932, 1158—1160, 1160—1169, 1169—1172).—I. Small yields of NH_3 and N_2H_4 have been obtained by the action of high-velocity electrons on mixtures of N_2 and H_2 . The long range of the electrons renders the method not very suitable for quant. investigation.

II. Investigation of the photochemical decomp. of NH_3 by the total radiation from a quartz-Hg arc by means of a flow method has proved the formation of N_2H_4 . The yield is increased by low temp. of the reaction vessel, a high rate of flow and rapid cooling of the gases leaving the reaction vessel. The yield of N_2H_4 may represent as much as 50% of the decomposed NH_3 . Very little N_2H_4 is obtained in the Hg-sensitised reaction. The decomp. of NH_3 by light is compared with that by ionising radiations.

III. In addition to NH_3 , traces of N_2H_4 are formed when mixtures of H_2 and N_2 are passed over a catalyst of Fe promoted by Al_2O_3 and K_2O . The relative yield of N_2H_4 is greater at lower temp. At 437°, with a very high rate of flow, the yield of N_2H_4 was approx. 4% by wt. of the NH_3 formed.

E. S. HEDGES.

Becquerel effect with zinc oxide. E. BURGIN (Z. wiss. Phot., 1932, 30, 334—358).—Results are detailed of the nature, permanence, and magnitude of the Becquerel effect with ZnO suspensions in H_2O ,

with and without the addition of cathodic depolarisers (dyes or metallic salts) or anodic depolarisers (glucose, glycerol, benzidine, or NHPh.NH_2), and with and without both. Experiments were made with and without access to air. The electrodes must be shielded from the light to prevent the small effect found to occur on exposure. The formation of ZnO_2 is postulated to account for alternation of the sign of the effect on alternation of exposure to light and dark, the potential rising in the dark, and the ZnO_2 being removed by cathodic depolarisation in the light. Experiments with gas electrodes are described. Baur's theory of sensitised photolysis is supported.

J. LEWKOWITSCH.

Theory of the Becquerel effect. E. BAUR (Z. wiss. Phot., 1932, 30, 359—363).—The Becquerel effect is the symptom of a hidden photochemical change in a material system. The application of Baur's theory of sensitised photolysis to explain the effect is upheld.

J. LEWKOWITSCH.

Hypersensitisation. I. Influence of silver ions on sensitivity of panchromatic plates. J. I. BOKINIK [with (FRL.) Z. LJUNA]. II. Action of hydrogen peroxide on sensitivity of panchromatic plates. J. I. BOKINIK (Z. wiss. Phot., 1932, 30, 322—329, 330—333).—I. Hypersensitisation by treatment of plates with AgNO_3 before exposure is due to (a) photochemical decomp. of the adsorption complex of AgNO_3 and the sensitising dye, and (b) a very slight effect caused by the strengthening of development by adsorbed Ag ions. TiNO_3 produces only effect (b).

II. H_2O_2 has a desensitising action which is greater in acid than in alkaline solution. Desensitisation of ordinary plates, and hypersensitisation of panchromatic plates, by a solution of AgNO_3 and H_2O_2 (Schmieschek, B., 1930, 793) is due to the action of H_2O_2 and AgNO_3 alone, respectively. N_2H_4 has a strong sensitising action. J. LEWKOWITSCH.

"Antagonism" of radiations in their effects on the photographic plate. E. MÜHLESTEIN (Ann. Guébhard-Séverine, 1930, 6, 123—140).—A summary of the theories of this subject with particular reference to the reversal of image observed in the action of rays from Ra-Em on photographic plates.

J. W. SMITH.

Photographic effect of pressure. N. T. ZÉ and C. L. CHAO (Compt. rend., 1932, 194, 1644—1646; cf. A., 1931, 319).—With const. pressure the reduction in density of a photographic plate ($d-d'$) increases as time of exposure increases from that of under- to that of correct exposure, and then decreases for over-exposure. It is also greater for light of shorter wavelength. The relative reduction, $(d-d')/d$, decreases logarithmically as time of exposure increases.

C. A. SILBERRAD.

Photographic emulsion: silver-ion and hydrogen-ion concentrations and sensitivity. B. H. CARROLL and D. HUBBARD (Bur. Stand. J. Res., 1932, 8, 481—505).—The rate of after-ripening increases with increasing $[\text{Ag}']$ and increasing p_{H} ; the corresponding effects on sensitivity are much larger than those produced by the direct effect of environment (after digestion). The effect of excess of Ag' is

reduced by combination of Ag^+ with gelatin. The distribution of excess of Br^- or Ag^+ in the emulsion with changing p_{H} has been studied. The desensitising action of Br^- (after digestion) increases with increasing acidity and the effect of p_{H} changes depends on the $[\text{Ag}^+]$. The spectral sensitivity of the emulsions is independent of $[\text{H}^+]$ or $[\text{Ag}^+]$; their influence on sensitivity appears to be through secondary reactions in latent image formation, and of these the elimination of Br^- is better explained by reaction with Ag_2S than with gelatin. The results are explained on the assumption that gelatin is adsorbed by Ag halides in preference to all other materials present. The nature of the adsorption is discussed in the light of the "Zwitterion" theory.

E. S. HEDGES.

Photosynthesis *in vitro*. G. MACKINNEY (J. Amer. Chem. Soc., 1932, 54, 1688—1689).—No procedure yet published enables conditions for obtaining CH_2O and carbohydrates *in vitro* to be reproduced.

C. J. WEST (c).

Progress in the theory of chemical reactions. M. POLANYI (Naturwiss., 1932, 20, 289—296).—A résumé.

W. R. ANGUS.

Alkali fluoborates, alkali fluorosulphonate, and potassium perrhenate. D. VORLANDER, J. HOLLATZ, and J. FISCHER (Ber., 1932, 65, [B], 535—538).—The following transition temp. are recorded for the conversion of the feebly doubly-refractive β -forms into the isotropic α -varieties of fluoborates: Na , 239—242°; K , 271—280°; Li , 203—206°; NH_4 , about 236°. $\text{Ag}(\text{H}_2\text{O})\text{BF}_4$ and LiBF_4 are described. NH_4 , K , and Rb fluorosulphonates are strongly doubly refractive and retain this property until melted or decomposed; they differ crystallographically from perchlorates and fluoborates. KReO_4 does not exhibit dimorphism.

H. WREN.

Alkali phosphates. I. Sodium pyrophosphate and the reaction pyrophosphate \rightleftharpoons orthophosphate. H. MENZEL and L. SIEG [with F. EBERT] (Z. Elektrochem., 1932, 38, 283—299).—The literature relating to analysis of ortho- and pyro-phosphates is critically reviewed, and the Debye-Scherrer diagrams of the Na salts and their various hydrates are described. The solubility curve (0—96°) of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ shows that transition to the anhyd. salt occurs at 79.5°; no other hydrate appears to exist. V.-p. measurements in the system $\text{Na}_4\text{P}_2\text{O}_7$ — $\text{Na}_4\text{P}_2\text{O}_{10} \cdot 10\text{H}_2\text{O}$ between 20° and 80° yield for the heat of hydration 124.5 kg.-cal. The action of dry gaseous or liquid NH_3 on $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ yields the anhyd. salt, but no ammoniate is produced at temp. down to -78.5°. $\text{Na}_4\text{P}_2\text{O}_7$ has m. p. $980^\circ \pm 2^\circ$; only one cryst. form exists between room temp. and the m. p. The isothermal decomp. of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ at 20°, and the v. p. of saturated solutions of this salt and of both the lower hydrates (7 and $2\text{H}_2\text{O}$) have been studied; the conditions necessary for the prep. of each hydrate are described. Thermal analysis does not serve to elucidate fully the reaction $2\text{Na}_2\text{HPO}_4 \rightleftharpoons \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$. Measurement of the decomp. pressure of Na_2HPO_4 between 130° and 208° is difficult, and the p - T curve obtained may represent either a univariant equilibrium between one vapour and two

solid phases, or a more complex process. Isothermal dehydration of Na_2HPO_4 at 211° yields cryst. $\text{Na}_4\text{P}_2\text{O}_7$; at 131° an amorphous form is produced, and this at a suitable H_2O v. p. may be reconverted into Na_2HPO_4 . The cryst. form of $\text{Na}_4\text{P}_2\text{O}_7$ combines very slowly with H_2O at 131°, and the equilibrium pressure is markedly higher than in the case of the amorphous salt.

H. F. GILLBE.

Formation of cupric sulphide, selenide, and telluride. H. PELABON (Bull. Soc. chim., 1932, [iv], 51, 377—380).—When Cu and S (Se or Te) are placed in contact in a solution of CuSO_4 , $\text{Cu}(\text{NO}_3)_2$, or $\text{Cu}(\text{OAc})_2$, CuS is formed with a velocity depending on the concn. of the Cu^{++} solution. The same effect is obtained if the Cu and S are joined by an electrical conductor such as Pt wire and also when solid S is replaced by a solution in CS_2 . The action is due to the formation of an electrolytic cell and a p. d. of about 0.2 volt has been observed. Thomson's formula is applicable.

E. S. HEDGES.

Conditions of reduction of Fehling's solution. A. HEIDUSCHKA and W. BIETHAN (J. pr. Chem., 1932, [ii], 133, 273—283).—The amount of auto-reduction of Fehling's solution increases as the following factors increase: time of heating, time of exposure to O_2 , concn. of the solution, and concn. of CuSO_4 , alkali, or Na K tartrate. A method, involving addition of $\text{K}_4\text{Fe}(\text{CN})_6$ to Fehling's solution, is described for determining glucose in 0.1—0.5% solution. By the modified process the amount of CuO reduced is exactly proportional to the amount of glucose oxidised; the results are independent of the time of heating and concn. of CuSO_4 , $\text{K}_4\text{Fe}(\text{CN})_6$, or alkali, but air must be excluded. Auto-reduction is influenced by the same factors as in the absence of this salt and is also increased by addition of glycerol and NaOH . By the modified process 1 mol. of glucose absorbs 4 atoms of O_2 , contrasted with 2—2.25 atoms by the usual method. Schaer's interpretation (Chem.-Ztg., 1904, 27, 912) of the auto-reduction is considered to be supported by the above results.

R. S. CAHN.

Berthollet's silver fulminate. P. C. VAN DER WILLIGEN (Chem. Weekblad, 1932, 29, 232).—An account of an explosion during the prep. of a small quantity of ammoniacal Ag solution.

S. I. LEVY.

Beryllium. H. BORCHERS (Metall.-Wirt., 1931, 10, 863—866; Chem. Zentr., 1932, i, 510).—Experiments in H_2 from low to atm. pressure gave no indication of compound formation; no change takes place in moist air, H_2O , or H_2O vapour. Finely powdered Be burns brightly in air; when heated in air it forms a white surface layer 200—300° below the f. p., and with rising temp. the metal is completely converted into this substance, a mixture of nitride and oxide. At higher temp. Be is very sensitive towards small quantities of O_2 . Above 1400° Be attacks SiO_2 , presumably forming BeO and Si . Al_2O_3 is analogously reduced by Be . The m. p., which depends on the purity, is 1285°, and the calc. heat of fusion is 345.0 g.-cal. The purity and electrolytic purification of Be are discussed.

A. A. ELDRIDGE.

Fluoberyllates and their analogy with sulphates. II. Fluoberyllates of bivalent metals.

N. N. RAY (Z. anorg. Chem., 1932, 205, 257—267; cf. this vol., 131).—The following salts have been prepared: CaBeF_4 , d_{10}^{25} 2.959; SrBeF_4 , d_{10}^{25} 3.736; $\text{NiBeF}_4 \cdot 7\text{H}_2\text{O}$; $\text{NiBeF}_4 \cdot 6\text{H}_2\text{O}$, d_{10}^{25} 1.941; $\text{NiBeF}_4 \cdot 3\text{H}_2\text{O}$; $\text{CoBeF}_4 \cdot 7\text{H}_2\text{O}$, d_{10}^{25} 1.867; $\text{CoBeF}_4 \cdot 6\text{H}_2\text{O}$, d_{10}^{25} 1.891; $\text{CoBeF}_4 \cdot 3\text{H}_2\text{O}$; $\text{CoBeF}_4 \cdot 2\text{H}_2\text{O}$; $\text{ZnBeF}_4 \cdot 7\text{H}_2\text{O}$; $\text{CdBeF}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$; $\text{FeBeO}_4 \cdot 7\text{H}_2\text{O}$, d_{10}^{25} 1.894; $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$. The Ni, Co, Zn, Fe^{II}, Cd, and Cu salts are isomorphous with the corresponding sulphates. F. L. USHER.

Trimagnesium phosphate. C. ZINZADZÉ (Compt. rend., 1932, 194, 1498—1500).—To obtain $\text{Mg}_3(\text{PO}_4)_2$ the p_{H} of the solution must be < 13 ; with greater acidity increasing quantities of MgHPO_4 result, and this alone with $p_{\text{H}} > 8$. To prepare $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, 2 parts of 20% aq. MgSO_4 (d_{15}^{15} 1.222) and 1 of 9% aq. Na_3PO_4 (d_{15}^{15} 1.1) are agitated together, and the ppt. is washed by decantation with less H_2O than was present at the first mixing. Drying must be effected below 30° (cf. A., 1924, ii, 676; B., 1926, 841; 1927, 55). C. A. SILBERRAD.

Perovskite (CaO, TiO_2) and titanite ($\text{CaO}, \text{TiO}_2, \text{SiO}_2$). K. IWASÉ and M. FUKUSIMA (Bull. Chem. Soc. Japan, 1932, 7, 91—102).—Perovskite and titanite were prepared by fusing together their constituents, using CaCO_3 instead of CaO . In the prep. of titanite, if the melt was allowed to supercool below about 1280° , perovskite and SiO_2 separated together with the titanite. Above this temp. only titanite separated, this compound being more stable than the mixture $\text{CaO}, \text{TiO}_2 + \text{SiO}_2$. This mixture melts at about 1390° , titanite at 1383° , Na_2SiO_3 at 1088° , Li_2SiO_3 at 1202° . D. R. DUNCAN.

Calcium aluminates. II. Crystallisation of calcium aluminate solutions at 40° . G. ASSARSON (Z. anorg. Chem., 1932, 205, 335—360).—The compounds crystallising from a mixture of freshly-prepared solutions of Ca aluminate and $\text{Ca}(\text{OH})_2$ at 40° have been investigated optically and analytically and the results recorded in a triangular diagram. The same aluminates have been identified as were previously obtained at 20° (A., 1931, 1370). Al hydroxide forms as a gel and also as a crypto- and micro-cryst. aggregate. The form first obtained has the composition $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, but the one obtained later is probably hydrargillite or bayerite. Pure aluminates separate from those solutions in which the mol. proportions $\text{CaO} : \text{Al}_2\text{O}_3 > 2$, the tetra-aluminate being always the first formed and other compounds following when the crystallisation of this is complete. Al hydroxide separates if the proportion lies between 1 and 2. Within a certain dilution range these solutions are metastable and deposit no Al hydroxide, although they cannot be unsaturated.

M. S. BURR.

Hydrothermal synthesis of calcium silicates under ordinary pressure. III. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 153—156B; cf. A., 1931, 1020, 1380).—A 1:1 $\text{CaO}-\text{SiO}_2$ mixture heated at $800-900^\circ$ first yields $3\text{CaO}, 2\text{SiO}_2$ but on further heating gives CaO, SiO_2 . A 3:2 $\text{CaO}-\text{SiO}_2$ mixture treated similarly yields at first $3\text{CaO}, 2\text{SiO}_2$, then $2\text{CaO}, \text{SiO}_2$. If CaO is replaced by CaCO_3 in

these and previous experiments results are not affected except by the time required to decompose the CaCO_3 .

C. IRWIN.

Action of thiocyanates on mercurous salts. J. FIALKOV (Z. anorg. Chem., 1932, 205, 235—240).—The transformation of Hg_2^{++} into $\text{Hg} + \text{Hg}^{++}$ is practically complete in presence of excess of KCNS, owing to the removal of Hg^{++} as a complex anion. The reaction has been used for the determination of Hg^I .

F. L. USHER.

Inhomogeneity of highly active salt of radium barium chloride. F. BEHOVNEK and O. KOBLEC (Physikal. Z., 1932, 33, 376—378).—The inhomogeneity is a primary property and arises from the concn. of RaCl_2 .

A. J. MEE.

Reactions of boron fluoride with alcohols and glycols. T. H. VAUGHN, H. BOWLUS, and J. A. NIEUWLAND (Proc. Indiana Acad. Sci., 1931, 40, 203—206).—The acidic substance formed when BF_3 is passed into MeOH is a co-ordination compound. When C_2H_2 is passed into MeOH containing BF_3 , MeOH, acetal is formed. Et_2O inhibits the reaction owing to preferential formation of a non-ionised compound with BF_3 .

CHEMICAL ABSTRACTS.

Valency relations of halides of periodic groups III, IV, and V. W. M. FISCHER and A. TAURINSCH (Z. anorg. Chem., 1932, 205, 309—320; cf. A., 1931, 613).—The following compounds with $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ (1:4) are described (figures denote temp. of decomp.; $\text{M} = \text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$): $2\text{M}, \text{BCl}_3$ 166° ; $3\text{M}, \text{BCl}_3$ 158° ; $3\text{M}, \text{AlBr}_3$ 155° ; $3\text{M}, 2\text{AlBr}_3$, $184-190^\circ$; $2\text{M}, \text{AlBr}_3$ $160-175^\circ$; $3\text{M}, \text{AlCl}_3$ 170° ; $3\text{M}, 2\text{AlCl}_3$, $182-184^\circ$; $4\text{M}, \text{SiCl}_4$ 163° ; $8\text{M}, \text{SiCl}_4$ 200° ; M, SiHCl_3 166° ; $2\text{M}, \text{TiCl}_4$ 215° ; M, TiCl_4 230° ; $\text{M}, 2\text{SnCl}_2$ $110-112^\circ$; M, SnCl_4 $50-55^\circ$; $2\text{M}, \text{SnCl}_4$; $2\text{M}, \text{SnBr}_4$ 65° ; $2\text{M}, \text{ThCl}_4$ 210° ; $3\text{M}, \text{PBr}_3$ $163-164^\circ$; $5\text{M}, \text{PCl}_5$ 172° ; $5\text{M}, \text{PBr}_5$ 172° , 194° ; $2\text{M}, \text{PhOPCl}_2$ 171° ; $4\text{M}, \text{PhOPCl}_4$ $170-173^\circ$; $3\text{M}, (\text{PhO})_2\text{PCl}_3$ $170-174^\circ$; $2\text{M}, \text{PI}_3$ 96° ; $3\text{M}, \text{AsCl}_3$ $175-176^\circ$; M, SbCl_5 151° ; $2\text{M}, 3\text{SbCl}_5$ 124° . The formation of the compounds is discussed with reference to the equivalence or otherwise of the halogen atoms.

F. L. USHER.

Action of anhydrous aluminium chloride (bromide) on some aliphatic alcohols and acetone. H. FUNK, J. SCHORMULLER, and W. HENSINGER (Z. anorg. Chem., 1931, 205, 361—368; cf. A., 1931, 1020).—The following compounds have been prepared by the action of AlCl_3 or AlBr_3 on some alcohols and COMe_2 : $\text{AlCl}_2(\text{OMe}), 2\text{AlCl}_3, 16\text{MeOH}$; $\text{Al}_3\text{Cl}_2\text{O}_2(\text{OMe})_3$ which may have either of the structural formulae $2\text{AlOCl}, \text{Al}(\text{OMe})_2$ or $2\text{AlO}(\text{OMe}), \text{AlCl}_2(\text{OMe})$; $\text{AlCl}_2(\text{OEt}), 2\text{AlCl}_3, 10\text{EtOH}$; $\text{AlBr}_2(\text{OMe}), 2\text{AlBr}_3, 16\text{MeOH}$; $\text{AlBr}_2(\text{OEt}), 2\text{AlBr}_3, 15\text{EtOH}$; $\text{AlCl}_2(\text{OPr}), 2\text{AlCl}_3, 5\text{PrOH}$; $\text{AlCl}_2(\text{OMe}), \text{AlCl}_3, 8\text{MeOH}$; $\text{Al}_3\text{Cl}_2\text{O}(\text{OMe})_4$; $\text{AlCl}_2(\text{CH}_2 \cdot \text{COMe}), \text{AlCl}_3, 2\text{COMe}_2$.

M. S. BURR.

Hydrothermal synthesis of muscovite. W. NOLL (Naturwiss., 1932, 20, 283).—Muscovite ($\text{K}_2\text{O}, 3\text{Al}_2\text{O}_3, 6\text{SiO}_2$) was prepared by heating an aq. solution of the corresponding colloid adsorption compound in a pressure bomb for 5 days at 300° .

The prep. thus obtained was identified as muscovite by its X-ray interference pattern. W. R. ANGUS.

Zeolites and salts slightly soluble in water. G. AUSTERWEIL (Compt. rend., 1932, 194, 1581—1583; cf. this vol., 30).—The whole salt, both cation and anion, can be removed from a solution by a zeolite saturated with a mobile cation that forms an insol. compound with the anion in solution, provided that this is more sol. than the resultant zeolite. Thus a zeolite saturated with a Pb salt will entirely remove Na_2CrO_4 or K_2CO_3 from aq. solution, PbCrO_4 or PbCO_3 being pptd. in the interstices of the zeolite. Conversely a Na zeolite, mixed with the correct amount of powdered $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, on lixiviation with H_2O yields an almost theoretical amount of Na_2SO_4 . It is impossible to extract Na_2CO_3 by lixiviating with H_2O a mixture of a Na zeolite and CaCO_3 , as CaCO_3 is less sol. than the resultant Ca zeolite.

C. A. SILBERRAD.

Compounds of higher valency in the rare earths. I. Lanthanum oxide. G. JANTSCH and E. WIESENBERGER (Monatsh., 1932, 60, 1—7).—Contrary to Kolthoff and Elmquist (A., 1931, 702) no appreciable increase in wt. is observed when La_2O_3 is heated at 1000—1300° in dry O_2 or air or in moist air. When a Pt boat is used slight adsorption of Pt by the oxide occurs.

H. A. PIGGOTT.

Anhydrous chlorides of the cerium group metals. P. BRAUMAN and S. TAKVORIAN (Compt. rend., 1932, 194, 1579—1580).—Excess of aq. NaOBz ppts. a neutral or slightly acid solution of a salt of La, Nd, Sm, etc. completely as $\text{M}(\text{OBz})_3 \cdot 3\text{H}_2\text{O}$, which is completely dehydrated at 110°. The anhyd. benzoate is treated with dry Et_2O saturated with HCl, the product washed with Et_2O , and treated with HCl at 60° and finally with dry air. The pure anhyd. chloride MCl_3 results.

C. A. SILBERRAD.

Germanium. IX. Germanates of alkali and alkaline-earth metals. R. SCHWARZ and F. HEINRICH (Z. anorg. Chem., 1932, 205, 43—48; cf. this vol., 117).—M.-p. curves of the systems $\text{Na}_2\text{O}-\text{GeO}_2$ and $\text{K}_2\text{O}-\text{GeO}_2$ indicate the existence of the following compounds (m. p. in parentheses): Na_2GeO_3 (1083°), $\text{Na}_2\text{Ge}_2\text{O}_5$ (799°), *Na tetragermanate* $\text{Na}_6\text{Ge}_4\text{O}_9$ (1052°); K_2GeO_3 (842°), $\text{K}_2\text{Ge}_2\text{O}_5$ (797°), $\text{K}_2\text{Ge}_4\text{O}_9$ (1038°). Each pair of salts forms a eutectic. Li_2GeO_3 forms no hydrate, Na_2GeO_3 a hexa- and hepta-hydrate. SrGeO_3 (anhyd.) and BaGeO_3 ($4\text{H}_2\text{O}$ and $5\text{H}_2\text{O}$) can be obtained cryst. from aq. solution, but not metagermanates of K, Mg, and Ca. F. L. USHER.

Influence of fusible reaction products or of pre-formed eutectics on the extent of interaction in mixed powders. J. A. HEDVALL and I. BERGSTRAND (Z. anorg. Chem., 1932, 205, 251—256; cf. A., 1931, 803).—The reaction between solid PbCl_2 and CaO is not appreciably influenced by small quantities of the fused reaction products or of an added fusible substance, but is considerably increased by quantities of the order of 40%. If the eutectic in question (e.g., $\text{PbCl}_2-\text{AgCl}$) is previously formed the effect is much more pronounced. F. L. USHER.

Mechanism of precipitation processes. IX. Reaction between lead bromide and sulphide

ions. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1932, 205, 268—272; cf. A., 1931, 323).—The reaction $2\text{PbBr}^+ + \text{S}^{2-} = \text{Pb}_2\text{Br}_2\text{S}$ occurs to a considerable extent when solutions of PbBr_2 and Na_2S are mixed. The amount of $\text{Pb}_2\text{Br}_2\text{S}$ in the ppt. decreases with time, and its formation is repressed by dilution, by increasing $[\text{H}^+]$ (except with HBr), by increasing the ratio $\text{Na}_2\text{S} : \text{PbBr}_2$, or by carrying out the pptn. more slowly. $\text{Pb}_2\text{Br}_2\text{S}$ is a red cryst. substance, stable at 70—80°, and is sol. in H_2O at 20° to the extent of 3.5×10^{-5} mol. per litre.

F. L. USHER.

Thorium nitride. Determination of nitrogen in incombustible inorganic substances. W. DUSING and M. HUNIGER (Tech. wiss. Abh. Osram-Konz., 1931, 2, 357—365; Chem. Zentr., 1932, i, 203—204).—By decomp. of Th halide at a glowing W wire in N_2 small quantities of a nitride having low electrical conductivity are formed. Compressed ThO_2 , graphite, and W are electrically heated at 2220—2600° in a non-oxidising atm. containing N_2 ; black crystals of Th_3N_4 are formed. In presence of traces of O_2 the crystals are coloured yellow or red owing to the presence of ThO_2 . For analysis the substance is melted in a Pt boat with $\text{Na}_2\text{S}_2\text{O}_7$ and the N_2 collected over alkaline pyrogallol solution.

A. A. ELDRIDGE.

Mechanism of the reaction between persulphate and iodide ions. A. VON KISS and I. BOS-SANYI (Rec. trav. chim., 1932, 51, 434—444; cf. A., 1929, 772).—A reply to criticisms by King and Jette and by Oostveen (A., 1929, 771, 1016). Earlier work has been repeated and its accuracy is confirmed.

F. L. USHER.

Selenites of sodium and potassium. J. JANITZKI (Z. anorg. Chem., 1932, 205, 49—76).—Solubilities of normal and acid selenites of Na and K have been determined, and the composition of the salts and their hydrates has been established by analysis. The hydrates $\text{Na}_2\text{SeO}_3 \cdot 8\text{H}_2\text{O}$, $\text{NaHSeO}_3 \cdot 3\text{H}_2\text{O}$, and $\text{K}_2\text{SeO}_3 \cdot 4\text{H}_2\text{O}$ have been prepared. MHSeO_3 and M_2SeO_5 are interconvertible in aq. solutions containing $\text{M}_2\text{O} + 2\text{SeO}_2$, whereas those containing $\text{M}_2\text{O} + 4\text{SeO}_2$ yield $\text{MH}_2(\text{SO}_3)_2$ only. The p_H of 0.05 or 0.1N solutions of all the salts has been determined. Na_2SeO_3 is hydrolysed about 0.1% at 0.1N concn.

F. L. USHER.

Oxidation of chromium hydroxide and chromite by atmospheric oxygen in presence of alkali. V. V. IPATIEV, jun., and M. N. PLATONOVA (Ber., 1932, 65, [B], 572—575).—Oxidation of $\text{Cr}(\text{OH})_3$ by air at 300°/100 atm. is quant. after 18 hr. in presence of sufficient KOH to give K_2CrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$. The change occurs also in presence of K_2CrO_4 solution. Diminution of temp. delays the reaction, which does not occur in absence of O_2 pressure. The rate of reaction decreases rapidly with fall in OH^- concn. Finely-divided chromite is oxidised more slowly than $\text{Cr}(\text{OH})_3$. Reaction does not occur in K_2CrO_4 solution. It is hastened by elevated temp. and an excess of alkali. 60% of the available Cr can be oxidised.

H. WREN.

Complex cyanide of tervalent molybdenum. R. C. YOUNG (J. Amer. Chem. Soc., 1932, 54, 1402—

1405).—The interaction of K_3MoCl_6 and KCN at room temp. in an atm. of N_2 gives the black compound $K_4Mo(CN)_7 \cdot 2H_2O$. B. A. SOULE (c).

Oxygen compounds containing fluorine. II. H. SEIFERT (Z. Krist., 1932, 82, 15—30; cf. this vol., 449).—Some more complicated "double salts," e.g., $(NH_4)_2MoOF_5$, $(NH_4)_3MoO_2F_5$, $K_5U_2O_4F_9$, etc., and minerals such as the humite-chondrodite series, are discussed on similar lines. Certain other compounds are shown to be "false," i.e., the F is not directly connected with the central atom, e.g., $R_3HS_2O_7F_3 \cdot H_2O$ (R—K, Rb, Cs) (cf. A., 1899, ii, 594), which are really only $2RHSO_4 \cdot RF \cdot HF$. C. A. SILBERRAD.

Chlorine hydrate. S. ANWAR-ULLAH (J.C.S., 1932, 1172—1176).—Under different conditions of temp., pressure, and concn. of the constituents, Cl hydrate has the composition $Cl_2 \cdot 6H_2O$. The higher hydrates previously recorded probably indicate incomplete reaction or imperfect drying.

E. S. HEDGES.

Bromine chloride hydrate. S. ANWAR-ULLAH (J.C.S., 1932, 1176—1179).—Cryst. $BrCl_4 \cdot 4H_2O$ is obtained by passing Cl_2 into Br under a layer of H_2O at temp. below 18° . It is more stable than the hydrates of Cl_2 or Br. The solubility of Br in H_2O is considerably enhanced by the presence of Cl_2 .

E. S. HEDGES.

[Reactions of iodine.] E. ABEL (Z. physikal. Chem., 1932, 159, 414).—Polemical against Angelescu and Popescu (A., 1931, 1369, 1372). R. CUTHILL.

Dehydration of salts with organic liquids. J. G. F. DRUCE (Chem. News, 1932, 144, 199—200).—By distilling PhMe over $MnSO_4 \cdot 4H_2O$ the salt was converted into the monohydrate. With $PhNO_2$ or a saturated hydrocarbon oil of b. p. 190 — 195° dehydration was carried a stage further and the anhyd. salt was formed. Both $MnSO_4 \cdot 4H_2O$ and $CuSO_4 \cdot 5H_2O$ could be completely dehydrated by warming with Ac_2O without having recourse to distillation (cf. Stephen, A., 1931, 182).

A. B. MANNING.

Highest oxide of rhenium. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (Nature, 1932, 129, 618).—Evidence that Re_2O_7 is the highest oxide of Re stable under ordinary conditions is advanced. The m. p. of Re_2O_7 is lowered by traces of H_2O and a specimen of m. p. approx. 150° gave a white sublimate without an increase in wt. $KMnO_4$ was not decolorised by any sublimates from Re_2O_7 (cf. A., 1929, 411). L. S. THEOBALD.

Rhenium oxychloride. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (J.C.S., 1932, 1104—1107).— ReO_2Cl_3 is prepared by heating (a) Re in dry mixtures of air and Cl_2 , (b) $ReCl_4$ in dry O_2 , (c) Re_2O_5 in dry Cl_2 . Method (a) is the most convenient. ReO_2Cl_3 has m. p. $23.9+0.2^\circ$; the liquid has d_{25}^{35} 3.359 and vaporises in vac. below 300° . It is decomposed by H_2O . E. S. HEDGES.

Thermite reaction with rhenium dioxide. J. G. F. DRUCE (Chem. News, 1932, 144, 247).—A mixture of ReO_2 and Al, ignited by means of a Mg fuse, yields Al_2O_3 and amorphous Re, which may be separated by treatment with HCl; fused Re could not

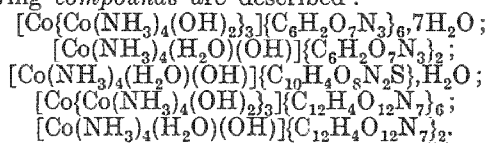
be obtained by this method. The product closely resembles that formed by reduction of ReS_2 by H_2 .

H. F. GILLBE.

Hydroxides and carbonates of metals. I. Ferric hydroxide. A. V. RAKOVSKI. **II. Chromic hydroxide.** A. V. RAKOVSKI and T. POLJANSKI (Trans. Inst. Pure Chem. Reag. U.S.S.R., 1931, No. 12, 3—10, 11—16).—I. The compositions of $Fe_2O_3 + H_2O$ gels prepared and dried under different conditions are given. Gels obtained by pptg. Fe^{+++} salts with alkali hydroxide or carbonate always contain CO_2 (up to 3%), which varies in amount with the H_2O present. Admixed SO_4^{--} , Cl' , etc. cannot be washed out of the gels but may be displaced by CO_3^{--} .

II. Cr hydroxide free from Cl' may be obtained by reducing $Na_2Cr_2O_7$ with CH_3O in presence of HCl, pptg. with NH_3 , and washing with dil. NH_3 and then with H_2O . Preps. made from the sulphate cannot be freed completely from SO_4^{--} . CO_2 is present in all the hydroxides obtained, which may be regarded as Cr carbonates in a dissociated state. Isotherms showing the relation of $(CO_2 + H_2O)$ in the hydroxides to the v. p. of H_2O in the surrounding air reveal hysteresis, which virtually disappears after repeated hydration and dehydration. T. H. POPE.

Ammines. V. Dihydroxotetramminocobaltic hydroxide and its derivatives. H. J. S. KING (J.C.S., 1932, 1275—1281).—The chemical reactions of the hydroxide solution obtained when $[Co(H_2O)_2(NH_3)_4]Cl_3$ is triturated with moist Ag_2O indicate the formula $[Co(NH_3)_4(H_2O)(OH)](OH)_2$ and no solid salts corresponding with a dihydroxotetramminocobaltic series can be isolated, even with acids which usually form very sparingly sol. salts of the type. Electrical conductivity measurements, however, support the formula $[Co(NH_3)_4(OH)_2]OH$. Corresponding salts appear to exist in solution, for concordant vals. for the mobility of $[Co(NH_3)_4(OH)_2]^+$ are obtained in these solutions. The mobilities of $[Co(NH_3)_4(H_2O)(OH)]^{++}$ and $[Co(NH_3)_4(OH)_2]^+$ at 0° are 60.8 and 23.0 mhos, respectively. The following compounds are described:



E. S. HEDGES.

Mode of formation of the cobaltite modification of Rinman's green. J. A. HEDVALL and T. NILSSON (Z. anorg. Chem., 1932, 205, 425—428).—The reaction by which the cobaltite modification of Rinman's green is formed is in accordance with the equation $ZnO + CoO, Co_2O_3 = ZnO, Co_2O_3 + CoO$ and is not an additive reaction between ZnO and Co_2O_3 . The instability of Co_2O_3 , even in O_2 , when heated below 300° is confirmed. Co_3O_4 is stable in air up to 900° , but above this temp. it is dissociated into CoO and O_2 . CoO is readily oxidised to Co_3O_4 . M. S. BURR.

Higher oxides of group VIII elements. Structure of nickel oxide hydrates. D. K. GORALEVITSCH (J. Gen. Chem. Russ., 1931, 1, 973—990).—The compounds $Ni_2O_3 \cdot 3, 4, 5$, and $6H_2O$, and $Ni_3O_4 \cdot 2$,

3, 5, and 6H₂O are formed when Cl₂ or Br is passed through alkaline solutions of Ni(OH)₂. Part of the H₂O of these compounds is constitutional, being eliminable only at temp. >120°, whilst the remainder is H₂O of crystallisation. The above compounds are hydrates of the acids H₄Ni₂O₅, H₄Ni₃O₆, H₂Ni₂O₄, and H₂Ni₃O₅. The relative proportions of these compounds in the product depend on the relative concn. of Ni(OH)₂ and Ni(OH)₃ at the moment of action of NaOBr or NaOCl. The structural formulæ of the above acids and of certain of their salts are discussed.

R. TRUSZKOWSKI.

Improved method of quantitative spectrographic analysis. C. C. NITCHIE and G. W. STANDEN (Ind. Eng. Chem. [Anal.], 1932, 4, 182—185; cf. A., 1929, 412).—The element is determined by measuring the intensity of one of its spectrum lines and comparing with the intensity of another line in the same spectrum due to another constituent known to be present in const. amount in all the samples. A recording microphotometer for measuring the intensities has been constructed. The max. deviation of the analyses from the mean is about 5% in the determination of 0.01% of Mg in an alloy, the chief error being connected with the excitation of the spectra.

E. S. HEDGES.

Molecular spectra and spectroscopic analysis. G. PICCARDI (Atti R. Accad. Lincei, 1931, [vi], 14, 578—582).—The usefulness of band spectra in qual. and quant. spectroscopic analysis is discussed.

O. J. WALKER.

Sensitivity of atomic analysis by X-rays. C. E. EDDY and T. H. LABY (Proc. Roy. Soc., 1932, A, 135, 637—656).—It is confirmed that a sensitivity of 1 or even 0.1 p.p.m. of a metallic element in an alloy can be obtained by at. analysis by X-ray spectroscopy (A., 1929, 867), but the sensitivity is greatly reduced when a poor vac. exists in the X-ray tube and when scattered radiation reaches the photographic plate. The conditions influencing the sensitivity are discussed. Although theoretically the sensitivity for an element of low at. no. alloyed with one of high at. no. should be less than that of the reverse case, 1 part of 29 Cu can be detected in 10⁶ parts of 82 Pb. For equiv. conditions of excitation the lines in the K series are approx. 20 times as intense as the L series. L lines due to 0.002% of 83 Bi in 50 Sn have, however, been observed. The X-ray method appears to be superior to the optical and chemical methods for the analysis of alloys.

L. L. BIRCUNSHAW.

Modern micro-chemical methods. K. JOSEPHSON (Svensk Kem. Tidskr., 1932, 44, 98—115).—A review.

Polarographic studies with the dropping mercury cathode. XXV. Increased sensitivity of micro-analytical determinations by compensation of current. D. ILKOVIČ and G. SEMERANO (Coll. Czech. Chem. Comm., 1932, 4, 176—180).—By compensating for the current required for charging the repeatedly renewed surface of the dropping Hg cathode, the sensitivity of polarographic analyses of electro-reducible substances has been increased 10-fold. A suitable circuit is described. In general, 5 × 10⁻⁷ g.-equiv. of reducible substance per litre,

i.e., 10⁻⁹ to 10⁻⁸ g. in the 0.2 c.c. of solution required, may be detected.

H. F. GILLBE.

Electrometric determination of p_H. H. D. VAN OORT (Intern. Sugar J., 1932, 34, 95—98).—Using the automatic H electrode apparatus for recording p_H (B., 1932, 431), a lightly platinised electrode was rapidly affected by As₂O₃, but buffer solutions to which brucine sulphate, indigo-carmin, KCN, KCNS, and Na₂S had been added failed to show any distinct poisoning effect. The nature of the poisoning observed in the case of beet juice was not ascertained.

J. P. OGILVIE.

Hydrogen effect as a source of error in p_H measurements. L. WOLF, (FRL.) L. P. USPENSKAJA, and K. ASKITOPOULOS (Naturwiss., 1932, 20, 297).—The H effect depends on the size of the electrode. p_H measurements on M/30-phosphate N-KCl and on M/120-Na₂HPO₄+N-KCl are given.

W. R. ANGUS.

Electrometric determination of the p_H using an antimony electrode. M. CATENACCI (L'Ind. sacc. Ital., 1931, 24, No. 8; Int. Sugar J., 1932, 34, 185).—An Sb electrode consists of a rod of the metal sealed into one end of a piece of glass tubing filled with Hg, and a wire connecting the Hg with the Hg₂Cl₂ cell. It functions at any p_H, and is unaffected by the presence of NH₃, SO₂, protein, and colloidal substances as found in sugar-factory products. Equilibrium is quickly established, and it gives results sufficiently accurate for technical work.

J. P. OGILVIE.

p_H chart. G. H. BELL and A. R. C. PATERSON (Biochem. J., 1932, 26, 454—457).—A chart is constructed to facilitate calculations on the measurement of p_H by the H electrode from p_H 1.5 to 12.0 at 18—25°.

S. S. ZILVA.

Bimetallic electrodes with nichrome in potentiometric acidimetry. A. MAZZUCHELLI (Gazzetta, 1932, 62, 265—270).—Nichrome and Pt in presence of a little H₂O₂ form a satisfactory pair of electrodes for potentiometric acidimetry. The p.d. across the electrodes is measured by means of a triode valve potentiometer.

O. J. WALKER.

Use of metallic electrodes as indicators. S. J. FRENCH and J. M. HAMILTON (Proc. Indiana Acad. Sci., 1931, 40, 171—174).—A review. In the titration of HCl, HNO₃, and H₂SO₄ the pair Al/Rose-metal gives accurate results.

CHEMICAL ABSTRACTS.

Sinalbin as an indicator. K. HARRISON (Biochem. J., 1932, 26, 88—89).—The glucoside of white mustard seeds (0.5% in 30% EtOH) is a suitable indicator for titration of weak acids and bases. The p_H range is 6.2 (colourless)—8.4 (yellow). Salt and protein errors are small.

A. COHEN.

Indicators. I. 2:6-Dinitrophenol. I. V. KULIKOV and S. V. PANOVA. II. Iodoeosin. I. V. KULIKOV and A. G. PUKIREV (Biochem. Z., 1932, 246, 87—96, 97—103).—I.—A method is described for nitration of o-nitrophenol in AcOH and H₂SO₄, the method giving 30—35% of 2:6-dinitrophenol. II.—The I content of iodoeosin is determined by fusion with NaOH+NaNO₃ and the iodate reduced with H₂SO₃. Iodoeosin from different sources

shows somewhat different degrees of iodination, but this does not affect its use as an indicator.

P. W. CLUTTERBUCK.

Micro-determination of water in coal and other solid materials. F. VETTER.—See B., 1932, 403.

Potentiometric determination of bromine, and octovalent and quadrivalent osmium in hydrobromic acid solutions. II. W. R. CROWELL (J. Amer. Chem. Soc., 1932, 54, 1324—1328; cf. A., 1929, 1029).—By heating Os^{VIII} at 100° in the presence of approx. 8*N*-HBr in a sealed tube, it becomes quadrivalent; an equiv. quantity of Br is liberated, and can be titrated potentiometrically with aq. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$. Similar treatment in approx. 0.1*N*-HBr causes complete oxidation of Os^{IV} to Os^{VIII} , and the excess of Br after heating measures the Os content. Because of its greater stability, N_2H_4 is better than TiCl_3 for titrating Br solutions.

W. T. HALL (c).

Calcium fluoride method for determination of fluoride, with special reference to analysis of nickel-plating solutions. S. G. CLARKE and W. N. BRADSHAW.—See B., 1932, 382.

Determination of fluorine. P. MOUGNAUD (Compt. rend., 1932, 194, 1507—1509; cf. this vol., 33).—Accurate determination of F as CaF_2 is possible by using excess of CaCl_2 and centrifuging with the min. quantity of H_2O . Thus a solution containing about 0.4 g. of KF is evaporated to 5 c.c., 4 c.c. of half-saturated aq. CaCl_2 are added, and the mixture is centrifuged and decanted, boiled twice with 5 c.c. of saturated aq. CaF_2 , and centrifuged, and the process repeated four times with 5 c.c. of H_2O . The loss in 7 experiments varied from 0.15 to 0.95%, average 0.51%.

C. A. SILBERRAD.

Detection of minute amounts of sulphur dioxide. J. BOUGAULT and E. CATTELAÏN (Ann. Falsif., 1932, 25, 138—140).—Paper impregnated with 0.5% starch solution and dried at 30° is moistened with 1—2 drops of 0.1% KI (iodate-free) and coloured blue by suspension over 0.1*N*-I for 5—10 sec. Food products (wines, ketchup, sausages, etc.) are tested directly by acidifying with dil. H_3PO_4 20 c.c. or g. in a stoppered flask and suspending the blue paper from the stopper. Decolorisation is effected in 5 min. by as little as 0.00002 g. of SO_2 in 10 c.c.

H. R. JENSEN.

Standards for, and standard methods of analysing, sulphuric, hydrochloric, and nitric acids. E. S. PRSHEVALSKI, A. V. FROST, and T. N. KARSKAJA (Trans. Inst. Pure Chem. Reag. U.S.S.R., 1931, No. 12, 49—69).—Max. limits are given for the proportions of the different impurities allowed in "pure," "chemically pure," and "pure for analysis" H_2SO_4 , HCl , and HNO_3 . Methods are given for the determination of the impurities, and the results of analysis of many brands of each acid. In HCl 0.0002% and in HNO_3 0.0004% of SO_4 , in HNO_3 0.00003% and in H_2SO_4 0.0001% of Cl , are detectable. For detecting HNO_3 in H_2SO_4 , the NHPh_2 reaction as described by Treadwell is suitable; for small proportions, the FeSO_4 reaction is better. Determination of Fe by the

thiocyanate method becomes more sensitive in presence of amyl alcohol. By Hefti's modification of the Gutzeit method, 0.000002% As may be detected in acids.

T. H. POPE.

Determination of sulphuric acid in presence of chromium salts by titration with alkali. B. I. LEONOV (J. Gen. Chem. Russ., 1931, 1, 1026—1034).—5 drops of 2% Na_2HPO_4 are added to the solution, containing H_2SO_4 and $\text{Cr}_2(\text{SO}_4)_3$, and 0.1*N*-NaOH is added to the appearance of the Tyndall effect due to separation of CrPO_4 . An error of $> 2\%$ is obtained when the $\text{Cr}_2(\text{SO}_4)_3$ content is > 2 g.

R. TRUSZKOWSKI.

Acidimetric determination of persulphates with and without catalysts. J. H. VAN DER MEULEN (Rec. trav. chim., 1932, 51, 445—451).—Solutions of persulphates are completely decomposed by boiling for 3—5 min. with excess of H_2O_2 , and the resulting M^+HSO_4 can be titrated with alkali. The reaction is accelerated by addition of AgNO_3 and/or MnSO_4 . The use of H_2O_2 entirely prevents oxidation of NH_3 when the NH_4^+ salt is used.

F. L. USHER.

Determination of ammonia without distillation. P. SORS (Chem.-Ztg., 1932, 56, 156).— NH_3 can be rapidly determined in solutions of NH_4 salts free from heavy metals by neutralisation with NaOH (Me-orange or *p*-nitrophenol), addition of a measured excess of NaOH, expulsion of the NH_3 by boiling, and titration of the excess NaOH.

A. R. POWELL.

Detection of nitrous oxides and iron in sulphuric acid. L. W. MARRISON.—See B., 1932, 419.

Micro-determination of phosphoric acid with strychnine molybdate. H. KLEINMANN (Mikrochem., 1932, 11, 139).—A reply to Rautenberg (this vol., 354).

F. L. USHER.

Reactions between certain metallic ions and ammonium aurintricarboxylate. J. H. YOE (J. Amer. Chem. Soc., 1932, 54, 1022—1023).—Reactions of As^{III} , Nb^{II} , Dy^{III} , Gd^{III} , Hf^{IV} , Ir^{IV} , Mo^{V} , Pr^{III} , Re , Rh^{III} , Ru^{III} , Sm^{III} , Ta^{V} , Te^{VI} , Tm^{III} , W^{VI} , $(\text{UO}_2)^{\text{II}}$, V^{II} , and Y^{III} with "aluminon" are described. None of these interferes with the detection of Al by the reagent.

R. H. CHERRY (c).

Titration of boric acid. J. C. KRANTZ, jun., and C. J. CARR (J. Amer. Pharm. Assoc., 1932, 21, 350—353).—Various methods of titration have been examined. The following modification of the U.S.P. method given by the Pacific Coast Borax Co. is the most accurate. A solution of 1.25 g. of boric acid in 25 c.c. of H_2O and 25 c.c. of glycerol (p_H of mixture 3.1) is titrated with *N*-NaOH, using phenolphthalein, and after the appearance of the pink colour this is discharged by the addition of a further 25 c.c. of glycerol (p_H of mixture 7.5) and the titration continued until the pink is restored (p_H 8.3). Theoretical results are obtained. The probable error of a single determination is 0.19%.

E. H. SHARPLES.

Use of fused sodium hydroxide in analytical chemistry. O. BRUNCK and R. HOLTJE (Angew. Chem., 1932, 45, 331—334).—The technique of fusion with NaOH is discussed with special reference

to the analysis of silicates, TiO_2 , titanates, corundum, aluminates, bauxite, monazite, tungstates, chrome ironstone, W, W-rich alloys, and cassiterite.

E. S. HEDGES.

Determination of silica in volcanic tufa. A. STEPOPOE (Bul. Chim. pura appl., Bukarest, 1931, 33, 11—17; Chem. Zentr., 1932, i, 845).—Results of the determination of sol. SiO_2 by means of alkali depend on the dispersion, time, concn., etc.

A. A. ELDRIDGE.

Analysis of compounds containing silica and alumina. J. DELFORGE (Bull. Soc. chim. Belg., 1932, 41, 95—97; cf. B., 1931, 491).—A reply to criticisms by Delfeld (B., 1931, 1091). In the separation of Ti and Fe, it is advantageous to reduce the latter with H_2S rather than with SO_2 .

F. L. USHER.

Carbonate content of volumetric sodium hydroxide solutions. J. E. S. HAN and T. Y. CHAO (Ind. Eng. Chem. [Anal.], 1932, 4, 229—232).—The methods of freeing "oil lye" and volumetric NaOH solutions from Na_2CO_3 have been investigated by determining the minute amount of Na_2CO_3 left in the solutions after the addition of various precipitants. $\text{Ba}(\text{OH})_2$ and Ba salts were found to be the best precipitants. The technique of Warder's differential titration method has been improved.

E. S. HEDGES.

Sensitive reaction for cyanates, especially in presence of cyanides. M. LINHARD and M. STEPHAN (Z. anal. Chem., 1932, 88, 16—23).—The solution containing CNO' in presence of CN' is pptd. with AgNO_3 . The filtered and dried ppt. is suspended in Et_2O and cyclohexene added with sufficient I to colour it. The 2-iodocyclohexylcarbimide (I) formed may be recognised by its pungent odour and the fact that it forms with NH_3 a white, flocculent ppt. of (I) consisting of very fine crystals. If the amount of CNO' is very small the ppt. appears only after a few min. as fine colourless needles. The test is unaffected by most inorg. ions. In the presence of CN' ICN is formed and this also gives a pungent additive compound with cyclohexene, so that the ppt. with NH_3 is necessary for distinguishing CNO' . The sensitivity of the method in aq. solution is determined by the solubility of AgCNO . 1 mg. of KCNO in 100 c.c. of H_2O gives no ppt. with AgNO_3 , but 3 mg. give a turbidity which results in an easily recognisable ppt. of (I).

M. S. BURR.

Analysis of helium without the aid of liquid air. A. CHEREPENNIKOV (Prirodn. Gaz., 1931, 2, 83—90).—Charcoal cooled by means of solid CO_2 is employed.

CHEMICAL ABSTRACTS.

Indirect volumetric determination of sodium based on reduction and titration of uranium in magnesium sodium uranyl acetate. N. H. FURMAN, E. R. CALEY, and I. C. SCHOONOVER (J. Amer. Chem. Soc., 1932, 54, 1344—1349).—The $\text{NaMg}(\text{UO}_2)_3(\text{OAc})_9 \cdot 6 \cdot 5\text{H}_2\text{O}$ is dissolved in 2% H_2SO_4 and reduced in a Jones reductor, then stirred for 5 min. while a rapid stream of air is passed through it to oxidise U^{III} to U^{IV} . After adding approx. 0.2N- $\text{Ce}(\text{SO}_4)_2$ and stirring vigorously for 5 min. the excess of $\text{Ce}(\text{SO}_4)_2$ is titrated potentiometrically with standard FeSO_4 solution. Instead of $\text{Ce}(\text{SO}_4)_2$, KMnO_4

can be used. 10 mg. or less of Na may be determined with an error of <0.1 mg. W. T. HALL (c).

Detection of beryllium in minerals. G. RIE-NACKER (Z. anal. Chem., 1932, 88, 29—38).—The sensitivity of Fischer's quinalizarin test for Be (A., 1927, 36; 1928, 385) has been confirmed. The test is unaffected by the presence of Al_2O_3 , SiO_2 , or TiO_2 , but Fe and Mg must be absent. Fe and Mg may be removed as hydroxides, without taking with them any adsorbed $\text{Be}(\text{OH})_2$, by fusing the mineral with NaOH, dissolving out the beryllate by treatment with ice, filtering, and washing the residue of $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, etc. The alkalinity of the filtrate is reduced to approx. 0.33N-NaOH by partial neutralisation with H_2SO_4 . A few drops of an alcoholic quinalizarin solution give the characteristic cornflower-blue coloration. A determination of the order of magnitude of the Be content may be obtained by diluting to the sensitivity limit. Direct colorimetric determination cannot be made. 0.01% Be may be recognised in 0.1 g. of mineral.

M. S. BURR.

Determination of beryllium. L. FRESSENIUS and M. FROMMES.—See B., 1932, 429.

Determination of beryllium in alloys. H. ECKSTEIN.—See B., 1932, 427.

Colour reactions for magnesium. N. A. TANANAEV (Z. anal. Chem., 1932, 88, 93—94).—Two colour reactions with test-papers are described, by one of which 0.006 mg. of Mg in 0.005 c.c. can be detected.

F. L. USHER.

Analysis of limestone. M. I. BLINOVA (Udobr. Urozhai, 1931, 3, 754—760).—Accurate results are obtained either by titration or by volumetric determination of CO_2 evolved. A modified Schübler calcimeter is described.

CHEMICAL ABSTRACTS.

Determination of calcium carbide in calcium cyanamide by means of cuprous acetylide. F. TROST.—See B., 1932, 420.

Determination of the hardness of water. J. LEICK.—See B., 1932, 450.

Determination of calcium, and its separation from magnesium by means of sodium tungstate. D. KATAKOUSINOS (Praktika, 1931, 4, 404; Chem. Zentr., 1932, i, 844).—Excess of Na_2WO_4 does not affect the result when the solution is hot, contains NH_4Cl , and is alkaline with NH_3 ; sufficient Na_2WO_4 must be added to make the reaction quant. The white ppt. is CaWO_4 ; the difference in wt. in two or more determinations is ± 0.004 g. A. A. ELDRIDGE.

Separation and determination of calcium and magnesium. 8-Hydroxyquinoline-saccharate method. A. C. SHEAD and R. K. VALLA (Ind. Eng. Chem. [Anal.], 1932, 4, 246).—Ca is pptd. as oxalate and Mg as the 8-hydroxyquinoline compound simultaneously. The mixed ppts. are ignited to the oxides and when in the freshly-ignited state are treated with 30% saccharate solution. CaO dissolves and MgO is insol.

E. S. HEDGES.

Determination of barium in ferriferous minerals. E. CHAUVENET and P. AVRARD (Compt. rend., 1932, 194, 1164—1166).— CCl_4 is passed over the mineral (about 1 g.) at 450° ; after about 30 min.

all Al and most of the Fe are removed as AlCl_3 and FeCl_3 , which mostly dissolve in condensed CCl_4 ; a further 2 hr. is required to convert into chlorides Ca, Mg, most of the Mn, and Ba present as BaCO_3 with a little as BaSO_4 . These are dissolved out, leaving the silicates, SiO_2 , BaSO_4 , and a little Fe as oxychloride. The amount of chlorides in solution is insufficiently appreciable to dissolve the BaSO_4 . This residue is fused with alkali and extracted with HCl , and the residue again treated with CCl_4 , which removes the Fe and Al which were in the silicates, and chlorinates any Mn and some more Ba. From the residue the Fe oxychloride is removed by aqua regia, and the insol. portion (BaSO_4 and SiO_2) treated with aq. HF .

C. A. SILBERRAD.

Methyl-red as an adsorption indicator. G. BATCHELDER and V. W. MELOCHE (J. Amer. Chem. Soc., 1932, 54, 1319—1323; cf. A., 1931, 925).— Na_2SO_4 solution cannot be successfully titrated with BaCl_2 in presence of Me-red, for the change from yellow to red at the equiv. point is not sufficiently sharp. Before the equiv. point is reached, the BaSO_4 tends to adsorb SO_4^{--} , but as soon as a slight excess of Ba^{++} has been added, Ba^{++} ions are adsorbed and tend to drag down OH^- rather than the negative dye ions, thus lowering the p_{H} .

W. T. HALL (c).

Determination of barium as chromate. LEMARCHANDS and SIROT (Compt. rend., 1932, 194, 1577—1579; cf. A., 1908, ii, 133; 1927, 223).—At 100° BaCrO_4 is sol. in H_2O to the extent of 11.81 mg. per litre, giving a solution $0.465 \times 10^{-4}N$. In aq. KCl as the concn. of KCl rises from 0.333*N* to 1.275*N* that of BaCrO_4 rises from $0.8415 \times 10^{-4}N$ to $9.73 \times 10^{-4}N$, giving for K ($=[\text{K}_2\text{CrO}_4][\text{BaCl}_2]/[\text{BaCrO}_4][\text{KCl}]$) 1.24×10^{-6} ; the activity coeff. of KCl falls from 1.08 for 0.333*N* to 0.873 for 1.275*N*.

C. A. SILBERRAD.

Determination of lead peroxide. III. A. V. PAMFILOV and (MISS) E. G. IVANCEVA (Z. anal. Chem., 1932, 88, 23—29).—Determination of PbO_2 by reducing with an alkaline solution of As_2O_3 and titrating the excess of As_2O_3 gives too high results. By using an acid solution of As_2O_3 and titrating the excess with NaBrO_3 , either by a simple potentiometric method or by the use of indicators such as indigo-carmin, the results approach in accuracy those obtained by the standard American method in which I is liberated from KI and titrated with $\text{Na}_2\text{S}_2\text{O}_3$, and the materials employed are considerably cheaper.

M. S. BURR.

Determination of lead in minerals. (Radioactive indicators in analytical chemistry.) G. VON HEVESY and R. HOBBIÉ (Z. anal. Chem., 1932, 88, 1—6).—Small quantities of Pb in minerals are determined by removing SiO_2 by HF , pptg. the sulphates, transforming into acetates, adding Ag_2SO_4 to both the acetate solution and the sulphate filtrate, pptg. Ag_2S and PbS together with H_2S , filtering, and dissolving in conc. HNO_3 . Sulphates are formed by oxidation and the solution is evaporated to dryness. The residue is dissolved in 0.001*N*- HNO_3 , carbamide added, and the solution electrolysed with an e.m.f. of 2 volts. PbO_2 is deposited on the Pt anode and weighed. Radioactive control of the completeness of the pptn. is exercised by adding a known quantity

of Ra-D before pptn. of the sulphides and comparing the activity of this with the activity of the final product, after correcting for the absorption of radiation by the PbO_2 deposit. If less Ra-D is pptd. than was originally added the deficiency represents the relative amount of Pb in the mineral which has not been deposited and a correction can be applied. The amount of pure PbO_2 present in the electrolytic deposit may be checked by a colorimetric method, using the reaction with $\text{CH}_3(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$.

M. S. BURR.

Determination of small quantities of thallium in presence of lead and bismuth. F. PAVELKA and H. MORTH (Mikrochem., 1932, 11, 30—33).—When a solution of a Tl salt ($2\text{--}10 \times 10^{-5}$ g. per c.c. as Tl^+) is treated with excess of phosphomolybdic acid Pb and Bi form sol. compounds, whilst Tl forms a yellow hydrosol the turbidity of which is compared with that of a standard. K and NH_4 compounds must be absent.

F. L. USHER.

Argentometric determination of thallium. M. V. TROITZKI (J. Gen. Chem. Russ., 1931, 1, 1083—1085).—0.4 g. of Tl^+ salt (sol. or insol.) is treated with 50 c.c. of 0.1*N*- AgNO_3 , 5 c.c. of 2*N*- HCl , and 10 c.c. of 15% NaOH , and the mixture is heated during 30 min. at 100° in absence of light. It is then filtered, and the washed residue of Ag, AgCl , and $\text{Tl}(\text{OH})_3$ is treated with 2 c.c. of conc. HNO_3 at 100° , whereby Ag and $\text{Tl}(\text{OH})_3$ are dissolved. The solution is diluted to 50 c.c., and AgNO_3 is determined by titration with NH_4CNS , when the no. of c.c. of 0.1*N*- NH_4CNS multiplied by 0.01022 gives the Tl^+ content in g. For the micro-determination of Tl^+ , 2 c.c. of solution, containing >5 mg. of Tl^+ , are treated with 1 c.c. of 0.1*N*- AgNO_3 , 2 c.c. of 0.1*N*- HCl , and 1 c.c. of *N*- NaOH , and the mixture is treated further as in the macro-method, substituting centrifuging for filtration, and taking 3 drops of HNO_3 in place of 2 c.c. An accuracy of 99.3—100.16% is obtained with the macro- and of 98.7—103.1% with the micro-method.

R. TRUSZKOWSKI.

Determination of thallium, using hypiodite. M. V. TROITZKI (J. Gen. Chem. Russ., 1931, 1, 1086—1088).—A solution of 0.1—0.5 g. of Tl^+ salt in 20—30 c.c. of H_2O is mixed with 25 c.c. of 0.1*N*-I, and 15% NaOH is added until the solution has a light yellow colour, when it is diluted to 100 c.c. After 15 min., the solution is filtered, and I, liberated by addition of dil. HCl , is determined in 50 c.c. of the filtrate. The Tl^+ content is calc. according to the equation $\text{TlNO}_3 + 2\text{I} + 3\text{NaOH} \rightarrow \text{Tl}(\text{OH})_3 + \text{NaNO}_3 + 2\text{NaI}$.

R. TRUSZKOWSKI.

Determination of copper. Clarke and Jones' method. L. C. HURD and J. S. CHAMBERS (Ind. Eng. Chem. [Anal.], 1932, 4, 236—238).—The method (A., 1929, 900) is suitable only under carefully controlled conditions and is not recommended for general use. If the method is used, the prep. of a series of colour standards of KMnO_4 is suggested.

E. S. HEDGES.

Determination of copper in presence of iron with salicylaldoxime. W. REIF (Z. anal. Chem., 1932, 88, 38—40).—Practically the same method is used as in the micro-determination of Cu (A., 1931,

927), but, in order to prevent pptn. of Fe, tartaric acid is first added to the acid solution and then aq. NH_3 until the solution is green, due to the mixture of the blue ammoniacal Cu and the yellow Fe tartrate complex. Saturated aq. NH_4OAc is then added drop by drop until the green colour disappears. Salicylaldoxime solution, prepared by Ephraim's method (A., 1930, 1393), is added in slight excess, and, after leaving for 20–30 min., the ppt. is collected on a sintered glass plate, dried at 105° , and weighed as $(\text{C}_7\text{H}_6\text{O}_2\text{N})_2\text{Cu}$. M. S. BURR.

Electrolytic micro-determination of copper in ammoniacal solution. A. OKAC (Z. anal. Chem., 1932, 88, 108–119).—The Cu compound, containing 0.2–5.0 mg. Cu, is dissolved in 6–7 c.c. of aq. NH_3 and electrolysed for 10 min. at 2 volts. A continuous stream of CO_2 keeps the liquid stirred and furnishes the necessary electrolyte. Examples of the method, which is rapid and accurate, are given.

F. L. USHER.

Electrolytic micro-determination of mercury. F. PATAT (Mikrochem., 1932, 11, 16–21).—A solution of a Hg salt in 0.1N- HNO_3 is electrolysed at 3 volts with a fine Au wire (0.1–0.15 g.) as cathode. 0.1–1.0 mg. of Hg can be determined. The cathode is weighed on a microbalance. The current (0.025 amp.) is passed for 20 hr. Org. acids should be absent. The method is accurate. F. L. USHER.

Micrometric determination of minimal quantities of mercury. V. MAJER (Mikrochem., 1932, 11, 21–30).—Hg (10^{-7} – 1.4×10^{-5} g. in 5 c.c. of liquid) may be determined by deposition on a fine Fe wire in presence of KCl and CuSO_4 . A stream of CO_2 from a capillary keeps the liquid stirred and protects the metal from oxidation. Reduction is complete (99%) in $1\frac{1}{2}$ hr. The wire is subsequently heated and the Hg condensed in a fine capillary in which the globules are measured under a microscope. The Hg need not all be in a single globule. F. L. USHER.

Determination of actinium in uranium minerals. (Mlle.) E. GLEDITSCH and E. FOYN (Compt. rend., 1932, 194, 1571–1572).—The Ac:U ratio has been determined (1) by extraction of Ac and (2) by pptn. of Pa with Ta, the radioactivities being measured with a Wulff electrometer. The ratios thus deduced from broeggerite (from Raade) average 2.7:100, and those from Cornish pitchblende 3.3:100, with a probable error $> 10\%$.

C. A. SILBERRAD.

Molecular spectra and spectroscopic analysis.

II. **Analysis of lanthanum.** G. PICCARDI and A. SBERNA (Atti R. Accad. Lincei, 1932, [vi], 15, 83–88).—La can be detected by an examination of the band spectra of LaO just as accurately as by the method of spark spectra; with small concn. and in presence of elements which give a complicated spectrum the method is more sensitive. Quantitatively, the accuracy is comparable with that obtainable by optical methods. O. J. WALKER.

Micro-test for aluminium. F. L. HAHN (Mikrochem., 1932, 11, 33–36).—Filter-paper soaked in a $\text{C}_5\text{H}_5\text{N}$ solution of 1:2:5:8-tetrahydroxyanthraquinone and subsequently dried is coloured violet by NH_3 and brown by AcOH vapour, but a spot made

with a drop of solution of an Al salt remains unchanged. 5×10^{-7} g. of Al can be detected in this way. When the test is carried out in a test-tube, 2×10^{-8} g. can be detected. Mg present in excess does not interfere.

F. L. USHER.

Permanganate reaction of manganese and a technique permitting it in a strongly chlorinated medium such as sea-water. G. DENIGES (Bull. Soc. chim., 1932, [iv], 51, 380–384).—The reaction $\text{Mn}^{++} \rightarrow \text{MnO}_4^-$ may be carried out conveniently by using H_2SO_4 and Bi peroxide. In the presence of halogens Mn^+ may be determined as MnO_4^- by adding conc. H_2SO_4 to the boiling solution, adding a drop of 5% AgNO_3 , and then $\text{K}_2\text{S}_2\text{O}_8$. The use of NaOCl with CuSO_4 as catalyst enables Mn^{++} to be determined colorimetrically as MnO_4^- in the presence of several thousand times the wt. of Cl^- . E. S. HEDGES.

Chromous sulphate as reducing agent in the volumetric determination of iron. W. M. THORNTON, jun., and J. F. SADUSK, jun. (Ind. Eng. Chem. [Anal.], 1932, 4, 240–243).— CrSO_4 solutions which are suitable for analytical purposes can be prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ by means of the Jones reductor. A solution of CrSO_4 containing $> 0.18\text{N}$ - H_2SO_4 can be kept without appreciable change for 2 months if properly stored; it is unnecessary to remove the dissolved Zn. Fe^{+++} in cold solution can be determined by potentiometric titration with CrSO_4 in the presence of a small quantity of KCNS .

E. S. HEDGES.

Determination of iron and manganese in natural carbonates. S. V. POTANENKO.—See B., 1932, 382.

Permanganometric determination of cobalt. J. LEDRUT and L. HAUSS (Bull. Soc. chim. Belg., 1932, 41, 104–114).—Determination of Co by pptg. with $\text{Na}_2\text{C}_2\text{O}_4$ in AcOH solution leads to results about 20% too high. By working in 25% HCO_2H the error is only a few tenths %, as under these conditions the ppt. has a const. composition (CoC_2O_4) and is sol. to the extent of about 6 mg. Co per litre. NH_4^+ and NO_3^- must be absent. F. L. USHER.

Analysis of nickel by Parr and Lindgren's method. G. I. SMIRNOV (Uchen. Zapiski Kazan. Gosudarst. Univ., 1930, 90, No. 6, 1025–1035).—Parr and Lindgren's modification of the dimethylglyoxime method is more exact than other methods generally used. CHEMICAL ABSTRACTS.

Electrometric titration of nickel in steel. W. BOHNHOLTZER.—See B., 1932, 430.

Colorimetric test for chromium. G. C. SPENCER (Ind. Eng. Chem. [Anal.], 1932, 4, 245–246).—Wool is dyed in 1% serichrome-blue R a bright crimson colour changed to navy-blue by immersion in $\text{H}_2\text{Cr}_2\text{O}_7$ solution. By preparing a series of colour standards the method may be used as an approx. method of determining small amounts of Cr. The reaction appears to be sp. for $\text{H}_2\text{Cr}_2\text{O}_7$.

E. S. HEDGES.

Test paper for molybdenum: application to the detection and rapid determination of molybdenum in steels. E. BERTRAND (Bull. Soc. chim. Belg., 1932, 41, 98–103).—Filter-paper is covered

with a thin layer of H_2WO_4 and a drop of the solution (acidified) to be tested is placed on it. On adding SnCl_2 in aq. HCl a greyish-blue stain, surrounded by a colourless ring, is produced if Mo is present, and the intensity and time of appearance can be used for the determination of Mo. 0.00005 mg. of Mo in a drop of solution can be detected. F. L. USHER.

Determination of molybdenum with potassium permanganate. E. CARRIERE and R. LAUTIE (Compt. rend., 1932, 194, 1167—1168, 1284).—When K_2MoO_4 (0.5 g.) dissolved in 150 c.c. of 18% aq. H_2SO_4 is reduced at 50—60° by 15 g. Zn as wire (any other form gives unsatisfactory results, as also does HCl in place of H_2SO_4), a salt of Mo_2O_3 or MoO_3 itself is obtained, and an arrest in the reduction occurs at the point corresponding with its formation. As soon as reduction is complete work must be carried on in CO_2 (cf. A., 1929, 165). C. A. SILBERRAD.

Determination of tin in stannic oxide and cassiterite by means of reducing vapours. G. L. CHABORSKI and M. N. BADESCU (Bul. Chim. pura appl., Bukarest, 1932, 32, 7—18; Chem. Zentr., 1932, i, 554).—Sn is determined by observing the difference in wt. when EtOH vapour is passed over SnO_2 for 5—10 min. at a high temp.; SnO_2 is reduced to Sn. A. A. ELDRIDGE.

Volumetric determination of tin. Application to the separation of antimony and tin. P. E. WINKLER (Bull. Soc. chim. Belg., 1932, 41, 115—137).— SnS_2 is dissolved in NaOH , neutralised with HCl , and Zn is added. The pptd. Sn is dissolved with excess of Zn in HCl , the H_2 liberated providing a reducing atm., and the solution obtained is titrated with I and $\text{Na}_2\text{S}_2\text{O}_3$. In the separation of Sb and Sn by the $\text{H}_2\text{C}_2\text{O}_4$ method, the Sn may be recovered quantitatively from the filtrate by removing the $\text{H}_2\text{C}_2\text{O}_4$ with HClO_3 and HCl . The result is uniformly slightly low, but a systematic correction may be made. E. S. HEDGES.

Determination of small quantities of vanadium in soils and rocks with *p*-phenylenediamine hydrochloride. D. KATAKOUSINOS (Praktika, 1931, 4, 448—451; Chem. Zentr., 1932, i, 845).—Dark-coloured complexes formed on addition of conc. solutions of *p*-phenylenediamine to cold solutions of V salts contain 37.72—37.80% V_2O_5 ; in dil. solution colours between yellow and dark green are produced. 0.005 mg. V in 10 c.c. H_2O can be detected. The colour in neutral solution is yellow, in HCl solution pink to red. A. A. ELDRIDGE.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXII. Separation of the earth acids from metals of the hydrogen sulphide group. E. F. WATERHOUSE and W. R. SCHOELLER (Analyst, 1932, 57, 284—289).—If the authors' method (this vol., 36) is extended to the separation of Ta and Nb from Sb, Bi, and Cu, it is found that treatment with H_2S at 60° of a solution of the H sulphate fusion in tartaric acid gives a ppt. which always contains a few mg. of earth acid owing to hydrolysis of the tartaric-earth acid complexes. On pouring a warm solution of this ppt. in conc. H_2SO_4 , to which 20% tartaric acid and excess

of NH_3 have been added, into fresh $(\text{NH}_4)_2\text{S}$, Bi and Cu are pptd. as sulphides, and after filtration the Sb may be obtained by acidification with AcOH and titrated with KMnO_4 . The final filtrate contains the contaminating earth acids, which are pptd. in the usual way (*loc. cit.*) and added to the ppt. from the tartaric hydrolysis of the first filtrate. The errors for 0.1—0.25 g. of earth acid are usually <1 mg. of earth acid, Sb_2O_3 , Bi_2O_3 , or CuO . J. GRANT.

Analytical application of catalytic reactions. F. FEIGL and E. FRANKEL (Ber., 1932, 65, [B], 539—546).—Pd is detected by pptn. of Ni from solutions of $\text{Ni}(\text{OAc})_2$ and NaH_2PO_2 , the limit of concn. being 1 in 4×10^5 ; Pt, Os, and Ru (1 in 6.6×10^6 , 2×10^7 , and 2×10^7 , respectively) behave similarly (possibly owing to presence of Pd), whereas Rh is inactive. The oxidation of $\text{Mn}(\text{OH})_2$ to NaMnO_4 by NaOBr is catalysed by Ni^{++} and Co^{++} in addition to Cu^{++} . Mn (1 in 20×10^6) is detected by the formation of KMnO_4 by the action of KBrO_3 and KBr in alkaline solution in presence of CuSO_4 ; if Co or Ni is also present, more CuSO_4 must be added. Alkali hypobromite solutions are decomposed in presence of Cu, Co, or Ni, but not of Bi, Pb, Cd, Fe, Mn, or Ba; in presence of MnSO_4 the decomposing action of CuSO_4 is enhanced. Ag (1 in 12×10^4 or 1 in 10^6) is detected by its ability to catalyse the reduction and consequent decolorisation of brown Mn^{+++} or Mn^{++++} solutions in 2.5*N*- HCl or Ce^{+++} solutions in dil. HNO_3 ; the reaction is applicable to mixtures of AgCl , PbCl_2 , and Hg_2Cl_2 from which the Hg_2Cl_2 has been removed by gentle ignition. SO_2 (1 in 125,000) is detected by the induced oxidation of $\text{Ni}(\text{OH})_2$ to Ni_2O_3 and identification of the latter by the blue colour with benzidine acetate solution. H. WREN.

High-precision constant-temperature bath. A. L. FERGUSON, K. VAN LENTE, and R. HITCHENS (Ind. Eng. Chem. [Anal.], 1932, 4, 218—219).—The bath is fitted with a special relay and a Hg-steel regulator, maintains a const. temp. to within 0.01° for periods of several months, and can be kept const. to within 0.001° for shorter intervals. The liquid used in the bath is "petrolatum" and freedom from all the usual disturbances is claimed.

E. S. HEDGES.

Thermostatic control operated by ordinary alternating current. J. B. RAMSEY and T. A. WATSON (Ind. Eng. Chem. [Anal.], 1932, 4, 164—165).—A circuit breaker operated by a.c. is described. The thermoregulator requires an inert atm. of the electrical contact in order to obviate fouling.

E. S. HEDGES.

Double-tube combustion furnace. C. B. DE WITT (Ind. Eng. Chem. [Anal.], 1932, 4, 225—226).—The furnace is designed for org. analysis. It has two combustion tubes, the temp. of each of which can be regulated at will without affecting the other; it dispenses with clay tiles and radiates less heat into the room.

E. S. HEDGES.

Laboratory furnace for high temperatures. H. S. BOOTH and R. WARD (Ind. Eng. Chem. [Anal.], 1932, 4, 199—200).—An electrically heated furnace, giving a temp. const. to $\pm 5^\circ$ between 1000° and 1500°, is described.

E. S. HEDGES.

Improvised micro-burner. LUDY, jun. (Pharm. Zentr., 1932, 73, 209—210).—A burner suitable for micro-sublimations is described.

N. H. HARTSHORNE.

Errors in thermal measurements. J. R. PARTINGTON (Nature, 1932, 129, 615—616).—Attention is directed to the neglect of the errors involved in the use of metal wire thermometers.

L. S. THEOBALD.

Method of regulating a water-bath to different fixed temperatures in succession. A. BECKEL (Chem.-Ztg., 1932, 56, 331—332).—The temp. of a H₂O-bath can be regulated to $\pm 0.1^\circ$ by means of hot and cold H₂O feeds controlled by screw pinch-cocks with indicators attached for fine adjustment. The temp. of the hot H₂O is controlled by a heating spiral or screened gas flame and the two supplies are mixed before they enter the H₂O-bath. The pressure head is regulated by open tanks in the feed.

C. IRWIN.

Apparatus for determination of m. p. M. MATSUI and H. KATO (J. Soc. Chem. Ind. Japan, 1932, 35, 168—171b).—A bar of Au-plated Cu has a groove 1 mm. deep on the upper surface, an electric heater at one end, and Cu and constantan wires fixed to the side forming a thermocouple. The substance is placed in the groove; the sharp line dividing the melted from the unmelted surface travels along the bar, and as it passes the thermocouple the reading is taken. A Leeds-Northrup potentiometer is used.

C. IRWIN.

Determination of m. p. of small volatile crystals. Detection of diacetyl in pyrogenic gases from sugars and sugar-like substances. H. SCHMALFUSS and H. BARTHEMEYER [with H. SCHAAKE] (Mikrochem., 1932, 11, 6—16).—A method of manipulating very small quantities of volatile cryst. ppts. is described. Ac₂ has been identified by the m. p. of its dioxime among products of the pyrogenic decomp. of sucrose, glucose, starch, cellulose, and tartaric acid.

F. L. USHER.

Infra-red spectrometer of large aperture. H. M. RANDALL (Rev. Sci. Instr., 1932, [ii], 3, 196—200).—An instrument for use from 50 to 300 μ is described. The parabolic concave mirror used is 24 in. in diameter and fills a grating 10 \times 22 in.

C. W. GIBBY.

Large grating spectrograph. A. L. LOOMIS and G. B. KISTIAKOWSKY (Rev. Sci. Instr., 1932, [ii], 3, 201—205).—Improvements consist in a rigid grating mounting and a const.-temp. attachment.

C. W. GIBBY.

Recording apparatus for potentiometric determinations. P. DUBOIS (Compt. rend., 1932, 194, 1162—1164).—The solution under examination is placed in a revolving beaker, in which is fixed a SiO₂ tube containing an electrical resistance, which serves as a stirrer and to regulate the temp. The progress of the reaction is measured electrically by means of a standard electrode and another in the solution. The reagent is added from a burette attached to a balance to the knife-edge support of which is attached a mirror. The record is made by light reflected from this and the mirror of the galvano-

meter connected with the two electrodes. The device has been used to determine Mn.

C. A. SILBERRAD.

Continuous measurement of p_H with quinhydrone electrodes. II. C. C. COONS (Ind. Eng. Chem. [Anal.], 1932, 4, 175—178).—An improved apparatus for continuous p_H measurement gives an error not exceeding $\pm 0.05 p_H$ between p_H 0 and 7.5. The error reaches ± 0.1 at p_H 8 and ± 0.2 at p_H 9. The time lag of the apparatus is negligible for most industrial applications, but may cause an error of $\pm 0.2 p_H$.

E. S. HEDGES.

Measurement of electromotive force by means of a valve null instrument and telephone. W. HILTNER (Chem.-Ztg., 1932, 56, 352).—A sensitive compensation method is described.

E. S. HEDGES.

Slotted watch glasses for use in electroanalysis. E. R. CALEY (Ind. Eng. Chem. [Anal.], 1932, 4, 223—224).—A watch glass having a radial slot cut by means of a thin carborundum wheel serves to prevent loss by spraying during electro-analytical determinations, whilst obviating the necessity of disconnecting the electrodes when the watch glass is removed or replaced.

E. S. HEDGES.

Measurement of the internal resistance of an accumulator, and of electrolytic resistances in general. E. DENINA and A. FRATES (Energia Elett., 1931, 8, 4 pp.; Chem. Zentr., 1932, i, 559).

Platinum resistance thermometry. III. Determination of low-temperature scale between 0° and -190° . S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1932, 35, 165—168b).—The equation $R_t = R[1 + At + Bt^2 + C(t-100)t^3]$ is chosen and the fixed points selected for calibration are the b. p. of liquid O₂ and the m. p. of Hg. Trustworthy results for the former could be obtained only after long-continued annealing of the bulbs at 400° with cooling to the b. p. of liquid air. An attempt to use the sublimation point of solid CO₂ in a Dewar flask with 3 compartments, the outer ones filled with the solid CO₂ and the centre one containing the bulb and the stirrer, was unsuccessful. The m. p. of Hg was determined by melting frozen Hg slowly with ice and the results were checked with the equations for the bulbs obtained from the b. p. of O₂.

C. IRWIN.

Apparatus for electrodialysis. E. J. KING (Ind. Eng. Chem. [Anal.], 1932, 4, 201—202).—The colloidal solution is placed in a large dialysing thimble and in it is immersed a smaller dialysing thimble through which distilled H₂O flows. The larger thimble is immersed in a beaker containing flowing, distilled H₂O. A Pt electrode is placed in the inner thimble and the other electrode is a layer of Hg at the bottom of the beaker.

E. S. HEDGES.

Apparatus for calibration of flowmeters. G. W. SMITH (Ind. Eng. Chem. [Anal.], 1932, 4, 224—245).—An apparatus and procedure for calibrating flowmeters of the resistance-tube type for use with low rates of gas flow are described.

E. S. HEDGES.

Multiple-range flowmeters. S. YUSTER (Ind. Eng. Chem. [Anal.], 1932, 4, 224).—Two forms of

apparatus for the study of gaseous reactions by flow methods are described. E. S. HEDGES.

Purification of materials by vacuum distillation. E. W. FLOSDORF and A. E. PALMER (*J. Rheology*, 1932, 3, 205).—A distillation flask with two side-arms enables two fractions to be collected without interrupting the process. E. S. HEDGES.

Anti-foam still-head. C. W. EDDY (*Ind. Eng. Chem. [Anal.]*, 1932, 4, 198—199).—Two forms of apparatus for use at low pressures are described.

E. S. HEDGES.

Determination of specific gravity. W. NORMANN (*Chem.-Ztg.*, 1932, 56, 297; cf. B., 1931, 399).—The method of suspending and weighing the apparatus formerly described is explained.

E. S. HEDGES.

Measurement of dissolution of metals in salt solutions. L. WHITBY (*Trans. Faraday Soc.*, 1932, 28, 474—478; cf. A., 1928, 1333).—An apparatus is described for following accurately the course of the corrosion of metals by periodic determinations of the H_2 and O_2 in the gas enclosed over the corroding liquid. O_2 is not absorbed appreciably during the dissolution of Mg in 0.0001N- and 0.001N-NaCl.

J. G. A. GRIFFITHS.

Apparatus for quantitative catalytic reduction. H. PAGET and W. SOLOMON (*J.C.S.*, 1932, 1198—1200).—Two forms of apparatus (for use at atm. pressure and at high pressures, respectively), which enable the amount of absorbed gas to be determined accurately, are described.

E. S. HEDGES.

Gas absorption pipette. H. TRAMM (*Brennstoff-Chem.*, 1932, 13, 146—147).—The pipette consists of three bulbs. The upper bulb is packed with glass beads. The intermediate bulb is connected with the larger lower bulb directly by a short capillary tube and also by a wider tube joining the top of the former to the bottom of the latter. The lower bulb may also be packed with beads. When the gas is drawn into the pipette it passes through the upper bulb and thence by way of the wide connecting tube to the lower bulb, and is subjected therein to the action of the stream of absorbing liquid which flows from the intermediate bulb through the capillary tube.

A. B. MANNING.

Apparatus for dispersoid analysis. H. LEHMANN (*Chem. Fabr.*, 1932, 149—150).—A pipette apparatus for determining the concn. of suspensions is described.

E. S. HEDGES.

Soxhlet apparatus for large amounts [of material]. F. N. SCHULZ (*Biochem. Z.*, 1932, 247, 474—475).—The apparatus is made mainly of metal (Sn plate, Cu, Ni) with linen or silk as filtering medium.

W. MCCARTNEY.

Apparatus for micro-extraction on Soxhlet's principle. A. WASITZKY (*Mikrochem.*, 1932, 11, 1—6).—A simple glass extraction apparatus for dealing with about 1 g. of material, and suitable for use at atm. or reduced pressure, is described.

F. L. USHER.

Extraction apparatus and its use in quantitative analysis. G. THOMIS (*Praktika*, 1931, 6, 248—251; *Chem. Zentr.*, 1932, i, 552).

Extraction apparatus for solids. H. WOLLENBERG (*Chem.-Ztg.*, 56, 1932, 332).—The material to be extracted rests on a filter plate beneath which a centrally placed horizontal paddle revolves in the extracting liquid. The latter is forced up through the central part of the solid and downward through the periphery.

C. IRWIN.

Impervious crucibles of magnesium oxide. P. S. ROLLER and D. RITTENBERG (*Ind. Eng. Chem.*, 1932, 24, 436—440).—The refractory powder, which must pass a 200-mesh sieve and have appropriate distribution of particle size, is moistened with dil. HCl and H_3PO_4 and pressed in two stages in such a manner that the base is welded to the walls and a structure of uniform density is obtained. The dried crucible is fired in a high-frequency induction furnace with a graphite inductor at 2600°, the time during which it is above 1800° being min. The crucible is translucent and retains molten slags (at 1500°) for long periods although slow dissolution of the MgO may occur.

J. G. A. GRIFFITHS.

Laboratory ball mill. R. BLOCK and C. ROSETTI (*Chem.-Ztg.*, 1932, 56, 196).—The mill comprises a porcelain or Fe jar containing pebbles or steel balls and closed with a clamped-on lid; the jar is rotated at 300 rev. per min. on a horizontal circular table with an eccentric drive so that the balls and material to be ground are thrown about vigorously by the centrifugal action combined with the eccentric motion.

A. R. POWELL.

Characteristics of porous plates. H. RUDOLPH (*Chem. Fabr.*, 1932, 137—140).—Porous plates are made by binding grains (diatomaceous earth, etc.) with a suitable medium, the size of grains used determining the size of the pores. They are used for filtration, as diaphragms for surface combustion, etc. The "pore no." is the no. of pores per sq. cm., the porosity is the percentage of pore vol. to total vol. Microscopic examination can be carried out only by reflected light. Indirect tests of filter plates include the determination of the quantity of H_2O passed under given conditions, a test which is subject to numerous errors unless pressure, thickness of plate, temp., and purity of H_2O are all standardised. Similar errors arise in the determination of rate of transmission of air, but the difficulties are not so great. The transmission of air alone does not offer the same problem as the passage of air in counter-current to a solution through which the air or gas is bubbled.

C. IRWIN.

Filling device for upward-flow viscosimeters. W. G. BURRASTON (*Analyst*, 1932, 57, 309).—The level of liquid in a viscosimeter is adjusted rapidly and accurately, and the risk of fouling the walls above the lower reference mark is avoided, by the use of a T-piece fitted to the air-outlet end, one arm of which leads to a cock and the other to a levelling tube of the eudiometer type.

J. GRANT.

Approximate calibration of apparatus for measuring absolute viscosity. C. H. WEISS and M. LOUIS (*J. Rheology*, 1932, 3, 217—220).—Sources of error are discussed.

E. S. HEDGES.

Speed regulator for small laboratory motors. A. TIAN (*Bull. Soc. chim.*, 1932, [iv], 51, 419—420).—

A rubber disc is affixed. During rotation its radius increases until the periphery touches a suitably placed object, thus providing a limiting max. speed.

E. S. HEDGES.

Use of sand in centrifuging precipitates. S. STENE (Mikrochem., 1932, 11, 131—132).—Admixture of sand when centrifuging a ppt. prevents the latter becoming too firmly consolidated, and from being stirred up when the centrifuge is stopped.

F. L. USHER.

Hair-type humidity control. M. C. MARSH (J. Sci. Instr., 1932, 9, 153—157).—Hairs extended vertically are pulled sideways by springs, and operate relays which control the humidifying or drying apparatus.

C. W. GIBBY.

Simplified method of calculating tangents by theory of least squares. F. T. GUOKER, jun. and H. J. BRENNEN (J. Amer. Chem. Soc., 1932, 54, 886—888).—By choosing equally spaced positive and negative vals. of the independent variable and making the y -axis pass through the point at which the tangent is desired, $dy/dx = \Sigma xy / \Sigma x^2$. R. H. CHERRY (c).

Albertus Magnus as chemist. F. PANETH (Nature, 1932, 129, 613).—A criticism.

L. S. THEOBALD.

Early history of platinum. E. P. C. MEYER (Science, 1932, 75, 438).—References to Pt dated 1735 have been found. Earlier references are probable.

L. S. THEOBALD.

Geochemistry.

Upper air temperatures and humidities in the Indian Peninsula. K. R. RAMANATHAN and K. P. RAMAKRISHNAN (Nature, 1932, 129, 615).

L. S. THEOBALD.

Phosphate, nitrate, and nitrite in the sea-water of regions adjacent to Cape Cod. N. W. RAKESTRAW (Science, 1932, 75, 417—418).—Data are recorded graphically.

L. S. THEOBALD.

Reducing power of sea-water. P. CHAUCHARD (Compt. rend., 1932, 194, 1256—1259).—Defining reducing power as the no. of c.c. of $M/300\text{-KMnO}_4$ reduced by 1 litre rendered alkaline, the reducing power of sea-water off Brest in fine weather (with E. wind) was 12—15, in stormy weather (W. wind) 16—24. After a long period of stormy weather several days of calm are required to diminish the reducing power. In calm weather the power is nearly const. to 100 m. depth, and then diminishes rapidly.

C. A. SILBERRAD.

Organic carbon content of various waters. PICON (Compt. rend., 1932, 194, 1175—1177).—The C content of 15 different waters was determined. Very little difference was found in the case of waters from rivers, wells, and springs, but water treated with hypochlorite showed markedly less, that from a forest pond markedly more, C. No relation was traceable between the amounts thus found and results with KMnO_4 .

C. A. SILBERRAD.

Iodine content of some waters of S.E. Dakota. C. B. STONE (Proc. S. Dakota Acad. Sci., 1927, 10, [xxvii], 35—45).—The I content is low.

CHEMICAL ABSTRACTS.

Occurrence of iodine. E. SCHANTL (Chem.-Ztg., 1932, 56, 341—342).—The H_2O pumped from deep wells (about 400 m.) in certain localities in the East Indies contains considerable quantities of KCl, NaCl, CaCl_2 , and MgCl_2 and about 0.015% of MgI_2 . Methods in use for extracting the I are described.

E. S. HEDGES.

Radioactivity of the sulphuretted water at Thues les Bains. E. CANALS (J. Pharm. Chim., 1932, [viii], 15, 397—400).—The radioactivities of the H_2O from several springs lie between 68×10^{-2} and 9.4×10^{-2} millicuries. There is no apparent relation

between the radioactivity and the chemical composition of the H_2O .

A. LAWSON.

Nitrogenous compounds and phosphate in the lake waters of Japan. S. YOSHIMURA (Proc. Imp. Acad., Tokyo, 1932, 8, 94—97).—Samples from about 80 Japanese lakes have been examined for free NH_3 , albuminoid NH_3 , NO_2' and NO_3' , sol. and total PO_4''' by colorimetric methods. Total N and PO_4''' are closely correlated in the different lake types.

W. R. ANGUS.

Spontaneous combustion in the marshes of Southern Louisiana. P. VIOSCA, jun. (Science, 1932, 75, 461—462).—Spontaneous ignition of the soil of a dried marsh is recorded.

L. S. THEOBALD.

New lime-precipitating bacterium from the Sevan Lake (Goktscha), *B. Sewanense*, spec. nov. P. KALANTARIAN and A. PETROSSIAN (Zentr. Bakt. Par., 1932, II, 85, 431—436).—The organism causes the pptn. of CaCO_3 as fine calcite crystals. No gas formation from sugars, starch, inulin, etc. occurs.

A. G. POLLARD.

Natural gases in Russia. G. A. SARKISYANTZ (Prirodn. Gaz., 1931, 2, 129—138).—Surakhani: CO_2 15—30, CH_4 75—79.5, C_2H_6 2—4, C_3H_8 and higher homologues 1.5—2%; gasoline 0.37—0.55 gallon per 1000 cu. ft. of gas. Bibi-Eibat: CO 4—8, CH_4 84—91, C_2H_6 2—4, C_3H_8 and higher homologues 3—4% (gasoline 0.77—1.00). Kirmaki: CO_2 4, CH_4 90—93, C_2H_6 2, C_3H_8 < 1% (gasoline 0.074—0.11). New Grozni: CO_2 trace, CH_4 18.3, C_3H_8 16.3, C_4H_{10} 27.8, C_5H_{12} and higher homologues > 31%. Old Grozni: CH_4 40, C_2H_6 7.08, C_3H_8 20.2, C_4H_{10} 18.4, C_5H_{12} and higher homologues > 13.6%. Maikop: CH_4 49, C_2H_6 13, C_3H_8 13, C_4H_{10} 7, C_5H_{12} and higher homologues > 8% (gasoline up to 12%).

CHEMICAL ABSTRACTS.

Radium and helium in petroleum beds. K. KREJCI-GRAF (Petroleum, 1932, 28, 12—14).—Contrary to a previous opinion (Salomon-Calvi, A., 1931, 1145), the Ra content of oil-bed waters is due to leaching alone. The reason for the comparative freedom from Ra of ordinary waters is that they contain SO_4'' ions. The storing of Ra and U in

organisms is shown to be probably without oleogeological significance. The He is derived from the disintegration of Em, which, being very sol. in petroleum, is conc. in it. N. H. HARTSHORNE.

Geochemistry of noble gases and radioactivity. V. G. CHLOPIN (Prirodn. Gaz., 1931, 2, 61—82).—Owing to the stability of He its accumulation in subterranean strata is governed by the total amount of radioactive elements.

CHEMICAL ABSTRACTS.

Escape of gas in sediments. H. KORN (Chem. Erde, 1932, 7, 1—23).—The decomp. of animal and vegetable remains in marine sediments may under certain conditions give rise to the generation of gases (H_2 , CH_4 , CO_2 , H_2S , NH_3) in considerable amounts. These gases may produce a porous texture in the rock or they may escape along channels. Examples are given of these channels in rocks, which have been described as fossil algae, worm tracks, and other problematical fossils. L. J. SPENCER.

Permian yellow sands of N.E. England. M. B. HODGE (Proc. Univ. Durham Phil. Soc., 1932, 8, 410—458).—Mechanical and mineralogical analyses of sands in Northumberland and Durham are given.

C. W. GIBBY.

Formation of flint. H. DOUVILLE (Compt. rend., 1932, 194, 1285—1289).—The SiO_2 of sedimentary deposits arises from the spicules of sponges, tests of *Radiolaria*, etc. and is thus produced as micelles regularly grouped in a protoplasmic medium. On decay of the organisms these micelles move with Brownian motion in the resultant muddy slime, gradually uniting to form a gel, which then slowly passes into cryptocryst. chalcedony where it replaces chalky deposits, and into cryst. fibrous chalcedony or even quartz in empty spaces. In this way is explained the formation of the chalk flints and their occasional geodes without assuming complete dissolution of SiO_2 .

C. A. SILBERRAD.

Veselyite from Vasko (Moravia). V. ZSIVNY (Z. Krist., 1932, 82, 87—110).—Veselyite is monoclinic, $a:b:c=0.7288:1:0.9542$, β $76^\circ 37'$, hardness 4, no cleavage, slightly pleochroic, blue and greenish-blue; $d_{20}^{20} 3.34_3$; analysis CuO 37.82, ZnO 26.69, PbO 0.05, FeO 0.06, NiO trace, P_2O_5 18.43, H_2O 16.87%, corresponding with $(Cu,Zn)_3(PO_4)_2 \cdot 3(Cu,Zn)(OH)_2 \cdot 4H_2O$, a formula applying equally to veselyite from Broken Hill, to the isomorphous arakawite, and probably also to kipushite, the differences depending on the relative amounts of Cu and Zn (cf. A., 1875, 546; 1881, 368).

C. A. SILBERRAD.

Narsarsukite. B. GOSSNER and H. STRUNZ (Z. Krist., 1932, 82, 150—151).—Narsarsukite consists of $1.027SiO_2 + 0.1707TiO_2 + 0.0394Fe_2O_3 + 0.0027Al_2O_3 + 0.006MgO + 0.006MnO + 0.260Na_2O + 0.0374F + 0.016H_2O$, and is composed of a mixture of $Na_2Ti(Si_4O_{11})$, $Na_2Fe(Si_4O_{10}F)$, and a little $Na_2(Mg,Mn)(Si_4O_9F_2)$, all three being isomorphous. It is tetragonal with a 10.78, c 7.99 Å., space-group probably C_{4h} , perhaps C_{3h} . C. A. SILBERRAD.

Hessite. L. TOKODY (Z. Krist., 1932, 82, 154—157).—Hessite from Botes (Hungary) contains Ag

59.41, Au 4.73, Te 35.97%, Fe trace; Sb, S, and SiO_2 are absent; d_{20}^{20} 8.350. It is probably monoclinic, the unit cell having a 5.98, b 6.31, c 5.56 Å., β $75^\circ 2'$, and containing 3 mols. (Ag_2Te), one of which must differ in some way from the other two.

C. A. SILBERRAD.

Geochemistry of gallium. V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Göttingen, 1931, 165—183; Chem. Zentr., 1932, i, 513).—The Ga content of many rocks and minerals has been determined, the arc spectrographic method being employed for quantities up to 0.01%. In the lithosphere Ga always accompanies Al, but the quant. relationship is not const. The at. ratio Ga:Al in the rocks of the lithosphere is $1:4-2 \times 10^4$. Ga occurs also in Fe meteorites and in technical Fe.

A. A. ELDRIDGE.

"Alkanasul," a new aluminium-bearing Chilean mineral. J. WESTMAN (Bol. min. Soc. Nac. Min., 1931, 43, 433—434; Chem. Zentr., 1932, i, 573).—The mineral, d 2.90, contains Al_2O_3 30.35, K_2O 5.61, Na_2O 3.70, SO_3 37.95, H_2O 16.11, Fe_2O_3 1.20, SiO_2 4.98%. On moderate roasting $Al_2(SO_4)_3$, K_2SO_4 , and Na_2SO_4 are obtained; heating at a higher temp., followed by extraction with H_2O , leaves a residue containing about 95% Al_2O_3 .

A. A. ELDRIDGE.

Genesis of oolites of Lorraine and Luxemburg. J. P. AREND (Compt. rend., 1932, 194, 1172—1175; cf. this vol., 493).—The origin of the Fe is discussed and an explanation of the formation of the "colloidal solid suspension" (this vol., 360) is offered.

C. A. SILBERRAD.

Spectrographic study of rocks and minerals of Katzenbuckel Mtn., Odenwald. F. SCHRODER (Neues Jahrb. Min., 1931, A, 63, 215—266; Chem. Zentr., 1932, i, 206).—The following elements are present in the minerals: Rb, Cu, (Au), (Be), Sr, Ba, Zn, Cd, rare earths, Ca, (In), Tl, Th, Sc, Sn, Pb, V, Mo, Cr, Mn, Co, Ni. The distribution of the elements is discussed.

A. A. ELDRIDGE.

Structural formula of hydromagnesite. G. R. LEVI and D. GHIRON (Gazzetta, 1932, 62, 218—220).—In four typical hydromagnesites from various localities (Val d'Aosta, Texas, and Euboea) the ratio $MgO:CO_2$ is very nearly 4:3 and not 5:4 (cf. A., 1930, 435).

O. J. WALKER.

Age of a monazite crystal from Portland, Connecticut. C. N. FENNER (Amer. J. Sci., 1932, [v], 23, 327—333).—Analysis gave Th 7.489, Pb 0.1007%; U absent. On the supposition that the Pb was derived from the Th by radioactive disintegration, this gives the age to be 2779×10^6 years, in good agreement with the age calc. from the analysis of a sample of uraninite from the same quarry (U.S. Geol. Survey Bull., 1889—1890, No. 78, 43).

N. H. HARTSHORNE.

Isomorphism of feldspars. E. SCHIEBOLD (Neues Jahrb. Min., 1931, A, 64, Bl.-Bd., 251—319; Chem. Zentr., 1932, i, 35—36).—A discussion.

A. A. ELDRIDGE.

Metallographic investigation of native silver. (Sir) H. C. H. CARPENTER and M. S. FISHER (Bull. Inst. Min. Met., 1932, No. 330, 22 pp.).—From micro-

graphic examination and heat-treatment tests on numerous samples of native Ag from 14 localities it is concluded that in the course of geologic ages native Ag may recrystallise at room temp. although the process is usually imperfect and localised. In deposits formed at a low temp., and never subjected to heat, some at least of the Ag retains its original structure, whilst that which has recryst. has not a uniform homogeneous structure like that of Ag recryst. by heat. Conversely, when native Ag has a homogeneous recryst. structure it may be assumed that the Ag was deposited at a high temp. or has subsequently been metamorphosed by heat. Native Ag from most localities has been deposited by meteoric waters or by cool hypogene solutions, but that found in N. Rhodesia, at Lake Superior, and in the Cobalt district has been deposited by hot juvenile solutions at above 200°. Both Ag and Cu at Lake Superior have been deposited at 200—250°. A natural alloy from Cobalt contained Ag 85.6, Sb 12.1, As 0.6, and Bi 1.2% and had a duplex Widmanstätten structure; it had probably been deposited from hot hypogene solutions as a homogeneous solid solution from which a second phase was subsequently pptd. to give the characteristic structure. Attempts to reproduce this structure with synthetic alloys of the same composition failed.

A. R. POWELL.

Graphic representation of rock weathering. G. GROSSER (Chem. Erde, 1932, 7, 130—176).—Bulk analyses and analyses of the portions sol. in acid and alkali solutions of fresh and weathered basalt from Oberlausitz, Saxony, are plotted on diagrams.

L. J. SPENCER.

Distribution of tungsten in the Bolivian metal province. F. AHLFELD (Chem. Erde, 1932, 7, 121—129).—Tungsten minerals, mostly wolframite (with ferberite and hubnerite), rarely scheelite and tungstite, are found at many localities in association with the Sn ores. They occur in the inner and outer contact zones of granodiorite and quartz-porphyry of Tertiary age, and belong mainly to a later, lower temp. phase than the Sn ore. Approx. analyses of wolframite and ferberite are given.

L. J. SPENCER.

Dehydration and rehydration of kaolin crystals. H. JUNG (Chem. Erde, 1932, 7, 113—120).—Kaolin can be partly dehydrated without destroying the crystal structure, and H₂O can then be reabsorbed. The completely dehydrated material is amorphous, but at 550° it passes into cryst. α -kaolin, Al₂Si₂O₇. The latter, if not strongly ignited, will absorb H₂O giving one or more hydrated Al silicates, which by further treatment may be reconverted into kaolin.

L. J. SPENCER.

Turquoise. H. JUNG (Chem. Erde, 1932, 7, 77—94).—Turquoise (*d* 2.719) from New Mexico gave, after deducting SiO₂ 2.24, P₂O₅ 34.41, Al₂O₃ 33.42, Fe₂O₃ 4.37, FeO 0.72, CuO 7.70, H₂O 19.35=99.97%, agreeing with the formula (Cu,Fe)O₃(Al,Fe)₂O₃·2P₂O₅·9H₂O. Previous analyses tabulated and plotted show considerable variation, as is to be expected with a mineral that was deposited in a colloidal form.

L. J. SPENCER.

Pyrochlore-romeite group. F. MACHATSCHKI (Chem. Erde, 1932, 7, 56—76).—The several minerals

(pyrochlore, hatchettolite, koppite, pyrrhite, micro-lite, neotantalite, atopite, schneebergite, romeite, weslienite, mauzeilite, lewisite, and monimolite) of this group have the general formula X₂Z₂(O,OH,F)₇, where X=Na, Ca, Ce, etc., and Z=Nb, Ta, Ti, Sb. They crystallise as small octahedra and have the same type of crystal structure with the edge of the unit cube ranging from 10.27 to 10.41 Å. As chemical varieties of one species they are distinguished as niobpyrochlore (for pyrochlore proper), tantalpyrochlore (microlite), antimonpyrochlore (romeite=atopite), titanantimonpyrochlore (mauzelite and lewisite), etc.

L. J. SPENCER.

Central American volcanic ashes. E. DEGER (Chem. Erde, 1932, 7, 51—55).—Chemical and mechanical analyses are given of the ash which fell on various dates (24 April—12 June, 1931) after the eruptions of the Izalco volcano in Salvador.

L. J. SPENCER.

Coloured efflorescences and encrustations on Elbe sandstone. E. BLANCK, A. SEIFERT, and F. GIESECKE (Chem. Erde, 1932, 7, 35—50).—Efflorescences of various alums and gypsum have long been known on the Elbe sandstone in northern Bohemia and Saxony. Red and reddish-violet encrustations (or rather surface impregnations) are noted from several localities in Saxony. Analyses are given of the yellow sandstone, the bleached zone, and the coloured encrustation zone. The last contains relatively more P₂O₅ (1.40%) and SO₃ (0.91%), and the colouring is ascribed to Fe and Mn phosphates.

L. J. SPENCER.

Brazilian salt-pans. F. W. FREISE (Chem. Erde, 1932, 7, 24—34).—Salt-pans in the interior of Brazil are with few exceptions confined to the outcrop of Permian rocks. The different types described are those carrying nitrates (K, Ca, Mg), carbonates (Na), sulphates (Na), and NaCl. Analyses of the salts are given.

L. J. SPENCER.

Genesis of the native copper and silver ore deposits in the Lake Superior region. K. NISHIO (Proc. World Eng. Cong., Tokyo, 1931, 37, 499—544).

CHEMICAL ABSTRACTS.

Iron ore from El Tofo, Chile. F. WUST (Bol. min. Soc. Nac. Min., 1931, 43, 381—385).—The ore, a mixture of magnetite and haematite, contained Fe 69.7% and V 0.21%, with little P and S.

CHEMICAL ABSTRACTS.

Liesegang phenomenon applied to Lake Superior iron formations. R. J. HARTMAN and R. M. DICKEY (J. Physical Chem., 1932, 36, 1129—1135).—The peculiar banding of the Fe formations is ascribed to the slow diffusion of sol. Fe³⁺ salts through a gel formed by the interaction of basic N compounds, CO₂, or carbonates with Na silicate, giving rise to irregularly-spaced bands of FeCO₃ separated by SiO₂.

F. URBAN (c).

Optical measurements with antimonite. A. CISSARZ (Neues Jahrb. Min., 1931, A, 64, Bl.-Bd., 137—162; Chem. Zentr., 1932, i, 512).

Action of heat on fluorite. L. DOMANGE (Compt. rend., 1932, 194, 1667—1669).—Seven samples of fluorite containing 0—1.12% SiO₂ broke into fragments and emitted violet (or in one case green)

luminescence at 200—300°. They lost 0.013—0.057 wt.-% (H₂O) at 150°, and an additional 0.0066—0.029% (gas) at 400°. Corresponding figures for a sample containing 15% SiO₂ are 300°, 0.54, and 0.51%. The *d* was unaltered, and if any allotropic change occurs, it is completely reversible.

C. A. SILBERRAD.

Transformation of brown coal into bituminous coal. G. STADNIKOV (Brennstoff-Chem., 1932, 13, 101—102).—The Tscheremchov seam (Siberia) consists of layers of coal separated by layers of shale or clay. The upper layers are typical brown coals whilst the lower layers are bituminous coals, an intermediate layer appearing to form a transition stage between the two varieties of coal. The seam is free from folds, faults, or igneous intrusions, so that no theory based on such phenomena can here explain the transformation of the brown coal into the bituminous coal. Theories based on temp. rises due to exothermic reactions also appear to be excluded.

A. B. MANNING.

Climate and parent material in soil formation in S.W. England. A. J. LOW (Nature, 1932, 129, 655).

L. S. THEOBALD.

Soils of the Nile and Gash. VIII. P. VAGELER and F. ALTEN (Z. Pflanz. Düng., 1932, 24 A, 179—242; cf. B., 1932, 476).—Mechanical and chemical data for numerous soils from several areas are recorded. The effectiveness of nutrients in these soils is largely dependent on the rate of H₂O movement through the soil mass. The characteristically high K content of many Egyptian and Sudan soils does not necessarily imply that K fertilisers would not prove beneficial. In these districts K acts not only as a fertiliser but also as an ameliorant by increasing H₂O mobility in the Na-clays. In this respect it is more effective than CaO or gypsum in penetrating to subsoil layers and breaking up the illuvial horizon. For the successful removal of Na salts, thorough surface working prior to leaching is essential.

A. G. POLLARD.

Hinojo meteorite. E. H. DUCLOUX (Anal. soc. cient. Argentina, 1931, 112, 247—252).—The meteorite (1155 g.) contained: SiO₂ 34.33, Al₂O₃ 2.22, FeO 12.29, Fe₂O₃ 16.53, MnO 0.59, NiO 1.39, CoO 0.04, CaO 2.27, MgO 20.04, K₂O 0.19, Na₂O 1.52, P₂O₅ 0.44, Fe 6.61, Ni 0.27, Co 0.01, S 0.54, P 0.08, H₂O and loss on ignition 0.69%. CHEMICAL ABSTRACTS.

Organic Chemistry.

Number of stereoisomeric and non-stereoisomeric paraffin hydrocarbons. C. M. BLAIR and H. R. HENZE (J. Amer. Chem. Soc., 1932, 54, 1538—1545; cf. this vol., 495).—Theoretical. A relationship is established between the no. of stereoisomeric and non-stereoisomeric paraffins and the alkyl groups of which the former may be considered to be composed. Recursion formulæ are advanced for calculating the no. of stereoisomeric and non-stereoisomeric paraffins in each of the structural types (arbitrarily chosen on the basis of their formulæ) from their C content, but their use involves the knowledge of total no. of stereoisomeric and non-stereoisomeric alkyl groups of *N*/2 and all smaller C contents.

C. J. WEST (b).

Thermal decomposition of *n*-butane into primary products. M. NEUHAUS and L. F. MAREK (Ind. Eng. Chem., 1932, 24, 400—402).—The method of Schneider and Fröhlich (this vol., 27) is applied to *n*-C₄H₁₀ pyrolysed at 600° and 650°. The primary products are the following (the no. of mols. for 100 mols. of C₄H₁₀ at each temp. are shown in parentheses): CH₄ and CH₃Me:CH₃, (48.5, 48.0), C₂H₆ and C₂H₄, (34.5, 37.7), H₂ and butylenes (16.0, 12.3), and C₃H₈ [0, (?) 1.0]. The results for the first two pairs agree with those predicted by Rice (A., 1931, 819). No butadiene, aromatic hydrocarbons, or hydrocarbons of mol. wt. higher than C₄H₁₀ were formed.

A. A. LEVI.

Preparation of $\alpha\beta\gamma\delta$ -tetrabromobutane. R. A. JACOBSON (J. Amer. Chem. Soc., 1932, 54, 1545—1548).— $\beta\gamma$ -Dibromobutane or crotyl chloride (I) is passed over soda-lime at 400—550° and the resulting gaseous products are absorbed in Br; the yields of $\alpha\beta\gamma\delta$ -tetrabromobutane (II) are 13.5—14.5% or 16.4—19.3%. The use of (I) is preferred. The

by-products formed with (II) are: $\alpha\beta$ -, $\alpha\gamma$ -, $\alpha\delta$ -, and $\beta\gamma$ -dibromobutanes, $\alpha\alpha\delta\delta$ -tetrabromobutane, an isomeride of (II), and *trans*- β -bromo- Δ^2 -butene.

C. J. WEST (b).

***p*-Nitrophenylcarbimide as a reagent for alcohols and amino-compounds.** C. W. VAN HOOGBRATEN (Rec. trav. chim., 1932, 51, 414—433).—The reaction between PhNCO and H₂O is unimol., the mean val. of *K* at 0° being 0.26. *p*-Nitrophenylcarbimide (I), m. p. 57° [modified prep. from COCl₂ and *p*-nitroaniline; occasional by-product, *p*-nitrocarbonyl chloride, m. p. indef. 120—135°, also prepared from (I) and dry HCl in C₆H₆], reacts violently with H₂O. Attempts to prepare 2:4-dinitrophenylcarbimide failed. When pure, (I) (solid or in solution) has little tendency to polymerise (cf. A., 1897, i, 410), but with a trace of pyridine in dry Et₂O or C₆H₆ forms a *polymeride*, m. p. 340° (block), stable to H₂O at 120° and to EtOH-NH₃, and with EtOH at 120° (not at 100°) forming Et *p*-nitrophenylcarbamate. With KOAc (below 90°) (I) forms (?) *tri-p*-nitrophenylcarbimide, m. p. above 360°. The following *p*-nitrophenylcarbamates were prepared: *n*-octyl, m. p. 111°; *n*-decyl and *n*-dodecyl, m. p. 117°; *n*-stearyl, m. p. 115°; *oleyl*, m. p. 85—91°; CH₂Ph, m. p. 157°; CHPh₂, m. p. 150°; *benzoin*, m. p. 183°; 5-hydroxy[? hydroxymethyl]furfuraldehyde m. p. 187°; *glycol*, m. p. 236°; *glycerol*, m. p. 216°; *Ph*, m. p. 161°; *resorcinol*, m. p. 232°. By reaction of (I) with the appropriate base the following substances were prepared: *N*-*p*-nitrophenyl-*N'*-ethyl- (m. p. 158°), *n*-propyl-, m. p. 151°, *n*-butyl-, m. p. 146°, *-dimethyl-*, m. p. 221°, *-diethyl-*, m. p. 162°, and *-di-n-propyl-*, m. p. 130°, *-carbamide*; *N*-*p*-nitrophenylcarbonyl-piperidine, m. p. 164°, and *-pyrrole*, m. p. 280°. Et *p*-nitrophenylallophanate,

m. p. 202° (formed only in presence of pyridine); *p*-nitrophenylhydantoic acid, m. p. 200° (*Et* ester, m. p. 168°); 1-*p*-nitrophenyl-hydantoin, m. p. 244°, -4- and -3-methyl- (m. p. 174° and 161°, respectively), and -4-isobutyl- (m. p. 181°)-hydantoic acid, and -4-dimethylhydantoin, m. p. 176°. The following semicarbazide derivatives, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHR}$, were prepared, R being the radical named: *Ph*, m. p. 211—213°; *p*-bromophenyl, m. p. 210°; *o*- (m. p. 225°), *m*- (m. p. 207°), and *p*- (m. p. 212°)-tolyl. Di-(*p*-nitrophenyl)semicarbazide has m. p. 246° and di-(*p*-nitroanilinoformyl)hydrazine, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH})_2$, m. p. 276°. The *p*-nitrophenylsemicarbazones of PhCHO and COMe_2 have m. p. 226° and 237°, respectively (from *p*-nitrophenylsemicarbazide, m. p. 186—187°). (I) is well suited for characterisation of alcohols and NH_2 -compounds, but does not react with $\text{CPh}_3 \cdot \text{OH}$. Indole and *Et* dihydrocollidinedicarboxylate do not react with PhNCO . Pyridine catalyses the reaction of (I) with amines, but also causes some polymerisation.

R. S. CAHN.

Stoichiometric additive compounds of alcohols and hydrogen chloride in the liquid state. G. KOHN (Ber., 1932, 65, [B], 589—595).—In confirmation of the hypothesis of the existence of liquid additive compounds of HCl and alcohols, it is shown that saturation of MeOH, EtOH, PrOH, BuOH, and amyl and octyl alcohol with HCl causes absorption of about 8% more HCl than is required to form the 1:1 compound. When amyl alcohol is shaken with aq. HCl the acid is not distributed between the two phases in conformity with the partition coeff., but accumulates in the alcohol with increasing concn. of the aq. phase. In presence of C_6H_6 , ligroin, or paraffin, the ratio HCl: alcohol = 1:1 persists after saturation. The solubility of the adducts differs in certain cases from that of the pure alcohols, the effect being noticeable when only a part of the stoichiometric amount of HCl has been absorbed. Addition of H_2O to the additive compound from EtOH and HCl causes a marked increase in viscosity which attains a max. at the ratio $\text{H}_2\text{O}:\text{HCl} = 1:1$. H_2O can be added to amyl alcohol-HCl until present in 2.4—2.5 times the amount of HCl; further addition causes separation into 2 phases.

H. WREN.

Preparation of absolute isopropanol. L. E. GILSON (J. Amer. Chem. Soc., 1932, 54, 1445).—Abs. Pr^iOH is obtained when the 91% azeotropic mixture is shaken with 10% of its wt. of flake NaOH, separated from the resulting aq. layer, shaken with a further small amount of NaOH, decanted, and distilled. Dil. Pr^iOH is concentrated by shaking with dry NaCl; the resulting upper layer (containing about 87% Pr^iOH and 2—3% NaCl), when distilled, gives practically the 91% mixture. Pr^iOH is recommended as a substitute for EtOH in biochemical work.

L. E. GILSON (b).

Reducing action of the Grignard reagent and the synthesis of *tert*-aliphatic carbinols. A. H. BLATT and J. F. STONE, jun. (J. Amer. Chem. Soc., 1932, 54, 1495—1499; cf. A., 1929, 675).—There is no definite and exact correlation between an increase in the complexity of the alkyl group and

the amount of reduction observed in the reaction between aliphatic ketones and Mg alkyl iodides. The synthesis of *tert*-aliphatic carbinols containing both straight and branched alkyl groups should be effected from branched-chain ketones and Mg *n*-alkyl halides. COPr_2 and MgPrBr give $\text{CPr}_2 \cdot \text{OH}$ (mainly) and $\text{CHPr}_2 \cdot \text{OH}$; COPr_2 and MgPr^iBr afford $\text{CPr}_2\text{Pr}^i \cdot \text{OH}$ (mainly), and small amounts of $\text{CHPr}_2 \cdot \text{OH}$ and a condensation product; COPrPr^i and MgPrBr yield $\text{CPr}_2\text{Pr}^i \cdot \text{OH}$ (mainly) and $\text{CHPrPr}^i \cdot \text{OH}$; COPrPr^i and MgPr^iBr furnish $\text{CPrPr}^i \cdot \text{OH}$; COPr^i and MgPrBr give $\text{CPrPr}^i \cdot \text{OH}$ (mainly) and $\text{CHPr}^i \cdot \text{OH}$.

C. J. WEST (b).

Constitution of the mannitol dibenzoate of Einhorn and Hollandt. P. BRIGL and H. GRUNER (Ber., 1932, 65, [B], 641—645).—Benzoylation of mannitol in presence of H_3BO_3 affords mannitol dibenzoate, m. p. 182°, identical with that prepared by Ohle and others (A., 1930, 191) and by Einhorn and Hollandt. Since it is oxidised by KMnO_4 to benzoylglycollic acid (not dibenzoylmesotartaric acid as assumed by Ohle), it cannot be a $\delta\epsilon$ -derivative. On grounds of probability it is regarded as an α -compound; this conclusion is strengthened by its inability to react with CPh_3Cl and by the introduction of a Bz group into the 6 position in the analogous benzoylation of glucose and its ethylmercaptal. The following compounds are incidentally described:

Pb glycollate, $\begin{matrix} \text{CH}_2\text{O} \\ \text{CO}_2 \end{matrix} \text{Pb}$; *r*-dibenzoyltartaric acid, m. p. 112—113°, and its *anhydride*, m. p. 182°; *meso*-dibenzoyltartaric *anhydride*, m. p. 207—208°; *benzoylglycollic acid*, m. p. 112°, and its *anhydride*, m. p. 126°.

H. WREN.

Ring contraction in formation of inner ethers from glycols. Oxidotetradecane from tetradecane- $\alpha\epsilon$ -diol. A. FRANKE, A. KROUPA, and T. PANZA (Monatsh., 1932, 60, 106—116).—Tetradecane- $\alpha\epsilon$ -diol, best prepared by reduction of Me dodecamethylenedicarboxylate with Na and amyl alcohol (cf. A., 1926, 499), gives on dehydration by distillation from 50% H_2SO_4 with superheated steam an *oxide*, $\text{C}_{14}\text{H}_{28}\text{O}$, b. p. 259—262°, in small yield, accompanied by much unsaturated material. Oxidation of the oxide with KMnO_4 in COMe_2 gives decoic acid in good yield, unaccompanied by succinic or oxalic acid. Succinic acid is destructively oxidised by KMnO_4 in COMe_2 , but not by aq. alkaline KMnO_4 ; further, oxidododecane gives *n*-hexoic acid alone with KMnO_4 in COMe_2 , but is known to give oxalic and succinic acids in addition with aq. alkaline KMnO_4 . The $\alpha\epsilon$ -oxide structure, $\text{C}_9\text{H}_{19} \cdot \text{CH} < \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} \end{matrix} > \text{CH}_2$, is therefore assigned to oxidotetradecane.

H. A. PIGGOTT.

Preparation, properties, and uses of glycerol derivatives. IV. ϵ -Piethylin, epiphenylin, and phenyl ethers. D. W. STEPHENS (Chem. and Ind., 1932, 375—378).—Improved prep. of glycidyl *Et* ether (*epiethylin*) (I) [from $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$ by NaOH in EtOH to give $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OEt}$ (67% yield), which, by further action of NaOH at 100°, the mixture being kept just acid to phenolphthalein, affords (1) a const. b. p. mixture of (I) and H_2O ,

b. p. 90—124° (25%), (2) (I), b. p. 124—126° (49%), and (3) b. p. >126° (26%), whence by salting out and fractionation a 78% yield of (I) is obtained], Ph glycidyl ether (epiphenylin) (II) [by addition of NaOH to PhOH and $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ at 70—80°, the reaction mixture being kept just acid to phenolphthalein, heating to 100°, and fractionation of the upper layer which gives a 65% yield of (II), b. p. 115—116°/3—4 mm., $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OPh}$, m. p. 80—81° (III), being obtained as a by-product], and $\text{OHCH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OPh}$, softens at 50°, becoming liquid at 68° [by a similar method from $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$, 59% yield], are described. (III) is similarly prepared from PhOH and $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ at 120° (70—75% yield). F.-p. diagrams for (II)-camphor [eutectic, 31.0°, 61.2 mol.-% of (II)], (III)-camphor [eutectic, 48.0°, 38.4 mol.-% of (III)], and (II)-(III) [eutectic 41.4°, 78.6 mol.-% of (II)], are plotted. (I) and (II) readily afford amino-ethers by the action of bases: $\text{NHR}_2 + \text{CH}_2\text{CH}_2\text{OR}' \rightarrow \text{NR}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OR}'$.

J. W. BAKER.

Esters of glycerol with amino-acids, and mixed esters with amino- and fatty acids. II. L. HASKELBERG (Bull. Soc. chim., 1932, [iv], 51, 212—230; cf. this vol., 364).—Glycerol heated with pyruvic acid at 105—110° for 3—4 hr. gives $2\text{H}_2\text{O}$, a solid (I), (?) $\alpha\gamma$ -ethylideneglycerol- α' -carboxy- β -lactone, m. p. 83.5°, b. p. 100—102°/6 mm. (cf. A., 1930, 193), and a liquid isomeride (II), (?) $\alpha\beta$ -ethylideneglycerol- α' -carboxy- γ -lactone, b. p. 118—119°/10 mm., converted by warm H_2O into (I). The isomeride, m. p. 62°, obtained by Brigl (*loc cit.*) was not observed. (I) gives a phenylhydrazone, m. p. 156° (Bz_2 derivative, m. p. 188°), whilst with $\text{Ba}(\text{OH})_2$ it gives the Ba salt of the corresponding acetal acid. (II) gives an oxime, m. p. 119° [Bz_3 derivative (III), m. p. 111—112°], and a phenylhydrazone, m. p. 114° (Bz_2 derivative, m. p. 152°), hydrolysed to pyruvic acid phenylhydrazone. Action of 1% NH_3 in EtOH gives the amide, m. p. 81°, of the corresponding acid (Ba salt). *iso*Propylideneglycerol with bromopropionyl bromide in presence of pyridine gives *isopropylideneglyceryl* α -bromopropionate, b. p. 138°/19 mm., 120°/5 mm., converted by NaNO_2 into the oximino-derivative, m. p. 43° [Bz derivative, m. p. 107° (softens 104°)], hydrolysed to *glyceryl* α -oximino-propionate, m. p. 118.5° [Bz_3 derivative, m. p. 78.5—79°, not identical with (III)]. A. A. LEVI.

Thionitrites. III. Thermal dissociation of alkyl thionitrites. H. RHEINOLDT and F. MOTT (J. pr. Chem., 1932, [ii], 133, 328—330; cf. A., 1931, 820).—*tert.*-Bu thionitrite (I) in CO_2 or air at 95—98°, or in boiling hexahydrotoluene gives NO and *tert.*-Bu disulphide, b. p. 74°/12 mm.; slow, spontaneous decomp. in air gives an oil and a little cryst. substance. (I) is stable to O_2 at 0°.

R. S. CAHN.

Preparation and properties of a double series of aliphatic mercaptans. L. M. ELLIS, jun., and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 1674—1687).—*n.* and α -*sec.*-Mercaptans from Me to nonyl and various intermediate alcohols and bromides are

prepared. Curves illustrating certain relationships between the mercaptans and alcohols are given. Vals. (new and lit.) of the b. p./760 mm., d_4^{20} , d_4^{25} , expansion per °C., n_D^{20} , and MR_D (found and calc.) for the alcohols from amyl to nonyl (both *n.* and *sec.*-isomerides), for the bromides, and for the mercaptans are given. C. J. WEST (b).

Action of some mercaptans in hydrocarbon solution on copper and copper sulphide. K. H. SLAGLE and E. E. REID (Ind. Eng. Chem., 1932, 24, 448—451).—The action of Cu compounds in removing mercaptans from hydrocarbon solutions is due to the formation of Cu mercaptides, and disulphides (cf. A., 1931, 1033). Measurements are recorded with CuS on Me to *n*-nonyl, Pr^i , Bu^i , and β -amyl mercaptans in C_6H_6 , *n*-heptane, and cyclohexane. *sec.*-Mercaptans higher than C_4 in C_6H_6 form sol. coloured Cu mercaptides. Repeated treatment with small amounts of CuS is more efficient than a single treatment. The effect of varying concn. was measured with CuS on Bu^iSH in C_6H_6 . HgS (black), PbS, Sb_2S_3 (black), CdS, and C are less effective than CuS, whilst other substances have little or no action. Sulphides and disulphides are not attacked. A. A. LEVI.

Addition of alkali alkoxide to esters. V. Ester-alkoxide compounds and acetoacetic condensation. F. ADICKES (Ber., 1932, 65, [B], 522—525; cf. A., 1931, 196).—A criticism of Scheibler's theories. H. WREN.

Addition of alkali enolates to esters. VI. F. ADICKES, W. BRUNNERT, O. LUCKER, and G. SCHAFER.—See this vol., 614.

Catalytic hydrogenation of esters to alcohols. II. K. FOLKERS and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1145—1154; cf. A., 1931, 598).—Various alkyl mono- and di-carboxylates are hydrogenated to the corresponding alcohols or glycols in 90—98% yields. The rate of hydrogenation is retarded by free acid or MeOH and is considerably modified by the nature of the alkyl group. Thus, cyclohexyl hexoate is reduced much more rapidly than the Et ester, whilst the latter is hydrogenated several times faster than the Me ester. The presence of a Ph, CO_2Et , or $\text{CH}_2\cdot\text{OH}$ group in the vicinity of a CO_2Et or $\text{CH}_2\cdot\text{OH}$ group (except with Et lactate) facilitates fission of the C-O linking; the CO_2Et (or $\text{CH}_2\cdot\text{OH}$) and CH-OH groups are thus reduced to Me and CH_2 , respectively. This reaction occurs almost exclusively when Ph is adjacent to CO_2Et , or when CO_2Et or $\text{CH}_2\cdot\text{OH}$ is α - to the ester group. Incorporation of Mg or Ca into the catalyst minimises the conversion of the α -Ph esters into the hydrocarbons. *N*-Hexoylpiperidine is hydrogenated to *N*-hexylpiperidine. The N-C linking in $-\text{N}\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{Et}$ undergoes fission under the conditions used for hydrogenation of the ester. With Et nipecotate, fission occurs (over Ni) at 165°, and 3-methyl-2-piperidone (or its reduction products) results. The rate of hydrogenation of Et laurate at pressures of 100, 200, and 300 atm. shows a 28-fold increase over this range. The hydrogenation of esters under the conditions used occurs at about 200° upward.

C. J. WEST (b).

Action of ammonia and amines on esters of unsaturated acids. I. Action of ammonia, methylamine, and diethylamine on ethyl crotonate. K. MORSCH (Monatsh., 1932, 60, 50—68).—Interaction of NH_3 and Et crotonate in abs. EtOH at room temp. gives an equilibrium (?) mixture of Et β -aminobutyrate and Et₂ $\beta\beta'$ -iminodibutyrate, accompanied, if the reaction is prolonged, by small amounts of β -aminobutyramide, m. p. 73—74.5°, but traces only of crotonamide. Addition to the double linking is therefore much more rapid than amidation. Similar results are obtained with liquid NH_3 at room temp., but at 100—155° aldehyde-ammonia and NH_4 oxamate are produced, presumably by hydrolytic fission at the double linking. Reaction is considerably more rapid with NH_2Me in abs. EtOH at room temp. or in absence of a solvent at 65°; Et β -methylaminobutyrate (I) is first formed (in 89% yield with 1.1 equiv. NH_2Me) and is converted by further action of NH_2Me into β -methylaminobutyrmethylamide. Neither crotonmethylamide nor an imino-ester was formed, and the latter could not be prepared by interaction of Et crotonate and (I). NH_4Et alone or in abs. EtOH at room temp. reacts very slowly to give Et β -diethylaminobutyrate as main product, but at 200° in absence of a solvent crotondiethylamide, b. p. 100—102°/13 mm., and unidentified basic products are formed. The above Et alkylaminobutyrate are readily hydrolysed by warm H_2O to β -methylamino-, m. p. 141—142° (+1 H_2O , m. p. 86—87°), and β -diethylamino-, m. p. 72.5—74.5°, -butyric acids. H. A. PIGGOTT.

New example of the allylic isomerisation. A. KIERNANN and R. RAMBAUD (Compt. rend., 1932, 194, 1168—1170).— Ac_2O converts Et α -hydroxy- Δ^{β} -butenoate into the corresponding Ac derivative, $\text{CH}_2\text{:CH-CH(OAc)-CO}_2\text{Et}$ (I), b. p. 89°/15 mm. (hydrolysed to the original acid), but PBr_3 gives Et γ -bromo- Δ^{α} -butenoate, converted by NaOAc into an Ac derivative, b. p. 119—120°/15 mm., isomeric with (I) and hydrolysed to an isomeric acid of the original acid. J. W. BAKER.

Conjugated double linkings. XXIV. Synthesis of cis-trans-isomeric methylated polyene-carboxylic acids. Synthesis and configuration of dehydrogeranic acid. R. KUHN and M. HOFFER (Ber., 1932, 65, [B], 651—660).—The synthesis of a series of cis-trans-isomeric methylated polyene-carboxylic acids is described. In view of the uncertainty of the configuration of the isomerides, it is recommended to apply the term "acid I" (probably trans with reference to the double linking vicinal to the CO_2H group) to the isomeride of higher m. p. and "acid II" (probably cis) to that of lower m. p. The requisite OH-esters are obtained from the ketone, $\text{CH}_2\text{Br-CH}_2\text{CO}_2\text{Me}$, and Zn in C_6H_6 , whereby aliphatic ketones require 15 min. ebullition and aromatic ketones 3 hr. Ethylideneacetone affords Me β -hydroxy- β -methyl- Δ^{γ} -hexenoate, b. p. 82—85°/12 mm., transformed by P_2O_5 in boiling C_6H_6 into Me β -methylsorbate, b. p. 80—84°/12 mm., hydrolysed by KOH-EtOH to β -methylsorbic acid I, m. p. 119—120°, and by aq. Ba(OH)_2 to β -methylsorbic acid II, m. p. 98—99° (in addition to

much ethylideneacetone and AcOH). Crotylideneacetone gives Me β -hydroxy- β -methyl- $\Delta^{\gamma\gamma}$ -octadienoate, b. p. 90—105°/3 mm., dehydrated to Me β -methyl-octatrienoate, b. p. 117—125°/11 mm., m. p. 33°, whence by KOH-EtOH , β -methyl- $\Delta^{\gamma\gamma}$ -octatrienoic acid I, m. p. 160—161° (corr.), and impure β -methyl- $\Delta^{\gamma\gamma}$ -octatrienoic acid II, m. p. 105—110° after softening at 97°; a similar mixture is obtained by means of Ba(OH)_2 . β -Methylcrotonaldehyde, COMe_2 , and aq. NaOH afford ζ -methyl- $\Delta^{\gamma\gamma}$ -heptadien- β -one, b. p. 86—87°/15 mm. [oxime, m. p. 108—109° (corr.)], transformed into the corresponding OH-ester, which with aq. Ba(OH)_2 yields $\beta\zeta$ -dimethyl- $\Delta^{\gamma\gamma}$ -octatrienoic acid II, m. p. 137° (corr.), and is converted by P_2O_5 in C_6H_6 into Me dehydrogeranate, b. p. 127—135°/12 mm., which gives $\beta\zeta$ -dimethyl- $\Delta^{\gamma\gamma}$ -octatrienoic acid I, m. p. 185—186° (corr.), identical with natural dehydrogeranic acid. Styryl Me ketone affords Me β -styrylcrotonate, b. p. 170—172°/12 mm., hydrolysed by KOH-EtOH to δ -phenyl- β -methyl- $\Delta^{\gamma\gamma}$ -pentadienoic acid II, m. p. 123.5—124.5°, isomerised by I in C_6H_6 in sunlight to δ -phenyl- β -methyl- $\Delta^{\gamma\gamma}$ -pentadienoic acid I, m. p. 160°. Cinnamylideneacetone slowly affords Me β -styrylacrylcrotonate, b. p. 160—180°/0.3 mm., hydrolysed by KOH-EtOH to a mixture of ζ -phenyl- β -methyl- $\Delta^{\gamma\gamma}$ -heptatrienoic acids, m. p. 202—203° and m. p. 167—169° (corr.), separable into its components by crystallisation from 96% EtOH or, more conveniently, by fractional digestion of the Ba salts with boiling H_2O . H. WREN.

Synthesis of dehydrogeranic acid and other compounds from β -methyl- Δ^{α} -butenal. F. G. FISCHER and K. LÖWENBERG (Annalen, 1932, 494, 263—284).— β -Methyl- Δ^{α} -butenal (I) (improved prep. given; cf. A., 1931, 335) with aq. Ba(OH)_2 in Et_2O gives (after repeated fractional distillation) impure dehydrocitril (II), b. p. 81—84°/0.3 mm. [semicarbazone, m. p. 223° (decomp.)], and impure β -methyl- $\Delta^{\beta\beta}$ -heptadien- ζ -one (III) [the pure ketone, b. p. 83—83.5°/9 mm., is prepared from (I) and COMe , in EtOH-NaOEt] [semicarbazone, m. p. 192° (decomp.)]; (III) is formed by hydrolytic fission of (II) or the intermediate aldol. (I) is converted by NaNH_2 in dry Et_2O and N_2 into 2-formyl-1:1:5-trimethyl- $\Delta^{2:4}$ -cyclohexadiene (IV) (50% yield), b. p. 85—86°/9 mm. (semicarbazone, m. p. 213°), oxidised by O_3 in EtCl at -30° to $\alpha\alpha$ -dimethyl-lævulic acid (1 mol.) and HCO_2H (2 mols.), and reduced to 2:2:4-trimethylhexahydrobenzaldehyde (semicarbazone, m. p. 222—223°), which is readily autoxidised to 2:2:4-trimethylhexahydrobenzoic acid, m. p. 93°. (IV), COMe , and NaNH_2 in N_2 give 1:1:5-trimethyl-2- γ -keto- Δ^{α} -butenyl- $\Delta^{2:4}$ -cyclohexadiene, b. p. 102—105°/0.8 mm. [semicarbazone, m. p. 190—191° (decomp.)]. Citral is converted by NaNH_2 in Et_2O into a compound, $\text{C}_{20}\text{H}_{30}\text{O}$ (probably 2-formyl-1-methyl-1:5-di- Δ^{γ} -isohexenyl- $\Delta^{2:4}$ -cyclohexadiene), b. p. 203—205°/9 mm., whilst crotonaldehyde similarly gives resinous material.

(I), $\text{CH}_2\text{Br-CH}_2\text{CO}_2\text{Et}$, and Zn in C_6H_6 give (after distillation of the intermediate with Zn dust) Et δ -methylsorbate, b. p. 82—83°/9 mm., hydrolysed to δ -methylsorbic acid II, b. p. 123—124°/9 mm., m. p. 17° (main product), and I, m. p. 109—110°, both of which are reduced catalytically to isoheptoic acid.

Hydrolysis of the twice-distilled ester from (III), $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn affords $\beta\zeta$ -dimethyl- $\Delta^{\alpha\alpha}$ -octatrienoic acid (V), m. p. 187–188° (decomp.), identical with the dehydrogeranic acid of Cahn *et al.* (this vol., 144); hydrolysis of the once-distilled ester gives a little (V) and (mainly) an oily acid, which when heated at 50–95° loses CO_2 forming the readily polymerised $\beta\zeta$ -dimethyl- $\Delta^{\alpha\alpha}$ -heptatriene, b. p. 53–54°/10 mm., m. p. –23° to –22°. H. BURTON.

Hydrogenation of arachis oil. H. I. WATERMAN and (FRL.) M. ZAAYER (Rec. trav. chim., 1932, 51, 401–406).—Selective hydrogenation (Ni) of linoleic acid and its glycerides in arachis oil occurs when Normann's but not when Wilbuschewitsch's apparatus is used. Linoleic acid is considered to occur in large quantities in natural edible fats, but to be oxidised when the fats are kept. R. S. CAHN.

Polymerisation and ring formation. XI. Use of molecular evaporation as a means for propagating chemical reactions. XII. Linear superpolyesters. XIII. Polyamides and mixed polyester-polyamides. XIV. Linear superpolyanhydride and cyclic dimeric anhydride from sebacic acid. XV. Artificial fibres from synthetic linear condensation superpolymerides. W. H. CAROTHERS and J. W. HILL. XVI. A polyalcohol from dimagnesium decamethylene bromide. W. H. CAROTHERS and J. E. KIRBY (J. Amer. Chem. Soc., 1932, 54, 1557–1559, 1559–1566, 1566–1569, 1569–1579, 1579–1587, 1588–1590).—XI. The use of mol. evaporation in reversible reactions involving the simultaneous formation of volatile and non-volatile products is advantageous. A new form of mol. still is described.

XII. The term superpolymeride is applied to linear polymerides of mol. wt. above 10,000. The previously described (A., 1930, 1272 and previous abstracts) linear polyesters derived from dibasic acids and glycols or from higher ω -OH-acids, when heated in a mol. still or in an inert gas, undergo self-reaction forming polyesters of much higher mol. wt. The new superpolyesters (ω -polyesters) are tough opaque solids; they show sharp X-ray powder diffraction patterns, become transparent at definite temp., and dissolve in CHCl_3 giving highly viscous solutions. The ω -trimethylene ester, m. p. 75–76°, M 3300, of hexadecamethylene- $\alpha\omega$ -dicarboxylic acid is prepared when the acid and 10% excess of the glycol are heated first at 180–200° for 3 hr. and then at 200°/1 mm. for 6 hr. When this ester is heated at 200° (bath)/10^{–3} mm. for 7 days in a mol. still a (non-distillable) product, M 12,000, results; the small amount of distillate contains (probably) unimol. trimethylene hexadecamethylenedicarboxylate, m. p. 124–125°. ω -Polyethylene succinate, a tough, somewhat elastic mass, softens at 95° to a very viscous and somewhat rubbery mass; fibres of this are short and rather brittle. The ω -polyester from λ -hydroxydecoic acid is a translucent tough, flexible mass. The ω -ester from ξ -hydroxypentadecic acid becomes transparent at 95°, and can be drawn into thin fibres and cold drawn.

XIII. The polyamide derived from ϵ -aminohexanoic acid (A., 1931, 205), when heated in the mol. still, undergoes a considerable change in physical properties,

indicating an increase in mol. wt. When ϵ -aminohexanoic (1–5 mols.) and 1 mol. of hexadecamethylene- $\alpha\omega$ -dicarboxylic acids are heated with $(\text{CH}_2)_3(\text{OH})_2$ (1 mol.+5% excess), mixed polyester-polyamides are obtained (the m. p. increases with the amount of NH_2 -acid). The properties of these substances are between those of the polyesters and the polyamides; like the superpolyesters they can be drawn out into strong, pliable, transparent fibres.

XIV. Sebacic α -anhydride, M about 5000, from the acid and AcCl or Ac_2O , is a linear polymeride. Smooth depolymerisation of this anhydride cannot be effected by ordinary vac. distillation, but when heated in the mol. still a (more complex) ω -anhydride (I), and the volatile β -anhydride (II), m. p. 68°, are obtained. (I) is very tough and can be drawn into exceedingly strong, pliable, lustrous, highly-oriented fibres. (II) is a cyclic (22-membered ring) dimeride. When heated above its m. p., (II) polymerises to a γ -anhydride, which resembles the α -anhydride. The behaviour of these anhydrides towards NH_2Ph is described and discussed.

XV. The linear condensation ω -polyesters, polyanhydrides, and mixed polyester-polyamides, described above, are easily drawn out into very strong, pliable, highly-oriented fibres which closely simulate natural silk and cellulose fibres. These materials also resemble cellulose and silk in the essential details of their mol. structure. If no stress is used in the prep. of the filaments they closely resemble the massive ester from which they are produced; if sufficient tension is applied the filaments are transparent and have a very high lustre. The tensile strength of rather thick fibres of the ω -trimethylene hexadecamethylene- $\alpha\omega$ -dicarboxylate, prepared by pulling filaments from the molten ester and subsequently orienting them by cold drawing, is approx. 16–24 kg. per sq. mm.; the dry (or wet) tenacity is about 1.1 g. per denier. The fibres are more elastic than those of any known artificial silk. The fibres from the anhydrides have a very high degree of strength, pliability, and lustre, but they gradually disintegrate on keeping, owing to hydrolytic degradation.

XVI. $(\text{CH}_2)_{10}(\text{MgBr})_2$ and HCO_2Me give an alcohol $[(\text{CH}_2)_{10}\text{CH}_2\text{OH}]_5$, m. p. 120–121°; various derivatives (e.g., Ac) are obtained as oils or tars. When heated in the mol. still, a product of the same composition but much higher mol. wt. results.

C. J. WEST (b).

Structure of the glutaconic acids and esters. III. α -Carbethoxyglutaconic esters. B. S. GIDVANI, G. A. R. KON, and C. R. WRIGHT (J.C.S., 1932, 1027–1040; cf., A. 1931, 608).—Carbethoxyglutaconic esters and NaOEt afford Na derivatives, partly hydrolysed by H_2O to an equilibrium mixture of $\alpha\beta$ - and $\beta\gamma$ -forms. The $\beta\gamma$ -ester is liberated from the remaining alkaline solution by CO_2 ; also by BzOH from the Na or K derivatives in a neutral solvent. All the esters studied alkylate in the α -position. The Na derivative of Et isoaconitate ($\beta\gamma$ -ester) reacts with MeI in EtOH to give an α -alkyl compound, which on ozonolysis affords Et glyoxylate and Et α -formylmethylmalonate (phenylhydrazone, m. p. 128°), and with NaOEt during 1 hr. affords Et α -methylglutaconate. Et β -chloro-crotonate and -iso-

crotonate with Et sodiomalonate afford distinct tricarboxylic esters, hydrolysed by 5% KOH to acids, m. p. 149° (from *trans*-ester) and m. p. 115—116° (from *cis*-ester), respectively. The K derivative of Et α -carbethoxy- β -methylglutaconate ($\alpha\beta$ - and $\beta\gamma$ -forms) affords with BzOH the pure $\beta\gamma$ -ester and with MeI, an α -Me compound, ozonised to Et glyoxylate and Et acetylmethylmalonate (*pyrazolone*, m. p. 176°). The methylated product and NaOEt afford Et $\alpha\beta$ -dimethylglutaconate, hydrolysed to the *cis*- $\alpha\beta$ -acid. Et phenylpropionate and Et sodiomalonate afford a yellow Na compound (Na in γ -position) which is not methylated in a neutral solvent. HCl liberates a liquid ester ($\alpha\beta$ - and $\beta\gamma$ -forms) affording a colourless Na derivative (Na in α -position) which suffers α -alkylation and affords the $\beta\gamma$ -isomeride with BzOH. The reaction product of Et phenylpropionate and Et sodiomethylmalonate with HCl (but not with BzOH) affords the $\beta\gamma$ -ester. γ -Me and -Et carbethoxyglutaconates react normally; the CH_2Ph ester, in the equilibrium state contains some $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}_2\cdot\text{C}(\text{CHPh})\cdot\text{CO}_2\text{Et}$, the K derivative of which affords with BzOH no $\alpha\beta$ -ester, although some benzylidene ester is formed. Reaction of the γ -Me ester with Al-Hg in Et_2O affords *Et* α -carbethoxy- γ -methylglutarate, b. p. 159—161°/14 mm. Interaction of Et α -carbethoxy- γ -methyl- α -ethylglutaconate and Et α -carbethoxy- α -methyl- γ -ethylglutaconate with NaOEt affords dibasic esters which immediately suffer interconversion and afford only mixtures of isomerides. J. L. D'SILVA.

Alkylaconitic acids. R. D. DESAI (J.C.S., 1932, 1088—1093).—Alkylation of Et aconitate affords a viscous product, and poor yields of the aconitic esters are obtained from $\text{CH}_2(\text{CO}_2\text{Et})_2$ or $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ with Et chlorofumarate and up to 3 mols. NaOEt. Et oxalacetate and Et bromopropionate with Zn in C_6H_6 afford *Et* α -methylcitrate, b. p. 195°/15 mm., in small yield and NPhEt_2 with Et α -bromotricarballylate affords mainly the lactone of Et_2H α -hydroxytricarballylate and some aconitic acid. Ozonolysis shows that Et α -cyanoaconitate (J.C.S., 1906, 89, 631) is a mixture of the $\alpha\beta$ - and $\beta\gamma$ -forms (I). Et oxalocyanacetate, one product of ozonolysis, affords with semicarbazide acetate 3-carbethoxy-1-carbamyl-4-cyanopyrazolone, m. p. 237° (decomp.). The K derivative of (I) affords with BzOH the $\alpha\beta$ -ester with some $\beta\gamma$ -ester (cf. A., 1930, 773). Methylation of the K salt affords Et α -cyano- Δ^4 -butene- $\alpha\beta\gamma$ -tricarboxylate, the isomeric " $\beta\gamma$ -ester" (J.C.S., 1906, 89, 631) containing some $\alpha\beta$ -ester. Further methylation of the $\alpha\beta$ - or $\beta\gamma$ -form affords the dimethylated ester. Hydration of α -methylaconitic anhydride affords the *cis*-acid, m. p. 105°, converted into the *trans*-acid by HCl or heat. With AcCl in CHCl_3 , α -methylaconitic acid affords the *anhydro*-acid(?), m. p. 110° (decomp. 140°). J. L. D'SILVA.

d-Talonic acid and γ -talonolactone. L. H. CRETCHER and A. G. RENFREW (J. Amer. Chem. Soc., 1932, 54, 1590—1594).—Freshly prepared solutions of *d*-talonic acid, $[\alpha]_D^{25} +18.24$ — 19.65° (cf. A., 1927, 340), give no evidence of γ -lactone when titrated with 0.1N-NaOH; nearly 4% is found after 1 hr. The % of γ -lactone calc. from titration vals. are definitely

higher than those calc. polarimetrically during the first 24 hr. The shape of the mutarotation curve for solutions of talonic acid indicates the formation of a dextrorotatory δ -talonolactone, in addition to the laevorotatory γ -lactone. γ -Talonolactone has m. p. 132—134°, $[\alpha]_D^{25} -34.65^\circ \rightarrow -28.4^\circ$ (5 days) in H_2O . C. J. WEST (b).

Manufacture of calcium gluconate by electrolytic oxidation of glucose. H. S. ISBELL, (Miss) H. L. FRUSH, and F. J. BATES (Ind. Eng. Chem., 1932, 24, 375—378).—The process already described (A., 1931, 1038) is made continuous for the prep. of Ca gluconate (yield 85%). Directions are given for recovery of the bromide. Basic Ca gluconate is $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_7)_2 \cdot 2\text{CaO}$. A. A. LEVI.

Micro-determination of uronic anhydride groups in pectic substances. H. W. BUSTON (Analyst, 1932, 57, 220—223).—In a modified micro-Zeisel apparatus, 6—10 mg. of the substance are refluxed with 4 c.c. of 13% HCl (90% saturated with NaCl) for 60—70 min. Any HCl is removed by Ag_2SO_4 and CO_2 is absorbed from a sintered glass plate in 0.02N-Ba(OH) $_2$. An aliquot portion of the Ba(OH) $_2$ solution is titrated with 0.01N- $\text{H}_2\text{C}_2\text{O}_4$. T. McLACHLAN.

Behaviour of methylglyoxal in weak alkaline solution. Y. ARAI (J. Biochem. Japan, 1932, 15, 151—161).—Methylglyoxal is rapidly transformed quantitatively into lactic acid when treated with alkali at reactions exceeding p_H 13.0, whilst at smaller degrees of alkalinity AcOH , HCO_2H , and unknown reducing substances are formed in addition to lactic acid, the proportions of the products depending on the degree of alkalinity and on the temp. KCN accelerates the disappearance of methylglyoxal and increases the yield of reducing substances. F. O. HOWITT.

Nitroso-compounds. I. Preparation and reduction of nitrosoketones. J. G. ASTON, D. F. MENARD, and M. G. MAYBERRY (J. Amer. Chem. Soc., 1932, 54, 1530—1538).—Ketones of the type $\text{CHMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{R}$, treated with an equiv. quantity of Et nitrite in HCl at about 50°, afford some of the bimol. compounds $(\text{NO}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{R})_2$. Thus COMePr^s gives 24% of bimol. *Me nitrosoisopropyl ketone* (I), m. p. 101.5—102° (decomp.); COEtPr^s affords 6.8% of bimol. *Et nitrosoisopropyl ketone*, m. p. 119—120°, and 27% of Pr^s α -oximinooethyl ketone, m. p. 92—93°. Reduction of (I) with SnCl_2 and HCl gives 62% of β -azoxy- β -methylbutan- γ -one, m. p. 60—61°, reduced further to COMePr^s and N_2H_4 . Reduction of bimol. β -nitroso- β -methylpentan- δ -one with SnCl_2 and HCl or Na-Hg and H_2O gives neither the corresponding amine nor hydrazine. There is no evidence that, as a rule, the NO group in aliphatic compounds is reduced to NH_2 or $\text{NH}\cdot\text{OH}$ except in small yields. C. J. WEST (b).

Constitution of certain carbohydrates. W. N. HAWORTH (Ber., 1932, 65, [4], 43—65).—A lecture. H. WREN.

Oxidation of the α - and β -forms of the sugars. H. S. ISBELL (J. Amer. Chem. Soc., 1932, 54, 1692—1693).—There are marked differences in the rates of oxidation of various sugars and of different forms of a given sugar with $\text{Br}\cdot\text{H}_2\text{O}$. β -Lactose is oxidised to

about 95% in 3 min., whilst α -lactose undergoes about 50% oxidation. This affords a method of determining the approx. amounts of the α - and β -isomerides in solution.

C. J. WEST (b).

Behaviour of phenolphthalein and methyl-orange in the oxidation of sugars by alkaline iodine. (Miss) C. A. MALLIN (Analyst, 1932, 57, 244—245).—With I in the presence of alkali, phenolphthalein forms tetraiodophenolphthalein and EtOH gives rise to CHI₃; together these may cause an error of 2% and account for the results of Slater and Acree (cf. A., 1930, 1165). Aq. methyl-orange is unaffected by alkaline I.

T. MCLACHLAN.

Synthesis of 2:3:6-trimethylglucose. J. C. IRVINE and J. K. RUTHERFORD (J. Amer. Chem. Soc., 1932, 54, 1491—1495).—2:3-Dimethylmethylglucoside and 30% HNO₃ in CHCl₃ give 89% of its 4:6-dinitrate, converted by NaI in COMe₂ at 100° into 6-iodo-2:3-dimethylmethylglucoside 4-nitrate. Treatment of this with AgOAc, hydrolysis (alkaline) of the product formed, and subsequent methylation gives 2:3:6-trimethylmethylglucoside 4-nitrate, reduced by Fe and AcOH to a trimethylmethylglucoside, b. p. 130—140°/0.2 mm., which is hydrolysed to 2:3:6-trimethylglucose, m. p. 114°.

C. J. WEST (b).

Determination of fructose and sucrose. J. FIEBE (Z. Unters. Lebensm., 1932, 63, 288—291).—The solution is heated on a water-bath for 30 min. with 10 c.c. of 5N-HCl, diluted to 50 c.c., and 5 c.c. are pptd. with 5 c.c. of 32% HCl and 0.625% phloroglucinol (cf. B., 1929, 146, 375, 955). Arabinose gave a bluish-green colour, and glucose, maltose, lactose, and wheat starch (1%) yellow colours, but no ppt.; 10 c.c. of 1% sucrose yielded 12.36 mg., and 5 c.c. of 1% fructose 11.71 mg. of hydroxymethylfurfuraldehyde, these results being reproducible within 0.5% if more than 11 mg. are weighed. Under these conditions 50 mg. of sucrose give the same wt. of ppt. as 26.3 mg. of fructose, but for more conc. solutions relatively higher wts. of ppt. are obtained.

J. GRANT.

Structure of α -fructose penta-acetate and α -fructose chloro[tetra]acetate. E. PACSU and F. V. RICH (J. Amer. Chem. Soc., 1932, 54, 1697—1698).—It is suggested that α -fructose chlorotetra-acetate is a derivative of the open-chain fructose with a Cl atom at C₆.

C. J. WEST (b).

Constitution of the anhydrofructose of Irvine and Stevenson. H. H. SCHLUBACH and H. ELSNER (Ber., 1932, 65, [B], 519—522; cf. A., 1929, 1046).—Treatment of anhydrofructose triacetate, m. p. 122°, [α]_D²⁰ —1° in CHCl₃, obtained from inulin by the method of Irvine and Stevenson, with NaOH and Me₂SO₄ followed by Ag₂O and MeI affords a product which, after depolymerisation with EtOH-H₂C₂O₄ and hydrolysis, yields 3:4:6-trimethylfructofuranose (phenylosazones, m. p. 78—80° and 123—125°, respectively), identical with that obtained by Haworth and Learner from trimethylinulin. The anhydrofructose has the constitution



The question of its identity with lavan is left open. Irvine and Stevenson's views concerning the heterogeneity of inulin are untenable.

H. WREN.

Heptamethylsucrose: a correction. J. C. IRVINE and E. T. STILLER (J. Amer. Chem. Soc., 1932, 54, 1486—1491).—The "heptamethylsucrose" described by Haworth (J.C.S., 1923, 123, 301) is a complex mixture containing 30% of octamethylsucrose. Hydrolysis of the mixture gives tetramethyl- γ -fructose (45%), tetramethylglucose (15%), trimethyl- γ -fructoses (8%), 17% of four isomeric forms of trimethylglucose, and 14% of a mixture of 2:3-dimethylglucose, one other isomeride, and monomethylglucoses. Evidence is obtained showing the order in which Me groups enter the sucrose mol.; so far as the glucose component is concerned, this is similar to that in starch. Methylation of sucrose may be accompanied to some extent by alteration in the position of the O ring in the glucose component.

C. J. WEST (b).

9:9-Diacetamido-compound of alizarin-glucoside. A. MÜLLER (Ber., 1932, 65, [B], 672—679; cf. A., 1931, 940).—1-Acetoxy-2-acetoglucoxyanthraquinone-9-imine (I) (improved prep.) is transformed by 15% NH₃-MeOH into 9:9-diacetamido-1-hydroxy-2-glucosoxyanthraquinone (II), m. p. 154—155° after becoming red at 120°, [α]_D²⁵ —59.26° in H₂O, obtained similarly from the N-Ac derivative of (I). It is stable towards alkali, but hydrolysed by 5% HCl to alizarin-glucoside. Passage of NH₃ into a solution of (I) yields a yellow diacetamido-compound, m. p. 153—154° after becoming red at 120°, which loses NH₃ when preserved over P₂O₅ and KOH and then becomes colourless. Treatment of (II) with Ac₂O in pyridine yields the compound C₃₃H₃₆O₁₆N₂; m. p. 177—178° after softening at 175°, [α]_D²⁵ —45.20° in CHCl₃, not readily hydrolysed and stable towards MeI and Ag₂O in COMe₂. 2-Hydroxy-2-glucosoxyanthraquinone-9-imine hydrate and BzCl in pyridine yield completely benzoylated alizarin-glucoside, m. p. 208° after softening at 156°, [α]_D²⁵ —32.72° in CHCl₃, obtained also from benzoglucosylalizarin. Methylation of (I) and 1-hydroxy-8-acetoglucoxyanthraquinone-9-imine is accompanied by elimination of N and production of acetylacetoglucoxyalizarin and 1-methoxy-8-acetoglucoxyanthraquinone, respectively.

H. WREN.

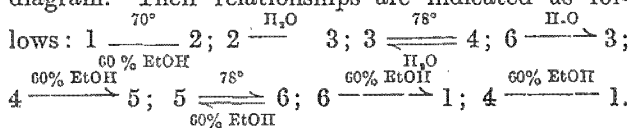
Dehydrogenation of sapogenin. Constitution and synthesis of sapotalin. E. SPATH and O. HROMATKA (Monatsh., 1932, 60, 117—128).—Dehydrogenation of sapogenin with Se at 300—340° gives sapotalin (18%) and unidentified hydrocarbons, m. p. 126—127°, b. p. 120°/0.0012 mm. (picrate, m. p. 161—163°), m. p. 116°, b. p. 170°/0.0012 mm. (picrate, m. p. 213—215°), m. p. 228—230.5° (sublimes about 210° in high vac.), and m. p. 304—305°. Sapotalin is oxidised by aq. KMnO₄ at 100° to trimellitic and mellophanic acids, whence it could be 1:2:6- (known), 1:4:6-, or 1:2:7-trimethylnaphthalene; it is shown to be the last-named by synthesis.

β -p-Tolyethyl bromide is condensed with CMeNa(CO₂Et)₂, and the resulting ester, b. p. 191—192°/14 mm., hydrolysed to β -p-tolyethylmethylmalonic acid, m. p. 160—161°, decarboxylated at 180° to γ -p-tolyl- α -methylbutyric acid (amide, m. p. 146—147°); the acid chloride with AlCl₃ in light petroleum gives 1-keto-2:7-dimethyl-1:2:3:4-tetrahydronaphthalene, b. p. 142—143°/16 mm. (semicarbazone, m. p.

204—206°). The last-named is condensed with MgMeI and the crude carbinol obtained dehydrated by Ac_2O at the b. p. to 1 : 2 : 7-trimethyl-3 : 4-dihydronaphthalene, which is dehydrogenated by Pd-charcoal at 190—200° or by Se at 300° to 1 : 2 : 7-trimethylnaphthalene, identical with sapotalin in all respects.

H. A. PIGGOTT.

α -Dextrin of Schardinger. M. ULMANN, C. TROGUS, and K. HESS (Ber., 1932, 65, [B], 682—686).—Simple treatment of α -amylose affords six modifications which differ from one another in Röntgen diagram. Their relationships are indicated as follows:



The transformations occur partly in solution, partly in course of heterogeneous decomp. Prep. (2) is probably identical with Schardinger's α -dextrin in which the presence of H_2O has been overlooked, whilst prep. (3) is probably the same as Miekeley's hydrate. The readiness with which the preps. are interconverted necessitates caution in judgment of compounds obtained from α -amylose by chemical action, since differences between initial and final material may simply be due to variation in separation and after-treatment of the "reaction product."

H. WREN.

Nitrates of starch. I. Nitrates of starch from potato starch. J. HACKEL and T. URBAŃSKI (Rocz. Chem., 1932, 12, 276—297).—The yield, N content, and viscosity of solutions of starch nitrates in COMe_2 increase with the concn. and relative quantity of HNO_3 , and diminish with rise in temp. above 0°. As the duration of reaction is increased, the above vals. at first rise to a max., thereafter regularly falling. The solubility in EtOH and the N content of starch nitrate are reduced by boiling with H_2O . Starch nitrate pptd. by H_2SO_4 is less stable than that pptd. by H_2O . The highest degree of nitration is given by mixtures of HNO_3 , H_2SO_4 , and H_2O in which the mol. concns. of H_2SO_4 and H_2O are approx. equal. When the relative concn. of H_2SO_4 to HNO_3 is <1 : 9, nitration proceeds differently from that of cellulose, probably owing to solubility of starch nitrate in such mixtures.

R. TRUSZKOWSKI.

Oxycellulose and its identity with β -cellulose and cellodextrin. E. PATERNO (Atti R. Accad. Lincei, 1932, [vi], 15, 20—26).—A sealed note, dated Nov. 7, 1926. Various oxycelluloses, obtained by the action of different oxidising agents, and including β -cellulose and cellodextrin, are identical, although varying in degree of purity; all are sol. in the moist state in 8—10% NaOH solution to give colloidal solutions from which acids ppt. them as a transparent jelly. The different oxycelluloses and the so-called viscose hydrocelluloses, that from silk included, contain only a single oxycellulose, which is of paramount importance in the prep. of viscose silk. Analysis indicates that oxycellulose contains only a small proportion of oxidised groups $\text{C}_6\text{H}_{10}\text{O}_6$.

T. H. POPE.

Exhausted cellulose. E. PATERNO (Atti R. Accad. Lincei, 1932, [vi], 15, 17—20).—"Exhausted

cellulose," prepared by repeated treatment of cellulose with 18% NaOH , is a pure product and, like cotton, yields rather more than the theoretical proportion of glucose on hydrolysis. Certain of the products classified as hemicelluloses are formed by the action of the air, especially in presence of H_2O or salts and, still more so, of alkali.

T. H. POPE.

Action of hydrogen fluoride on carbohydrates.

III. B. HELFERICH and O. PETERS (Annalen, 1932, 494, 101—106).—Cellan (A., 1930, 72) is methylated (Me_2SO_4 and aq. KOH) to a product (OME about 44%), $[\alpha]_D^{25} +145.1^\circ$ in CHCl_3 , hydrolysed by 2% MeOH-HCl to a mixture of methylated methylglucosides; hydrolysis of the glucoside fraction, b. p. up to 110°/0.2 mm., with 5% aq. HCl gives a little 2 : 3 : 4 : 6-tetramethylglucose (I). The % condensations (determined by the diminution in reducing power) occurring when 2 : 3 : 4- and 2 : 3 : 6-trimethylglucoses, (I), and glucose are treated with anhyd. HF are 58, 59, 68, and 95, respectively. These results indicate that cellan is not built up uniformly from glucose residues. Dissolution of cellulose (II) in anhyd. HF and addition of anhyd. Et_2O (after 10 min.) gives an almost F-free product which is largely insol. (or slightly sol.) in H_2O ; more prolonged treatment affords a product containing 3.9—4.7% F. Similar short treatment of glucosidyl fluoride (III) gives a H_2O -sol. product (8.1% F); the F content after more prolonged treatment is 7.4%. Fredenhagen's view (A., 1931, 1119) that (III) is produced from (II) and HF is criticised.

H. BURTON.

Cellulose sulphuric esters. II. W. TRAUBE, B. BLASER, and E. LINDEMANN (Ber., 1932, 65, [B], 603—612; cf. A., 1928, 621).—Prolongation of the action of ClSO_3H on cellulose in presence of pyridine does not lead to the production of a homogeneous trisulphate, whereas esters with less than 3 SO_3H groups per $\text{C}_6\text{H}_{10}\text{O}_5$ cannot be isolated by the action of SO_3 on cellulose. In the last-named reaction it is advantageous to replace gaseous SO_3 by a solution of SO_3 in CS_2 and to use the cellulose in excess. The product is poured into an excess of KOH , unattacked cellulose is removed, and the filtrate worked up for the K_3 salt (cf. *loc. cit.*). The corresponding $(\text{NH}_4)_3$ salt is described. Addition of pyridine to the solution of SO_3 in CS_2 followed by evaporation of the latter and addition of cellulose gives an ester with 2.6 SO_3H groups. The esters obtained by the pyridine process (K and Na salts described) are more closely allied to cellulose than those obtained by means of SO_3 , for which the nomenclature "hydrocellulose sulphates" is proposed. The viscosities of aq. solutions, Cu no., and $[\alpha]_D^{25}$ for the two series are recorded. The wide variation, particularly in viscosity, appears to indicate that the micellar structure of cellulose is not destroyed unless all the OH groups are replaced by the SO_3H residue. The behaviour of K hydrocellulose trisulphate as protective colloid and its inhibition of the pptn. of BaSO_4 , HgCrO_4 , and PbI_2 (properties shared by the "pyridine" sulphate) indicate a high mol. wt. confirmed by the non-elevation of the b. p. of H_2O , in which, however, it has marked electrical conductivity. H_3 hydrocellulose trisulphate is quantitatively hydro-

lysed by MeOH-HCl, which does not attack the K_2 salt.
H. WREN.

Relation of cellulose to lignin in wood. K. FREUDENBERG (Papier-Fabr., 1932, 30, 189—195).—The results of chemical, X-ray, and microscopical investigations indicate that cellulose is built up from glucose or cellobiose residues and lignin from coniferyl alcohol or phenolic residues in order to produce the structure of the wood fibre. There is no combination between cellulose and lignin, but the whole structure resembles reinforced concrete in that the cellulose micelles are held in position by lignin and hemi-cellulose.
B. P. RIDGE.

Basis for the physiological activity of -onium compounds. IX. Derivatives of homologues of betaine. R. R. RENSHAW and M. E. MCGREAL (J. Amer. Chem. Soc., 1932, 54, 1471—1474).—The following trialkyl-carbomethoxy- and -carbethoxy-methylammonium bromides are prepared from $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Me}(\text{Et})$ and the requisite trialkylamine: triethyl-carbomethoxy-, m. p. 132°, and -carbethoxy-, m. p. 104°; tri-*n*-propyl-carbomethoxy-, m. p. 138°, and -carbethoxy-, m. p. 134°; tri-*n*-butyl-carbomethoxy-, m. p. 113°, and -carbethoxy-, m. p. 83°; triisooamyl-carbomethoxy-, m. p. 99.5°; phenyldimethylcarbomethoxy-, m. p. 99°; benzoyldimethyl-carbomethoxy-, m. p. 151°, and -carbethoxy-, m. p. 114.5°; dibenzylmethyl-carbomethoxy-, m. p. 128°, and -carbethoxy-, m. p. 148°; methylammonium bromides. Triisooamylcarboxyanilido-, m. p. 169°, triethylcarboxy-, m. p. 190°, tri-*n*-propylcarboxy-, m. p. 177°, and triisooamylcarboxy-, m. p. 144°, -methylammonium bromides are also prepared. The $\cdot\text{CO}_2\text{H}$ compounds have no action on the autonomic nervous system; the activity of the esters varies with the different *N*-alkyl groups.

C. J. WEST (b).

Reactions between sugars and amino-acids. II. Syntheses of some amino-acid glucosides. K. MAURER and B. SCHIEDT (Z. physiol. Chem., 1932, 206, 125—132; cf. A., 1926, 602).—Tetra-acetylsarcosine ester glucoside with HCl in Et_2O gives the hydrochloride, m. p. 78°. Sarcosine amide glucoside with pyridine- Ac_2O affords the Ac_5 derivative, m. p. 176°, $[\alpha]_D^{25} +13.66^\circ$ in CHCl_3 . Treatment of sarcosylglycine with HCl in EtOH gives the *Et* ester (I), m. p. 88—89°; (I) condenses with acetobromoglucose to tetra-acetylsarcosylglycine ester glucoside, m. p. 125°, $[\alpha]_D^{25} +7.52^\circ$ in CHCl_3 . Sarcosine *Et* ester and acetobromocellobiose yield hepta-acetylsarcosine ester cellobioside, m. p. 164°, $[\alpha]_D^{25} -8.1^\circ$ in CHCl_3 (hydrochloride, m. p. 89°), which gives a syrupy amide glucoside with NH_3 in MeOH and on reacylation of the latter, octa-acetylsarcosine amide cellobioside, m. p. 254° (decomp.), $[\alpha]_D^{25} -11.43^\circ$ in CHCl_3 . (I) with acetobromocellobiose affords hepta-acetylsarcosylglycine ester cellobioside, m. p. 212°, $[\alpha]_D^{25} -8.32^\circ$ in CHCl_3 .

J. H. BIRKINSHAW.

Configurative behaviour of isoleucine in the Walden inversion. E. ABDERHALDEN and F. SCHWEITZER (Z. physiol. Chem., 1932, 206, 116—124).—dl- α -Bromo- β -methyl-*n*-valeryl derivatives of the NH_2 -acids: dl-leucine, m. p. 120—124° (sinters about 114°), -glycine, m. p. 120—122°, and *l*-tyrosine were not attacked by trypsin or yeast maceration juice.

The four optically active derivatives of leucine were obtained; d- α -bromo- β -methyl-*n*-valeryl-d-leucine, m. p. 128°, $[\alpha]_D^{25} +62.0^\circ$; d-*l*-, m. p. 157°, $[\alpha]_D^{25} +5.15^\circ$, *l*-*l*-, m. p. 128° $[\alpha]_D^{25} -62.1^\circ$; *l*-d-, m. p. 157°, $[\alpha]_D^{25} -5.03^\circ$ (all rotations in EtOH). The rate of elimination of Br by *N*-alkali was greater in the compounds containing components opposite in configuration (*l*-d- and d-*l*-). From this fact and the sp. rotation it is concluded that in the conversion of isoleucine into the corresponding α -bromo-fatty acid and in formation of the NH_2 -acid from the latter by amination there is no change in configuration.

J. H. BIRKINSHAW.

Determination of the ionisation constants of guanidine and its alkylated derivatives. T. L. DAVIS and R. C. ELDERFIELD (J. Amer. Chem. Soc., 1932, 54, 1499—1503).—The following new salts are reported: butylguanidine sulphate, m. p. 206°, nitrate, m. p. 69°, and picrate, m. p. 154.5°; heptylguanidine sulphate, nitrate, and picrate, m. p. 244° (decomp.), 86°, and 140.5°, respectively; benzylguanidine sulphate, nitrate, and picrate, m. p. 204°, 165°, and 185.5°; piperidoguanidine nitrate, m. p. 154° (decomp.); NN'-dimethylguanidine sulphate and nitrate, m. p. 264—265° and 68° (decomp.), respectively; NN'-diethylguanidine sulphate, m. p. 234—235° (decomp.); NN'-diamylguanidine sulphate and picrate, m. p. 190—191° (decomp.) and 108°, respectively; NN'-trimethylguanidine sulphate, nitrate, and picrate, m. p. above 345°, 276°, and 214.5°, respectively. The vals. of $K \times 10^{-1}$ are given for some of the guanidines; the basic strength of the alkylguanidines appears to be a function only of the positions of the substituents. Introduction of a Ph group into guanidine lowers the basicity. General details for the synthesis of amines are given in the prep. of heptylamine.

C. J. WEST (b).

ϕ -Halogenes. XIX. 1. Action of halogen on fulminic acid and fulminates. 2. Trihalogeno-nitrosomethanes. L. BIRCKENBACH and K. SENNEWALD (Ber., 1932, 65, [B], 546—552; cf. this vol., 505).—Hg fulminate in aq. suspension is converted by Cl_2 into dichloroformoxime (I) (40%) and dichlorofuroxan, whereas the latter substance is almost quantitatively obtained in EtCl at -80° . The yields of dibromofuroxan and dibromoformoxime (II) from Hg fulminate and Br in H_2O , *N*- H_2SO_4 , and 5*N*- H_2SO_4 are 30% and 25%, respectively. (I) in 50% EtOH gives di-iodofuroxan in 90% yield. The course of the reaction of halogen and Hg fulminate in presence of halogen acid [not mineral acids as stated by Endres (this vol., 257)] is governed by the liberation of fulminic acid and not by hydrolysis of the primary product $[\text{CHal}_2\text{N}\cdot\text{O}]_2\text{Hg}$ in acid medium.

Dichlorobromonitrosomethane, b. p. 21°/24 mm., obtained by successive addition of Br and NaOAc to (I) in H_2O , is transformed by Br into dichlorodibromomethane, b. p. 135°, and reduced by H_2S in MeOH to (I). $\text{CBr}_3\cdot\text{NO}$, b. p. 34—39°/14 mm., prepared by addition of Na fulminate to NaOAc and Br in dil. AcOH, is transformed by hot H_2O into CHBr_3 and CBr_4 . (II), treated successively with HgCl_2 , Br, and NaOAc, affords chlorodibromonitrosomethane, b. p. 24°/20 mm., passing into CClBr_3 , b. p. 158—159.5°, m. p. 55°, when heated with Br. Dibromoformoxime

hydrate, m. p. 40°, prepared in 80% yield from Na fulminate and Br in presence of 20% H_2SO_4 , gives *chlorobromoformoxime*, m. p. 36°, when treated with HgCl_2 in H_2O . Addition of Na fulminate to (I) suspended in EtOH and conc. H_2SO_4 afford *di-iodoformoxime hydrate*, m. p. 52°. H. WREN.

Alkylation of nitriles in liquid ammonia. J. B. CLOKE (J. Amer. Chem. Soc., 1932, 54, 1690—1691).—The alkylation of nitriles in liquid NH_3 reported by Nieuwland and Baldinger (this vol., 382) has been previously observed by the author (A., 1931, 1031). C. J. WEST (b).

Configuration of simple amino-nitriles and diamines. H. REIHLEN, E. WEINBRENNER, and G. VON HESSLING (Annalen, 1932, 494, 143—158).—(—)-*l*- α -Aminopropionitrile (I), $[\text{M}]_D -18.4^\circ$ in H_2O (cf. Delépine, A., 1904, i, 148) [*H* tartrate (+ H_2O), $[\text{M}]_D +23.2^\circ$ in H_2O], is hydrolysed by cold conc. HCl to the hydrochloride, $[\text{M}]_D +13.1^\circ$ in H_2O , of (+)-*l*- α -aminopropionamide, $[\text{M}]_D +7.2^\circ$ in H_2O . The (—)-*Ac* derivative (II), m. p. 102°, of (I) is reduced catalytically (PtO_2) in Ac_2O (cf. this vol., 256) to (—)-*l*- α -diacetamidopropene, m. p. 153°, $[\text{M}]_D -64^\circ$ in EtOH, hydrolysed by conc. HCl to (+)-*l*- α -propylenediamine. Reduction (H_2 - PtO_2) of (II) in EtOH and subsequent benzoylation gives (—)-*l*- α -benzamido- β -acetamidopropene, m. p. 163°, whilst similar reduction (in Ac_2O) of the Bz derivative, m. p. 128° (lit. 123.5°), of (I) affords (—)-*l*- β -benzamido- α -acetamidopropene, m. p. 187°. Phenylethylenediamine is resolved by *d*-tartaric acid into *l*-, b. p. 104°/1—2 mm., m. p. 4—5°, $[\text{M}]_D -47.8^\circ$ [tartrate, m. p. 220° (decomp.), $[\text{M}]_D +116.6^\circ$ in H_2O]; (—)-*Ac*₂, m. p. 174°, and (—)-*Bz*₂, m. p. 227°, derivatives], and *d*-forms [*H* tartrate, m. p. 180° (decomp.), $[\text{M}]_D +29^\circ$ in H_2O]. α -Aminophenylacetonitrile is partly resolved through its *H* tartrate to the *l*-form [(—)-*Ac* derivative, m. p. 130.5°, $[\text{M}]_D -23^\circ$ in CHCl_3], the (+)-*Bz* derivative, m. p. 151°, $[\text{M}]_D +8^\circ$ in CHCl_3 , of which is reduced (H_2 , PtO_2 , Ac_2O) to (—)- β -benzamido- α -acetamido- β -phenylethane, m. p. 190—193°. The configurations (denoted by *l*) assigned to the derivatives of α -aminophenylacetic acid are determined essentially by Freudenberg and Rhino's method (A., 1924, i, 1173). In the above cases (\pm) represents the sign of rotation. Vals. of $[\text{M}]_D$ for the *Ac* and *Bz* derivatives of the *d*-series of the above NH_2 -compounds and $\text{NH}_2\text{-CHPhMe}$ in various solvents are recorded.

H. BURTON.

Aliphatic germanium derivatives. I. Triethylgermanium compounds; their properties and reactions. C. A. KRAUS and E. A. FLOOD. II. Diphenyldiethylgermane, germanium diethyl oxide, and germanium diethyl dibromide. E. A. FLOOD (J. Amer. Chem. Soc., 1932, 54, 1635—1644, 1663—1667).—I. GeEt_3 is obtained in 91% yield from GeBr_4 and MgEtBr . Addition of a 50% solution of Br in EtBr to GeBr_4 during 6 days gives 82% of *Ge Et*₃ bromide, b. p. 190.9°/760 mm., f. p. —33°, hydrolysed to *Ge Et*₃ oxide, ($\text{GeEt}_3)_2\text{O}$, b. p. 253.9°, which is stable towards oxidation, is converted by halogen acids into GeEt_3X , and with Li in NH_3Et gives (probably) a mixture of LiGeEt_3 and LiO-GeEt_3 . *Ge Et*₃ fluoride, b. p. 149°/751 mm., chloride, b. p.

175.9°, and iodide, b. p. 212.3°, are described; the fluoride is more stable towards hydrolysis than the other halides. GeEt_3Br and liquid NH_3 afford a 1:1-compound having a v. p. of 10 mm. at room temp. GeEt_3Br is ammonolysed in liquid NH_3 ; the lower liquid phase formed in the reaction contains *diethylgermaniumimine*, b. p. about 100°/0.1 mm., which reacts with H_2O to form the oxide. The halides react with Li in NH_3Et to give (GeEt_3)₂ (not a satisfactory method of prep.); GeEt_3Br and Na heated at 210° for 12 hr. and then at 270° during 5 days, give *hexaethyldigermene* (I), b. p. 265°/758 mm. (I) and Br in EtBr give GeEt_3Br ; with Na in liquid NH_3 no appreciable reaction occurs, whilst with Li in NH_3Et LiGeEt_3 [which ammonolyses (more completely in NH_3) to GeHEt_3 and LiNH_3Et (or LiNH_3)] results; if NH_3 is passed into the reaction vessel after removal of the NH_3Et , *triethylgermane*, b. p. 124.4°/751 mm., is obtained. This decolorises Br in EtBr, does not react with Na in liquid NH_3 , and gives H_2 with KNH_2 . (I) and K in NH_3Et give *K triethylgermanide*, which with EtBr affords GeEt_4 .

II. GePh_2Br_2 and MgEtBr in Et_2O give 95% of *diphenyldiethylgermane*, b. p. 316°, converted by Br in *s*- $\text{C}_2\text{H}_4\text{Br}_2$ into PhBr and GeEt_2Br_2 . Hydrolysis of the product from GeEt_3F and Br in EtBr with NaOH give *Ge Et*₂ oxide, amorphous, m. p. 175°, and unstable liquid (termol.) forms; the latter (f. p. about 18°) is transformed into the solid at room temp. in a few hr., the process being accelerated by a trace of H_2O ; transition between the two forms occurs about 110°. The oxide and HBr give *Ge Et*₂ dibromide, b. p. 202°, hydrolysed to the oxide and converted by liquid NH_3 into *diethylgermaniumimine*, b. p. 100°/0.01 mm. C. J. WEST (b).

cycloPropane hydrocarbons: general methods of preparation. R. LESPIEAU and R. L. WAKEMAN (Bull. Soc. chim., 1932, [iv], 51, 384—400).—Hexane- $\beta\delta$ -diol and PBr_3 give $\beta\delta$ -dibromohexane, b. p. 81.5—83°/10 mm., debrominated with Zn and EtOH to 1-methyl-2-ethylcyclopropane, b. p. 63.9—64.9°. $\beta\delta$ -Dibromo- $\beta\delta$ -dimethylpentane, prepared from the corresponding diol, similarly affords a small yield of 1:1:2-trimethyl-2-ethylcyclopropane, b. p. 103.5—104.5°. γ -Bromo- $\alpha\gamma$ -diphenyl- Δ^3 -propene, m. p. 54—54.5° (dibromide, m. p. 130.5—131.5°), gives $\alpha\gamma$ -dibromo- $\alpha\gamma$ -diphenylpropane, debrominated to 1:2-diphenylcyclopropane, b. p. 164—166°/13 mm. (cf. Kishner, A., 1915, i, 952). MgPrBr and β -bromobutaldehyde, b. p. 42—44°/12 mm., afford β -bromohexan-3-ol, b. p. 99—101°/10 mm., which forms with HBr $\beta\delta$ -dibromohexane, b. p. 99—100°/12 mm., debrominated to 1-methyl-2-propylcyclopropane, b. p. 92—93°. For determination of the amount of olefine present in the cyclic hydrocarbons, reaction with KBr-KBrO_3 gives good results. The general methods of prep. of cyclopropane hydrocarbons are discussed.

F. R. SHAW.

Bromination of organic compounds in presence of activated charcoal. L. A. NIKOLAEV (J. Gen. Chem. Russ., 1931, 1, 1035—1038).—Freshly ignited animal charcoal first treated with Br and then with C_6H_6 causes rapid formation of PhBr and *p*- $\text{C}_6\text{H}_4\text{Br}_2$, although there is no action with Cl_2

or I. Similarly, from EtOH and Br, EtBr, ethylene dibromide, and a lachrymatory oil, b. p. 128°, are obtained; Cl₂ and I do not react with EtOH in presence of charcoal. It is suggested that in spite of being rapidly absorbed by charcoal, Cl₂ is incapable of bringing about the polarisation of a non-polar mol. such as C₆H₆, being less activated than Br. Activated Br has a more powerful polarising effect owing to its greater residual valency and also reacts more rapidly with polar mols. G. A. R. KON.

Polymethylbenzenes. V. Separation of mesitylene from ψ -cumene. VI. Separation of durene from isodurene. VII. Jacobsen reaction. II. L. I. SMITH and O. W. CASS (J. Amer. Chem. Soc., 1932, 54, 1603—1609, 1609—1614, 1614—1621).—V. Xylene, MeCl, and AlCl₃ give a mixture of trimethylbenzenes [also obtained in about 15% yield from xylene (4 pts.) and AlCl₃ (1 pt.) at 130—140°] containing no 1:2:3-derivative. Sulphonation of the mixture and treatment of the mixed sulphonic acids with HCl (const. b. p.) at 80° causes hydrolysis of mesitylenesulphonic acid (I) (+2H₂O), m. p. 78°, m. p. (anhyd.) 98.5—100°, to mesitylene (II) which is removed by steam-distillation at 80° under reduced pressure [in order to obtain pure (II) the above processes must be repeated]. ψ -Cumene-5-sulphonic acid (III) (+1.5H₂O), m. p. 111—112°, m. p. (anhyd.) 128—131°, separates from the reaction mixture after removal of (II), and is converted into ψ -cumene (IV) by steam-distillation from 50% H₂SO₄ at 135—145°. Pure (III) can be obtained from a mixture of (I) and (III) by washing with CHCl₃, whereby (I) is removed, but cannot be isolated pure. The refractive index of a mixture of (II) and (IV) is a linear function of the composition.

VI. The mixture of tetramethylbenzenes produced in the above methylation is cooled to -15°, whereby durene (V) [sulphonic acid (+2H₂O), m. p. 113°] separates. The filtrate from this contains isodurene (VI) [sulphonic acid (+2H₂O), m. p. 79°] saturated with (V); prehnitene [sulphonic acid (+2H₂O), m. p. 104°] is not present. Details are given for the separation of (V) and (VI) from the above filtrate; the method involves fractional sulphonation and hydrolysis.

VII (cf. A., 1929, 1433). The Jacobsen reaction occurs either (a) by the shift of Me (alkyl) groups from mol. to mol., giving higher and lower methylated benzenes, or (b) by internal rearrangement of Me groups to a system more stable towards H₂SO₄ or other strong dehydrating agents. Of the polymethylbenzenes, only (V), (VI), and C₆HMe₅ (VII) undergo the reaction; (V) and (VI) react according to (b), giving prehnitene (VIII), whilst (VII) reacts according to (a), giving (VIII) and C₆Me₆. Mixtures of (V) and (VI) can thus be used in the prep. of (VIII). By-products of the reactions are SO₂, black H₂O-sol. material, and brown amorphous H₂O-insol. material, the last constituting 10—30% of the total materials recovered. Rearrangement of the sulphonic acid (not the hydrocarbon) occurs; the dehydrating agent (P₂O₅ or H₂SO₄) is necessary, since the acids alone are stable. The shift of the Me groups is accompanied by reduction of the sulpho-group of part of the material

used. The orientation effects of the Jacobsen reaction and those of direct methylation of C₆H₆ hydrocarbons are entirely opposite in the case of tetramethylbenzene. C. J. WEST (b).

Polymerides from benzyl chloride and related compounds. R. A. JACOBSON (J. Amer. Chem. Soc., 1932, 54, 1513—1518).—CH₂PhCl is polymerised by a little AlCl₃ to (mainly) an insol. hydrocarbon (C₇H₈)_x and a small amount of a sol. resin of the same empirical formula. The proportions of these are reversed when FeCl₃ is used, whilst with SnCl₄, the sol. polymeride results. The mol. wt. of the sol. resin is 1260—2250. The polymerides are not readily attacked by oxidising agents. Polymerisation of *p*-C₆H₄Br·CH₂Cl proceeds similarly; the unit of both the insol. and sol. polymerides is C₇H₅Br and the mol. wt. of the resin varies from 1300 to 1500. Polymerides have been obtained from *p*-C₆H₄Br₂ and *p*-C₆H₄(CH₂Br)₂ by the Wurtz reaction; the former gives a sol. polymeride, whilst the latter affords an infusible insol. polymeric hydrocarbon (C₈H₈)_x. C. J. WEST (b).

Diphenyl and its derivatives. XI. New derivatives of 2-methyldiphenyl and influence of methyl on reactions of the amino-group in the 2'-position. L. MASCARELLI and D. GATTI [with P. LAVAZZA] (Atti R. Accad. Lincei, 1932, [vi], 15, 89—91; cf. this vol., 509).—2-Nitro-2'-methyldiphenyl, m. p. 57—58°, was prepared from *o*-iodotoluene, *o*-iodonitrobenzene, and Cu. 2-Amino-, m. p. 37°, b. p. 157—158°/17 mm. (hydrochloride, m. p. 128°, decomp. 130—131°), 2-chloro-, b. p. 174°/50 mm., 276°/755 mm., 2-bromo-, b. p. 285—286° (decomp.) or 156—157°/27 mm., 2-iodo-, m. p. 38—39°, b. p. 186—187°/30 mm., and 2-cyano-, b. p. 213—214°/63 mm., 2'-methyldiphenyl were prepared. The formation of no compounds (carbazole, diphenylene oxide, iodonium base) indicating closure (by means of NH, O, I) of a third nucleus on the 2:2'- or 2:6'-position was observed. Hence, not only is the 2-Me not expelled during the diazo-reaction and subsequent decomp. of the diazo-compound by means of H₂O, CuCl(Br), or KI, but it does not disturb the reactions of the 2'-NH₂-group. T. H. POPE.

Variations in the behaviour of phenyl-ethylenes and -ethanes during catalytic hydrogenation. W. H. ZARTMAN and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1668—1674).—Increase in the no. of Ph groups in the phenylethylenes increases the temp. and/or pressure required for hydrogenation to the corresponding phenyl- and cyclohexyl-ethanes and decreases the rate of hydrogenation under comparable conditions. The increased difficulty of hydrogenation with rise in mol. wt. is not large, since CPh₂:CPh₂ is converted into the ethane at 100°, and CPh₃:CHPh₂ into pentacyclohexylethane at 125°, at reasonably rapid rates. The successive substitution of Ph groups in C₂H₆ materially lowers the stability of the C-C linking, so that when three Ph groups are in the mol. the ethane can be cleaved at 200° over a Cu-Cr oxide catalyst. CPh₃:CHPh₂ undergoes fission over Ni at 125°. The labilising effect (if any) of cyclohexyl groups on the ethane C atoms is very small, since pentacyclohexylethane is

stable at 200° over Ni or Cu-Cr oxide catalysts. $\alpha\alpha\beta$ -*Tricyclohexylethane*, b. p. 191—192°/8 mm., $\alpha\alpha\alpha\beta$, m. p. 112—114°, and $\alpha\alpha\beta\beta$ -*tetracyclohexylethane*, m. p. 158—159°; β -*phenoxy- α -diphenylethane*, b. p. 214—217°/8 mm., m. p. 64—65°; *pentacyclohexylethane*, m. p. 191—192°, and β -*phenoxy- α -diphenylethylene*, b. p. 235°/23 mm., m. p. 58—59°, are incidentally described. Data are given for the reduction of styrene, stilbene, tri- and tetra-phenylethylenes, β -phenoxy- α -diphenylethylene, $\alpha\alpha$ - and $\alpha\beta$ -di- and penta-phenylethanes, and also the cleavage products of several of these compounds.

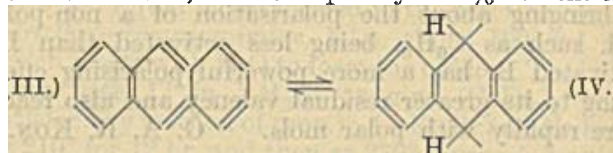
C. J. WEST (b).

Syntheses of alkylphenanthrenes. I. 1-, 2-, 3-, and 4-Methylphenanthrenes. R. D. HAWORTH (J.C.S., 1932, 1125—1133).—Reduction of β -1- and β -2-naphthoylpropionic acids (prep. described) by Clemmensen's method and cyclisation with 85% H_2SO_4 affords 1- (I) and 4-keto-1:2:3:4-tetrahydrophenanthrene. MgMeI and (I) afford a carbinol (*picrate*, m. p. 127—128°) [the 4-keto-compound affords 4-hydroxy-4-methyl-1:2:3:4-tetrahydrophenanthrene, m. p. 111—112° (*picrate* from cold MeOH , m. p. 96—98°, from hot MeOH , m. p. 110°)]. Either carbinol when dehydrated with HCO_2H at 100° and then treated with Se affords 1-methylphenanthrene, m. p. 118° (*picrate*, m. p. 135—136°; quinone, m. p. 191°), and 4-methylphenanthrene, m. p. 49—50° (lit. 117°) [*picrate*, m. p. 140—141° (lit. 125°); quinone, m. p. 187° *quinoxaline*, m. p. 178°]. 1-Keto- and 4-keto-1:2:3:4-tetrahydrophenanthrene afford with $(\text{CO}_2\text{Et})_2$ and KOEt , *Et* 1-keto-1:2:3:4-tetrahydrophenanthrene-2-glyoxylate (I), m. p. 84—85°, and *Et* 4-keto-1:2:3:4-tetrahydrophenanthrene-3-glyoxylate, m. p. 75—76°, also prepared by cyclisation of γ -1-naphthyl- α -methylbutyric acid with 85% H_2SO_4 . Reaction of C_{10}H_8 with methylsuccinic anhydride in PhNO_2 containing AlCl_3 affords β -2-, m. p. 165—166°, and β -1-naphthoyliso-butyric acid, m. p. 123—124°, which are reduced to γ -2-naphthyl- α -methylbutyric acid, m. p. 85—86°, converted by H_2SO_4 into 4-keto-3-methyl-1:2:3:4-tetrahydrophenanthrene, m. p. 64—65°, and thence into 3-methylphenanthrene, m. p. 62—63° (lit. 65°) [*picrate*, m. p. 137—138° (lit. 141°); quinone, m. p. 205—206°; *quinoxaline*, m. p. 207—208°], by reduction and dehydrogenation, and γ -1-naphthyl- α -methylbutyric acid, m. p. 90°, cyclised by H_2SO_4 to 1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene and thence to 2-methylphenanthrene, m. p. 55—56° (lit. 52—53°) (*picrate*, m. p. 118—119°; quinone, m. p. 147—148°; *quinoxaline*, m. p. 186—188°).

J. L. D'SILVA.

Polynuclear aromatic hydrocarbons. XII. Distribution of the double linkings in condensed aromatic hydrocarbons. E. CLAR (Ber., 1932, 65, [B], 503—519; cf. A., 1931, 1282, 1292).—The absorption spectra of the following compounds are described: 2:3:6:7-dibenzanthracene-9:10-diyl (I) and its 9:10- Cl_2 -derivative; 2:3-benzanthracene (II); 1:2:3:4-dibenzanthracene; 2':3'-naphtha-2:3-phenanthrene; 2':1'-anthraceno-1:2-anthracene; 7:7'-dimethyl-2':3'-naphth-1:2-anthracene. The formation of the first bands in the region of longer wave-length in the case of anthracene derivatives

(A bands) is attributed to unpaired electrons of the *meso*-C atoms. This condition (*R* state), in which these C atoms possess electron septets, is in equilibrium with the *o*-quinonoid state (III \rightleftharpoons IV). $\text{Log } \epsilon_{\text{max}}$ of the A bands, and consequently the % content of



the anthracenes in the *R* state, increases with increasing reduction potential of the *o*-quinones from which the anthracenes are evolved, and conversely. The displacement of the first A bands in comparison with those of anthracene is a measure of the valency demand of the *o*-arylene residues. In polynuclear aromatic hydrocarbons of the anthracene type, the *o*-arylene residues replacing the *o*-phenylene group of anthracene are so united to the central ring that the union in the *R* state is formed by a double linking. The structure of the naphthylene residue is unsymmetrical in linear, symmetrical in angular, union.

(I) and PCl_5 in boiling $\text{C}_6\text{H}_4\text{Me}_2$ yield an additive product which passes into 9:10-dichloro-2:3:6:7-dibenzanthracene-9:10-diyl, decomp. 305° when rapidly heated, oxidised by air in sunlight to 2:3:6:7-dibenzanthraquinone. It reacts slowly with *p*-benzoquinone, very rapidly with maleic anhydride. (II), m. p. 341°, prepared by distilling tetrahydro-2:3-benzanthraquinone over Zn dust and Cu powder, reacts more readily than anthracene with maleic anhydride in boiling $\text{C}_6\text{H}_4\text{Me}_2$, and is smoothly oxidised by air in ultra-violet light to 2:3-benzanthraquinone. 9:9'-Dianthryl has m. p. 308—310°; 9:10-endo-2:3-benzanthracene-, m. p. (indef.) 273—282° (decomp.), and 9:10-endo-1:2-benzanthracene-, m. p. 242°, $\alpha\beta$ -succinic anhydride are described.

H. WREN.

N-Chlorosulphonyl-amides and -sulphonamides. Reactivity of sulphuryl chloride. J. MEYBECK (Ann. Chim., 1932, [x], 17, 129—206).—Action of SO_2Cl_2 on sodioformanilide (improved prep.) gives *N*-chlorosulphonylformanilide (I), m. p. 80—81° (yield 27.4%). Similarly are obtained *N*-chlorosulphonyl-acetanilide (II), m. p. 71° (yield 30%) (together with a little *p*-chloroacetanilide), and -benzanilide (III), m. p. 109.5—110° (yield 10—15%), also obtained from the K derivative (yield 33%), from the product of interaction of MgEtBr and NHPhBz (together with Br) (yield 9%), and from the similar product using MgPrCl (yield 58%); *N*-chlorosulphonyl-*p*-toluenesulphonanilide (IV), m. p. 138.5—139° (yield 23%), -*o*- (V), m. p. 107.5—108° (yield 20%), -*p*- (VI), m. p. 106.5—107.5°, and -*m*-toluidide (VII), m. p. 125.5—126°. These substances when heated with Cu evolve SO_2 and give unidentified products [from (II) a substance, m. p. 180—185°, is obtained]. With conc. H_2SO_4 HCl is evolved. Hydrolysis with H_2O , acids, or alkalis gives the original anilides, except (I), which with NaOH gives PhNC , whilst (II) gives NH_2Ph . With NaOH in $\text{EtOH-H}_2\text{O}$ at room temp. sulphamates are probably formed, e.g., $\text{NPhBz}\cdot\text{SO}_3\text{Na}$. The action of heat gives SO_2 , HCl , and unidentified products, AcCl and BzCl being formed from (II) and (III),

respectively. (II) with EtOH gives EtOAc and HCl. (I) and (III) react similarly, whilst (IV), (V), (VI), and (VII) are unattacked. Interaction of sodio-*p*-toluenesulphonamide and (IV) gives a substance, m. p. 195–197°. NH_2Ph and (IV) give $\text{NH}_2\text{Ph}\cdot\text{HCl}$, *p*-toluenesulphonamide, and coloured products, similar products being obtained from (VI) together with (?) sulphondianilide (cf. this vol., 261). (VI) with NH_3 gives (?) sulphamide and trisulphimide, $(\text{SO}_2\cdot\text{NH})_3$, whilst with *o*-phenylenediamine 2:3-diaminophenazine is formed. The action of SO_2Cl_2 on formanilide, acetanilide, benzanilide, and *p*-toluenesulphonanilide and *o*-toluidide in CCl_4 and CHCl_3 gives chlorinated anilides. A. A. LEVI.

p-Aminophenylguanidine: preparation of the nitrate, hydrochloride, and sulphate, and attempted preparation of the free base. C. E. BRAUN (J. Amer. Chem. Soc., 1932, 54, 1511–1513).—*p*-Aminophenylguanidine hydriodide and AgNO_3 in H_2O give 30.1% of the nitrate, m. p. 189–190°. *p*-Phenylenediamine and *S*-ethylisothiocarbamide hydrochloride in H_2O give 15% of *p*-aminophenylguanidine hydrochloride, m. p. 167–168.5°; the sulphate, decomp. 279°, is prepared similarly. The sulphate and aq. $\text{Ba}(\text{OH})_2$ give (probably) the amorphous dihydrate, m. p. 182° (decomp.), of the free base, which when heated above 100° gives NH_3 and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$. C. J. WEST (b).

Stereochemistry of derivatives of ethane. III. Stereochemical course of ring fission of $\alpha\beta$ -diphenylethyleneimines. A. WEISSBERGER and H. BACH (Ber., 1932, 65, [B], 631–636; cf. this vol., 259).—Addition of HCl to *dl*-*cis*-, *dl*-*trans*-, *l*-*trans*-, and *d*-*trans*- $\alpha\beta$ -diphenylethyleneimine yields quantitatively *dl*-*iso*-, *dl*-, *l*-, and *d*- β -chloro- α -aminodibenzyl, respectively. Ring fission leads stereochemically exclusively to the chloroaminodibenzyls from which the imines are derived. Addition of the elements of H_2O to the *dl*-*cis*-, *dl*-*trans*-, *l*-*trans*-, and *d*-*trans*-imines in presence of $2\text{N}\cdot\text{H}_2\text{SO}_4$ gives mainly *dl*-*iso*- with little *dl*-, mainly *dl*- with little *dl*-*iso*-, mainly *l*- with little *l*-*iso*-, and mainly *d*- with little *d*-*iso*- α -amino- β -hydroxydibenzyl, respectively. Racemisation is not observed. All the changes are mixtures of *cis*- and *trans*-addition. It is considered that only one C-N linking is ruptured during ring fission. *iso*- α -Acetamido- β -acetoxydibenzyl has m. p. 145–146° (corr.). H. WREN.

Alkylation of orange-I. A refutation. K. H. T. PFISTER (J. Amer. Chem. Soc., 1932, 54, 1521–1526).—A criticism of the work of Slotta and Franke (A., 1931, 344). Alkylation of orange-I is normal; the methylation, ethylation, propylation, butylation, and hexylation products are described. The Na salt (+2 H_2O) of the Me ether has no val. as an indicator. The ethers are readily hydrolysed by acids, especially at higher temp. The use of HCl by Slotta and Franke probably resulted in the regeneration of the original material. C. J. WEST (b).

Configuration of phthalylbenzidine. E. E. TURNER (J.C.S., 1932, 1294–1295).—Contrary to Gugliemelli and others (this vol., 171), phthalylbenzidine (I) (prep. from benzidine phthalate described) can be

diazotised and coupled with β -naphthol, and dissolution in 1% NaOH affords the Na salt of the phthalamic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, which is obtained by acidification of the NaOH solution. (I) is therefore *N*-4-(4'-aminodiphenyl)phthalimide (A., 1926, 1131) and does not possess the structure based on the Kaufler formula. J. W. BAKER.

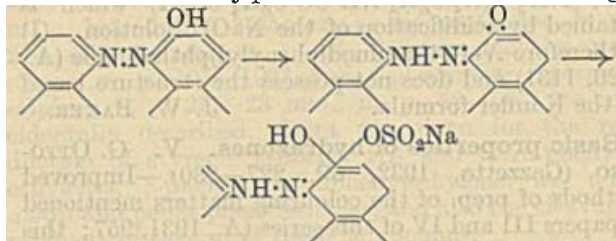
Basic properties of hydrazones. V. G. OTTO-LINO (Gazzetta, 1932, 62, 227–230).—Improved methods of prep. of the colouring matters mentioned in papers III and IV of this series (A., 1931, 957; this vol., 51) are described. E. E. J. MARLER.

Action of diazo-compounds on unsaturated compounds. VII. A new case of anomalous coupling. A. QUILICO and M. FRERI (Gazzetta, 1932, 62, 253–264).—Addition of *p*-propenyldimethylaniline, *p*-dimethylaminobenzaldehyde, or *pp'*-tetramethyldiaminobenzhydrol to EtOH suspensions of diazonium salts results in elimination of the side-chain, which is replaced by the group N_2R giving *p*-azo-derivatives of NPhMe_2 . An explanation of the mechanism is given. E. E. J. MARLER.

Azo-sulphites of disazonaphthols and their fission into the corresponding aminoazo-naphthols. A. T. KING (J.C.S., 1932, 1265–1271).—Extension of azo-sulphite formation (A., 1927, 1180) to disazo-dyes of the type $\text{XN}:\text{N}\cdot\text{Y}\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ (β) (X and Y=aromatic nuclei) permits the stabilisation of one azo-linking towards reducing agents, the unprotected azo-linking suffering fission either by the action of NaHSO_3 itself or by suitable reduction, with the formation of monoazo-dyes with an NH_2 group at the point of fission. By reactions of this type, the following are obtained, the disazo-sulphite usually being obtained at 0° in the presence of pyridine, fission to the monoazo-derivative occurring at 60°. 2-Hydroxy-1-naphthaleneazo-*m*-tolueneazobenzene-*m*-trimethylammonium chloride with 5% NaHSO_3 at 60° gives its sulphite, converted by $\text{Na}_2\text{S}_2\text{O}_4$ into Na *p*-amino-*m*-tolueneazo- [converted by dil. NaOH into *p*-amino-*m*-tolueneazo- β -naphthol (Ac derivative, m. p. 251°)]; Na diphenyldisazo-4-sulpho- α -naphthylamine-8-sulpho-, converted into Na 4'-aminodiphenylazo-8-sulpho- (and 4'-amino-diphenylazo- β -naphthol-8-sulphonic acid); Na diphenyldiazo-4:8-disulpho- α -naphthol-8-sulpho-; Na diphenyldisazosalicylic acid-3:6-disulpho- and Na 4'-aminodiphenylazo-3:6-disulpho-; Na *p*-sulphobenzeneazobenzeneazo-8-sulpho-; Na monosulpho-4-amino- α -naphthaleneazo- α -naphthaleneazo-6-sulpho-; Na diphenyldisazophenetole-6:8-disulpho-; Na 4'-aminodiphenylazo-6:8-disulpho-; Na diphenyldisazo-3:6:8-trisulpho- α -naphthol-; Na 4'-aminodiphenylazo- [and 4'-aminodiphenylazo- β -naphthol (Ac derivative, m. p. 275°)]; Na ditolyldisazo-3:6:8-trisulpho- α -naphthol-; and Na *p*-aminoditolylazo- [reduced to *p*-aminoditolylazo- β -naphthol (Ac derivative, m. p. 233°)]- β -naphthyl sulphite. J. W. BAKER.

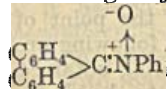
Sulphites of azo-compounds containing two hydroxyls. A. T. KING (J.C.S., 1932, 1271–1275).—Contrary to Voroschtov's view (A., 1916, i, 293) dyes containing one azo-linking and two naphtholic OH groups do not give disulphites, since assump-

tion of the ketonised form by one of the β -naphthol nuclei automatically prevents the other from so doing:



This supports the hydrazone as opposed to the azo-structure for such compounds. Thus *Na* 4-sulpho-2-hydroxy- α -naphthaleneazo-, *Na* 4-sulpho-5-nitro-2-hydroxy- α -naphthaleneazo-, and *Na* 5-sulpho-2-hydroxy-benzeneazo- β -naphthyl sulphite are obtained. These are stable in NaHSO_3 solution at 60° , and at 70° are reconverted into the original dye, no fission taking place (cf. preceding abstract). On the other hand, disulphites are formed from disazo-compounds containing two β -naphthol nuclei, and thus *Na* diphenyl-disazobis-8-sulpho-, and *Na* 2:5:2':5'-tetramethyl-triphenylmethane-4:4'-disazobis-3:6-disulpho- β -naphthyl disulphites are obtained, although *Na* 2:2'-disulphodiphenyldisazobis- β -naphthol affords only a monosulphite. The significance of these results and those in the preceding abstract relative to SO_2 faults in dyed fabrics is discussed. J. W. BAKER.

A reaction of fluorene. A. J. HALLWOOD and R. ROBINSON (J.C.S., 1932, 1292—1293).—Fluorene condenses with PhNO_2 in presence of Na in xylene at 100° to give fluorenylideneaniline oxide, probably (I)



, m. p. 193° , hydrolysed by boiling 40% H_2SO_4 to fluorenone and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in EtOH to fluorenylaniline, m. p. $122\text{--}123^\circ$ (Ac, m. p. 177° , and nitroso-, m. p. 104° , derivatives), also obtained from fluorenyl chloride and NH_2Ph with anhyd. NaOAc in $\text{iso-C}_2\text{H}_5\cdot\text{OH}$.

J. W. BAKER.

Resolution of 2-aminocyclohexanol. R. M. GODCHOT and M. MOUSSERON (Compt. rend., 1932, 194, 981—983).—2-Aminocyclohexanol (A., 1903, i, 680) is regarded as the *trans*-isomeride. Fractional crystallisation from EtOH of the *d*-tartrate of the *dl*-base, m. p. $152\text{--}153^\circ$, $[\alpha]_D +17.25^\circ$, affords the *d*-tartrate of *l*-trans-2-aminocyclohexanol, m. p. $177\text{--}178^\circ$, $[\alpha]_D -2.73^\circ$, and the *d*-tartrate of *d*-trans-2-aminocyclohexanol, m. p. $170\text{--}171^\circ$, $[\alpha]_D +31.2^\circ$. KOH liberates the *d*- and *l*-bases, m. p. $83\text{--}84^\circ$, $[\alpha]_D \pm 40.2^\circ$ (hydrochlorides, m. p. $147\text{--}148^\circ$, $[\alpha]_D \pm 31.60^\circ$). Catalytic reduction of *o*-amino- and *o*-acetamido-phenol yields cyclohexylamine and acetylcyclohexylamine and not *cis*-2-aminocyclohexanol.

J. L. D'SILVA.

Formation of *cis-cis*-muconic acid and benzoquinone in the oxidation of phenol with peracetic acid. J. BOESEKEN and R. ENGELBERTS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1292).—When PhOH is oxidised with 20% AcO_2H a 62% yield of *cis-cis*-muconic acid (I) is obtained and benzoquinone is formed. Pyrocatechol with AcO_2H gives

an excellent yield of (I). These reactions appear to afford the simplest means of transition from aromatic to aliphatic compounds. E. S. HEDGES.

Hexyl and hexenyl derivatives of phenol. C. D. HURD and R. W. MCNAMEE (J. Amer. Chem. Soc., 1932, 54, 1648—1651).— Δ^a -Hexen- γ -ol (propylvinylcarbinol) and PCl_3 in C_6H_6 give α -chloro- Δ^a -hexene (I), b. p. $42\text{--}44^\circ/40\text{ mm.}$, $120\text{--}122^\circ/751\text{ mm.}$, the structure of which is established by reduction to *n*-hexyl chloride and hydrolysis to Δ^a -hexen- α -ol. α -Bromo- Δ^a -hexene (II), b. p. $43\text{--}45^\circ/10\text{ mm.}$, $50\text{--}53^\circ/25\text{ mm.}$, is prepared from the carbinol, HBr , and conc. H_2SO_4 . (I) or (II) and NaOPh in EtOH give α -phenoxy- Δ^a -hexene (*Ph* γ -propylallyl ether) (III), b. p. $105\text{--}107^\circ/4\text{--}5\text{ mm.}$, also formed from (II) [but not (I)], PhOH , and K_2CO_3 . (I) and NaOPh in Et_2O give α -*o*-hydroxyphenyl- Δ^a -hexene (*o*- γ -propylallylphenol), b. p. $144^\circ/20\text{ mm.}$ Catalytic reduction of (III) gives *Ph* hexyl ether (α -phenoxyhexane), b. p. $125\text{--}128^\circ/11\text{ mm.}$, m. p. -19° , also prepared from hexyl chloride and NaOPh in EtOH . γ -Bromohexane and NaOPh give γ -phenoxyhexane, b. p. $129\text{--}132^\circ/12\text{ mm.}$, m. p. -35° to -33.5° ; when heated at $210\text{--}215^\circ$, (III) gives γ -*o*-hydroxyphenyl- Δ^a -hexene, b. p. $120\text{--}122^\circ/7\text{ mm.}$ C. J. WEST (b).

Bromination of phenyl γ -chloro- Δ^a -propenyl ether. L. BERT and E. ANDOR (Compt. rend., 1932, 194, 1079—1081).— Br in CHCl_3 converts this ether (I) into the corresponding *p*-bromophenyl ether, b. p. $153^\circ/13\text{ mm.}$ (also synthesised in 60% yield from $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$ and $\text{CHCl}_3\text{CH}_2\text{CH}_2\text{Cl}$), the HBr formed reacting with (I) to give PhOH (and hence $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$) and α -bromo- γ -chloro- Δ^a -propylene (this vol., 362). J. W. BAKER.

Aryl ethers of ψ -carbamide. M. BATTEGAY and H. SILBERMANN (Compt. rend., 1932, 194, 988—990).—By heating a mixture of cyanamide dihydrochloride and a phenol at a high temp. for several hr. in a stream of dry HCl , an aryl ether of ψ -carbamide is formed. *O*-*m*-Tolylcarbamide hydrochloride, m. p. $215\text{--}216^\circ$ [picrate, m. p. $243\text{--}244^\circ$ (decomp.)], is described. These aryl ethers are unstable in the free state, NH_3 resolving them into PhOH and cyanamide. Ethers of *o*- and *m*-cresol, α - and β -naphthol, and of resorcinol are prepared by the above method.

J. L. D'SILVA.

Condensation of phenols with formaldehyde.

I. Formation of phenol alcohols. F. S. GRANGER (Ind. Eng. Chem., 1932, 24, 441—448).—Action of CH_2O on PhOH in presence of NaOH gives mono-, di-, and tri-hydroxymethylphenols (cf. A., 1894, i, 577). Similarly *o*-cresol with 2 mols. of CH_2O gives 4:6-dihydroxymethyl-*o*-cresol, m. p. 94° , and a small amount of (?) dihydroxydihydroxymethylditolymethane, m. p. 155° . With 1 mol. of CH_2O mono- and di-alcohols are formed. *m*-Cresol gives resins and the *Na* salt of (?) 2:4:6-trihydroxymethyl-*m*-cresol. *m*-2- and -6-Xylenols give CH_2Ph_2 derivatives, the former more quickly. A similar product is obtained from ψ -cumenol. The $\text{OH}\cdot\text{CH}_2$ derivatives of *p*- and *o*-5-xylenols react slowly with a second mol. of CH_2O (cf. A., 1899, i, 34). Attempts to prepare a trihydroxymethyl derivative from *m*-5-xylenol gave resinous products. A. A. LEVI.

Mono- and di-bromo-derivatives of *m*-cresol.

R. C. HUSTON and J. A. HUTCHINSON (J. Amer. Chem. Soc., 1932, 54, 1504—1506).—*m*-Cresol and Br (1 mol.) in the cold give 4- and 6-bromo-*m*-cresol (benzoate, m. p. 82.5—83°; benzenesulphonate, m. p. 79—80°; *p*-toluenesulphonate, m. p. 84—85°), also prepared from the corresponding bromotoluidines. Dibromination gives 2 : 6- (benzoate, m. p. 80—81°) and 4 : 6 dibromo-*m*-cresol (benzoate, m. p. 84—85°).

C. J. WEST (b).

Action of aromatic alcohols on aromatic compounds in presence of aluminium chloride. VIII.

Benzoylation of *m*-cresol. R. C. HUSTON and A. L. HOUK (J. Amer. Chem. Soc., 1932, 54, 1506—1510; cf. A., 1931, 1047).—*m*-Cresol, $\text{CH}_2\text{Ph}\cdot\text{OH}$, and AlCl_3 in light petroleum at 35° give 4-benzyl-*m*-cresol (I), b. p. 153—155°/4 mm., m. p. 46—47° (2 : 6- Br_2 derivative, m. p. 102—103°; benzoate, b. p. 215—220°/5 mm., m. p. 58—59°), 6-benzyl-*m*-cresol, b. p. 168—170°/5 mm., m. p. 93—94° (2 : 4- Br_2 derivative, m. p. 86—87°; benzoate, m. p. 70—71°), and 4 : 6-dibenzyl-*m*-cresol, b. p. 230—232°/5 mm., m. p. 106—107° (2- Br derivative, m. p. 65—67°; benzoate, m. p. 88—89°). *m*-Cresol, CH_2PhCl , and Na in PhMe give (I), *m*-tolyl benzyl ether, b. p. 142—145°/5 mm., m. p. 45—46°, 2-benzyl-*m*-cresol, b. p. 157—159°/5 mm., m. p. 71—72° (benzyl ether, m. p. 71—73°; 4 : 6- Br_2 derivative, m. p. 106—107°; benzoate, m. p. 71—73°), and 2 : 4-dibenzyl-*m*-cresol, b. p. 216—218°/5 mm. (benzoate, b. p. 235—240°/5 mm.). C. J. WEST (b).

Tervalent carbon. XI. Labile radical peroxides. K. ZIEGLER and P. ORTH (Ber., 1932, 65, [B], 628—631).—The rate of absorption of O_2 by solutions of C_6Ph_3 in PhMe or CHCl_3 is considerably greater than that of dissociation of the ethane. A portion of the C_6Ph_3 is directly oxidised without previous dissociation into CPh_3 , probably owing to the formation of a particularly active, labile peroxide (cf. Haber and Willstätter, this vol., 352). Di-9-phenylfluorenyl is converted by a small excess of chloroanil in hot CHCl_3 into tetrachloroquinol di-9-phenylfluorenyl ether; the solution is indifferent to air. If a deficiency of chloroanil is used, the resulting solution very readily absorbs O_2 with formation of chloroanil. The intermediate production of a labile peroxide is postulated: $\text{R}\cdot\text{O}\cdot\text{C}_6\text{Cl}_4\cdot\text{O}\cdot\text{R} + \text{O}_2 = \text{O}\cdot\text{C}_6\text{Cl}_4\cdot\text{O} + \text{R}\cdot\text{O}\cdot\text{O}\cdot\text{R}$. H. WREN.

Synthesis of thyroxine. A. I. BOLSCHUHIN (J. Gen. Chem. Russ., 1931, 1, 1070—1074).—The condensation product of 3 : 4 : 5-tri-iodonitrobenzene with quinol Me ether (A., 1927, 358) is usually difficult to purify from accompanying tarry matter; 3 : 5-di-iodo-4-(4'-ethoxyphenoxy)nitrobenzene (I), m. p. 148—149°, is much more readily purified. Reduction of (I) with SnCl_2 in AcOH gives 3 : 5-di-iodo-4-(4'-ethoxyphenoxy)aniline hydrochloride, m. p. 220—223° in open and 224—227° in sealed capillary; the free amine has m. p. 100—101°. G. A. R. KON.

Synthesis of derivatives of myristicin. W. BAKER, (MISS) L. V. MONTGOMERY, and H. A. SMITH (J.C.S., 1932, 1281—1283).—Methylenation of pyrogallol 1-Me ether gives 1-methoxy-2 : 3-methylenedioxybenzene, m. p. 41°, which is nitrated to give the 5- NO_2 -compound, m. p. 146—148° (lit. 143—144°); attempts

to prepare myristicin acid from the corresponding NH_2 -derivative were unsuccessful. Myristicin aldehyde is synthesised from methylene sulphate and 4 : 5-dihydroxy-3-methoxybenzaldehyde, and oxidised to the acid, each identical with the compound prepared from natural myristicin. F. R. SHAW.

Conversion of *l*-phenylmethylcarbinol into dextro- and lævo-rotatory α -chloroethylbenzene. A. H. J. HOUSSA and H. PHILLIPS (J.C.S., 1932, 1232—1235).— COCl_2 reacts with *l*-CHPhMe·OH in the presence of either K_2CO_3 (when the *dl*-carbinol gives the chloroformate, converted into CHPhMeCl by distillation at 80—90°/13 mm.) or quinoline (1.25 mols.) to give lævorotatory CHPhMeCl, but with 3 mols. of quinoline a dextrorotatory chloride is obtained. Since, in the latter case, decomp. of the additive compound of the chloroformate and quinoline intervenes, inversion probably occurs in this case (cf. this vol., 251). *l*-CHPhMe·OH *p*-toluenesulphinate does not react smoothly with a 4% solution of HOCl at 0°, much *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and styrene and only a little CHPhMeCl of low dextrorotation being obtained; hence it is not possible to decide whether the change in sign of rotation is due to inversion. With aq. solutions of Cl_2 or Br the *p*-toluenesulphinate yields dextrorotatory α -chloro- and α -bromo-ethylbenzene, with less by-product, whilst with ICl the *dl*-sulphinate reacts smoothly to give *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{I}$ and CHPhMeCl. The results are discussed from the viewpoint of the Walden inversion. J. W. BAKER.

Isomerisation of phenylglycide. Affinity of the primary alcohol grouping. P. WEILL and (MLLE.) M. DARMON (Compt. rend., 1932, 194, 977—979).—Phenylglycide at 275° in a N_2 atm. affords $\text{CH}_2\text{Ph}\cdot\text{CHO}$ and products of isomerisation, from which $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, transformed into $\text{CH}_2\text{Ph}\cdot\text{CHO}$ by heat, is isolated. The reaction indicates that the affinity of the $\text{CH}_2\cdot\text{OH}$ group is less than that of the Ph group. J. L. D'SILVA.

Preparation of an optically active triaryl-carbinol. E. S. WALLIS (J. Amer. Chem. Soc., 1932, 54, 1695—1696).—*d*-, $[\alpha]_D^{20} +5.8^\circ$ in CCl_4 , and *l*-, $[\alpha]_D^{20} -5.4^\circ$, -phenyldiphenyl- α -naphthylcarbinols have been prepared from *l*- and *d*-phenyldiphenyl- α -naphthylthioglycolic acids, respectively. The *d*-, $[\alpha]_D^{20} +21.6^\circ$, and *l*-, $[\alpha]_D^{20} -22.7^\circ$ in Et_2O , -*Et* ethers of the carbinols are obtained from the *d*- and *l*-acids, respectively. C. J. WEST (b).

Amino-alcohols. VIII. Benzoic esters of arylalkanolamines. W. H. HARTUNG, J. C. MUNCH, and E. B. KESTER (J. Amer. Chem. Soc., 1932, 54, 1526—1530; cf. this vol., 157).— α -Chloro- β -benzamido- α -phenylpropane, m. p. 125° (corr.), prepared by benzoylating the amine, rearranges when heated with moist Bu^nOH to β -amino- α -benzoyloxy- α -phenylpropane hydrochloride, m. p. 208° (corr.), which has a marked local anæsthetic action and about one tenth of the relative pressor action of β -amino- α -hydroxy- α -phenylpropane.

C. J. WEST (b).

Action of oxidising agents on derivatives of ergosterol. A. GUITERAS, Z. NAKAMIYA, and H. H. INHOFFEN (Annalen, 1932, 494, 116—126).—

α -Methylisovaleraldehyde (*semicarbazone*, m. p. 129—130°, $[\alpha]_D^{20}$ —52.2° in EtOH) is obtained in 13.5—31% yield by the action of 6% O_3 (in AcOH) on ergosterol (cf. Reindel and Kipphan, this vol., 267) and (a) ergosteryl- B_1 and - B_3 acetates, lumisterol, vitamin- D_2 , suprasteryl I allophanate, and suprasterol II, (b) the additive compounds from maleic anhydride and ergosterol and dehydroergosteryl acetate and from citraconic anhydride and tachysterol acetate, and (c) dihydroergosterol, showing that the side-chain double linking is not involved in (a) isomerisations by mineral acid or irradiation, (b) the conjugated system in the sterols, and (c) the addition of 2H to ergosterol. Oxidation of α -ergostenyl acetate and ergostanol with CrO_3 in AcOH gives small amounts of a liquid ketone containing 9 C atoms (probably Me γ -methylisohexyl ketone) (*semicarbazone*, m. p. 156°, $[\alpha]_D^{20}$ —16.45° in $CHCl_3$). Cholesterol, ergosterol, and sitosterol may contain the same ring systems but different side-chains. The so-called cyclopentadienetricarboxylic acid obtained by Reindel and Niederländer (A., 1930, 1578) from ergosterol and HNO_3 is probably toluene-2:3:4:5(or 2:3:5:6)-tetracarboxylic acid (M_{e4} ester, m. p. 123—124°), and is also obtained by HNO_3 -oxidation of dehydroergosterol and lumisteryl acetate (but not from vitamin- D_2 or ergosteryl- B_1 and - B_3 acetates). Contrary to Reindel and Niederländer it is not stable to oxidising agents; alkaline $KMnO_4$ converts it into benzenepentacarboxylic acid.

H. BURTON.

Benzoic esters and electronic affinities of radicals. III. A. KAKI (J.C.S., 1932, 1184—1188).—Nitration of $BzO\cdot[CH_2]_n\cdot OBz$ affords 80.8, 74.8, and 75.3% of *m*-derivative (subsequently given in parentheses) when $n=1, 2$, and 3, respectively, the corresponding vals. for $BzO\cdot[CH_2]_n\cdot H$ being 72.6, 69.9, and 71.8%, and for $BzO\cdot[CH_2]_n\cdot Cl$, 81.9, 75.8, and 77.7%. Hence *m*-nitration induced by substitution in a saturated side-chain increases in the order $H < O < Cl$. The vals. obtained for cyclohexyl (67.0), 2- (65.4), 3- (67.2), and 4- (67.3) -methylcyclohexyl, compared with those for Me (72.6) and *n*- C_6H_{13} (63.7) benzoates confirm the increased electrochemical repulsion due to increased alkyl substitution in the saturated C chain, and indicate only a slight increase (3%) in *m*-nitration due to ring closure, which cannot, therefore, be entirely responsible for the relatively large difference (20%) between benzylpiperidine (72%) and $CH_2Ph\cdot N\cdot Et_3$ (51%). The proportion of *m*-nitration observed with *p*-nitrophenyl (88%), *o*- (76%), *m*- (73%), and *p*- (75%) -nitrobenzyl benzoates indicates the order $Me > NO\cdot C_6H_4\cdot CH_2\cdot$ for directive power. The proportion of *m*-nitration of NH_2Bz (69%), benzoylpiperidine (31%), and $NBzEt_2$ (29.5%) indicates decreased *m*-substitution by substitution in the NH_2 group, but is unaffected by addition of $Be(NO_3)_2$ during nitration.

J. W. BAKER.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. III. Carbonyl group in ethyl benzoate. J. W. BAKER and L. HAY (J.C.S., 1932, 1226—1231).—Partition of $BzOEt$ between ligroin and H_2SO_4 and

its nitration in oleum- HNO_3 (with varying concns. of SO_3), both with and without added $(NH_4)_2SO_4$, give results exactly comparable in type with those obtained with $PhCHO$ and $PhAc$ (A., 1931, 485, 486), indicating that the same type of consecutive ionic equilibria must be present in such H_2SO_4 solution, but

hydrolysis of the oxonium salt $PhC(OEt)\cdot OH\cdot O\cdot SO_3H$, and repression of its ionisation by $(NH_4)_2SO_4$, are more marked than in the previous cases. The proportion of *m*-nitration (74.8%) when $BzOEt$ is nitrated in HNO_3 (d 1.53) alone is increased gradually to 93.7% when nitration is effected in the presence of H_2SO_4 containing increasing amounts (up to 5.5%) of free SO_3 , addition of $(NH_4)_2SO_4$ to the H_2SO_4 - HNO_3 medium causing a depression (8—9%) of the *m*-isomeride in each case. Addition of N_2O_5 to the HNO_3 (d 1.53) causes no appreciable increase in *m*-nitration (75.8%), indicating that, in agreement with the previous suggestion (*loc. cit.*), no true oxonium nitrate is formed.

J. W. BAKER.

Nuclei of *cis*-cinnamic acid. A. W. K. DE JONG (Rec. trav. chim., 1932, 51, 397—400).—No definite concn. of a solution of *cis*-cinnamic acid (I), m. p. 68°, in ligroin exists which will with certainty induce crystallisation in this form (cf. A., 1914, i, 173). A method is described for determining the rate of disappearance of nuclei of (I) from solution in ligroin.

R. S. CAHN.

Abietic acid. H. BERGER (J. pr. Chem., 1932, [ii], 133, 331—349).—Na abietate, when heated with NaOH at 240—280°, gives amongst other products H_2 , CH_4 , CO_2 , a substance (A), tetrahydrotetene or 2:3:2'-trimethyl-4'-isopropylidiphenyl, m. p. 104°, $[\alpha]_D^{20} +106^\circ$ in MeOH, and a substance (B), $C_{17}H_{16}$ or $C_{18}H_{18}$ (possibly impure retene), m. p. 86°. (A) gives retene when heated with S, but did not yield a quinone. (B) with CrO_3 gives (?iso)butyric acid and an *o*-quinone (? impure retenequinone), m. p. 195° (quinoxaline derivative, m. p. 163°); (B) is unchanged by heating with S. Attempts to reduce retene catalytically and to condense 2-bromophenanthraquinone with Pr^iBr failed. *o*-Nitrobenzaldehyde, K *m*-bromophenylacetate, and $ZnCl_2$ in hot Ac_2O give *o*-nitro- α -*m*-bromophenylcinnamic acid, trans-form, m. p. 238—239°, cis-form, m. p. 164°, reduced by $FeSO_4$ and aq. NH_3 to *o*-amino- α -*m*-bromophenylcinnamic acid, trans-form, m. p. 155° (decomp.), whence by diazotisation and treatment with Cu powder 2-bromophenanthrene-9-carboxylic acid was obtained; attempts to remove CO_2 from this acid failed. *oo'*-Ditolyl with S at 250° (not with Se) gives a 50% yield of phenanthrene.

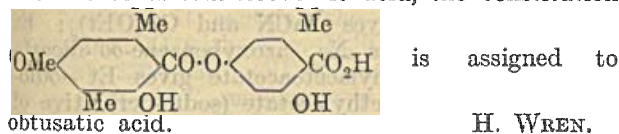
R. S. CAHN.

***l*-p-Methoxyphenylalanine.** L. D. BEHR and H. T. CLARKE (J. Amer. Chem. Soc., 1932, 54, 1630—1634).—*l*-N-Acetyltyrosine (I), a resin, $[\alpha]_D^{20} +46.2^\circ$ in H_2O , prepared from Ac_2O and tyrosine in hot aq. suspension (whereby about 10% racemisation occurs), separates from dioxan with 1 mol. of solvent, with m. p. 107—109° and (after cooling) 138—140°; the dioxan is removed only with difficulty. Me_2SO_4 and (I) in aq. $Ba(OH)_2$ give N-acetyl-*p*-methoxyphenylalanine, m. p. 150—151°, $[\alpha]_D^{20} +67.6^\circ$ in EtOH, hydrolysed by dil. mineral acids to *l*-*p*-methoxyphenyl-

alanine (II), m. p. 264—265° (corr.), $[\alpha]_D^{20}$ -5.9° in *N*-HCl [sulphate, m. p. 191° (corr.); hydrochloride, m. p. 237—238° (corr.); Cu salt, decomp. 250° (corr.); picrolonate, m. p. 174° (decomp., corr.); Bz derivative, m. p. 136—137°, $[\alpha]_D^{20}$ -3.7° in EtOH; benzene-sulphonyl derivative, m. p. 136—137°, $[\alpha]_D^{20}$ $+6.3^\circ$ in EtOH]. The phenylhydantoic acid, m. p. 176—177° (corr.), $[\alpha]_D^{20}$ $+123.6^\circ$ in EtOH, from (II) and PhNCO when boiled with 10% HCl gives the phenylhydantoin, m. p. 134—135°; the α -naphthylhydantoic acid, m. p. 167—168°, $[\alpha]_D^{20}$ $+63.3^\circ$ in EtOH, similarly affords the α -naphthylhydantoin, m. p. 155—157°.

C. J. WEST (b).

Lichen substances. XI. Constitution of obtusatic acid. Y. ASAHINA and F. FUJIKAWA (Ber., 1932, 65, [B], 580—583).—Maceration of *Ramalina calicaris* with COMe₂ followed by evaporation of the extract affords *d*-usnic acid, m. p. 200°, $[\alpha]_D^{20}$ $+499^\circ$ in CHCl₃, evernic acid, m. p. 169°, and obtusatic acid, m. p. 205° after loss of CO₂ at 195° when rapidly heated. Since *Me obtusate* *Me*₂ ether, m. p. 126—127°, is hydrolysed to rhizomic acid *Me* ether and *isoevernic* acid, the constitution



H. WREN.

Lichen substances. XII. Synthesis of diffractaic acid. Y. ASAHINA and F. FUJIKAWA (Ber., 1932, 65, [B], 583—584; cf. this vol., 396).—*Me* β -orcinolcarboxylate and dimethyl- β -orcinolcarboxyl chloride in COMe₂ and *N*-NaOH afford *Me diffractate*, m. p. 127—128°, identical with the product derived from diffractaic acid and diazomethane and hydrolysed to diffractaic acid, the constitution of which (*loc. cit.*) is thereby established.

H. WREN.

Cyanohydrins of type Ph·[CH₂]_n·CH(OH)·CN and Ph·[CH₂]_n·CHMe·CH(OH)·CN and the corresponding α -hydroxy-acids. (Mlle.) D. BIQUARD (Compt. rend., 1932, 194, 983—985).—The H sulphite compound (freed from aldehyde) of the appropriate aldehyde with KCN in H₂O at room temp. affords excellent yields of cyanohydrins. Hot conc. HCl hydrolyses them to the corresponding acids. Many cyanohydrins are prepared by this method. α -Hydroxy- β -phenylbutyronitrile, b. p. 133°/3 mm., and α -hydroxy- β -phenylbutyric acid, m. p. 121—122°, are described.

J. L. D'SILVA.

Preparation of diarylphthalides. F. F. BLICKE and O. J. WEINKAUFF (J. Amer. Chem. Soc., 1932, 54, 1446—1453).—Mg *o*-ethoxymethylphenyl bromide (I) reacts with various methoxybenzophenones giving *tert*-carbinols, the -CH₂·OEt groups of which are oxidised to CO₂H with the spontaneous formation of OMe derivatives of diarylphthalides. The following substituted triphenylcarbinols are prepared from (I) or *o*-Me·C₆H₄·MgBr and the appropriate benzophenones: 2-methyl-, m. p. 100—101°; 2':4''-dimethoxy-2-methyl-, m. p. 152—154°; 4':4''-dimethoxy-2-methyl-, m. p. 109—110°; 2-ethoxymethyl-, m. p. 81—82°; 2'-methyl-2-ethoxymethyl-, m. p. 108—109°; 3'-methoxy-2-ethoxymethyl-, an oil; 4'-methoxy-2-ethoxy-

methyl-, m. p. 100—101°; 2':2''-dimethoxy-2-ethoxy-methyl-, m. p. 103—104°; 2':4''-dimethoxy-2-ethoxy-methyl-, m. p. 107—108°; 4':4''-dimethoxy-2-ethoxy-methyl-, m. p. 74—76°; 3':4''-dimethoxy-2-ethoxy-methyl-, m. p. 83—84°. 9-*o*-Tolyl- and 9-*o*-ethoxy-methylphenyl-xanthohydrols have m. p. 165—166° and 153—154°, respectively. The colorations of these compounds with H₂SO₄ are given. The following are obtained by oxidation of the requisite carbinols: diphenylphthalide; 2'-, m. p. 127—128°, 3'-, and 4'-methoxydiphenylphthalides, gums; 2':2'', m. p. 151—152°, 2':4'', m. p. 127—128°, 4':4'', m. p. 101—102°, and 3':4'', m. p. 200—201°, -dimethoxydiphenylphthalides; fluoran. 4'-Hydroxydiphenylphthalide, fluoran, isophenolphthalein, phenolphthalein, and 3':4''-dihydroxydiphenylphthalide, amorphous, are prepared by demethylation of the appropriate OMe derivatives. *iso*Phenolphthalein has no laxative effect.

2-Hydroxy-5-*o*-hydroxybenzoylbenzophenone, m. p. 131—132°, is obtained as a by-product in the prep. of 2-hydroxybenzophenone from *o*-anisoyl chloride, C₆H₅, and AlCl₃. Details are given for the prep. of 4-hydroxy- and 2:4'- and 3:4'-dihydroxy-benzophenone. Attempted prep. of *iso*phenolphthalein from 2-*o*-hydroxybenzoylbenzoic acid (cf. Orndorff and Barrett, A., 1925, i, 35) gave phenolphthalein (40%), a little fluoran, and tar.

C. J. WEST (b).

Halogen derivatives of diarylphthalides. II. F. F. BLICKE, F. D. SMITH, and J. L. POWERS (J. Amer. Chem. Soc., 1932, 54, 1465—1471; cf. A., 1929, 926).—2:6-Dichloro- and -dibromo-phenols, obtained in 80—85% yield from 3:5-dichloro- and -dibromo-4-hydroxybenzoic acids and quinoline at 190—200°, are methylated (Me₂SO₄) to 2:6-dichloro-, b. p. 105—106°/20 mm., and 2:6-dibromo-, b. p. 129—130°/20 mm., -anisoles. Condensation of 2-halogenoanisoles with phthalyl chloride (I) gives the 3:3'-dihalogenophenolphthalein *Me*₂ ethers: the dichloro-, m. p. 136—138°, dibromo- (II), and di-iodo-, m. p. 177—179° (demethylated to 3':3''-di-iodophenolphthalein, m. p. 245—246°), derivatives are prepared. 2:6-Dichloroanisole, phthalyl chloride, and AlCl₃ in CS₂ give di-2:6-dichlorophenyl phthalate, m. p. 142—144° (di-2:6-dibromophenyl ester, m. p. 216—218°), formed by demethylation of the anisole to the phenol, which then reacts with (I). 3':5':3'':5''-Tetrachloro- (*Me*₂ ether, m. p. 180—182°) and -tetrabromo-phenolphthaleins are obtained by direct halogenation of phenolphthalein. (II) is also prepared from Mg *o*-ethoxymethylphenyl bromide and 3:3'-dibromo-4:4'-dimethoxybenzophenone by oxidation of the resulting carbinol, m. p. 148°. Attempts to obtain diphenoxypthalide are described.

C. J. WEST (b).

Preparation of homophthalic acid by oxidation of indene. A. MEYER and R. VITTENET (Compt. rend., 1932, 194, 1250—1252).—Homophthalic acid, m. p. 189—190°, is prepared in a max. yield of 66% by oxidation of indene with K₂Cr₂O₇ and H₂SO₄, indanone being formed intermediately. The oxidation of chloroindane and of indanone with the same reagent follows an identical course.

H. A. PIGGOTT.

Decolorised cinnamylidenemalonic acid. A. MADINAVEITIA and J. MADINAVEITIA (Anal. Fis. Quim., 1932, 30, 120—127).—2 : 4-Diphenylcyclobutane-1 : 3-bismethylenemalonic acid (I) (Kohler, A., 1902, i, 788), obtained by insolation of cinnamylidenemalonic acid, is reduced catalytically (Pt oxide) to the *bismethylenemalonic acid* (II), m. p. 203°, which is converted by vac. distillation into the *bispropionic acid* (III), m. p. 185°. Although (III) belongs to the *trans*-series, it yields with Ac_2O an oily *anhydride* reconvertible into the acid by NaOH . Conc. H_2SO_4 causes depolymerisation of (I), but not of (II). The 4-ring in (III) is unattacked by HCl or HI . The aromatic nucleus in cinnamylidenemalonic acid can be completely hydrogenated, using Pt oxide, yielding an *acid*, $\text{C}_{12}\text{H}_{20}\text{O}_4$, m. p. 90°, and *Et* α -truxillate similarly yields an *ester*, $\text{C}_{22}\text{H}_{36}\text{O}_4$, m. p. 85°, but in α - and γ -truxillic acids, as in (I), the nuclei are unattacked.

R. K. CALLOW.

Formation and stability of β -lactones. A. KANDIAH (J.C.S., 1932, 1215—1226).—Moist Ag_2O converts bromo-acids of the type $\text{CO}_2\text{H}\cdot\text{CR}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ in Et_2O solution into β -lactones $\text{CR}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{O}$ (I)

which are the probable intermediates in the formation of the OH-acids, the sole products obtained when Na_2CO_3 replaces Ag_2O . Distillation converts (I) into the anhydrides $\text{CR}_2\cdot\text{CH}(\text{CO})\cdot\text{CO}$.

simulation of γ -lactonic properties in the conversion OH-acid \rightarrow β -lactone observed when $\text{R}_2=\text{Pr}_2$ (Bains and Thorpe, J.C.S., 1923, 123, 2742) is not observed when $\text{R}_2=\text{C}_5\text{H}_{10}$, even with an additional α -Me substituent. PCl_5 and Br convert 1-carboxycyclohexane-1-acetic acid into its α -Br-derivative, m. p. 142°, whence by Ag_2O in Et_2O is obtained the β -lactone, m. p. 129° (NH_2Ph salt, m. p. 116°), of α -hydroxy-1-carboxycyclohexane-1-acetic acid, m. p. 135° (anhydride, b. p. 170°/11 mm., m. p. 86°; *anilic acid*, m. p. 187°; *anil*, m. p. 108°), readily oxidised by cold KMnO_4 to the α -keto-acid, m. p. 132° (quinoxaline derivative, m. p. 249°), and finally to cyclohexane-1 : 1-dicarboxylic acid. By similar methods are obtained: α -bromo-1-carboxycyclopentane-1-acetic acid, m. p. 135°, the β -lactone, m. p. 81° (NH_2Ph salt, m. p. 118°), of the α -OH-acid, m. p. 125° (anhydride, m. p. 141°; *anilic acid*, m. p. 151°), oxidised to the α -keto-acid, m. p. 133°, and cyclopentane-1 : 1-dicarboxylic acid; α -bromo- β -methyl- β -ethylsuccinic acid, m. p. 126°; β -lactone, not cryst. (NH_2Ph salt, m. p. 102°), and the β -lactone, m. p. 51°, of β -methyl- β -ethyl- and $\beta\beta$ -dimethyl-malic acid. α -Bromo-2-carboxy-trans-hexahydrohydrindene-2-acetic acid, m. p. 136°, affords the β -lactone, m. p. 110° (NH_2Ph salt, m. p. 116°), of the α -OH-acid, m. p. 134°, and the *cis*-acid, m. p. 164°, affords the β -lactone, m. p. 125° (NH_2Ph salt, m. p. 135°), of the α -OH-acid, m. p. 192°. Condensation of cyclohexanone cyanohydrin with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ and subsequent methylation affords *Et* 1-cyanocyclohexane-1- α -cyanopropionate, m. p. 51°, hydrolysed to 1-carboxycyclohexane-1- α -propionic acid, m. p. 110° (anhydride, m. p. 165°/10 mm.; *anilic acid*, m. p. 165°; *anil*, m. p. 100°), brominated in ultra-violet light to the α -Br-acid, m. p. 142° (bromoanhydride, m. p. 55°), whence the β -lactone,

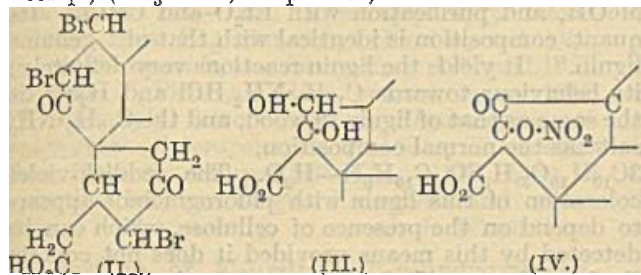
m. p. 46°, of the α -OH-acid, m. p. 73·4°, is obtained. Bromotrimethylsuccinic acid, m. p. 185°, similarly gives the β -lactone. Malonic acid and COPr_2 with Ac_2O and H_2SO_4 give α -carboxy- β -hydroxy- β -n-propyl-hexolactone, $\text{CO}_2\text{H}\cdot\text{CH}(\text{COPr})\cdot\text{O}$, m. p. 89°, 1-hydroxycyclopentane-, m. p. 73°, and 1-hydroxycyclohexane-, m. p. 95°, -1-malonolactone being similarly obtained from cyclopentanone and -hexanone.

J. W. BAKER.

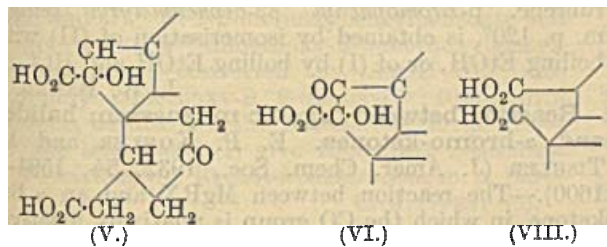
Addition of alkali enolates to esters. VI. F. ADICKES, W. BRUNNERT, O. LÜCKER, and G. SCHAFER (J. pr. Chem., 1932, [ii], 133, 305—330; cf. A., 1931, 196).— BzOEt , *Et o*- and *p*-chlorobenzoate, trimethylacetate (best prepared by esterification by HCl and MeOH), triphenylacetate, benzylfluorene-9-carboxylate, benzenesulphonate, Et_4 methanetetracarboxylate, Et_3 chloromethanetricarboxylate and trimesate, Et_6 ethanehexacarboxylate, Et_2 dibenzyl- and diphenoxy-malonate, cyclopropane-1 : 1-dicarboxylate, and fluorenylsuccinate do not react with NaOEt in dry Et_2O . The following do not form additive compounds but react as stated: *Et* cyanofornate gives NaCN and $\text{CO}(\text{OEt})_2$; *Et o*-nitrobenzoate gives Na_2 azoxybenzene-*oo'*-dicarboxylate; *Et* dimethylacetoacetate gives *Et* sodio- α -acetoacetyl- α -dimethylacetate (sodio-derivative of $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$); *Et* fluorene-9-carboxylate gives the sodio-derivative, $\text{C}_{12}\text{H}_8\cdot\text{CN}\cdot\text{CO}_2\text{Et}\cdot\text{EtOH}$; *Et* triethoxyacetate, Et_2 diethoxy- and dichloromalonate, Et_3 fluorene-9 : 9-dicarboxylate (from ClCO_2Et and *Et* fluorene-9-carboxylate in pyridine, or with NaOEt in dry Et_2O) (m. p. 99·5° after sintering at 88·5°, β p. 220—222°/13 mm., monoclinic, β 114° 36', $a : b : c$ 0·8224 : 1 : 0·8346), and Et_4 oxalomethanetricarboxylate decompose; Et_2 benzylidene-malonate and -fumarate add NaOEt at the ethylenic linking; *Et* cinnamate reacts very slowly. *Et* phenylglyoxylate and trimethylpyruvate, Et_3 phthalonate and ketomalonate add 1 mol. of NaOEt either at the CO_2Et or CO group. Parallelism exists between the ability of an ester to add NaOEt and of the corresponding ketone to form a hydrate, but no parallelism with the dissociation const. of the acid. The additive compound of *Et* trifluoroacetate and NaOEt is not colloidal, since it passes through a "Cella" filter. R. S. CAHN.

Constitution of the bile acids. XXXVII. Degradation of ring III. XXXVIII. Oxidation of 3 : 7-dihydroxycholenic acid. Structure of ring III. H. WIELAND and E. DANE (Z. physiol. Chem., 1932, 206, 225—242, 243—254; cf. A., 1931, 957).—XXXVII. Bromination of the diketodicarboxylic acid, $\text{C}_{23}\text{H}_{34}\text{O}_8$ (I), in AcOH yields a tribromodiketodicarboxylic acid, $\text{C}_{23}\text{H}_{31}\text{O}_8\text{Br}_3$ (II), m. p. 203—207° (decomp.), reduced by Zn dust and HCl in AcOH to (I). Aq. $\text{Ba}(\text{OH})_2$ converts (II) into a bromodihydroxyketotricarboxylic acid, $\text{C}_{23}\text{H}_{33}\text{O}_9\text{Br}$ (III), m. p. 250—252° (decomp.) (*Me* ester, m. p. 135°), probably by autooxidation of the primarily formed diketone to the hydroxydiketone, which then undergoes a benzilic acid transformation. (III) liberates about 60% of the theoretical amount of CO with conc. H_2SO_4 . Oxidation of (III) with fuming HNO_3 gives

a nitrate, $C_{23}H_{30}O_{11}NBr$ (IV), m. p. 215—223° (decomp.) (Me_3 ester, m. p. 168°).



Oxidation of (III) with CrO_3 in AcOH yields a *lactonic acid*, $C_{22}H_{30}O_9$, m. p. 210—213° (isomeric lactone, m. p. 253—256°; Me ester, m. p. 115°). Reduction of (III) with Zn dust or catalytically gives the *acid*, $C_{23}H_{34}O_9$ (V), m. p. 238—240° (Me_3 ester, m. p. 131°, contains two OH groups, gives an Ac derivative, m. p. 122°), also obtained by the action of Zn dust and AcOH on (IV). Oxidation of (V) with $Pb(OAc)_4$ or CrO_3 gives an *acid*, $C_{23}H_{32}O_9$ (VI), m. p. 226—228°, $[\alpha]_D -11.9^\circ$, titrating as tribasic in the cold, tetrabasic on heating. It contains the $C(OH) \cdot CO_2H$ group, liberating CO with conc. H_2SO_4 . When heated in vac. at 220—230°, (VI) yields an *acid*, $C_{23}H_{30}O_8$, m. p. 190—195°, monobasic in the cold, tribasic at 100°, giving an *acid*, $C_{22}H_{32}O_7$, m. p. 205°, on acidification of the hot titrated solution. Oxidation of (V) with fuming HNO_3 affords biloidanic acid (VII), with CrO_3 in AcOH, a *ketotetracarboxylic acid* (VIII), $C_{22}H_{32}O_9$, m. p. 153° (+ H_2O of cryst.) $[\alpha]_D +62.0^\circ$ (Me_4 ester, m. p. 103°). KOBBr oxidises (VIII) to (VII). In high vac. at 330—335°, (VIII) gives a *product*, $C_{21}H_{30}O_8$, m. p. 170—175°. (VIII) is also obtained by CrO_3 oxidation of norcilianic acid. KOBBr oxidises (VI) and (V) to a *pentabasic acid*, m. p. 250—252°. The lactone ring is not opened on hot titration.



Oxidation of (III) with $Pb(OAc)_4$ gives an *acid* (IX), $C_{23}H_{31}O_9Br$, m. p. 183—185° (decomp.), from which the Br is eliminated on titration. On treatment with Zn dust and AcOH, the Br is replaced by H, yielding (VI). Oxidation of (IX) with CrO_3 gives (VIII).

XXXVIII. Oxidation of 3:7-dihydroxycholenic acid (I) with alkaline $KMnO_4$ affords *tetrahydroxycholenic acid* (II), $C_{24}H_{40}O_6$, m. p. 223—225°, which is further oxidised by fuming HNO_3 forming the *nitrate* (III), m. p. 223° (decomp.), of (IV) (below). Reduction of (III) in AcOH with Zn dust and HCl or with hyposulphite gives *dihydroxyisodeoxybilianic acid* (IV), m. p. 290° (decomp.) (Me_3 ester, m. p. 187°), which, when boiled with HCO_2H , gives a doubly unsaturated *acid*, $C_{24}H_{32}O_7$, m. p. about

192°, and with HI and red P in AcOH gives *mono-hydroxyisodeoxybilianic acid*, m. p. 280—285° (decomp.). Thermal decomp. of (IV) yields a *pyro-acid*, $C_{23}H_{30}O_4$. Oxidation of (II) with $Pb(OAc)_4$ gives a small amount of an *acid*, $C_{24}H_{38}O_6$, m. p. 200—202° (decomp.). Oxidation of (I) with BzO_2H in $CHCl_3$ yields *dihydroxycholenic acid oxide*, m. p. 181—182° (intense orange-brown colour with $Ac_2O \cdot H_2SO_4$), which with H_2O at 115° affords *dihydroxycholadienic acid*, m. p. 242—244°, giving apocholic acid on catalytic hydrogenation. The group $:CHMe$ in ring III is thus probably between C_1 and C_9 but may be between C_{11} and C_{12} . J. H. BIRKINSHAW.

Photobiological properties of bile acids. I. Formation of β -cholic acid from cholic acid by ultra-violet irradiation. Z. URAKI (Z. physiol. Chem., 1932, 207, 16—24).— Me α -cholate (ordinary Me cholate) on ultra-violet irradiation in $CHCl_3$ yields an isomeric Me β -cholate, m. p. 162°, $[\alpha]_D^{20} +25.0^\circ$ in $CHCl_3$, giving a very slow Mylius reaction and regenerating α -cholic acid on hydrolysis. A *resin*, $[\alpha]_D^{20} +26.6^\circ$ in MeOH, probably a polymeride, yielding on hydrolysis an *acid*, $[\alpha]_D^{20} +25.0^\circ$, is also produced. Irradiation of cholic acid in EtOH produced a change in rotation, but no β -cholic acid was found. With Na cholate and Et deoxycholate there was no change. Both Me α - and β -cholates give the same Me dehydrocholate on oxidation with CrO_3 . The change from α - to β -form probably involves steric inversion at the OH group in ring III. J. H. BIRKINSHAW.

Autooxidation of some benzaldehyde derivatives. P. A. A. VAN DER BEEK (Rec. trav. chim., 1932, 51, 411—413).—*p*-Bromo- (I), *o*-, *m*-, and *p*-chloro-benzaldehyde in Ac_2O absorb 1 mol. of O_2 in 1—2 weeks to form peroxides almost quantitatively. (I) gives a *substance*, m. p. 66.6°, probably $C_6H_4Br \cdot CO \cdot O_2 \cdot Ac$. In $COMe_2$ only 1 atom of O is absorbed and little peracid is formed. R. S. CAHN.

Characteristics of vanillin and coumarin. R. M. HITCHENS (Ind. Eng. Chem., 1932, 24, 418—419).—A measurement of solubilities of vanillin and coumarin in EtOH- H_2O and in glycerol- H_2O mixtures. A. A. LEVI.

Nitration of *O*-benzylvanillin. P. V. NAIR and R. ROBINSON (J.C.S., 1932, 1236—1239).—Nitration of *O*-benzylvanillin with HNO_3 (*d* 1.46) at 0° affords a mixture of *O*-*o*- (I), m. p. 174—176° (*phenylhydrazone*, m. p. 190—192°; *oxime*, m. p. 142—144°; *phenylimine*, m. p. 138—140°), and *O*-*p*- (II), m. p. 212—214° (main product) (*phenylhydrazone*, m. p. 208°; *oxime*, m. p. 158—160°; *phenylimine*, m. p. 192—193°), *nitrobenzyl-6-nitrovanillin*, also obtained by similar nitration of *O*-*o*-, m. p. 128—130°, and *O*-*p*-, m. p. 124°, *nitrobenzylvanillin* (obtained by heating vanillin, the $NO_2 \cdot C_6H_4 \cdot CH_2Cl$, and K_2CO_3 in $COMe_2$), respectively. Oxidation of (I) or (II) with $KMnO_4$ gives, respectively, *O*-*o*-, m. p. 201—202°, and *O*-*p*-, m. p. 208°, *nitrobenzyl-6-nitrovanillic acid*, converted by boiling HNO_3 (*d* 1.42) into *O*-*p*-*nitrobenzyl-4:5-dinitroguaiacol*, m. p. 178—180°, hydrolysis and methylation of which gives 4:5-dinitroveratrole. Hydrolysis of (II) with conc. H_2SO_4 at 50—60° affords 6-*nitrovanillin*, m. p. 207° (*phenylhydrazone*, m. p. 198°). J. W. BAKER.

Arylviny- and aralkylvinyl-carbinols; conversion into β -homoacraldehydes. R. DELABY (Compt. rend., 1932, 194, 1248—1250).—The following are prepared by interaction of acraldehyde with the appropriate Grignard reagent: vinylphenyl-, b. p. $77^{\circ}/2$ mm.; *o*-tolyl-, b. p. 92 — $93^{\circ}/2$ mm.; *p*-tolyl-, b. p. $90^{\circ}/2$ mm.; benzyl-, b. p. 111 — $113^{\circ}/12.5$ mm.; β -phenylethyl-, b. p. $105^{\circ}/3$ mm., and γ -phenylpropylvinylcarbinol, b. p. $112^{\circ}/2$ mm. They are converted by HBr or PBr₃ into bromides of the type CHR:CH·CH₂Br, viz., cinnamyl bromide, b. p. 111 — $114^{\circ}/4$ mm.; β -*o*-tolyl-, b. p. 115 — $116^{\circ}/2$ mm.; β -*p*-tolyl-, β -benzyl-, b. p. 126 — $130^{\circ}/10.5$ mm.; β -(β' -phenylethyl)-, b. p. $117^{\circ}/1$ mm., and phenylpropyl-allyl bromide, b. p. 117 — $120^{\circ}/0.7$ mm. Condensation of these with hexamethylenetetramine, and hydrolysis of the resulting quaternary bromides (cf. A., 1913, i, 1395) gives the corresponding aldehydes, e.g., β -*o*-tolyl-, b. p. 139 — $141^{\circ}/16$ mm., β -*p*-tolyl-, b. p. 145 — $146^{\circ}/16$ mm., β -(β' -phenylethyl)-, b. p. 115 — $117^{\circ}/2$ mm. (semicarbazone, m. p. 195.5°), and β -(γ' -phenylpropyl)-acraldehyde, b. p. 126 — $128^{\circ}/2.5$ mm. (semicarbazone, m. p. 172.7°). H. A. PIGGOTT.

Lignosulphonic acids. P. KLASON (Svensk Kem. Tidskr., 1932, 44, 85—89).—A discussion of the chemical constitution of the α - and β -acids.

H. F. HARWOOD.

Lignin. VI. Distillation of alkali-lignin with zinc dust in an atmosphere of hydrogen. M. PHILLIPS and M. J. GOSS (J. Amer. Chem. Soc., 1932, 54, 1518—1521; cf. A., 1931, 469).—Alkali-lignin, isolated from maize cobs, heated with Zn dust in H₂ at a max. temp. of 400° , gives an oily distillate separable into phenolic and "neutral" fractions. Guaiacol and 4-propylguaiacol are isolated from the former, whilst oxidation of the latter fraction with KMnO₄ affords anisic acid. The results indicate that the lignin mol. contains at least two aromatic nuclei or groups readily convertible into aromatic nuclei.

C. J. WEST (b).

Lignin of Coniferae. XVI. P. KLASON (Ber., 1932, 65, [B], 625—628; cf. this vol., 57).—Drastic treatment accomplishes the complete methylation of α -ligninsulphonic acid and partly affects the phenolic OH. The double linkings of the acid can be methylated, doubtless in consequence of primary addition of H₂O. Oxidation of the trimeric acid with H₂O₂ in presence of FeCl₃ gives a partly demethoxylated carboxylic acid pptd. as the naphthylamine salt, 2C₁₀H₁₀O₃·C₉H₈O₃·O·H₂SO₃·C₁₀H₉N, or, after neutralisation with alkali, as the salt 2C₁₀H₁₀O₃·C₉H₈O₃·O·H₂SO₃·2C₁₀H₉N. β -Lignin-sulphonic acid is hydrolysed by H₂SO₃ at 130° ; the product yields the mixed naphthylamine salts, 2C₉H₉O₄·H₂SO₃·C₁₀H₉N—H₂O and C₁₀H₁₀O₃·H₂SO₃·C₁₀H₉N—H₂O. Methylation of the β -acid removes its tendency to polymerise; the methylated acid is indifferent to H₂O₂, is not pptd. by C₁₀H₇NH₂ or hydrolysed by H₂SO₃. Methylation of melaligninsulphonic acid followed by dialysis and pptn. with β -C₁₀H₇NH₂ gives a salt, 2C₉H₉O₄·C₁₀H₁₀O₃·H₂SO₃·C₁₀H₉N—H₂O, the "aldol H₂O" being methylated but not the two phenolic OH groups. Free, alcohol-sol., reserve lignin is isolated

by treating the finely-divided wood with Et₂O to remove fat and resin, extraction of the residue with MeOH, and purification with Et₂O and CHCl₃. Its quant. composition is identical with that of "genuine lignin." It yields the lignin reactions very definitely; its behaviour towards C₁₀H₇NH₂·HCl and H₂SO₃ is the same as that of lignin in wood, and the C₁₀H₇NH₂ salt has the normal composition, 3C₁₀H₁₀O₃·H₂SO₃·C₁₀H₉N—H₂O. The reddish-violet coloration of this lignin with phloroglucinol appears to depend on the presence of cellulose, which can be detected by this means provided it does not contain lignin. Reserve lignin does not contain sugar. It is formed independently between the annual rings where high pressure exists. The hemicellulose is not combined with the lignin. H. WREN.

Phosphorus-chlorine derivatives of dibenzoylmethane. R. BURET (Compt. rend., 1932, 194, 1353—1356).—Interaction of CH₂Bz₂ and PCl₅ gives different products according to the solvent used; these could not be purified, but gave pure CH₂Bz₂, HCl, and H₃PO₄ with H₂O, and were also decomposed by EtOH. In Et₂O and C₆H₆, respectively, the compounds C₁₅H₁₁O₂·PCl₄, m. p. 115 — 116° , and C₁₅H₁₂O₂·POCl₃, m. p. 137 — 138° , and in CHCl₃ a substance, m. p. 180° , are formed.

H. A. PIGGOTT.

Acetylenic arylcarbinols. Diphenyl-*p*-bromophenylacetylenylcarbinol and its derivatives: conversion into the ethylenic ketone. N. DRISCH (Compt. rend., 1932, 194, 1170—1172).—MgPhBr and *p*-C₆H₄Br·C≡CH afford diphenyl-*p*-bromophenylacetylenylcarbinol (I), m. p. 99 — 100° (60% yield), converted by cold conc. H₂SO₄ and ROH into its Me, m. p. 144 — 145° , and Et, m. p. 108 — 109° , ether, and by PCl₃ into α -chloro- $\alpha\alpha$ -diphenyl- γ -(*p*-bromophenyl)- Δ^{β} -propinene (II), m. p. 108 — 109° (decomp.), slow heating causing decomp. at 95° into a dibromorubrene. *p*-Bromophenyl $\beta\beta$ -diphenylstyryl ketone, m. p. 120° , is obtained by isomerisation of (II) with boiling EtOH, or of (I) by boiling EtOH and HCl.

J. W. BAKER.

Reaction between organic magnesium halides and α -bromo-ketones. E. P. KOHLER and M. TISHLER (J. Amer. Chem. Soc., 1932, 54, 1594—1600).—The reaction between MgRX and an α -Br ketone, in which the CO group is relatively inactive, is: CHR:Br·CO·R + R'MgBr \rightarrow CHR:CR·OMgBr + R'Br. Thus, MgMeI and Ph α -bromo- $\alpha\beta$ -triphenylethyl ketone give (after decomp. with dil. acid) Ph $\alpha\beta$ -triphenylethyl ketone; with MgPhBr, the enolate CHPh₂·CPh:CH·OMgBr (the free enol absorbs O₂ from the air forming a peroxide) results. MgPhBr and Ph α -iodo- $\beta\beta$ -diphenylethyl ketone, m. p. 184 — 185° (decomp.), give PhI and CHPh₂·CH:CH·OMgBr, converted by CO₂ into α -benzoyl- $\beta\beta$ -diphenylpropionic acid (Et ester, m. p. 135 — 136° , also prepared from CH₂Bz·CO₂Et, CHPh₂Br, and NaOEt) and by BzCl into $\alpha\alpha$ -dibenzoyl- $\beta\beta$ -diphenylethane.

C. J. WEST (b).

Reaction between keto-oxido-compounds and Grignard reagents. E. BERGMANN and H. A. WOLFF (J. Amer. Chem. Soc., 1932, 54, 1644—1647).—Anisyl styryl ketone and alkaline H₂O₂ in MeOH give

α-anisoyl-β-phenylethylene oxide, m. p. 75°, converted by MgPhBr into *α*-*γ*-dihydroxy-*α*β-*γ*-triphenyl-*γ*-anisylpropane, m. p. 131—132°. Diphenylstyryl ketone, m. p. 165°, from Ph₂, cinnamoyl chloride, and AlCl₃ in CS₂, yields an oxide, two forms, m. p. 126° and 162°, which with MgPhBr affords a pinacol, m. p. 181°, of Ph diphenylstyryl ketone, and *α*-*γ*-dihydroxy-*α*β-*γ*-triphenyl-*γ*-diphenylpropane, m. p. 159°. The results confirm Kohler's interpretation (A., 1931, 354) of the reaction between Grignard reagents and oxido-ketones. C. J. WEST (b).

Preparation of 4'-hydroxy-2-p-hydroxybenzoylbenzophenone. F. F. BLICKE and O. J. WEINKAUFF (J. Amer. Chem. Soc., 1932, 54, 1454—1459).—The Me₂ ether (I), m. p. 157—159° [dioxime, m. p. 177—178° (decomp.); diphenylhydrazone, m. p. 171—173°], of 4'-hydroxy-2-p-hydroxybenzoylbenzophenone (II), m. p. 225—226°, is prepared from (a) o-C₆H₄(CO)₂O and p-OMe-C₆H₄·MgI, (b) Me 2-anisylbenzoate and p-OMe-C₆H₄·MgI, (c) phenolphthalein, and (d) 4:4'-dimethoxytriphenylmethane-2-carboxylic acid (converted by conc. H₂SO₄ into 2:6-dianisyl-3:4-benzofuran, m. p. 126—127°); (I) is demethylated to (II). (I) and N₂H₄·H₂O in AcOH give 6-dianisyl-4:5-benzopyridazine, m. p. 205—206°. The compound described (lit.) as "dihydroxyphenylanthranol" is (II). C. J. WEST (b).

Preparation of substituted anthrones. F. F. BLICKE and O. J. WEINKAUFF (J. Amer. Chem. Soc., 1932, 54, 1460—1464).—Anthraquinone and p-OMe-C₆H₄·MgI (I) give 9-hydroxy-9-p-anisyl-10-anthrone, m. p. 206—207°. 2-p-Methoxybenzylbenzoic acid and conc. H₂SO₄ give 2-methoxy-9-anthrone, m. p. 94—95° (structure proved by oxidation), which with (I) affords 2-methoxy-9-anisylanthracene, m. p. 175—176°, oxidised by Na₂Cr₂O₇ in AcOH to 9-hydroxy-2-methoxy-9-anisyl-10-anthrone, m. p. 199—201°, also formed from 2-methoxyanthraquinone and (I). Et 2-p-methoxybenzylbenzoate and (I) give 4'':4'''-dimethoxy-2-p-methoxybenzyltriphenylcarbinol, converted by AcOH-HCl into the gummy 2-methoxy-9:9-dianisyl-9:10-dihydroanthracene, oxidised to the 10-anthrone, m. p. 182—183°; the latter and (I) give 10-hydroxy-2-methoxy-9:9:10-trianisyl-9:10-dihydroanthracene, m. p. 193—194°. C. J. WEST (b).

Benzoylbenzoic acids and their transformation into anthraquinones. A. OLIVERIO (Gazzetta, 1932, 62, 231—243).—A crit. examination of previous work. E. E. J. MARLER.

Synthesis of munjistin. P. C. MITTER and H. BISWAS (Ber., 1932, 65, [B], 622—625).—2-Chloro-6-methoxytoluene is converted by phthalic anhydride in presence of CS₂ and AlCl₃ into o-2'-chloro-4'-methoxy-3'-methylbenzoylbenzoic acid, m. p. 202°, transformed by H₂SO₄ into 4-chloro-2-methoxy-3-methylanthraquinone (I), m. p. 197°. (I) and AlCl₃ at 200° afford 4-chloro-2-hydroxy-3-methylanthraquinone, m. p. 324—325°, oxidised by treatment with H₂SO₄ and 3:3 and then with NaNO₂ to a substance, m. p. 231°, which does not depress the m. p. of natural munjistin (1:3-dihydroxyanthraquinone-2-carboxylic acid), but is not free from Cl. (I) and SO₂Cl₂ in

presence of PhNO₂ transform 3-methylalizarin into 4-chloro-3-methyl-1:2-dihydroxyanthraquinone, m. p. 178—180°, oxidised at 160—165° to purpurin, but yielding at 145—150° a compound with the same m. p. as 1:2:4-trihydroxyanthraquinone-3-carboxylic acid, but not free from Cl. Repeated reduction of this compound with Na₂S₂O₄ and NH₃ followed by treatment with boiling aq. Ba(OH)₂ yields an insol. Ba salt from which a Cl-free product, m. p. 229—230°, is obtained which does not depress the m. p. of natural munjistin. H. WREN.

Tautomerism of anthraquinone-1:5-dicarboxyl chloride and synthesis of members of the hetero-coerdianthrene series. Stereochemistry of difficultly hydrolysable esters. R. SCHOLL, H. K. MEYER, and W. WINKLER (Annalen, 1932, 494, 201—224).—The Friedel-Crafts reaction with anthraquinone-1:5-dicarboxyl chloride (I) and ArH resembles that with anthraquinone-1-carboxyl chloride (this vol., 274), and gives mixtures of 1:5-diaroylanthraquinones and 9:10-dihydroxy-9:10-diaryl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactones. The former is usually the main product when a little FeCl₃ is the catalyst (at high temp.) in absence or presence of PhNO₂, whilst the latter predominates with a stoichiometrical proportion of AlCl₃ in PhNO₂, usually at 0—20°. Interconversion (under the conditions of their formation) of these products has not been accomplished.

[With S. HASS.] (I) and a little FeCl₃ in boiling m-xylene give 65% of 1:5-di-2':4'-dimethylbenzoylanthraquinone, m. p. 263° (bis-o-diazine, m. p. 330°). With AlCl₃ in PhNO₂ at 0—20°, the main product is the dilactone, m. p. 328.5—329°, of 9:10-dihydroxy-9:10-m-4'-xylyl-9:10-dihydroanthracene-1:5-dicarboxylic acid; a little 1-2':4'-dimethylbenzoylanthraquinone-5-carboxylic acid, m. p. 288—289° (decomp.), is also produced.

[With H. VON HOESSLE.] 1:5-Di-2':5'-dimethylbenzoylanthraquinone, m. p. 273—274°, and the dilactone, m. p. 327—328° (slight decomp.), of 9:10-dihydroxy-9:10-di-p-xylyl-9:10-dihydroanthracene-1:5-dicarboxylic acid are similarly prepared from (I) and p-xylene.

(I) and C₆H₆ give 1:5-dibenzoylanthraquinone, m. p. 277—279°, sublimes at 300—350°/20 mm., and the dilactone, m. p. above 360°, of 9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene-1:5-dicarboxylic acid (II). This dilactone is reduced by red P and HI (d 1.7) in AcOH to 9:10-diphenylanthracene-1:5-dicarboxylic acid (III) (Et ester, m. p. 233—234°, prepared by the Ag salt method), whilst (II) is reduced by Zn dust, aq. NH₃, and a little CuSO₄ to 9:10-diphenyl-9:10-dihydroanthracene-1:5-dicarboxylic acid (IV) (Et ester, m. p. 186—188°), also formed from (III), Zn dust, and 10% NaOH at 200°. (III) and conc. H₂SO₄ at 50—60° give a green solution of hetero-coerdianthrene (7':7'') (V), bronze with violet reflex [the unknown parent hydrocarbon (V, where :O=H₂) is designated hetero-coerdianthrene], also formed when (IV) is heated at about 350° or treated with conc. H₂SO₄ at 80°, from (III) and Ac₂O containing a trace of mineral acid, and by treatment of the dilactone of (II) with Al powder and conc.

H_2SO_4 . (V) undergoes oxidation in various solvents in sunlight to the 9:10-dihydroxy-9:10-dihydro-derivative, colourless, which is readily reduced (even when warmed with org. solvents) to (V). Reduction of (V) with red P and HI (*d* 1.7) at 200° and treatment of the reaction product with Zn and pumice gives 1:2:7:8-dibenzperylene in very small yield. Reduction of (V) with alkaline $\text{Na}_2\text{S}_2\text{O}_4$ and treatment of the blue vat with $\text{Et}_2\text{O}-p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COCl}$ afford 3:9-di-*p*-bromobenzoyloxy-1:2:7:8-dibenzperylene. The following are also

prepared: 10-dihydroxy-9:10-di-*p*-tolyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone; 1:5-di-*p*-chlorobenzoylanthraquinone, m. p. 333—334°; 9:10-dihydroxy-9:10-di-*p*-chlorophenyl-9:10-dihydroanthracene-1:5-dicarboxylic acid (dilactone, not melted at 360°), converted by conc. H_2SO_4 and Al powder at 25° into 5':5''-dichloro-hetero-coerdianthrone, violet.

[With C. SEER and O. DISCHENDORFER.] 9:10-Dihydroxy-9:10-di- α -naphthyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone, not melted at 360°, obtained with (probably) 1:2:7:8-dinaphthoperylene-3:9-quinone from (I), C_{10}H_8 , and AlCl_3 in PhNO_2 at 0°, when heated with soda-lime at 350° gives C_{10}H_8 and anthraquinone.

[With A. KELLER.] 4:8-Dichloroanthraquinone-1:5-dicarboxyl chloride, C_6H_6 , and AlCl_3 in PhNO_2 at 0—20° give almost entirely 4:8-dichloro-9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone; this dissolves in conc. H_2SO_4 to a colourless solution which when treated with Cu at 100° gradually becomes green owing to coerdianthrone formation.

[With G. LANGBEIN.] 2:4:6:8-Tetrabromo-1:5-diaminoanthraquinone, m. p. about 340° (from the diamino-compound and Br in H_2O), is converted by the usual method into 2:4:6:8-tetrabromoanthraquinone-1:5-dicarboxylic acid, darkens about 310° (*Et* ester).

[With H. DEHNERT.] 1:5-Dicyano-2:6-dimethylanthraquinone, darkens at 350°, not melted at 420°, is hydrolysed by H_2SO_4 at 170—175° to 2:6-dimethylanthraquinone-1:5-dicarboxylic acid, decomp. about 350° (previous darkening); the chloride and FeCl_3 in boiling C_6H_6 give mainly 9:10-dihydroxy-9:10-diphenyl-2:6-dimethyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone, m. p. 382—383° (previous darkening).

Et 9:10-diphenylanthracene-1:5-dicarboxylate (above) is hydrolysed only to the extent of 10% by 25% $\text{MeOH}-\text{KOH}$ after 30 hr.; this difficulty of hydrolysis is ascribed to diplanar configuration of the ester mol., the CO groups being screened by Ph.

H. BURTON.

Podophyllin. W. BORSCHÉ and J. NIEMANN (Annalen, 1932, 494, 126—142).—Podophyllotoxin (I), extracted from *Podophyllum indicum*, is $\text{C}_{22}\text{H}_{22}\text{O}_8$ (cf. Dunstan and Henry, J.C.S., 1898, 73, 209), m. p. (anhyd.) 114—118° (+ $\text{H}_2\text{O}, 0.5\text{EtOH}$) 106—108° (decomp.) (+0.5 $\text{H}_2\text{O}, 0.5\text{CO}_2\text{Me}_2$) 114—117 (decomp.) (+ $\text{H}_2\text{O}, 0.5\text{C}_6\text{H}_6$) 112—115° (de-

comp.), $[\alpha]_D^{25}$ —101.3° in EtOH , contains 3 OMe and 2 OH groups (Zerevitinov), and gives (with Ac_2O alone) an *Ac* derivative, m. p. 179—181°, $[\alpha]_D^{25}$ —134.9° in CHCl_3 . (I) is isomerised by 2*N*- Na_2CO_3 in MeOH , 10% NaOAc in EtOH , and during attempted reduction (colloidal Pd, H_2 , MeOH) to picropodophyllin (II) (+ MeOH and EtOH), m. p. 227°, $[\alpha]_D^{25}$ +5.32° in CHCl_3 , also containing 3 OMe and 2 OH groups and acetylated ($\text{Ac}_2\text{O}-\text{NaOAc}$) to an *Ac* derivative (III), m. p. 215—216°, $[\alpha]_D^{25}$ +17.7° in CHCl_3 , also formed by similar acetylation of (I). (I) and (II) are unaffected by diazomethane (i.e., no phenolic OH groups), do not contain $\cdot\text{CHO}$ or $\cdot\text{CO}$, and are converted by *N*- NaOH into podophyllin acid, $\text{C}_{22}\text{H}_{20}\text{O}_9$ (+3 H_2O) (IV), m. p. 163—165° (decomp.), $[\alpha]_D^{25}$ —102.8° in EtOH (*Na* salt), also formed similarly from (III). When (IV) is heated alone or in H_2O or EtOH , (II) results. (III) and conc. H_2SO_4 in Ac_2O give apocicropodophyllin, $\text{C}_{22}\text{H}_{20}\text{O}_7$, m. p. 214—216°, $\alpha=0^\circ$ [also formed from (II) and $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ or PCl_5 in CHCl_3 , but not by thermal decomp. of (I) or (II)], reduced (H_2 , Pt-black, AcOH) to deoxypicropodophyllin, $\text{C}_{22}\text{H}_{22}\text{O}_7$, m. p. 169—170°, and converted by *N*- NaOH into apocicropodophyllin acid, $\text{C}_{22}\text{H}_{22}\text{O}_8$, m. p. 160—165° (decomp.). (I) and (II) are considered to be structural isomerides. Oxidation of (IV) with KMnO_4 gives a small amount of an acid, $\text{C}_{21}\text{H}_{18}\text{O}_9$, m. p. 213—214° (*Me* ester, m. p. 126—127°), whilst (II) is reduced by HI (*d* 1.7) in AcOH to podophyllomeronic acid, $\text{C}_{13}\text{H}_{10}\text{O}_4$, m. p. 236—237° (*Me* ester, m. p. 121—123°; *Ac* derivative, m. p. 103—104°; dinitro-derivative, darkens at 250° and decomp. slowly without melting).

H. BURTON.

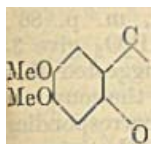
Chemistry of polyene pigments. Condensation product of benzylideneacetone. I. J. POSTOVSKI and B. P. LUGOVKIN (J. Gen. Chem. Russ., 1930, 1, 1006—1011).—Benzylideneacetone treated with KOH in EtOH gives an orange-red substance, $\text{C}_{30}\text{H}_{26}\text{O}$ (I), m. p. 247—250°, which is approx. dimeric in C_6H_6 solution. (I) gives characteristic colour reactions, forms a brownish-black bromide, and is readily oxidised in the air, giving a yellow compound, $\text{C}_{28}\text{H}_{24}\text{O}_5$, which gradually loses 2O in the dark (more rapidly on heating) but later tends to absorb it again.

G. A. R. KON.

Conjugated double linkings. XXIII. Dihydro-compound of the isomeric bixins and the electronic configuration of polyenes. R. KUHN and A. WINTERSTEIN (Ber., 1932, 65, [B], 646—651).—The isomerisation of bixin to β -bixin and of methylbixin to β -methylbixin differs from that of β -carotene to isocarotene in that it can be effected with minute amounts of I. Since dihydrobixin is obtained from bixin and β -bixin and dihydromethylbixin from methylbixin and β -methylbixin, the *cis-trans*-isomerism of the bixins is established. It is very probable that addition of the H atoms occurs at the ends of the system of conjugated double linkings as in the case of the amalgam reduction of $\omega\omega'$ -diphenylpolyenes. The views on electronic configuration of Radulescu (A., 1931, 1351) and of Wittig and Wiemer (*ibid.*, 92) are criticised: there appears no immediate reason to abandon the classical conception of double linkings

when assigning structural formulæ to the natural polyene dyes. H. WREN.

Toxicarol. III. Relation between toxicarol and the rotenone group of fish poisons. E. P. CLARK (J. Amer. Chem. Soc., 1932, 54, 1600—1602; cf. A., 1931, 1065).—Oxidation of dehydrotoxicarol (I) with KMnO_4 in COMe , gives rissic and 2-hydroxy-4:5-dimethoxybenzoic acids, the former being obtained in small and variable quantities. (I) boiled gently with EtOH-KOH affords an acid apparently analogous to deguelic and derric acids, oxidised by alkaline KMnO_4 to derric acid. Toxicarol contains the annexed grouping, as do rotenone, deguelin, and tephrosin.



C. J. WEST (b).

Carotene. IV. Hydrogenation of carotenes from different sources, of dihydrocarotene, and of lycopene. J. H. C. SMITH (J. Biol. Chem., 1932, 96, 35—51; cf. A., 1931, 491).—The substances were hydrogenated in a micro-apparatus with PtO freshly reduced to Pt as catalyst and with $\text{Bu}_2\text{O} + \text{AcOH}$, cyclohexane and AcOH , and *p*-menthane as solvents. Carotenes from various sources all absorb approx. 20H per mol. of pigment. Caroteneloses only one double linking on reduction by Al-Hg . Lycopene absorbs 26H per mol. (cf. A., 1928, 1016).

F. O. HOWITT.

Vegetable, fish, and insect poisons. III. Rotenone, the physiologically active constituent of *Derris elliptica*: constitution of rotenone. III. A. BUTENANDT and W. MCCARTNEY (Annalen, 1932, 494, 17—41; cf. A., 1930, 478).—Rotenone is assigned a structure [identical with that suggested by La Forge and Haller (this vol., 401)] which explains all its reactions. Formulæ are also assigned to the numerous degradation products prepared by Butenandt, Kariyone, Takei, and Haller and La Forge.

Derrisic acid is oxidised by H_2O_2 in dil. KOH at 60—100° to derric acid, m. p. 165° (Me_2 , m. p. 66°, and Et_2 , m. p. 62°, esters). Rissic acid, m. p. 257° (Me_2 ester, m. p. 84°), distils unchanged at 265—270°/0.4 mm.; when heated at atm. pressure and then distilled, decarboxyrissic acid, m. p. 115° (Me ester, m. p. 45°), is obtained. Oximation of dihydro-rotenone in alkaline solution (cf. *loc. cit.*) gives the isooxime, m. p. 201°. Rotenonone is converted by boiling 20% MeOH-KOH into rotenononic acid and 10—15% of derritol. Netoric acid, obtained by oxidation of rotenol with H_2O_2 in 5% EtOH-KOH at 100° (bath) (cf. La Forge and Smith, A., 1931, 227), exists in two interconvertible modifications, m. p. 87° and 131°. Rotenone is oxidised by dil. HNO_3 to an unidentified acid, $\text{C}_8\text{H}_3\text{O}_8\text{N}_3$ (?), m. p. 212—213°.

H. BURTON.

Isoprene and caoutchouc. XXXVI. Constitution of caoutchouc. H. STAUDINGER (Angew. Chem., 1932, 45, 276—280, 292—295).—The isoprene residues in caoutchouc (I) are in long chains. The primary colloid particles, which exist in a dil. solution, are identical with mols. Homopolar mol. colloids, such as (I), are differentiated from heteropolar, micellar colloids, such as soap. Work on the mol. wt. (I) is reviewed.

E. S. HEDGES.

Physico-chemical properties of terpin hydrate. N. SCHOORL (Natuurwetensch. Tijds., 1932, 14, 35—40).—The behaviour of terpin hydrate on dehydration and rehydration confirms the view that the compound is a true monohydrate. The dissociation pressure at 15° is about 0.6 mm. Dehydration is complete but slow at 70—80°. Terpin (m. p. 105°) and its hydrate form at 95° a eutectic containing 10% of the hydrate; no second hydrate appears to exist. The phase diagram of the system terpin hydrate- H_2O indicates an upper crit. solution temp. of 158°, and a lower of 59°, the composition in both cases being 45—50% terpin hydrate. The m. p. of terpin hydrate falls on addition of H_2O to 114° (20% H_2O), when the system becomes heterogeneous; homogeneity is reattained at 84% H_2O .

H. F. GILLBE.

Δ^1 -Dehydroisopulegol from citral. O. ZEITSCHSEL and H. SCHMIDT (J. pr. Chem., 1932, [ii], 133, 370—373).— Δ^1 -Dehydroisopulegol (Δ^1 -4-isopropylidenemethylcyclohexen-3-ol) (I) [modified prep. (25—30% yield) from citral], b. p. 218—219° (acetate, b. p. 234—235°), has the physical consts. recorded (A., 1899, i, 768) but an odour of isopulegol. The presence of two ethylenic linkings is proved by titration with Br . The dihydrochloride, an oil, with 2% aq. KOH gives an oil and a few crystals. (I) loses H_2O when heated with acids or, better, a trace of I , to yield *p*-cymene. (I) with CrO_3 in COMe_2 gives much hydrocarbon and a little ketone, an oil (semicarbazone, m. p. 193°; oxime), and when reduced (Ni) affords a mixture of menthols, b. p. 214—215°, containing neomenthol and giving isomenthone on oxidation. Attempts at partial reduction of (I) failed.

R. S. CAHN.

Disubstituted derivatives of eucalyptol. A. SOLDI (Gazzetta, 1932, 62, 221—227).— α -Bromoketocineole with $\text{NH}_2\text{OH.HCl}$ gives an oxime, $\text{C}_{10}\text{H}_{16}\text{O}_2\text{NBr}$, m. p. 165°, which on further treatment with NH_2OH in presence of anhyd. NaOAc gives the hydroxylamine-oxime, $\text{C}_{12}\text{H}_{21}\text{O}_3\text{N}_2$, m. p. 83°, and with gaseous NH_3 in anhyd. Et_2O the amino-oxime [monohydrate, m. p. 226°; chloroplatinate, m. p. 252° (decomp.); hydrochloride dihydrate] of ketocineole and a substance m. p. 232°, and with piperidine gives the oxime, m. p. 173°, of α -piperidinoketocineole.

E. E. J. MARLER.

New solid *dl*-fenchyl alcohol from American pine oil. O. ZEITSCHSEL and K. TODENHÖFER (J. pr. Chem., 1932, [ii], 133, 374—376).—The alcohols from American pine oil yield a mixture of borates; a portion of this, m. p. 119—122°, is stable to aq. NaOH but with hot KOH-EtOH gives a new *dl*-fenchyl alcohol (I), b. p. 201.4°/770 mm., m. p. 38—39°, $[\alpha]_D$ -0.20° (acetate, m. p. -0.5°, b. p. 79°/5 mm., $[\alpha]_D$ -0.7°; formate, m. p. 21°, b. p. 207—208°, $[\alpha]_D$ -0.11°; phenylurethane, m. p. 104°), which with Beckmann's mixture affords *dl*-fenchone, $[\alpha]_D$ +2.25°. The optically active constituent could not be removed. (I) is thus an isomeride (H , OH) of the known *dl*-fenchyl alcohol. *l*-Fenchyl formate has m. p. -13°, b. p. 77°/6 mm., $[\alpha]_D$ -76°.

R. S. CAHN.

Orientation in the furan nucleus. 2-Methyl-3-furoic acid. H. GILMAN, R. R. BURTNER, and E. W. SMITH (Rec. trav. chim., 1932, 51, 407—410).—Et 5-nitro-2-methyl-3-furoate [from Et 2-methyl-3-

furoate (modified prep.)] is hydrolysed by 33% H_2SO_4 or, better, 20% HCl to 5-nitro-2-methyl-3-furoic acid (I), m. p. 154—154.5°, also obtained from 2-methyl-3-furoic acid by fuming HNO_3 in Ac_2O at -10° . (I) with quinoline and a little Cu-bronze at 200—205° affords 5-nitro-2-methylfuran (thereby proving the position of the NO_2 -group) and with Br gives 5-bromo-2-methyl-3-furoic acid, m. p. 118°. R. S. CAHN.

β -Substituted furans. H. GILMAN, R. R. BURTON, and G. F. WRIGHT (J. Amer. Chem. Soc., 1932, 56, 1696).—Furan-3-carboxylic acid is obtainable by pyrolysis of furan-2:4-dicarboxylic acid. 3-Iodo-2:5-dimethylfuran readily forms a Grignard reagent. C. J. WEST (b).

Introduction of furylalkyl groups by means of sulphonic esters. H. GILMAN and R. E. BROWN (Iowa State Coll. J. Sci., 1931, 6, 11—15).—Toluene-*p*-sulphonyl chloride with tetrahydrofurfuryl alcohol afforded the toluene-*p*-sulphonate, from which volatile impurities were removed at 145—150°/11 mm. The ester reacted with $\text{CH}_2\text{Ph-MgCl}$ to give tetrahydrofurfurylphenylmethane. Tetrahydrofurfuryl chloride, bromide, and iodide were prepared.

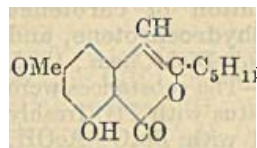
CHEMICAL ABSTRACTS.

Isomerism of tetrahydropyrones. R. CORNUBERT and P. ROBINET (Compt. rend., 1932, 194, 1081—1083).—The pyrone-like compound (I), m. p. 175°, of 2:6-dimethylcyclohexanone (A., 1928, 416) is converted by dil. HCl at 125—140° into PhCHO , the tetrahydropyrone (II), m. p. 206° (*loc. cit.*, m. p. 197—198°), and the original ketone, which with PhCHO and HCl at -15° gives only the tetrahydropyrones, m. p. 175° and m. p. 216° (III) (*loc. cit.*). Similar hydrolysis of (II) occurs only partly and with difficulty, giving a ketone from which a small quantity of (II) can be regenerated. Hydrolysis of (III) gives PhCHO and the ketone, the quantity available bring too small for further investigation. The isomerism of these derivatives is discussed and, in this connexion, it is found that condensation of acetonedicarboxylic acid with PhCHO in the presence of HCl affords 2:6-diphenyltetrahydropyrone, m. p. 131°, and a geometrical isomeride, m. p. 76°, with the same chemical properties. J. W. BAKER.

Hydroxy-carbonyl compounds. VI. Application of the Simonis reaction to *p*-cresol. A. ROBERTSON and W. F. SANDROCK (J.C.S., 1932, 1180—1184).—Condensation of *p*-cresol and Et acetoacetate in the Simonis reaction gives 4:6-dimethylcoumarin, m. p. 152° (lit. 148°), which is converted by NaOH and subsequent methylation into 2-methoxy- β :5-dimethylcinnamic acid, m. p. 120°, oxidised to 2-methoxy-5-methylacetophenone (semicarbazone, m. p. 201—202°). *p*-Cresol and Et α -ethylacetoacetate with 84% H_2SO_4 afford 4:6-dimethyl-3-ethylcoumarin, m. p. 106°, converted into 2-methoxy- β :5-dimethyl- α -ethylcinnamic acid, m. p. 113°, but with P_2O_5 , mainly 2:6-dimethyl-3-ethyl-1:4-benzopyrone, b. p. 140—158°/6 mm., is obtained, which with piperonal and NaOEt yields 2-(3':4'-methylenedioxy-2-ethyl-1:4-benzopyrone), m. p. 154°, also obtained from the product of ring closure of 2-hydroxy-5-methyl-*n*-butyrophenone with NaOAc and Ac_2O . 4-Phenyl-6 methyl-

coumarin, m. p. 131°, is prepared from *p*-cresol, Et benzoylacetate, and H_2SO_4 , but NaOAc and Ac_2O give with 2-hydroxy-5-methylbenzophenone the acetate, m. p. 65°, of the ketone. 6-Methylflavone and its 3-*Bz* derivative, m. p. 184°, result from vigorous benzoylation of 2-hydroxy-5-methylacetophenone, and also in small amount from *p*-cresol, Et benzoylacetate, and P_2O_5 together with a compound, m. p. 86°. *p*-Cresol, Et α -chloroacetoacetate, and P_2O_5 give 3-chloro-4:6-dimethylcoumarin. It is suggested that the only trustworthy method of detecting the coumarin structure is by conversion into the corresponding 1-*O*-methylcinnamic acid. F. R. SHAW.

Lichen substances. XIII. Olivetoric acid. II. Y. ASAHINA and J. ASANO (Ber., 1932, 65, [B], 584—586; cf. this vol., 521).—Short treatment of olivetoric acid with diazomethane in Et_2O affords the



(II.)

Me ester of the Me_2 ether (I), m. p. 132°, hydrolysed by 95% HCO_2H to olivetonide Me ether (II), m. p. 57°, obtained also from olivetonide and diazomethane. Treatment of (I) with KOH-EtOH affords olivetonide Me ether and Me olivetolcarboxylate

o-Me ether, (corresponding acid, m. p. 105°). The constitution of olivetoric acid (*loc. cit.*) is thus confirmed. H. WREN.

Hydroxychrysin (5:7:8-trihydroxyflavone, norwogonin). M. NIERENSTEIN (Acta Phytochim., 1932, 6, 173—175).—5:7:8-Trihydroxyflavone, m. p. 227—228° (this vol., 64), is probably a hydrate of the anhyd. form, m. p. 305° (A., 1912, i, 292), and is identical with hydroxychrysin. R. S. CAHN.

5:7:8-Trihydroxyflavone. S. HATTORI (Acta Phytochim., 1932, 6, 177—178).—A reply to Nierenstein (cf. preceding abstract). 5:7:8-Trihydroxyflavone (synthetic or from wogonin), recryst. from AcOH and a few drops of H_2O , contains $1\text{H}_2\text{O}$ (lost above 100° in vac.), but the hydrated and anhyd. forms melt at 227—228°. It is not identical with hydroxychrysin. R. S. CAHN.

Spectrography of flavones. V. Relations between absorption of light and hydroxyl substituents among flavone derivatives. S. HATTORI (Acta Phytochim., 1932, 6, 131—154; cf. this vol., 64).—The absorption spectra, partly new, of many hydroxyflavones are described. It is possible by their means to determine the positions of OH groups in the flavone series. The auxochromic effect of OH groups is not affected by methylation or glucoside formation, but is destroyed by acylation. Resacetophenone Me_2 ether, Me *o*-methoxybenzoate, and Na at 120—125° give 2:4:2'-trimethoxybenzoylacetophenone, m. p. 96—97°, whence by HI first 7:2'-dimethoxy-, m. p. 176—177°, and then 7:2'-dihydroxy-flavone, m. p. above 300°, were obtained. Resacetophenone Me ether and *m*-methoxybenzaldehyde in hot KOH-EtOH give 2-hydroxy-4:3'-dimethoxychalkone (I), m. p. 93° after sintering at 91° (lit. 80—81°), and 7:3'-dimethoxyflavanone (II),

m. p. 104° [also obtained from (I) and 5% H_2SO_4 in hot EtOH]; (II) with PCl_5 in hot C_6H_6 affords 7:3'-dimethoxyflavone, m. p. 153°, which with HI gives 7:3'-dihydroxyflavone, m. p. 276—277°. Me gallate Me_3 ether, *o*-methoxyacetophenone, and Na at 130—135° give 2:3':4':5'-tetramethoxybenzoylacetophenone, m. p. 105—107°, which with HI yields 3':4':5'-trihydroxyflavone, m. p. above 280° (Me_3 ether, m. p. 174—175°; Ac_3 derivative, m. p. 195—196°). β -Resorcyraldehyde Me_3 ether and *o*-hydroxyacetophenone in hot NaOH-EtOH give 2-hydroxy-2':4'-dimethoxychalkone, m. p. 107°, which with aq. NaOH forms 2':4'-dimethoxyflavanone, m. p. 131—132°, whence 2':4'-dimethoxy-, m. p. +1.5 H_2O 135°, anhyd. 221°, and 2':4'-dihydroxy-flavone, m. p. 268—270°, were obtained. 2:4:5-Trimethoxyacetophenone (prepared by a Friedel-Crafts reaction), m. p. 102°, with BzOEt and Na at 120—125° yields 2:4:5-trimethoxybenzoylacetophenone, m. p. 104—105°, which with HI gives 6:7-dimethoxy-, m. p. 189°, and 6:7-dihydroxy-flavone, m. p. 252° (after sintering (anhyd. or + H_2O) [not 135° (+ H_2O) (lit.)].

R. S. CAHN.

Synthetical experiments in the chromone group. VII. Synthesis of 7:8:4'-trihydroxy-, 7:8:3':4'-tetrahydroxy-, and 7:8:3':4':5'-, 5:7:3':4':5'-, and 3:7:3':4':5'-pentahydroxy-flavones. I. C. BADHWAR, K. S. KANG, and K. VENKATARAMAN (J.C.S., 1932, 1107—1112).—2'-Acetoxy-4:3':4'-trimethoxychalkone dibromide, m. p. 133°, and KOH give 7:8:4'-trimethoxy-, m. p. 189—190°, demethylated to trihydroxy-flavone, m. p. 299—300° (decomp.) (Ac_3 derivative, m. p. 183°). 2'-Acetoxy-3:4:3':4'-tetramethoxychalkone dibromide, m. p. 118°, 7:8:3':4'-tetramethoxy-, m. p. 198—199°, and tetrahydroxy-flavone (I), m. p. 309—310° (decomp.) (Ac_4 derivative, m. p. 218°), are similarly prepared. Et veratrate, gallacetophenone Me_3 ether, and Na yield 2:3:4:3':4':5'-pentamethoxy- ω -benzoylacetophenone, m. p. 105°, which gives (I) on treatment with HI. 2:3:4:3':4':5'-Hexamethoxy- ω -benzoylacetophenone, m. p. 125°, and 7:8:3':4':5'-pentahydroxyflavone, m. p. above 345° (Ac_5 derivative, m. p. 263°), are similarly prepared. Trimethylgallic anhydride and K trimethylgallate with ω -methoxyresacetophenone and phloracetophenone give, respectively, 7-hydroxy-3:3':4':5'-tetramethoxy-, m. p. 246° (Ac derivative, m. p. 146°), demethylated to 3:7:3':4':5'-pentahydroxy-, m. p. 310—312° (decomp.) (Ac_5 derivative, m. p. 175—176°), and 5:7-dihydroxy-3':4':5'-trimethoxy-, m. p. 264—265°, demethylated to 5:7:3':4':5'-pentahydroxy-flavone, decomp. about 310°. The colour reactions of the above flavones are described.

F. R. SHAW.

Constitution of dye of toad-flax petals (*Linaria vulgaris*). L. SCHMID and W. RUMPEL (Monatsh., 1932, 60, 8—25).—The hydrocarbon previously isolated from the degradation products of the aglucone (A., 1931, 738) is found to have been present in the original dye, and is hentriacontane, m. p. 67—69°. Alkaline degradation of the hydrocarbon-free aglucone gives anisic acid and unidentified phenolic substances. Demethylation (2Me) with HI gives scutellareine. Acetylation gives the Ac_2

derivative of 6:4'-dimethylscutellareine (cf. A., 1930, 1295); this Me ether, m. p. 218°, and the aglucone, m. p. 201°, are dimorphic, the latter being formed by hydrolysis of the Ac_2 derivative or by prolonged heating of the former at its m. p., and being converted into the former by crystallisation from EtOH. The original glucoside is unaffected by diazomethane. It is accompanied in the petals by mannitol.

H. A. PIGGOTT.

A rearrangement in the flavone series. F. WESSELY and F. KALLAB (Monatsh., 1932, 60, 26—31).—Interaction of 1:2:3:5- $\text{C}_6\text{H}_2(\text{OMe})_4$, AlCl_3 , and AcCl gives 2-hydroxy-3:4:6-trimethoxyacetophenone and a dihydroxydimethoxyacetophenone, m. p. 160—162° (cf. A., 1911, i, 211); the former on condensation with Na or K anisate and anisic anhydride gives the expected 5:7:8:4'-tetramethoxyflavone, m. p. 206—207°, identical with the product of methylation of 7-hydroxy-5:8:4'-trimethoxyflavone (cf. A., 1930, 1295). This on demethylation gives scutellareine and not 5:7:8:4'-tetrahydroxyflavone as stated by Hattori (this vol., 64). Condensation of 2:4-dihydroxy-3:6-dimethoxyacetophenone with Na anisate and anisic anhydride gives 5:7-dihydroxy-6:4'-dimethoxyflavone, dimorphic, m. p. 218° (from EtOH), 206° (fused or sublimed) (cf. A., 1930, 1295).

H. A. PIGGOTT.

Dye of yellow dahlias. L. SCHMID and A. SEEBALD (Monatsh., 1932, 60, 32—49).—The yellow dye, $\text{C}_{15}\text{H}_{10}\text{O}_5$, decomp. 324° (darkens >315°; sublimes >165°/vac.), is extracted from the petals with EtOH, separated from apigenin by extraction with Et_2O , and, after treatment with solvents, purified by sublimation. It is not a glucoside, is free from OMe groups, and gives negative results on distillation with Zn dust. Ac_2O at its b. p. gives a substance, m. p. 178°, and in presence of NaOAc a substance, decomp. 345—350°; both are produced in small yields and fail to regenerate the original dye on hydrolysis. A Me_3 ether (I), m. p. 175.5°, is formed with Me_2SO_4 and alkali, but the dye has three OH groups (Zerevitinov). Fusion of the dye with NaOH at 220° in H_2 gives *p*-hydroxybenzoic acid and unidentified phenols (in poor yield); it is therefore most probably a flavone derivative. (I) with 20% KOH in EtOH at 100° gives anisic acid and unidentified phenols.

H. A. PIGGOTT.

Thioxanthhydrol: action of acids. C. FINZI (Gazzetta, 1932, 62, 211—218).—Gaseous HCl converts thioxanthhydrol (I) in dry Et_2O into the red thioxanthonium chloride (J.C.S., 1911, 99, 158), which with NH_3 in dry Et_2O gives dithioxanthenylamine, m. p. 168°, but the main product is a mixture of thioxanthone and thioxanthene. The same mixture is obtained by the action on (I) of AcOH, dil. HCl, or heat. Conc. H_2SO_4 gives only thioxanthone.

E. E. J. MARLER.

Action of Grignard reagents on pyrrolones. General synthesis of 1:2:5-trisubstituted pyrrolones. R. LUKES (Coll. Czech. Chem. Comm., 1932, 4, 181—192).—The action of the Grignard reagent on pyrrolones gives the trisubstituted pyrroles with some γ -diketones and pyrrolines as by-products. MgMeBr and 1:5-dimethylpyrrol-2-one, subsequently treated with NH_2Me , afford 1:2:5-trimethylpyrrole,

and similarly 1-methyl-5-ethylpyrrol-2-one (I) gives 1 : 2-dimethyl-5-ethylpyrrole, b. p. 186—187°/761 mm., but with MgEtBr yields 1-methyl-2 : 5-diethylpyrrole, b. p. 89.0—89.2°/13 mm., 1-methyl-2 : 5 : 5-triethyl- Δ^2 -pyrroline, b. p. 116°/10 mm., and dipropionylethane. (I) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ afford dibenzyl and an inseparable mixture of diketone and pyrrole, converted by NH_2Me into 5-benzyl-1-methyl-2-ethylpyrrole, b. p. 162°/10 mm., obtained also mixed with diketone by the action of MgEtBr on 5-benzyl-1-methylpyrrol-2-one (II). MgMeBr and (II) form 5-benzyl-1 : 2-dimethylpyrrole, m. p. 50—51°, and 1 : 2 : 2-trimethyl-5-benzyl- Δ^2 -pyrroline (isolated as the perchlorate, m. p. 188°). (II) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ yield 2 : 5-dibenzyl-1-methylpyrrole, m. p. 92—93°, and no diketone.

F. R. SHAW.

Basis for the physiological activity of -onium compounds. X. Heterocyclic -onium compounds. R. R. RENSHAW and E. W. SHAND (J. Amer. Chem. Soc., 1932, 54, 1474—1476).—Methyl- β -phenoxyethylpiperidinium bromide, m. p. 112—113° (all m. p. are corr.), and iodide, m. p. 121.2°; methyl- β -phenoxyethylpyrrolidinium iodide, m. p. 86.5—87.5°; methyl-, m. p. 119—121°, and ethyl-, m. p. 97—99°, - β -phenoxyethylpyrrolidinium iodides are prepared from the requisite *N*- β -phenoxyethyl-base and alkyl iodide. β -Phenoxyethylpyridinium and 3-hydroxy- β -phenoxyethylpyridinium bromides, m. p. 80—83° and 126—127°, respectively, and 2- and 3-acetamidopyridine methiodides, m. p. 177° and 220—221°, respectively, are also prepared. These compounds have no pronounced effect on the autonomic nervous system.

C. J. WEST (b).

Cationoid reactivity of aromatic compounds. I. W. BRADLEY and R. ROBINSON (J.C.S., 1932, 1254—1263).—The action of $\text{C}_6\text{H}_{11}\text{N}$, and NaNH , gives (a) with PhNO_2 , *p*-nitrophenylpiperidine, m. p. 103—103.5°; (b) with 1-nitronaphthalene, 1-nitro-4-piperidinonaphthalene, m. p. 73.5—74° [reduced to 1-amino-, m. p. 78—79° (*Bz* derivative, m. p. 213—214°)], and a piperidino- α - β -dinaphthazine, m. p. 257—258°; (c) with *p*-nitrotoluene, 4 : 4'-dinitrodibenzyl; (d) with 8-nitroquinoline, diluted with C_6H_6 , 8-nitroquinolylpiperidine (possibly 4 or 7), m. p. 131.5—132.5°; (e) with 5-chloro-8-nitroquinoline, 8-nitro-5-piperidinoquinoline, m. p. 105.5—106.5°; (f) with 2-chloro-8-nitroquinoline, 8-nitro-2-piperidinoquinoline, m. p. 87°; and (g) with benzanthrone, piperidinobenzanthrone, m. p. 176.5—178°. With liquid NH_3 and NaNH_2 , PhNO_2 forms a base, $\text{C}_{12}\text{H}_8\text{ON}_2$, m. p. 215° (decomp.), and a phenolic base, m. p. 230—231°. General cationoid reactions are discussed.

F. R. SHAW.

Mercuric iodide compound of pyridine. II. V. V. ZAPOLSKI (U.S.S.R. State Inst. Tobacco Inv. Bull., 1931, No. 81, 113—117; cf. A., 1930, 1594).—The following compounds are described: $2\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$, m. p. 103°, and $\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$, m. p. 87°. Unstable products containing higher proportions of HgI_2 , and apparently consisting of mixtures of $\text{C}_5\text{H}_5\text{N}\cdot 2\text{HgI}_2$ and $\text{C}_5\text{H}_5\text{N}\cdot 3\text{HgI}_2$ were also obtained. At room temp., the compounds containing HI (*loc. cit.*) lose all their HI and part of their $\text{C}_5\text{H}_5\text{N}$ when treated with alkali, giving $\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$. The latter has the

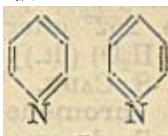
normal mol. wt. in freezing C_6H_6 but $2\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$ dissociates.

T. H. POPE.

Behaviour of the pyridine group on electrochemical oxidation. II. Picoline. M. YOKOYAMA (Bull. Chem. Soc. Japan, 1932, 7, 69—72).—The oxidation of α -picoline, dissolved in dil. H_2SO_4 , at a Pb-PbO₂ anode gave rise to picolinic acid, together with smaller quantities of HCO_2H , AcOH , NH_3 , HNO_3 , picolylalkine, CO, and CO_2 . Using a Pt anode, the same products were obtained in much smaller yields. Picolinic acid under the former conditions gave CO, CO_2 , HCO_2H , NH_3 , CH_2O , NH_2Me , NHMe_2 , and NMe_3 .

D. R. DUNCAN.

New type of isomerism in the pyridine series. I. A. KIRPAL and W. BOHM (Ber., 1932, 65, [B], 680—682).—Oxidation of 2- and 4-aminopyridine with 30% H_2O_2 and fuming H_2SO_4 affords 2- and 4-nitropyridine, m. p. 50°. Oxidation of 2-aminopyridine with KOC yields 2 : 2'-azopyridine, m. p. 87°, in addition to the known isomeride, m. p. 81°, which differ in appearance, m. p., solubility, and lower crit. solution temp., but show identical absorption spectra. The isomerism is accounted for in accordance with (I). Reduction of 2-nitropyridine with Na_3AsO_3 and NaOH gives exclusively the compound m. p. 87°.



[Halogeno-derivatives of] pyridine[carboxylic acids]. M. DOHRN and P. DIEDRICH (Annalen, 1932, 494, 284—302).—3 : 5-Di-iodochelidamic acid (I) [chloride, m. p. 149°; *Me*, m. p. 173°, *Et* (II), m. p. 169°, and benzyl, m. p. 200° (decomp.), esters] and Me_2SO_4 in aq. KOH at 35° give 3 : 5-di-iodo-*N*-methylchelidamic acid (III), m. p. 174° (decomp.) (*Me* ester, m. p. 194—195°), whilst the Ag salt of (II) and MeI in xylene afford the *Et* ester, m. p. 100—101°, of 3 : 5-di-iodo-*O*-methylchelidamic (3 : 5-di-iodo-4-methoxy-pyridine-2 : 6-dicarboxylic) acid, decomp. 176°. 3 : 5-Di-iodo-4-ethoxy-, m. p. 174° (decomp.) (*Me* ester, m. p. 131°), -propoxy-, m. p. 156° (decomp.) (*Me* ester, m. p. 89°), -butoxy-, m. p. 145° (decomp.) (*Me* ester, m. p. 82°), and -benzyloxy-, m. p. 167° (decomp.) (*Me* ester, m. p. 120°), -pyridine-2 : 6-dicarboxylic acids are prepared similarly. (III) heated at 170° gives 3 : 5-di-iodo-*N*-methyl-4-pyridone, m. p. 214—215°, also prepared from 3 : 5-di-iodo-4-pyridone (IV), m. p. 321° (decomp.), and Me_2SO_4 in aq. KOH ; (IV) is obtained from 4-pyridone and ICl in dil. HCl and by hydrolysis of its *N*-Ac derivative, m. p. 245° (decomp.) [from (I) and boiling Ac_2O]. (I) and (IV) with ClSO_3H give the corresponding *N*-sulpho-derivatives, m. p. 210° (decomp.) and 183° (decomp.), respectively, hydrolysed by H_2O to H_2SO_4 and (I) and (IV). 3 : 5-Di-iodo-4-pyridone-*N*-acetic acid, m. p. 240° (decomp.), is prepared from (IV) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$. 4-Pyridone-2-carboxylic acid (V) and I in aq. KOH give the 3 : 5- I_2 -derivative, decomp. 250° [*N*-*Me*, m. p. 159° (decomp.), and *N*- $\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 223° (decomp.), derivatives]; 2-pyridone-6-carboxylic acid similarly affords the 3 : 5- I_2 -derivative, decomp. 272° [*N*-*Me* derivative, m. p. 194° (decomp.)], also formed by iodination of 2-pyridone-5 : 6-dicarboxylic acid. 3 : 5-Dichloro-, m. p. above 300° (*N*-*Me* derivative, m. p. 166°), and 3 : 5-dibromo-, m. p. above 300°

[*N-Me* derivative, m. p. 170° (decomp.)], -4-pyridone-2-carboxylic acids are obtained by halogenation of (V). Et 3:5-dichlorochelidamate, m. p. 96°, and PCl_5 give the Et ester, m. p. 35°, of 3:4:5-trichloropyridine-2:6-dicarboxylic acid, decomp. 150°. 4-Chloro-, m. p. 232° (decomp.) (Et ester, m. p. 111°), and 4-bromo-, m. p. 186° (decomp.) (Et ester, m. p. 98—99°), -3:5-di-iodopyridine-2:6-dicarboxylic acids are prepared from (II) and $\text{PCl}_5 + \text{POCl}_3$ and PBr_5 . The Et ester of 3:4:5-tribromopyridine-2:6-dicarboxylic acid, m. p. 180° (decomp.), has m. p. 67°.

3:4:5-Trichloropyridine, m. p. 76—77°, from 3:5-dichloro-4-pyridone, PCl_5 , and POCl_3 at 125°, with EtOH-KHS gives 3:5-dichloro-4-thiopyridine, m. p. 188°, oxidised by alkaline KMnO_4 to 3:5-dichloropyridine-4-sulphonic acid, m. p. above 300°. 4-Chloro-3:5-dibromo-, m. p. 98°, and 4-chloro-3:5-di-iodo-, m. p. 175°, -pyridines are similarly converted by way of 3:5-dibromo-, m. p. 222°, and 3:5-di-iodo-, m. p. 206° (decomp.), -4-thiopyridines into 3:5-dibromo- (VI) and 3:5-di-iodo- (VII), decomp. 308°, -pyridine-4-sulphonic acids. 3:5-Dibromo- and 3:5-di-iodo-pyridine-2-sulphonic acids, both decomp. above 300°, are prepared similarly. (VI) and aq. NH_3 (d 0.91) at 130° give 3:5-dibromo-4-aminopyridine, m. p. 169—170°; 3:5-dibromo-4-anilino-, m. p. 167°, and 4-o-carboxyanilino-, m. p. 252° (as Et ester, m. p. 105—106°), -pyridines are formed, using NH_2Ph and $\text{o-NH}_2\text{C}_6\text{H}_4\text{CO}_2\text{Et}$, respectively. When an aq. solution of (VI) is heated, 3:5:3':5'-tetrabromo-N-4'-pyridyl-4-pyridone, m. p. above 300°, and SO_2 are formed. 3:5:3':5'-Tetraiodo-N-4'-pyridyl-4-pyridone, decomp. above 300°, is obtained similarly from (VII).

H. BURTON.

Action of phosphorus pentachloride on acetanilide. O. G. BACKEBERG (J.C.S., 1932, 1138—1142).—The action of 1, 2, or 3 mols. of PCl_5 on NHPhAc gives, respectively, diphenylchlorovinylacetamide and a small amount of 4-anilinoquinoline hydrochloride, (I), m. p. 243—245° (decomp.) (lit. 222°), the free base having m. p. 135—136° (lit. about 130°); in the cold, (I) and diphenylacetamide, and on heating, ω -dichloroacetanilide (cf. Michael, A., 1887, 481). An explanation of the reactions is given.

F. R. SHAW.

Quinoline derivatives. XXXIX. H. JOHN (J. pr. Chem., 1932, [ii], 133, 350—354; cf. this vol., 523).—By interaction with the appropriate base 4-bromo-2-phenylquinoline affords 4-ethylamino-, m. p. 82° (EtOH at 160—170°), 4-N'-N'-dimethyl-p-phenylenediamino-, m. p. 177° (amyl alcohol at 100°), and 4-(4'-hydroxy-5'-carboxyanilino)-, m. p. 283° (boiling amyl alcohol), -2-phenylquinoline, and NN'-di-(2-phenylquinolyl-4-ethyl)enediamine, m. p. above 300° (EtOH at 140—150°). Inorg. and complex salts of these bases are described.

R. S. CAHN.

Trypanocidal action of some derivatives of anil and styryl quinolines. II. C. H. BROWNING, COHEN, K. E. COOPER, and R. GULBRANSEN (Roy. Soc., 1932, B, 110, 372—377; cf. A., 1929, 1109; 1931, 763).—2-Methyl-6-acetyl-lactamidoquinoline, m. p. 141—142° (methosulphate, methochloride), from 6-amino-2-methylquinoline and acetyl-lactyl

chloride (A., 1904, i, 966) in CHCl_3 , yields on deacetylation 2-methyl-6-lactamidoquinoline, m. p. 192° (methosulphate). The acetyl-lactamido-derivatives of PhCHO , m. p. 114—115°, and of 2-methylbenzthiazole, m. p. 153—155° (methosulphate), yield on appropriate condensation the 2-(p-aminostyryl)acetyl-lactyl and 2-(p-acetyl-lactamidostyryl) derivatives of aminobenzthiazole methochloride. p-Aminobenzaldehyde or nitrosodimethylaniline with the appropriate 2-methylquinoline at 100° in presence of piperidine yield 2-(p-aminostyryl)-6-acet- and -6-lact-amidoquinoline methochloride and the corresponding 2-(p-dimethylaminoanil) derivatives. Condensation of acetyl-lactamidobenzaldehyde with 6-amino-2-methylquinoline methochloride results in simultaneous hydrolysis of the Ac group, giving 2-(p-lactamidostyryl)-6-aminoquinoline methochloride. Similarly, 6-acetamido-2-methylquinoline methiodide yields 2-(p-lactamidostyryl)-6-acetamidquinoline methiodide. Glyceric acid, treated successively with AcCl and SOCl_2 , gives diacetyl-glyceryl chloride, b. p. 75—85°/15 mm, which with 6-amino-2-methylquinoline and then MeI , gives 6-diacetyl-glycerylamido-2-methylquinoline methiodide, m. p. 217—219° (decomp.). Condensation of the appropriate benzaldehyde in MeOH with piperidine yields the 2-(p-aminostyryl) and 2-(p-acetamidostyryl) derivatives of 6-glycerylamidoquinoline methochloride (methiodide), the two Ac groups of the glyceryl group being hydrolysed. 6-R-Amino-2-methylquinoline (methiodide), where R=octoyl, nonoyl, undecoyl, and lauryl, were prepared by treating the acid chloride with 6-amino-2-methylquinoline in AcOH at 100° for 1 hr. Condensation of these products yielded the methiodides and methochlorides of the corresponding 2-(p-dimethylaminoanil) derivatives. None of the above anil derivatives exhibits marked trypanocidal activity; the styryl derivatives are more active. Acetylation of the NH_2 in the quinoline nucleus does not generally increase the trypanocidal potency, but occasionally tends to produce convulsive effects.

F. O. HOWITT.

Relation between constitution, colour, and reactivity of heterocyclic compounds. Derivatives of homophthalimide. A. MEYER and R. VITTENET (Ann. Chim., 1932, [x], 17, 272—411).—Indene with $\text{K}_2\text{Cr}_2\text{O}_7$ and hot H_2SO_4 gives a 65% yield of homophthalic acid and a little indanone. The prep. of homophthalimide (I) is modified. With the appropriate diazo-compound in aq. Na_2CO_3 at 0° 2:4-dihydroxyquinoline affords 3-benzene-, m. p. 263—264°, -o-chlorobenzene-, decomp. 284—285°, -m- and -p-nitrobenzene-, m. p. 295—296° (decomp.) and 332—333° (decomp.), respectively, -o- and -p-toluene-, m. p. 267—268° (decomp.) and 268—269° (decomp.), respectively, -o- and -m-nitro-p-toluene-, m. p. 282—284° (decomp.) and 312—314° (decomp.), respectively, -m-xylene-, m. p. 264—265°, -1- and -2-naphthalene-, m. p. 267—268° and 264°, respectively, -m-carboxybenzene-, m. p. 308—310° (decomp.), -azo-2:4-dihydroxyquinoline, di-(2:4-dihydroxyquinoline-3-azo)-pp'-diphenyl, decomp. above 320°, -di-o-tolyl, m. p. above 320° (decomp.), and -di-o-anisyl, decomp. above 320°. (I) yields similarly 4-benzene-, -o-chlorobenzene-, m. p. 281—283°, -o- and -p-nitrobenzene-, m. p. 276—277° and 290—291°, respectively, -o-,

-m-, and -p-toluene-, m. p. 266—267°, 228—230°, and 240—242°, respectively, -o- and -m-nitro-p-toluene-, m. p. 270—272° and 305—307°, respectively, m-xylene-, m. p. 260—261°, -1- and -2-naphthalene-, m. p. 283—285° (decomp.) and 262—264°, respectively, -o- and -m-carboxybenzene-, decomp. about 315° and m. p. 305—307° (decomp.), respectively, antipyrine-, m. p. 252—254° (decomp.), -homophthalimide, dihomophthalimide-4-azo-pp'-diphenyl-, ditolyl-, and -dianisyl-, decomp. above 320°, and the Na salts of the following acids: homophthalimide-4-azo-benzene-p-sulphonic, -m-xylene-o-sulphonic, -β-naphthol-6:8-disulphonic, -naphthionic, -naphthol-2:4-disulphonic acid, and -primuline. Substantive dyes are produced by addition of (I) to an alkaline solution of tetrazotised benzidine, tolidine, and dianisidine, already coupled once (in both acid and alkaline solution, when different products result) with H, G, J, naphthionic, and Neville and Winther's acid, and with benzidine already coupled once with salicylic and Schaeffer's acid and 2-p-nitrobenzenazo-H acid. (I), when heated with the appropriate primary amine, gives at least 75% yields of N-phenyl-, m. p. 191° (lit. 188°) [oximino-derivative, m. p. 234—236° (decomp.)], -p-tolyl-, m. p. 173° (oximino-derivative, decomp. 241—243°), -α- and -β-naphthyl-, m. p. 212° and 220°, respectively, -homophthalimide; these substances are fairly readily hydrolysed; the oximino-derivatives are very stable. Oximinohomophthalimide decomposes at 242—243°. By means of MeI or EtI and hot KOH-EtOH were prepared N-phenyl-4:4-dimethylhomophthalimide, m. p. 149—150°, N-phenyl-, m. p. 146°, N-p-tolyl-, m. p. 177—178°, and N-α-naphthyl-, m. p. 224°, -4:4-diethylhomophthalimide; these substances have no physiological action. Coupling at 0° with diazotised NH₂Ph gives 4-benzenazo-N-phenyl-, -p-tolyl- (m. p. 258—259°), -α- and -β-naphthyl- [m. p. 283—284° (decomp.) and 262—263°, respectively] -homophthalimide. By treatment with the appropriate NO-compound in warm EtOH were prepared p-dimethylaminophenyl-, m. p. 243°, p-diethylaminophenyl-, m. p. 196—197°, antipyrinyl-, m. p. 224—225°, p-tolylantipyrinyl-, m. p. 227—228° (decomp.), -iminophthalonimide, C₆H₄ $\left\langle \begin{smallmatrix} \text{C(NR)} \\ \text{CO-NH} \end{smallmatrix} \right\rangle \text{CO}$, antipyrinylphthalon-N-phenyl-, m. p. 210°, -p-tolyl-, m. p. 223—224°, -α- and -β-naphthyl-, m. p. 239—240° (decomp.) after sintering at 235°, and 180—181° (decomp.), respectively, -imide; these substances are red or bluish-violet, are decomposed rapidly by dil. alkali or acid or by prolonged boiling in neutral solvents, and are immediately reduced by boiling aq. Na₂S₂O₄. By means of the appropriate aldehyde and a few drops of piperidine or NH₄Et, in hot EtOH were prepared N-phenyl-, m. p. 193—194°, N-p-tolyl-, m. p. 185—186°, N-α- and -β-naphthyl-, m. p. 225° and 204°, respectively, -4-benzylidenhomophthalimide, N-phenyl-, m. p. 244—245°, N-p-tolyl-, m. p. 245—246°, N-α- and -β-naphthyl-, m. p. 141° and 159—160°, respectively, -4-p-dimethylaminobenzylidenehomophthalimide. The antipyrinyliminohomophthalimides with hot 15% HCl give 85—90% yields of phthalonimide (II), m. p. 228—229° (lit. 224°), phthalon-phenyl- (III) (m. p. 220—221°, sublimes from 215°), -p-tolyl- (IV) (m. p. 238°, sublimes from

220°), -α-naphthyl- (V) [m. p. 239—240° (decomp.) after sintering from 200°], and -β-naphthyl- (VI) [m. p. 268—269° (decomp.)] -imide; these substances dissolve in alkali giving (probably) phthalonic acid and substituted phthalonamides. The phenylhydrazones of these phthalonimides are identical with the products of coupling (I) with diazotised NH₂Ph; the following derivatives of the phthalonimides are described: (II) phenylmethylhydrazone, m. p. 242·5°, and oxime, decomp. 242—244°; (III) phenylmethylhydrazone, m. p. 204°, oxime, m. p. 234—236° (decomp.), and semicarbazone, m. p. 230—231° (decomp.); (IV) phenylmethylhydrazone, m. p. 199°, oxime, decomp. 241—243°, and semicarbazone, decomp. 236—237°; (V) and (VI) phenylmethylhydrazone, m. p. 212° and 199—200°, respectively. o-Phenylenediamine in hot EtOH gives phenazine derivatives with (II) (m. p. 267°), (III) (m. p. 238—239°), and (IV) (m. p. 232—233°).

The colours of the above compounds are discussed and considered to be in accord with analogy. The azo-dyes are considered to have the azo- rather than the hydrazone structure, excepting those from (I) itself, which are considered to be thermolabile mixtures of both forms.

R. S. CAHN.

Determination of constitution of bases obtained from protein. III. C₁₀H₁₄O₂N₂. F. WREDE (Z. physiol. Chem., 1932, 206, 146—154; cf. this vol., 284).—The base C₁₀H₁₄O₂N₂ (I) (A., 1931, 245) when boiled for a short time with dil. HCl loses 1 mol. of AcOH and forms dl-3-acetamido-2-homopiperidone, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH-CO-CH}_2\text{-NHAc}$, m. p. 163°, which on longer boiling (4 hr. with 10% HCl) gives dl-lysine and 1 mol. of AcOH. d-Lysine by Troensegaard's method, or on heating the dihydrochloride with AcOH and AcCl to 100°, yields (I), which is therefore $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N-CO-NaCMeO}$. Ornithine similarly gives a compound, C₉H₁₂O₂N₂ (chloroaurate, darkens at 175°, m. p. 184°), which on hydrolysis yields dl-3-acetamido-2-piperidone and finally ornithine.

J. H. BIRKINSHAW.

Derivatives of 4:5-diketopyrazoline. F. D. CHATTAWAY and A. ADAIR (J.C.S., 1932, 1022—1026; cf. A., 1927, 776).—2:5-Dichlorophenylhydrazine hydrochloride and dihydroxytartaric acid give diketosuccinic acid 2:5-dichlorophenylosazone (I), m. p. 195° (decomp.), converted by Ac₂O into the anhydride, m. p. 233°. Diketosuccinophenylhydrazide 2:5-dichlorophenylosazone, m. p. 286°, is obtained from the corresponding anhydride and NHPh-NH₂. (I) or its anhydride and EtOH-HCl form Et 4:5-diketo-1-(2':5'-dichlorophenyl)pyrazoline-3-carboxylate 4-(2'':5'':dichlorophenylhydrazone) (II), m. p. 213° [acid, m. p. 214° (decomp.)], also obtained by the action of EtOH-HCl on Et diketosuccinate 2:5-dichlorophenylosazone, m. p. 207°, which may be prepared from the corresponding hydrazone, m. p. 101° (formed by the action of Et oxalacetate on diazotised 2:5-dichloroaniline). Diketosuccinic acid 2:4:5-trichlorophenylosazone and its anhydride, m. p. 295—300°, are similarly prepared. Diazotised trichloroaniline and Et oxalacetate afford the hydrazone,

converted into *Et diketosuccinate* 2:4:5-trichlorophenylosazone, m. p. 224°, forming with EtOH-HCl, 4:5-diketo-1-(2':4':5'-trichlorophenyl)pyrazoline-4-(2'':4'':5'':trichlorophenylhydrazone), m. p. 308—310° (decomp.), with elimination of the CO₂H group. *Carbethoxyglyoxal*-2:4:5-trichlorophenylhydrazone, m. p. 118°, prepared from diazotised trichloroaniline and Et sodioformylacetate, gives the *osazone*, m. p. 242°, which cannot be hydrolysed; the corresponding *carboxyglyoxal*-2:4:5-trichlorophenylosazone, m. p. 284°, is obtained from dibromopyruvic acid and 2:4:5-trichlorophenylhydrazine hydrochloride.

F. R. SHAW.

Fission of the glyoxaline ring in a base C₉H₁₁ON₃, prepared from protein. F. WREDE and G. FEUERRIEGEL (Z. physiol. Chem., 1932, 205, 198—200; cf. this vol., 284).—The compound, m. p. 185°, formed by the action of *m*-nitrobenzoyl chloride on the base C₉H₁₁ON₃ (A., 1931, 245) is 4-[βγ-di-(*m*-nitrobenzamido)-Δ^β-propenyl]-2:5-dimethyloxazole. BzCl similarly yields 4-[βγ-di(benzamido)-Δ^β-propenyl]-2:5-dimethyloxazole, m. p. 172° (cf. Windaus, A., 1910, i, 283). The presence of a glyoxaline ring in the base is thus confirmed.

J. H. BIRKINSHAW.

Chloroaurates of histamine and glyoxaline. F. HORN (Z. physiol. Chem., 1932, 207, 111—112).—When ordinary histamine chloroaurate, B₂HAuCl₄, is dissolved in hot H₂O and rapidly cooled, an irregular *chloroaurate*, B₂HAu₂Cl₅, sinters 165—166°, decomp. 179—182°, is formed. This seems to be a characteristic of the glyoxaline ring, since ordinary iminazole chloroaurate, B₂HAuCl₄, on similar treatment gives an irregular *chloroaurate*, B₂AuCl₃, decomp. 190°.

J. H. BIRKINSHAW.

Substituted piperazines. I. 2:5-Dimethyl- and tetramethyl-piperazines. II. Bistetramethylenepyrazine and bistetramethylenepiperazine. M. GODCHOT and M. MOUSSERON (Bull. Soc. chim., 1932, [iv], 51, 349—360, 360—372).—I. Reduction of 2:5-dimethylpyrazine by H₂ in presence of Ni at 150—155° affords the *α*- or *trans*-piperazine, m. p. 118°, and no trace of the *cis*-compound, but in presence of Pt a small amount of *cis*- is also formed, a similar result being obtained when oximinacetone is hydrogenated with Pt as catalyst. Tetramethylpyrazine cannot be reduced in presence of Ni, but with Pt two tetramethylpiperazines, m. p. 38° and 69—70° (*chloroplatinate*; *picrate*, m. p. about 170°) (cf. Kipping, A., 1930, 223), are obtained, the same products resulting from reduction of oximinomethyl Et ketone.

II. The following salts of bistetramethylenepyrazine (I) have been prepared: *hydrochloride* (+H₂O); *hydrobromide* (+3H₂O); *hydriodide* (+3H₂O); *sulphate* (+2H₂O); *oxalate*; *tartrate*, decomp. 190°; *citrate*, decomp. 200°; *benzoate*, decomp. 190°; *salicylate*; *chloroaurate* (+3H₂O); *mercurichloride*; and *chlorostannate*. Reduction of (I) with Na and EtOH gives *bistetramethylenepiperazine*, m. p. 132—133°, also obtained by hydrogenation in presence of Al-Hg and of Ni, but with Pt two stereoisomeric *piperazines*, m. p. 105—106° (*dimitroso*-derivative, m. p. 182°), and m. p. 62—63° (*dimitroso*-derivative, m. p. 107°), result. Reduction does not take place with Et₂O

and Na, Sn and HCl, and SnCl₂. It is suggested that isolation of the three isomerides is connected with the multiplanar configuration of the 6-membered rings.

F. R. SHAW.

Mechanism of the formation of indigotin in the von Baeyer synthesis. L. TANASESCU and A. GEORGESCU (Bull. Soc. chim., 1932, [iv], 51, 234—240).—Condensation of *o*-NO₂-C₆H₄-CHO with PhAc in presence of Na₃PO₄ gives *Ph β-o-nitrophenyl-β-hydroxyethyl ketone*, (II), m. p. 108—109° [Bz derivative (I), m. p. 152°], also obtained together with Ph *o*-nitrostyryl ketone by using alkali in place of Na₃PO₄ (cf. A., 1902, i, 879). (I) and (II) with Zn and AcOH at 100° give 2-phenylquinoline. (II) with Zn and AcOH at 0° followed by treatment with FeCl₃ gives a *substance*, m. p. 121°, probably *o*-nitrobenzoyl-acetophenone. The action of light on Me β-*o*-nitrophenyl-β-hydroxyethyl ketone (improved prep.) in pyridine gives a *substance*, m. p. 170°, and in EtOH a *substance*, m. p. 150° (previous softening). Similar results are obtained with the Bz derivative and with (I) and (II), formation of indigotin being observed in some cases.

A. A. LEVI.

Preparation of 7:7'-dimethyl- and 5:7:5':7'-tetramethyl-8:8'-diquinolyl. H. P. WARD and M. G. WARING (J. Amer. Chem. Soc., 1932, 54, 1697).—2-Iodo-3-nitrotoluene and Cu give 6:6'-dinirodi-*o*-tolyl, which is reduced and then converted (Skraup) into 7:7'-dimethyl-8:8'-diquinolyl, m. p. 213—215°. 5:7:5':7'-Tetramethyl-8:8'-diquinolyl is similarly prepared from 4-iodo-5-nitro-*m*-xylene.

C. J. WEST (b).

Reactions of allantoxanic acid and allantoxidine with alkali hydrogen sulphites. J. BOUGAULT and (Mlle.) PENGUET (Compt. rend., 1932, 194, 979—981).—A mixture of aq. solutions of alkali allantoxanate or allantoxidine and alkali H sulphite affords an additive product. These products are decomposed by mineral acids and by I, affording allantoxanic acid and allantoxidine. The following are described: C₄H₂O₄M.MHSO₃·2H₂O and C₄H₂O₂N₃.MHSO₃·H₂O (M=K or Na).

J. L. D'SILVA.

Preparation of dimethylalloxantin. H. BILTZ and P. NACHTWEY (Ber., 1932, 65, [B], 565—567).—Contrary to Büllmann and Mygind (A., 1930, 1193), the method of Biltz (A., 1913, i, 166) is trustworthy for the prep. of dimethylalloxantin from theobromine. Reduction of methylalloxan by SnCl₂-HCl must be effected slowly at 0°.

H. WREN.

Chlorophyll. XX. Conversion of chlorin *e* trimethyl ester into deoxypyrrhæophorbide. H. FISCHER and H. SIEBEL. **XXI. Conversion of deoxophylloerythrin and phylloerythrin into chloroporphyrin *e*₅; chloroporphyrin *e*₄.** H. FISCHER, J. HECKMAIER, and J. RIEDMAIER (Annalen, 1932, 494, 73—86, 86—100).—XX. Chlorin *e* Me₃ ester (I) boiled with Na₂CO₃ and pyridine for 72 hr. gives 37% of unchanged (I) and 10% of *deoxypyrrhæophorbide* (II), m. p. 230° (*oxime*), which appears to be identical with the product similarly formed (much more readily) from phæophorbide *a*. (II) is a (mono) Me ester, is unaffected by Na₂CO₃ and pyridine, is reduced by HI in AcOH at 55° to phyllo-

erythrin, and is oxidised by O_2 and $MeOH-KOH$ in $EtOH$ -pyridine to a chlorin (reduced by HI to rhodoporphyrin). Chlorin e_7 (III) (Cu salt) with Na_2CO_3 and pyridine gives much unchanged (III) and a porphyrin similar to chloroporphyrin e_5 . (III) and moist Ag_2O in boiling $EtOH$ afford a salt, $C_{35}H_{36}O_6N_4Ag$ (reduced to porphyrins showing the spectra of chloroporphyrins e_5 and e_6), whilst (I) gives a salt, $C_{37}H_{40}O_6N_4Ag$. Conant and Hyde's method (A., 1930, 225) of decarboxylating methylphæophorbide affords pyrroporphyrin and phylloerythrin and not a pyrrophæophorbide. The phase test with all deoxypyrrophæophorbides is negative. The production, by ring closure, of (II) from (I) is strong evidence for the authors' formula for (I).

XXI. Deoxyphylloerythrin (IV) (and phylloerythrin) with 20% oleum at room temp. for 42 hr. give chloroporphyrin e_5 (formylrhodoporphyrin) (V); after 24 hr., (IV) affords small amounts of (IV) and (V) and phylloporphyrinsulphonic acid. (V) crystallises from Et_2O in two forms [data by STEINMETZ]. Condensation products could not be obtained from chloroporphyrin e_4 (Me (Fe and Cu salts) or Me , esters (Fe and Cu salts) with Et_2CO_3 , $CH(OEt)_3$, HCO_2Et , $Et_2C_2O_4$, $CH_2(CO_2Et)_2$, or $CO(CH_2CO_2Et)_2$ (rhodo- and phyllo-porphyrins are generally formed), or with $PhCHO$, $p-NO_2 \cdot C_6H_4 \cdot CHO$, or $p-NO \cdot C_6H_4 \cdot NMe_2$ [the production of (V) is determined spectroscopically]. Chloroporphyrin e_4 is oxidised to (V) by short treatment with cold 20% oleum and by O_2 and $MeOH-KOH$ in $EtOH$ -pyridine; its conversion (by ring closure) into phylloerythrin could not be effected.

H. BURTON.

Derivatives of ætioporphyrin I. H. FISCHER and W. NEUMANN (Annalen, 1932, 494, 225—245).—Ætioporphyrin I (I) [Zn , m. p. (Pregl block) 343° , Ni ($+0.5C_5H_5N$), m. p. (block) 327° , Co , m. p. (block) 337° , Ag , and complex Sn salts; K , derivative, formed from (I) and K in xylene and dry CO_2 , whereby only 1 atom of H is produced] and Br (20 mol.) in boiling $AcOH$ give a compound, $C_{32}H_{36}N_4Br_8$, converted by dissolution in $AcOH-HCO_2H$ and pptn. with H_2O into a substance, $C_{32}H_{35}O_3N_4Br_8$, and by treatment with $COMe_2$ into an O -containing compound containing about 2 Br per mol. (I) in $AcOH-HCl$ treated with H_2O_2 at about 40° gives the dihydrochloride ($+COMe_2$) (II), m. p. (block) 250° , (tube) 290° (not sharp), of tetrachloroætioporphyrin, decomp. 400° (block) without melting. (II) and pyridine at 30° afford dichloroætioporphyrin (III), m. p. 331° (dihydrochloride), whilst at the b. p. (I) is regenerated. Direct chlorination of (I) gives (III); a monochloro-derivative could not be prepared. The conversion of (II) into ætio-xanthoporphyrinogen by PbO_2 indicates that substitution of the β -side-chains does not occur. (I) and an excess of H_2O_2 in $AcOH-HCl$ give a compound, $C_{10}H_{12}O_{10}Cl$. (I) and aq. $NaNO_2$ in conc. H_2SO_4 below 70° give a dinitronitrosoætioporphyrin, unaffected by H_2O_2 in H_2SO_4 at -5° , and apparently also formed (spectrum) from dihydroxyætioporphyrin (Cu salt), aq. $NaNO_2$, and H_2SO_4 .

[By A. TREIBS.] (I) and HNO_3 (d 1.4) give a nitroætioporphyrin, m. p. (block) 287° [Cu salt, m. p. (block) 325°], also formed with HNO_3 (d 1.48) and

carbamide. In another case, using HNO_3 -free HNO_3 (d 1.48), dinitroætioporphyrins, m. p. 301° (Cu salt, m. p. 325°) and 293° , resulted. (I), HNO_3 (d 1.48), and $NaNO_2$ give a trinitroætioporphyrin, m. p. 293° (Cu salt, m. p. 316°), spectroscopically identical with the $(NO_2)_3$ -compound previously described (A., 1928, 1382). (I) and $NaNO_2$ in $AcOH-H_2SO_4$ afford a nitro-compound, $C_{32}H_{36}O_4N_6$, m. p. 275° (Cu salt, m. p. 321°). In the above cases, nitration is probably accompanied by oxidation.

(I) and $Et_2O-MgMeI$ give ætiophyllin, $C_{32}H_{36}N_4Mg(+MeOH)$, m. p. (block) $347-349^\circ$ (crystallographic data given), which with picric acid in Et_2O affords the dipicrate of (I). The catalytic reduction of (I) and ætiohæmin is investigated; (I) absorbs $6H$ with colloidal Pt in $AcOH+10\%$ HCl at 36° , but under similar conditions, ætiohæmin is not reduced. The Ag salts of mesoporphyrin Me , ester and protoporphyrin are described.

H. BURTON.

Ring synthesis of porphyrins with substituted and unsaturated side-chains. III. Synthesis of α -5-carbethoxy-2:4-dimethyl-3-pyrrolysuccinic acid. H. FISCHER, P. HARTMANN, and H. J. RIEDL (Annalen, 1932, 494, 246—263).— Et 2:4-dimethylpyrrole-5-carboxylate and acetylenedicarboxylic acid at 110° give 5-carbethoxy-2:4-dimethyl-3-pyrrolymaleic acid, m. p. 257° (decomp.), reduced by 3% $Na-Hg$ and H_2O at $3-5^\circ$ to the 5- Et ester, m. p. 240° (decomp.), of α -5-carboxy-2:4-dimethyl-3-pyrrolysuccinic acid, m. p. $172-173^\circ$ (decomp.).

Et 2:4-dimethyl-3- $\beta\beta$ -dicyanovinylpyrrole-5-carboxylate (A., 1924, i, 543) and aq. KCN in $EtOH$ give (after acidification) the alkali-sol. Et 2:4-dimethyl-3- $\alpha\beta\beta$ -tricyanoethylpyrrole-5-carboxylate (I), m. p. 163° , hydrolysed by 1% $NaOH$ (about 3 mols.) to 3-formyl-2:4-dimethylpyrrole-5-carboxylic acid (II) and by $EtOH-HCl$ to a 5-carbethoxy-2:4-dimethyl-3-pyrrolysuccinic acid mononitrile, m. p. 185° (Me ester, m. p. 166°). (I) and Br in boiling $MeOH$ afford Et 2:4-dimethyl-3- $\alpha\beta\beta$ -tricyanovinylpyrrole-5-carboxylate, m. p. 194° . $Me(2)$ $Et(5)$ 4-methyl-3- $\beta\beta$ -dicyanovinylpyrrole-2:5-dicarboxylate and KCN similarly give the 3- $\alpha\beta\beta$ -tricyanoethyl derivative, m. p. 167° , hydrolysed by 66% $NaOH$ to 3-formyl-4-methylpyrrole-2:5-dicarboxylic acid, decomp. 260° . Et 2:4-dimethyl-3- β -cyano- β -carbethoxyvinylpyrrole-5-carboxylate and KCN afford Et 2:4-dimethyl-3- $\alpha\beta$ -dicyano- β -carbethoxyethylpyrrole-5-carboxylate, m. p. 108° , hydrolysed by $EtOH-HCl$ to the 3- α (or β)-cyano- β (or α)-carbethoxy- β -carbethoxyethyl derivative, m. p. 183° , by 1% $NaOH$ to (II), and by $EtOH-KOH$ to 2:4-dimethyl-3- β -cyano- β -carbethoxyvinylpyrrole-5-carboxylic acid, m. p. 240° , or its 5- Et ester, m. p. 241° , according to the amount of KOH used. Et 3-formyl-2:4-dimethylpyrrole-5-carboxylate (III) does not react with $CH_2(CO_2H)_2$ in $EtOH-NH_2Ph$; the anil, m. p. 138° , of (III) (converted by KCN into Et 2:4-dimethyl-3-anilinocyanomethylpyrrole-5-carboxylate, m. p. 133°) is produced. 2:4-Dimethyl-3- $\beta\beta$ -dicyanovinylpyrrole and KCN give 2:4-dimethyl-3- $\alpha\beta\beta$ -tricyanoethylpyrrole, m. p. 188° ; 2:4-dimethyl-3- β -cyano- β -carbethoxyvinylpyrrole-5-carboxylic acid similarly affords the 3- $\alpha\beta$ -dicyano- β -carbethoxyethyl derivative, m. p. 180° , hydrolysed (alkali) to (II). 2:4-Dimethyl-3- $\beta\beta$ -

dicyanovinylpyrrole-5-carboxylic acid, m. p. 204°, is obtained from (II) and $\text{CH}_2(\text{CN})_2$ in $\text{EtOH-NH}_2\text{Et}$ at 65°. Et 2:4-dimethyl-3- α -dicarbethoxyethylpyrrole-5-carboxylate and carbamide in EtOH-NaOEt at 105–110° give (5-carbethoxy-2:4-dimethyl-3-pyrrolyl)methylbarbituric acid, m. p. 240°; with EtOH-NH_3 at 130°, a monoamide, m. p. 191°, results.

Carboxyhämatic acid, obtained by oxidation of mesoporphyrin II with CrO_3 in dil. H_2SO_4 , has m. p. 154° (decomp.) (cf. A., 1927, 1088), and is identical with the "natural" acid. H. BURTON.

Constitution of bile pigments. VII. "Ætiomesobilirubin" and the nature of the Gmelin reaction. H. FISCHER and E. ADLER (Z. physiol. Chem., 1932, 206, 187–200; cf. A., 1931, 1420).—5-Bromo-4:3':5'-trimethyl-3:4'-diethylpyrromethene hydrobromide when heated with KOAc in AcOH yields 5-hydroxy-4:3':5'-trimethyl-3:4'-diethylpyrromethene (I). Treatment of (I) with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ equiv. to 2 mols. of Br gives a mixture of hydrobromides from which there were isolated: *product A*, $\text{C}_{31}\text{H}_{36}\text{O}_3\text{N}_4$, dark violet plates, Gmelin reaction negative, but gives blue colour; *product B*, $\text{C}_{31}\text{H}_{38}\text{O}_2\text{N}_4$, emerald-green needles, m. p. 263–265°, Gmelin reaction positive; *product C*, $\text{C}_{31}\text{H}_{38}\text{O}_2\text{N}_4$, bluish-violet prisms, m. p. 253° [trihydrobromide (II), violet plates, Gmelin reaction positive, $\text{Zn}(\text{OAc})_2$ reaction positive]. Reduction of (II) with Zn dust in AcOH gives *ætiomesobilirubin*, $\text{C}_{31}\text{H}_{40}\text{O}_2\text{N}_4$, Gmelin reaction as for mesobilirubin. If the Gmelin reaction with mesobilirubin is interrupted at the blue phase the CHCl_3 solution gives the same $\text{Zn}(\text{OAc})_2$ reaction as (II). Condensation of neobilirubic acid with *p*-nitrobenzaldehyde in 25% aq. HCl affords *p*-nitrobenzylideneneobilirubic acid, m. p. 252° (corr.), with *p*-dimethylaminobenzaldehyde, *p*-dimethylaminobenzylideneneobilirubic acid, m. p. 282°, positive Gmelin reaction. The pigments isolated probably correspond with the various colour phases of the Gmelin reaction.

A bilirubin prep. from liver echinococcus on analysis gave figures corresponding with the C_{33} bilirubin formula. J. H. BIRKINSHAW.

Bile pigments. XI. Ferro- and glauco-bilin. H. FISCHER, H. BAUMGARTNER, and R. HESS (Z. physiol. Chem., 1932, 206, 201–210; cf. A., 1931, 497).—Mesobilirubin with FeCl_3 in hot AcOH gives *ferrobilin* (I), $\text{C}_{33}\text{H}_{38}\text{O}_6\text{N}_4\cdot\text{FeCl}_3\cdot\text{HCl}$, m. p. 260° (decomp.) [Me_2 ester (II), m. p. 255° and m. p. 244°]. With NaOH (I) gives *glauco-bilin* (*dehydromesobilirubin*) (III), sinters at 205–220°, m. p. 304° (decomp.) [Me_2 ester (IV), violet, m. p. 216°, or blue, m. p. 222°]. With aq. Na_2CO_3 , (II) yields (IV). FeCl_3 reconverts (III) into (I), (IV) into (II). In a sealed tube at 215° for 5 min. (III) gives mesobilirubin. Reduction of (III) or (I) with Na-Hg gives mesobilirubinogen. Reduction of (III) with Zn dust in MeOH affords a substance, $\text{C}_{33}\text{H}_{40}\text{O}_6\text{N}_4\cdot 0.5\text{CHCl}_3$ (from CHCl_3), blackening at 230–240°, m. p. 280° (decomp.). Heating mesobilirubin for 6 hr. in conc. H_2SO_4 at 100° or in boiling HCO_2H gives (III). Neoxanthobilirubic acid in boiling HCO_2H also gives (III). A second *ferrobilin* (?), $\text{C}_{37}\text{H}_{46}\text{O}_6\text{N}_4\cdot\text{FeBr}_3\cdot\text{HBr}$, m. p.

228°, is obtained from mesobilirubin by the action of HBr and FeBr_3 in HCO_2H . J. H. BIRKINSHAW.

Uteroverdin, the green pigment of the dog's placenta. R. LEMBERG and J. BARCROFT (Proc. Roy. Soc., 1932, B, 110, 362–372).—*Uteroverdin hydrochloride*, the extraction of which is described, in abs. MeOH-HCl gave the *Me* ester, $\text{C}_{35}\text{H}_{38-42}\text{O}_6\text{N}_4$, m. p. 199° (corr., decomp.), which contains 2OMe and is not identical (optical examination) with the *Me* ester of oocyan (A., 1931, 1066). The two pigments, however, give a similar Gmelin reaction and show similar absorption (acid and neutral solution). Uteroverdin, $\text{C}_{33}\text{H}_{34-38}\text{O}_6\text{N}_4$, is provisionally given a structural formula based on that for bilirubin (*ibid.*, 1420).

F. O. HOWITT.

Constitution of cytochrome. K. ZEILE (Z. physiol. Chem., 1932, 207, 35–47).—Repeated reduction and oxidation of hæmin or amorphous hæmatohæmin in pyridine with $\text{Na}_2\text{S}_2\text{O}_4$ and $\text{K}_3\text{Fe}(\text{CN})_6$, respectively, gives a hæmin insol. in pyridine, sol. in neutral and slightly acid aq. media. It resembles cytochrome, but differs in that the porphyrin obtained by elimination of Fe is insol. in Et_2O . Treatment of the product obtained by the action of HBr-AcOH on natural hæmin with glycine *Me* ester gives a complex, $\text{C}_{40}\text{H}_{48}\text{O}_8\text{N}_6$, m. p. 164° (corr.), similar in spectroscopic properties and solubility to cytochrome C and its corresponding porphyrin. It could not, however, be converted into an Et_2O -sol. porphyrin with HBr-AcOH.

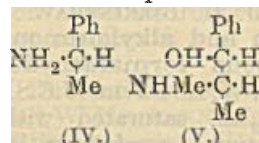
J. H. BIRKINSHAW.

Interaction of ammonium and alkylammonium sulphides with aqueous formaldehyde. (MRS.) C. G. LE FEVRE and R. J. W. LE FEVRE (J.C.S., 1932, 1142–1148).—Aq. NH_2Me , saturated with H_2S , gives with aq. CH_2O a mixture of a substance (I), $\text{C}_2\text{H}_7\text{NS}$, m. p. 138–139°, and methylthioformaldin (II), (I) being converted into (II) by aq. COMe_2 . NH_2Et , H_2S , and CH_2O form a substance isolated as the hydrochloride, $\text{C}_4\text{H}_9\text{NS}\cdot\text{HCl}$, m. p. 100–150°; piperidine gives a compound, $\text{C}_{12}\text{H}_{26}\text{ON}_2\text{S}$, m. p. 56°; $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ yields a compound, m. p. 248–250° (decomp.), whilst the substances formed from NHMe_2 , NH_2Et , and NH_2Ph cannot be characterised and are hydrolysed to thioformaldehyde. The action of aq. CH_2O on $(\text{NH})_2\text{S}$ results in a compound, m. p. 200° $\text{CH}_2\text{S}\cdot\text{CH}_2$ (cf. A., 1931, 573), which is probably $\text{N}\cdot\text{CH}_2\cdot\text{N}$ (III) $\text{CH}_2\text{S}\cdot\text{CH}_2$ and a scheme for its formation is suggested.

F. R. SHAW.

Configuration of ephedrine bases. W. LEITHE (Ber., 1932, 65, [B], 660–666).—The configuration of one of the centres of asymmetry of ephedrine is correlated with that of mandelic acid, whereas that of the other is brought into relationship with phenylalanine. l-(+)-Mandelamide is converted by MgMeI into acetylphenylcarbinol, the oxime of which is reduced to *r*-norephedrine containing a small proportion of (+)-norephedrine [oxalate, m. p. 245° (decomp.), $[\alpha]_D^{25} +22^\circ$ in 2*N*-HCl; hydrochloride, m. p. 165–170°, $[\alpha]_D^{25} +30^\circ$]. *dl*- α -Benzylethylamine, b. p. 204°, prepared by reduction of $\text{CH}_2\text{Ph Me}$ ketoxime with Na in abs. EtOH, is resolved by *d*-tartaric acid

in EtOH giving (+)- α -benzylethylamine (I), d^{20}_D 0.940, $[\alpha]^{20}_D +35.6^\circ$, $[d]^{20}_D +29.9^\circ$, $+37.6^\circ$, $+35.8^\circ$, $+54.3^\circ$, $+36.2^\circ$, $+34.5^\circ$, and $+29.4^\circ$ in Et₂O, C₆H₆, cyclohexane, CCl₄, CHCl₃, EtOH, and MeOH, respectively [*H* tartrate, m. p. 182°, $[\alpha]^{20}_D +20.8^\circ$ in *N*-HCl; Bz derivative, m. p. 159—160°, $[\alpha]^{20}_D -17^\circ$, -14.8° , $+67^\circ$, and $+72^\circ$ in C₆H₆, CHCl₃, EtOH, and MeOH, respectively; hydrochloride (II), m. p. 156°, $[\alpha]^{20}_D +24.8^\circ$ in H₂O]. Treatment of (II) with MeI and KOH affords (+)-deoxyephedrine, thereby establishing the configurative relationship for all natural ephedrine bases. Attempts to correlate (I) with l(-)- α -phenylethylamine (III) by optical comparison of the bases, their Bz derivatives, and hydrochlorides lead to conflicting results, so that it is necessary to eliminate the disturbing influence of the Ph group. Catalytic hydrogenation of (III) affords α -cyclobenzylethylamine, d^{20}_D 0.875, $[\alpha]^{20}_D +3.2^\circ$ (oxalate, m. p. 132°; hydrochloride, m. p. 242°, $[\alpha]^{20}_D -5.0^\circ$ in H₂O; Bz derivative, m. p. 162°, $[\alpha]^{20}_D +16.8^\circ$, $+21.4^\circ$, and $+19.2^\circ$ in CHCl₃, EtOH, and MeOH, respectively). (I) is hydrogenated to α -cyclohexylmethylethylamine, $[\alpha]^{20}_D +8.4^\circ$ (oxalate, m. p. 180° (decomp.); hydrochloride, m. p. 186°, $[\alpha]^{20}_D -1.8^\circ$ in H₂O; Bz derivative, m. p. 108°, $[\alpha]^{20}_D +20.3^\circ$, $+31.8^\circ$, $+39.6^\circ$, and $+40.7^\circ$ in C₆H₆, CHCl₃, MeOH, and EtOH, respectively). (+)-Benzylethylamine is therefore configuratively related to l(-)-phenylethylamine. The same configuration is assigned to its *N*-Me derivative, and since all natural *Ephedra* alkaloids can be referred to this compound the asymmetry centre (IV) occurs



l-phenylalanine which has the *l*-configuration proper to natural NH₂-acids.

H. WREN.

Methylisopelletierine and α -2-*N*-methylpiperidylpropan- β -one. K. HESS and O. LITTMANN (Annalen, 1932, 494, 7—17).—Re-investigation (cf. A., 1919, i, 345; 1925, i, 425) of the synthesis of α -2-*N*-methylpiperidylpropan- β -one (I) (revised data for various derivatives given) confirms Meisenheimer and Mahler's statement (A., 1928, 905) that methylisopelletierine (II) is (I). (II) is only partly demethylated by Diels and Fischer's method (A., 1914, i, 989); the resulting isopelletierine (III) is separable from unchanged (II) by treatment of the mixture with sufficient 2*N*-HCl to neutralise (III) and extraction [of (II)] with Et₂O. Codeine, but not atropine or ψ -pelletierine, can be completely demethylated by Diels and Fischer's method. Edlbacher's method (A., 1918, ii, 336) for the determination of NMe gives vals. of 0.6—0.8% Me with NMe-free substances. Revised data are given for α -2-piperidylpropan- β -one [i.e., (III)] and its derivatives.

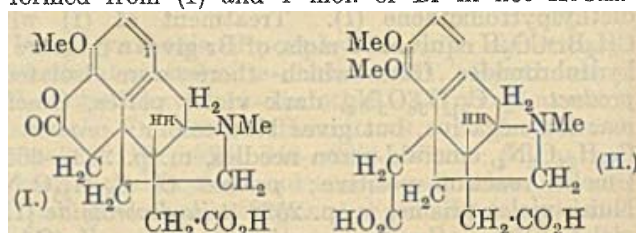
H. BURTON.

Synthesis and pharmacological action of a homoisopapaverine (and laudanoline). I. Synthesis of 6 : 7-dimethoxy-2-methylquinoline. F. KONEK [with J. DOKTAY] (Math. Nat. Anz. Ungar. Akad. Wiss., 1930, 47, 779—786; Chem. Zentr., 1931, ii, 3485).—6 : 7-Dimethoxy-2-methylquinoline, m. p.

103° [hydrochloride, decomp. 220—225°; chloroplatinate, $+2H_2O$, m. p. 238—240°; picrate, m. p. 218° (decomp.)], was obtained from veratrole by way of nitroveratrole and veratrylamine.

A. A. ELDRIDGE.

Sinomenine. XXX. Sinomenic acid. K. GOTO, K. TAKUBO, and S. MITSUI (Annalen, 1932, 494, 1—6).—Sinomeninone and 30% H₂O₂ in AcOH at 100° give sinomenic acid (I), m. p. 291° (decomp.), $[\alpha]^{20}_D +88.9^\circ$ (all rotations are in H₂O) [methiodide, m. p. 239° (softens at 160°), $[\alpha]^{20}_D +61.8^\circ$; hydrochloride, m. p. 278—280° (decomp.), $[\alpha]^{20}_D +81^\circ$], which is recovered unchanged when its solution in aq. NH₃ is evaporated. 1-Bromosinomeninone is similarly oxidised to 1-bromosinomenic acid, m. p. 251°, $[\alpha]^{20}_D +70.25^\circ$ [methiodide, m. p. 276° (decomp.), $[\alpha]^{20}_D +49.7^\circ$; hydrobromide, m. p. 306° (decomp.), $[\alpha]^{20}_D +54.82^\circ$; hydrochloride, m. p. 292° (decomp.)], also formed from (I) and 1 mol. of Br in hot AcOH.



Methylsinomenic acid (II), m. p. 295° (decomp.), $[\alpha]^{20}_D +12.38^\circ$ (Ba salt, decomp. above 300°), and 1-bromosinomenic acid (III), m. p. 261—262° (decomp.) $[\alpha]^{20}_D +34.6^\circ$ (Ba salt, decomp. above 300°; methiodide, decomp. 249°, $[\alpha]^{20}_D +45.77^\circ$), are obtained by oxidation of methylsinomeninone and the

diketone from 1-bromosinomenine (A., 1930, 1049), respectively. The absorption curves of (I), (II), and (III) are similar to that of sinomeninone, which is almost identical with that of sinomenine (IV). (IV) and Br (2 mols.) in EtOH give a perbromide, decomposed by cold Na₂SO₃ to 1-bromosinomenine (70% yield), supporting the view (A., 1931, 1171) that bromination at C₅ is by decomp. of the perbromide.

H. BURTON.

Identification of corynanthine. J. SIVADJIAN (J. Pharm. Chim., 1932, [viii], 15, 352—353).—Corynanthine could not be distinguished from yohimbine by a colour reaction. With either Frode's, Mandelin's, or Meillere's reagent they give identical colours and also in the (new) reactions with vanillin or piperonal and H₂SO₄ (violet) or with epichlorohydrin and chloranil (brown changing to cherry-red on adding HNO₃).

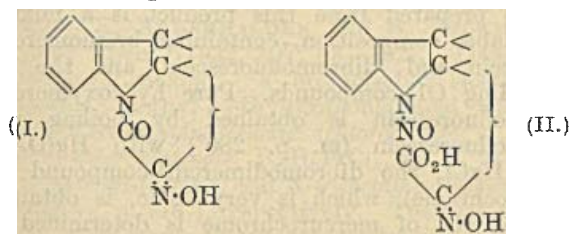
E. H. SHARPLES.

Strychnine and brucine. XIX. Reduction of strychnine methosulphate by means of sodium amalgam in the presence of carbon dioxide. (The late) W. H. PERKIN, jun., R. ROBINSON, and J. C. SMITH (J.C.S., 1932, 1239—1254).—Reduction of strychnine methosulphate by Na—Hg in presence of CO₂ gives tetrahydromethylstrychnine (amorphous) (I), C₂₂H₂₈O₂N₂, cryst. by-products of m. p. 200°,

m. p. 277°, m. p. 267°, and strychnine. Electrolytic reduction of (I) yields *tetrahydromethylstrychnidine*, b. p. 240–243°/1 mm., and distillation of (I) gives a mixture ($C_{22}H_{26}ON_2$; b. p. 245°/0.3 mm.) of *anhydro*-, m. p. 200–201° (reduced to *di*-, m. p. 160°, and *tetrahydro*-derivatives, m. p. 163–164°), and *demethyleneanhydro-tetrahydromethylstrychnine*, m. p. 172–173° [*methiodide*, m. p. 250–252° (efferv.)]; reduced catalytically to *dihydro*-derivative, m. p. 160–162° (*methiodide*, m. p. about 170°), a further hydrogenation compound being unobtainable pure; and reduced at a Pb cathode to *dihydrodemethylenetetrahydromethylstrychnidine*, m. p. 98–100°, a hydrate, $C_{22}H_{28}O_2N_2$, m. p. 182–184° [*methiodide*, m. p. 250° (decomp.)], a base, $C_{22}H_{28}ON_2$, m. p. 217–218° [*methiodide*, m. p. 250° (efferv.)], and a syrup which forms a *methiodide*, m. p. 265–270° (decomp.), a *methochloride*, m. p. 255° (efferv.), and a *methine*, m. p. 70–75°. The constitution of these compounds is discussed.

F. R. SHAW.

New reactions of Strychnos alkaloids. XI. H. WIELAND and W. GÜMLICH (Annalen, 1932, 494, 191–200).—Strychnine and brucine with Et nitrite and EtOH–NaOEt at 40–80° give *oximinostrychnine* (as I), darkens above 200°, not melted at 300°, and *oximinobrucine*, respectively. Dihydrostrychnine similarly affords *oximinodihydrostrychnic acid nitrosoamine* (as II), m. p. about 190° (decomp.); *oximinodihydrobrucic acid nitrosoamine* decomposes at 170° (darkens at 120°). In the prep. of dihydrobrucine hydrate, decomp. 255° (cf. A., 1930, 1455), from



dihydrobrucine (III) and EtOH–KOH, an *isomeride*, m. p. 218°, $[\alpha]_D^{25} -20.1^\circ$ in $CHCl_3$ [*methiodide*, m. p. 230° (decomp.)], of (III) is also produced. Brucine and (III) form additive (1:1) compounds, decomp. 218–220° and 240–242°, respectively, with $CNBr$ in $CHCl_3$ at 40–50°, which when heated with Zn dust and AcOH regenerate the alkaloids. Tetrahydrostrychnine (IV) and $BzCl$ in pyridine give the *benzoate*, m. p. 172°, of the Bz_2 derivative of (IV), hydrolysed by EtOH–NaOH to the *N-Bz* derivative, m. p. 235°, of (IV). Brucine and maleic anhydride in AcOEt give an additive (1:2) compound, decomp. 240°, decomposed by H_2O into its components; (III) affords a similar compound (+1.5AcOEt), m. p. 125° (decomp.).

H. BURTON.

Aconitum alkaloids. IX. Molecular formula of oxonitine; oxonine. R. MAJIMA, H. SUGINOME, and H. SHIMANUKI (Ber., 1932, 65, [B], 595–598).—Analyses and determinations of Bz, OMe, and NMe in oxonitine (I), pyroxonitine, and pyroxonine lead to the abandonment of the formula $C_{25}H_{33}ON$ for (I); the results agree more closely with those of Henry (A., 1931, 636) than with those recorded by Späth (*ibid.*, 243). Treatment of (I) with KOH–EtOH

affords *oxonine*, $C_{22}H_{35}O_{10}N_4H_2O$, m. p. (indef.) 175° after softening at 160°.

H. WREN.

Aconitum alkaloids. X. New Aconitum alkaloid. R. MAJIMA and S. MORIO (Ber., 1932, 65, [B], 599–602; cf. this vol., 178).—Lucidusculine, $C_{22}H_{37}O_4N$ (+1.5 H_2O), decomp. 248–250°, $[\alpha]_D^{25} -95.5^\circ$ in $CHCl_3$, yields a *hydrobromide*, decomp. 248–250°, $[\alpha]_D^{25} -62.7^\circ$ in H_2O ; *hydrochloride* (+3.5 H_2O), m. p. (hydrated) 98–115°, (anhyd.) decomp. 245–265°; *perchlorate*, decomp. 260–265°, $[\alpha]_D^{25} -70.3^\circ$ in EtOH; *picrate*, m. p. 173–176°; *chloroplatinate*, decomp. 225° after darkening at 217°; and *methiodide*, m. p. 197° after swelling at 187–193°, $[\alpha]_D^{25} -65.0^\circ$ in EtOH. Luciculine, m. p. 115–117°, $[\alpha]_D^{25} -11.4^\circ$ in EtOH, yields a *hydrochloride* (+1.5 H_2O), decomp. 198–203°, $[\alpha]_D^{25} -9.4^\circ$ in H_2O . *Acetyl-lucidusculine* (*diacetyl-luciculine*) has m. p. 155–157°, $[\alpha]_D^{25} -76.0^\circ$ in $CHCl_3$ [*hydrochloride* (+3 H_2O), m. p. 113–117°, anhyd. decomp. 139–144°, $[\alpha]_D^{25} -50.4^\circ$ in H_2O].

H. WREN.

Alkaloids of ergot. A. SOLTYS (Ber., 1932, 65, [B], 553–560).—Ergotinine and ergotamine give analytical data in harmony with the respective formulæ $C_{35}H_{39}O_5N_5$ and $C_{33}H_{35}O_5N_5$ after being dried in air in the dark. Ergotamine, dried in the air, has the composition $C_{33}H_{35}O_5N_5 \cdot 3H_2O$; it loses about 2 H_2O over P_2O_5 at 16 mm. and room temp. and becomes anhyd. over P_2O_5 at 100°/16 mm. The difficulties of analysis are due to unusual hygroscopicity. Ergotoxine does not appear to be a hydrate of ergotinine, but the composition is left undecided. The four alkaloids are sol. in acid and alkali hydroxide and are pptd. by CO_2 from the latter solutions. They do not contain OMe, but 2 NMe groups appear present. With boiling alkali hydroxides they evolve 1 NH_3 , yielding acids the salts of which are not decomposed by CO_2 . The same acid appears to be derived from each alkaloid, but final judgment is hindered by the non-cryst. nature of the acids and their salts. Since the bases evolve β -methylbutyramide when heated, the presence of the group $CHMe_2 \cdot C \cdot CO \cdot NH_2$ is suggested.

Oxidation with $KMnO_4$ and HNO_3 affords BzOH and $p\text{-NO}_2 \cdot C_6H_4 \cdot CO_2H$, respectively. Double linkings do not appear present. 4 active H atoms are detected, one of which is assigned to OH and two to $\cdot CO \cdot NH_2$.

H. WREN.

Precipitating agents for alkaloids. C. C. FULTON (Amer. J. Pharm., 1932, 104, 244–271).—A review and classification. Suitable concns. are given, and some new reagents suggested.

A. A. LEVI.

Organic germanium derivatives. V. Reaction of sodium triphenylgermanide with halogenated methanes in liquid ammonia. C. A. KRAUS and H. S. NUTTING (J. Amer. Chem. Soc., 1932, 54, 1622–1630; cf. A., 1930, 1602).— $NaGePh_3$ and RX in liquid NH_3 give NaX and $GePh_3R$. Thus, MeI gives $GePh_3Me$, m. p. 70.5–71°, which does not react with Na in liquid NH_3 ; EtBr gives $GePh_3Et$, m. p. 78–78.5°, which reacts readily with Br, apparently with the substitution of a Ph group. CH_2Cl_2 gives $GePh_3Me$, $(GePh_3)_2O$, and *ditriphenylgermanylmethane*, $CH_2(GePh_3)_2$, m. p. 134.5°. The last-named compound is the normal reaction product; the other

compounds are formed thus: $2\text{GePh}_3 + \text{CH}_2\text{Cl}_2 + \text{NH}_3 \rightarrow 2\text{Cl}^- + \text{GePh}_3\text{Me} + \text{GePh}_3\text{NH}_2$ (hydrolysed to the oxide). The same compounds are formed with CHCl_3 as with CH_2Cl_2 but in different proportions. $\text{CH}_2(\text{GePh}_3)_2$ and $(\text{GePh}_3)_2\text{O}$ form solid solutions, separable only with difficulty. The reaction with CCl_4 is similar to but more complex than that with CHCl_3 and CH_2Cl_2 ; free GePh_3 is not formed, but $(\text{GePh}_3)_2\text{O}$ and unidentified compounds are produced. NH_3 probably takes part in the reaction.

C. J. WEST (b).

Arsenical derivatives of thiophen. V. C. FINZI (Gazzetta, 1932, 62, 244—252).—*Thiophen-2-arsenious oxide*, m. p. 115—116°, 5-nitro-, m. p. 171—172° (decomp.), 5-bromo-, m. p. 191°, 5-bromo-4-nitro-, m. p. 245° (decomp.), 5-iodo-, m. p. 233—234°, and 5-iodo-4-nitro-, m. p. 157°, *thiophen-2-arsenious oxides*, di-2:2'-dithienylarsenious oxide, m. p. 73°, and di-5:5'-dinitro-2:2'-dithienylarsenious oxide, m. p. 222°, are prepared by reduction of the corresponding arsenic acids (A., 1926, 186) with SO_2 and a trace of HI . In the prep. of iodothiophen-arsinic acid (*loc. cit.*) di-5-iodo-2-thienylarsinic acid, m. p. 184° with formation of an anhydride, is also obtained. Nitration of 5-bromothiophen-2-arsinic acid gives 5-bromo-4-nitrothiophen-2-arsinic acid, m. p. 288—290°. 5-Bromothiophen-2-arsenious oxide with MeI and KOH in MeOH gives methyl-5-bromothiophen-2-arsinic acid [2-(5-bromothiophenyl)methylarsinic acid], m. p. 192°. 5-Nitrothiophen-2-arsinic acid on reduction with H_3PO_3 followed by heating with excess of S gives 5-nitrothiophen-2-arsenious sesquisulphide, $(\text{NO}_2 \cdot \text{C}_4\text{H}_4\text{S} \cdot \text{As})_2\text{S}_3$, m. p. 60—80°.

E. E. J. MARLER.

Nitroso-derivatives of the phenarsazine series. Action of nitrosyl chloride on derivatives of trivalent arsenic. G. A. RAZUVAYEV and D. A. GODINA [with T. I. JEMELJANOVA] (Ber., 1932, 65, [B], 666—672).—The action of HNO on 10-chloro-5:10-dihydrophenarsazine or phenarsazinic acid does not yield the expected NO-derivative. Addition of HCl to a solution of NaNO_2 and 10-methyl-5:10-dihydrophenarsazine in EtOH affords the 5-nitroso-derivative, m. p. (indef.) 108—110° without evolution of NO . If NaNO_2 is added to the phenarsazine and HCl , NO is evolved and the formation of the NO-compound is accompanied by that of 10:10-dihydroxy-10-methylphenarsazine (isolated as the oxide), the production of which is not due to direct oxidation by HNO_2 , since 5-acetyl-10-methyl-5:10-dihydrophenarsazine is unaffected by HNO_2 , although readily oxidised by I and H_2O to 10:10-dihydroxy-5-acetyl-10-methyl-5:10-dihydrophenarsazine, m. p. (indef.) 225—240°. 5-Nitroso-10-ethyl-5:10-dihydrophenarsazine is a viscous liquid; the 10-Ph derivative has m. p. 143—145° (decomp.). In C_6H_6 or EtOH the NO-compounds are rapidly transformed into red, resinous masses owing to partial conversion into NO_2 -compounds and partial oxidation. In presence of HCl the NO_2 -compound is not produced; As becomes quinquivalent and NO is evolved. The NOCl initially formed appears to be added to the As atom with production of 10-chloro-10-nitroso-10-methyl-5:10-dihydrophenarsazine, rapidly hydrolysed to 10-chloro-10-hydroxy-10-methyl-5:10-di-

hydrophenarsazine, m. p. 204°, and thence to the corresponding $(\text{OH})_2$ -compound; the 10-Cl-compound is also derived from NOCl and 10-methyl-9:10-dihydrophenarsazine. AsPh_3 and NOCl in C_6H_6 afford $\text{AsPh}_3\text{Cl} \cdot \text{OH}$. AsPh_3Cl and NOCl in C_6H_6 yield the substance $(\text{Ph} \cdot \text{AsCl}_2)_2\text{O}$, m. p. 117°, hydrolysed to diphenylarsinic acid. H. WREN.

Mercuration in the aromatic series. VII. Mercury derivatives of *m*-cresol. E. MAMELI and F. PIAGGESI (Gazzetta, 1932, 62, 158—174; cf. A., 1927, 268).—*m*-Cresol with $\text{Hg}(\text{OAc})_2$ under various conditions gives a mixture containing *m*-cresol-4-mercuriacetate (I), m. p. 130°, *m*-cresol-6-mercuriacetate (II), m. p. 155°, *m*-cresol-4:6-dimercuriacetate (III), m. p. 195°, and *m*-cresol-2:6-dimercuriacetate (IV), decomp. at 232—235°. Further mercuration of (I) or (II) gives (III). With benzene-diazonium chloride (II) and (III) give 4:6-diphenylazo-*m*-cresol and a compound, m. p. above 210°; (II) also gives 6-benzeneazo-*m*-cresol. By treatment of (I), (II), and (III) with NaCl , NaNO_3 , or Na_2SO_4 *m*-cresol-4-mercuri-chloride, m. p. 209°, -nitrate, and -sulphate, -6-mercuri-chloride, m. p. 212°, -nitrate, and -sulphate, and -4:6-dimercuri-chloride, m. p. 215°, -nitrate, and -sulphate are obtained, respectively.

E. E. J. MARLER.

Toxicity and chemical constitution of mercurochrome. M. A. PHILLIPS (Quart. J. Pharm., 1932, 5, 1—5).—Bromination of fluorescein in glacial AcOH solution gives dibromofluorescein hydrobromide and unchanged fluorescein. Hence mercurochrome prepared from this product is a mixture of variable composition, containing bromomercurofluorescein and -dibromofluorescein, and the corresponding OH-compounds. Pure hydroxymercurodibromofluorescein is obtained by boiling pure dibromofluorescein (m. p. 280°) with $\text{Hg}(\text{OAc})_2$. Using HgCl_2 the dibromodimercuri-compound (dimercurochrome), which is very toxic, is obtained. The toxicity of mercurochrome is determined by the amount of free Hg present. J. B. BATEMAN.

Mercuration of pyridine. N. P. McCLELAND and R. H. WILSON (J.C.S., 1932, 1263—1265).—Mercuration of $\text{C}_5\text{H}_5\text{N}$ and pptn. with brine (cf. Sachs and Eberhartinger, A., 1924, i, 110) affords a mixture containing 3-chloromercurypyridine, m. p. 278—280° (decomp.) and (after treatment with KI) pyridine tri-iodomercuriate, m. p. 152—154° (also prepared from $\text{C}_5\text{H}_5\text{N}$, HI , and HgI_2). F. R. SHAW.

Derivatives of thiodiphenylamine. C. FINZI (Gazzetta, 1932, 62, 175—189; cf. A., 1927, 685).—Alkylation of thiodiphenylamine (I) occurs normally only with MeI and EtI . When heated under pressure with Bu^tI (I) gives *N*-($\alpha\gamma\gamma$ -tetramethylbutyl)thiodiphenylamine, $\text{S} \langle \text{C}_6\text{H}_4 \rangle \text{N} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CMe}_3$, m. p. 209°; with higher alkyl iodides there is no reaction. With PhI , Cu powder, and K_2CO_3 in PhNO_2 (I) gives *N*-phenylthiodiphenylamine (II), m. p. 89—90°, oxidised by KMnO_4 to the corresponding sulphone, m. p. 204—205°; with CH_3PhCl it gives *N*-benzylthiodiphenylamine (III), m. p. 130° (sulphone, m. p. 215—216°). *N*-Methyl- and *N*-ethyl-thiodiphenylamines with $\text{Hg}(\text{OAc})_2$ in boiling EtOH give *N*-methylthiodiphenylamine-

mercuriacetate (IV), m. p. 165°, and -2:7-dimercuriacetate (V), decomp. without melting at 290—300°, oxidised by HNO_3 to 2:7-dinitro-*N*-methylthiodiphenylamine sulphoxide (A., 1919, i, 222), and *N*-ethylthiodiphenylamine-2-mercuriacetate (VI), m. p. 153°, and -2:7-dimercuriacetate (VII), decomp. at 300°. With NaCl (IV) gives *N*-methylthiodiphenylamine-2-mercurichloride (VIII), m. p. 234—235°, giving with (I) 2-iodo-*N*-methylthiodiphenylamine, m. p. 107°, and (V) gives *N*-methylthiodiphenylamine-2:7-dimercurichloride (IX), decomp. at 280—290°, giving with Br 2:7-dibromo-*N*-methylthiodiphenylamine, m. p. 198°. With AsCl_3 (VIII) gives *N*-methylthiodiphenylamine-2-arsenious chloride, oxidised by alkaline H_2O_2 to the corresponding arsenic acid, m. p. 283° (decomp.), and (IX) gives *N*-methylthiodiphenylamine-2:7-diarsenious chloride, m. p. 195° (acid, decomp. at 230—240°). (II) and (III) do not give mercuriacetates with $\text{Hg}(\text{OAc})_2$ but are oxidised.

E. E. J. MARLER.

Selenobenzaldehyde. L. SZPERL and W. WIOROGÓRSKI (Rocz. Chem., 1932, 12, 270—275).—Vanino and Schinner's (A., 1915, i, 117) α - and γ -selenobenzaldehydes, m. p. 83—84° and 166°, could not be obtained by their procedure. A dimeride of PhCHSe , m. p. 92—93°, and a trimeride, m. p. 189—193°, are identified; the latter, which is the chief product of interaction of H_2Se with PhCHO , differs from Vanino's β -selenaldehyde in its lower m. p.

R. TRUSZKOWSKI.

Identification of *l*(+)-isoleucine as component of brain proteins. Separation of leucine mixtures. E. ABDERHALDEN and S. BECKMANN (Z. physiol. Chem., 1932, 207, 93—102).—Treatment of α -bromo-*n*-hexoic, α -bromoisobutylacetic, and α -bromo- β -methyl- β -ethylpropionic acid with NMe_3 gives *N*-trimethylnorleucine (chloraurate, m. p. 137—138°; chloroplatinate, $\text{B}_3\text{H}_2\text{PtCl}_6$, m. p. 215—216°), *N*-trimethylleucine, and *N*-trimethylisoleucine (chloraurate, m. p. 178°), respectively. The rate of elimination of Br serves to separate norleucine from leucine and isoleucine. The chloraurates aid identification. The proteins of brain tissue contain *l*(+)-isoleucine.

J. H. BIRKINSHAW.

Optical activity and coagulation of the degradation products of caseinogen. I. B. JIRGENSONS (Biochem. Z., 1932, 246, 219—228).—The optical activity and coagulation of the peptone-like products obtained by degrading caseinogen in glycerol are investigated. From the rotation curve it is concluded that these degradation products have the same configuration as the natural NH_2 -acids. Aq. solutions of these products are not coagulated by EtOH , but if the p_{H} is somewhat increased, coagulation occurs with various alcohols and COMe_2 . The degree of pptn. is not proportional to the amount of alcohol, but shows a max. and a min. which differ for the different alcohols.

P. W. CLUTTERBUCK.

Combination curves, hydrogen-ion regulating power, and equivalents of ovalbumin. E. B. R. PRIDEAUX and D. E. WOODS (Proc. Roy. Soc., 1932, B, 110, 353—361).—1.0 and 0.1% aq. solutions of cryst., heat-coagulated, EtOH -denatured, and commercial dried ovalbumin were titrated electrometric-

ally against 0.1*N*- HCl and - NaOH . The solutions of cryst. ovalbumin were dialysed against H_2O and finally against 0.01*N*- AcOH until the NH_3 content was 6×10^{-6} equiv. per litre. The lack of inflexion on the acid side of the isoelectric point excludes a definition of the acid saturation capacity, the basic groups being progressively opened as the p_{H} diminishes. Below p_{H} 3.0 is a slight downward turn peculiar to denatured albumin. Titration on the alkaline side appears to be accompanied by formation of metaprotein: there is no inflexion, and hence ovalbumin, unlike gelatin (A., 1931, 683), shows no sign of saturation with alkali, whilst the buffering power is less const. Ovalbumin, as an acid, has p_{K_a} 3.5 and equiv. 1130 for p_{H} 2.6—4.4; as an alkali, it has equiv. 1390 for p_{H} 10.3—11.3 or 10.0—11.6.

F. O. HOWITT.

Metal tube in micro- and semimicro-combustion analysis. S. AVERY, J. BRACKENBURY, and W. D. MACLAY (Ind. Eng. Chem. [Anal.], 1932, 4, 238—239).—The use of Cu combustion tubes with H_2O -jacketed ends is recommended for the micro-determination of C, H, and N. A tube of Ag is recommended for the combustion of compounds containing halogens. A boat-inserter is described.

E. S. HEDGES.

Acidimetric determination of chlorine and bromine in organic substances. II. Semimicro-determination. F. VIEBOCK (Ber., 1932, 65, [B], 586—588).—The method (this vol., 529) can be applied without modification to semimicro-practice except that the larger quantities of CO_2 evolved render it desirable to boil the H_2O_2 solution towards the end of the titration.

H. WREN.

Determination of sulphur in organic substances by combustion in an air-stream. F. SEELIG (Angew. Chem., 1932, 45, 281).—A claim for priority (cf. this vol., 291).

E. S. HEDGES.

[Determination of sulphur in organic substances by combustion in an air-stream.] J. SIELISCH and R. SANDKE (Angew. Chem., 1932, 45, 281—282).—A reply to Seelig (cf. preceding abstract).

E. S. HEDGES.

Volumetric sulphate determination. Determination of sulphur in organic compounds. A. CHALMERS and G. W. RIGBY (Ind. Eng. Chem. [Anal.], 1932, 4, 162—164).—The org. substance is oxidised in a Parr S bomb and the $\text{SO}_4^{''}$ produced is treated with excess of standard BaCl_2 , the excess being determined by aq. Na_2CO_3 and phenolphthalein. Metals which form insol. carbonates must be removed previously, and $\text{PO}_4^{'''}$, $\text{AsO}_4^{'''}$, BO_2' , and $\text{CrO}_4^{''}$ interfere.

E. S. HEDGES.

Microanalytical identification of organic substances. V. STANEK and T. NEMES (Z. Zuckerind. Czechoslov., 1932, 56, 390—395).—A micro-method is described in which org. matter is oxidised with iodate in the presence of H_2SO_4 , the amount of O thus utilised by many substances agreeing closely with that calc.

J. P. OGILVIE.

Determination of hydrocarbons in air. E. POZNER and R. A. MELIKOVA (J. Appl. Chem., Russia, 1931, 4, 932—939).—Unsaturated hydrocarbons are removed with $\text{Pb}(\text{OAc})_2$, aromatic hydrocarbons with

$\text{H}_2\text{SO}_4 + \text{Ag}$, and naphthenes and paraffins with activated C by passing the air through these reagents in series. The method is applicable to the analysis of low-boiling hydrocarbon mixtures.

CHEMICAL ABSTRACTS.

Colorimetric determination of the vapours of amyl alcohol and amyl acetate in air. I. M. KORENMAN (J. Appl. Chem., Russia, 1931, 4, 940—949).—The vapours are absorbed in EtOH and the filtered solution is treated with furfuraldehyde and H_2SO_4 , the coloration being compared with that of a standard.

CHEMICAL ABSTRACTS.

Determination of acetaldehyde in presence of ethyl alcohol. J. D. PELGROMS (Natuurwetensch. Tijds., 1932, 14, 44—48).—The MeCHO is converted into the HSO_3 compound, the EtOH is determined by the Northrup method, and the MeCHO is determined by decomp. of the HSO_3 compound and titration of the liberated KHSO_3 with I solution. In a method recommended for rapid determinations, HgO is added to one half of the aq. solution, the EtOH is removed by distillation and determined by the $\text{K}_2\text{Cr}_2\text{O}_7$ method; in the other half the total MeCHO + EtOH is determined with $\text{K}_2\text{Cr}_2\text{O}_7$ and the MeCHO is calc. by difference. Practical details are indicated.

H. F. GILLBE.

Refractometric determination of organic acids. (MNE.) G. ALLARD (Bull. Soc. chim., 1932, [iv], 51, 372—376).— $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ (0.0025—0.25N) may be determined by measuring n during pptn. by $\text{Pb}(\text{OAc})_2$. For the individual acids the error is up to 2%; in mixtures, the error in $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ does not exceed 3% and 6%, respectively.

E. S. HEDGES.

Detection of diacetyl in pyrogenic gases from sugars etc. H. SCHMALFUSS and H. BARTHEMEYER.—See this vol., 592.

Conditions of reduction of Fehling's solution. A. HEIDUSCHKA and W. BIETHAN.—See this vol., 582.

Amino-acid content of ox-horn. Detection of I(+)-norvaline. E. ABDERHALDEN and K. HEYNES.—See this vol., 637.

Improvement in Carobbio's reaction for the detection of traces of resorcinol. L. BEY (Bull. Soc. chim., 1932, [iv], 51, 230—233; cf. A., 1906, ii, 809).— CdSO_4 is 8 times as sensitive as ZnCl_2 and is applicable over wider ranges of concentration.

A. A. LEVI.

Colloidal condition of cholesterol, cholesteryl ester, and lecithin. VI. **Catalytic properties of cholesterol.** I. REMESOV (Biochem. Z., 1932, 246, 431—445; cf. A., 1930, 415).—Provided that O_2 (air) is present, cholesterol (<0.005%) in true or colloidal solution in CHCl_3 gives an immediate emerald-green colour with a mixture of equal vols. of fresh 1% aq. dimethyl-*p*-phenylenediamine and 2:4-diaminotoluene. The intensity of the blue colour, to which the green soon changes, is proportional to the amount of sterol present. The p_{H} should be between 6.2 and 8.2 (optimum at 7.0). Addition of conc. aq. NH_3 causes the CHCl_3 layer to become pink. The reaction is sp. for cholesterol, but impure oleates and lecithin also

give it; with them, however, no pink colour is produced when aq. NH_3 is added. It is probable that a "peroxide" form of cholesterol, which acts as an adsorbed catalyst (analogous to the oxidases), is responsible for the reaction, which consists in dehydrogenation of the amines. Two diamines must be present together in order to satisfy energy requirements. The so-called "oxidones" of Battelli and Stern (A., 1915, i, 346) probably consist of cholesterol. It is possible that there exists, in addition to the biological oxidation system involving Fe, a system involving sterols instead.

W. MCCARTNEY.

Mohler's test for benzoic acid. E. T. ILLING (Analyst, 1932, 57, 224—232).—Grossfeld's modification of Mohler's test has been standardised to give concordant results. The excess of NaOH over BzOH should be as small as possible. Determinations are made on approx. 3 mg. of BzOH. BzOH gives rise to an orange colour, easily distinguishable from the yellow given by salicylic acid or the brown colour of cinnamic acid. When volatile acids sol. in H_2O are present, the BzOH is extracted from the distillate by light petroleum before nitration, and an alkaline oxidation is necessary for distillates from coffee extracts, cordials, and similar products.

T. MCLACHLAN.

[Detection of] novocaine and tutocaine. E. KALLSTROM (Svensk farm. Tidskr., 1931, 35, 617—619; Chem. Zentr., 1932, i, 425).—The oil obtained by interaction of tutocaine with HgCl_2 (Rosenthaler, A., 1926, 531) gradually affords crystals which, however, differ in habit from those of the corresponding novocaine compound.

A. A. ELDRIDGE.

Reactions of anæsthesin. L. EKKERT (Pharm. Zentr., 1932, 73, 226—227).—Anæsthesin (0.02—0.03 g.) in H_2O (2 c.c.), treated with HCl (5—10 drops) and then Cl-water gives a white ppt. which on shaking becomes orange-red, sol. in Et_2O or CHCl_3 . The α - and β -naphthol colour reactions show anæsthesin when 1 in 10^5 . A solution of the hydrochloride gives a red ppt. with 20% bleaching-powder solution.

E. H. SHARPLES.

Microchemical reactions of the furols. M. WAGENAAR (Pharm. Weekblad, 1932, 69, 449—456).—Several condensation reactions are found suitable for microchemical detection. The most sensitive are those with NH_2Ph and with barbituric acid, by means of which 0.1 mg. may be detected.

S. I. LEVY.

Reactions of arecoline. L. EKKERT (Pharm. Zentr., 1932, 73, 227).—The D.A.B. VI and Rosenthaler's reactions are described. When the hydrobromide is evaporated with H_2O_2 and HCl, the residue dissolved in H_2O and treated with resorcinol and H_2SO_4 , an intense reddish-violet colour is formed which quickly changes to violet and finally to rose. In ultra-violet light it is citron-yellow and on saturation with NH_3 it changes to bluish-violet.

E. H. SHARPLES.

Determination of glutamine in presence of asparagine. A. C. CHIBNALL and R. G. WESTALL.—See this vol., 660.

Determination of amides in presence of carbohydrates. F. BAERTS and P. DELVAUX.—See this vol., 666.

Biochemistry.

Determination of carbon monoxide in blood. J. HERRMANNSEN and H. W. KNIPPING (*Z. physiol. Chem.*, 1932, 206, 168—176).—The gas mixture containing CO is passed over heated I_2O_5 and the liberated I absorbed in aq. KI and determined by titration. The gas stream must be carefully dried and volatile org. substances removed by passage through suitable absorbents. CH_4 and H_2 do not interfere. CO is liberated from blood by $K_3Fe(CN)_6$ and washed out by a neutral gas.

J. H. BIRKINSHAW.

Rate of sinking of red blood-corpuscles. W. M. BENDIEN, J. NEUBERG, and I. SNAPPER (*Biochem. Z.*, 1932, 247, 306—321; cf. A., 1931, 973).—There is not necessarily any connexion between the charge on blood-corpuscles and their rate of sinking. The lability of the proteins of plasma, and, in particular, increases in the amounts of fibrinogen and globulin greatly affect the agglutination and hence the rate of sinking. Small amounts of Na salicylate (but not of NaOBz) stabilise the proteins and hence greatly reduce this rate. Consideration of the factors in the Stokes formula and of the condition of the blood in anæmia lead to the adoption for anæmic blood of a modification of the formula previously given for calculating rate of sinking. True auto-agglutination cannot occur at 30° and is thus distinguished from pseudo-agglutination (van der Hoeden and Verbeek, *Ned. Tijds. Geneesk.*, 1931) which is promoted at this temp.

W. MCCARTNEY.

Permeability of vital membranes. The red blood-corpuscle. D. L. WOODHOUSE and F. A. PICKWORTH (*Biochem. J.*, 1932, 26, 309—316).—The permeability of the red corpuscles to various inorg. ions, dyes, and org. compounds of physiological importance is given. 0.4% aq. CH_2O produces no change in the structure of the corpuscles or in the relative permeabilities to bromide and sulphate, nor does 0.5% saponin solution affect the permeability of bromide or sulphate. Veronal and streptococcus toxin in the concns. used also produced no appreciable changes on the permeability. Egg-white as well as the lipid envelope exerts a selective permeability to salts.

S. S. ZILVA.

Non-protein-sulphur content of blood-corpuscles. N. HAJDU (*Z. physiol. Chem.*, 1932, 206, 217—224).—A part of the non-protein-S of the blood-corpuscles is diffusible and part non-diffusible. The concn. of the non-diffusible portion is 4.85—5.25 mg. per 100 c.c. of blood. The diffusible S of the corpuscles is 55% of the plasma-S concn. An equation is derived for calculation of the non-diffusible corpuscular-S from whole blood-S and plasma-S.

J. H. BIRKINSHAW.

Polycythæmia in the rat on a milk-iron-copper diet supplemented by cobalt. J. M. ORTEN, F. A. UNDERHILL, E. R. MUGRAGE, and R. C. LEWIS (*J. Biol. Chem.*, 1932, 96, 11—16).—Rats fed on a milk-Fe diet supplemented by Cu and Co (0.5 mg. as $CoSO_4$ or $CoCl_2$ per day) develop a marked increase

in red blood-cells and hæmoglobin with no change in the leucocyte or differential leucocyte counts.

F. O. HOWITT.

Lectures on blood-sugar. S. L. BHATIA (Mysore Univ. J., 1931, 5, 1—99).

Blood-sugar in abnormal mental states. P. K. McCOWAN and J. H. QUASTEL (*Lancet*, 1931, 221, 731—736).—The hyperglycæmic index has been defined so as to give a quant. expression of the amount of hyperglycæmia sustained after 2 hr., the time required for the blood-sugar level to return to normal in the ordinary way. Sugar tolerance curves are discussed on this basis for 85 psychotic cases. In cases of benign stupor and mania the index is generally low. Arteriosclerosis is not a cause of a high index. During menstruation normal and psychotic cases both show a departure from the normal sugar tolerance curve.

L. S. THEOBALD.

Absence of abnormal forms of glucose from blood dialysates. D. J. BELL (*Biochem. J.*, 1932, 26, 349—352).—The apparent low optical activities of the dialysates may be accounted for by the presence of the levorotatory Na d -lactate without assuming the presence of any γ -glucose.

S. S. ZILVA.

Occurrence of thiocyanic acid in blood in normal and pathological conditions, particularly in renal insufficiency; thiocyanic acid-decomposing power of blood. E. BECHER [with K. HAMANN and F. DOENECKE] (*Münch. med. Woch.*, 1932, 79, 1—6; *Chem. Zentr.*, 1932, i, 831).—The CNS' content of the serum and plasma is smaller than that of whole blood; the erythrocytes contain large quantities. In renal insufficiency, particularly in uræmia, the amount rises to 3—5 times the normal. The red corpuscles can decompose CNS-compounds. In the deproteinisation of blood by $CCl_3\cdot CO_2H$ decomp. of CNS' to H_2S occurs.

A. A. ELDRIDGE.

Bile salts. I. Are there any bile salts in normal blood? S. TASHIRO. II. Pettenkofer reaction of different bile salts and of blood filtrates. S. TASHIRO, E. B. TIETZ, and U. TANGE. III. Pettenkofer reaction of lipins and of blood filtrates. S. TASHIRO, L. H. SCHMIDT, and E. B. TIETZ. IV. Reciprocal relationship between blood-sugar and Pettenkofer-positive substances in mercury poisoning. E. B. TIETZ and S. GOLDBLATT. V. Reciprocal relationship between blood-sugar and Pettenkofer-positive substances in blood during intestinal obstruction. S. TASHIRO and L. H. SCHMIDT. VI. Antagonistic action of glycerol towards bile salts in blood coagulation. S. TASHIRO and O. P. LEE. VII. Antagonistic action of cholesterol to bile salts in blood coagulation. S. TASHIRO and C. A. MILLS. VIII. Antagonistic power of glycerol and cholesterol to bile salts in gastric ulcer formation. S. TASHIRO and S. OLIVER. IX. Antagonistic action of sugars to bile salts in blood coagulation. J. J. KOBES. X. Antagonistic action of

lipins to bile salts in gastric ulcer formation. T. TSURUTA. XI. Antagonistic action of various lipins to bile salts on frog muscles. T. TSURUTA. XII. Antagonistic action of lipins to the toxic action of bile salts. T. TSURUTA. XIII. Antagonistic action of cholesteryl oleate to bile salts in gastric ulcer formation. K. ISHII. XIV. Relation of sex to susceptibility to the toxicity of bile salts. T. TSURUTA. XV. Relation of thyroid activity to the production of gastric ulcer by bile salts. S. TASHIRO and L. H. SCHMIDT. XVI. Relation of blood-phospholipins to experimental gastric ulcer. S. TASHIRO and L. H. SCHMIDT. XVII. Effect of administration of bile salts on Pettenkofer-positive substances and blood-lipin-phosphorus. S. TASHIRO and L. H. SCHMIDT. XVIII. Eczema, an expression of hepatic insufficiency and its cure with bile salt. W. B. WHERRY and S. TASHIRO (Med. Bull. Univ. Cincinnati, 1931, 6, 40—50, 51—61, 62—73, 74—83, 84—89, 90—97, 98—99, 100—101, 102—109, 110—116, 117—123, 124—129, 130—133, 134—136, 137—143, 144—150, 151—155, 156).—I. Normal blood contains slightly $>0.1\%$ of compounds sol. in abs. EtOH or in EtOH+COMe₂ (1:1) and giving a strong Pettenkofer reaction; the substances, which are determined colorimetrically, are pptd. by BaCl₂ or Ba(OH)₂ or by Mg salts in slightly alkaline medium. Cholic acid appears to be absent.

II. The application of the colorimetric method to cholic acid, deoxycholic acid, and mixtures with "blood salts" was studied. The method of determination of Pettenkofer-positive substances in blood can be applied to pure bile salts. When a bile salt is added to the EtOH+COMe₂ extract of plasma the resulting colour val. is less than the sum of the separate colour vals.; apparently a lipid substance renders some of the pigment insol. It is not proved that blood contains deoxycholic acid.

III. The Pettenkofer reactions of lecithin and cephalin are similar to those of deoxycholic acid and "blood salts"; the colours are intensified when the substances are added to blood filtrate. Cholesteryl oleate has the reverse effect. The ultra-violet fluorescence (3660 Å. used) of "blood salts" and of deoxycholic acid is purplish, that of cholic acid being reddish-purple. Normal horse blood contains $<0.0027\%$ of cholic acid, if any.

IV. Increase in blood-sugar was reduced, and the "blood salt" was increased from sub- to super-normal, by intravenous injection of HgCl₂ into cholecystotomised dogs with resected common bile duct.

V. In dogs with operative salivary, œsophageal, or intestinal obstruction nearly all fluctuations in blood-sugar were accompanied by reverse changes in "blood salts" content of the blood.

VI. Delay in clotting caused by Na taurocholate in small quantity is checked by glycerol.

VII. Cholesterol counteracts delay in clotting caused by bile salts.

VIII. Neither glycerol nor cholesterol counteracts.

IX. Glucose, maltose, fructose, rhamnose, and arabinose (in that order of diminishing effect), but not sucrose, antagonise the delay in coagulation

time of citrated horse plasma on recalcification caused by Na taurocholate.

X. Lecithin or crude brain phosphatide counteracted the effect of Na glycocholate.

XI. Crude phosphatide mixture, lecithin, sulpholipin, and cephalin (in that order of diminishing effect) antagonise the tetanic effect of bile salts.

XII. The toxic effects of cholic and deoxycholic acids on frogs and guinea-pigs are compared. Glucose, olive oil, and phosphates have no antagonistic effect.

XIII. Cholesteryl oleate antagonises the action of bile salts.

XV. Feeding thyroxine lowers the ulcer-producing dose of bile salt in guinea-pigs, possibly by reduction of the phospholipins as a result of increased general lipin metabolism.

XVI. Changes in (rabbits') blood-phospholipins on treatment with gastric ulcer-producing agents are recorded; a decrease occurs in all the treatments.

XVII. Oral administration of Na taurocholate and glycocholate (0.1—0.2 g. per day for 14 days) to normal and pathological human subjects resulted in the "blood salts" becoming more nearly normal; in all normal cases the lipin-P decreased.

CHEMICAL ABSTRACTS.

Determination of ergothioneine in blood-filtrates. J. A. BEHRE (Biochem. J., 1932, 26, 458—460).—Salt's results (A., 1931, 1440) are criticised.

S. S. ZILVA.

Photochemical degradation of hæmoglobin and its reaction-relationship to chlorophyll. G. KOEGL (Strahlenther., 1931, 42, 379—383; Chem. Zentr., 1932, i, 533).—Chlorophyll is decomposed by light more rapidly in presence than in absence of quinones. Hæmoglobin is decomposed to complete decolorisation in presence of hæmatin or K glutathione.

A. A. ELDRIDGE.

Blood-glutathione. V. SCHELLING (J. Biol. Chem., 1932, 96, 17—24).—The reduced glutathione in the blood as determined by Mason's method (A., 1930, 803) averages 0.0213% in males and 0.0227% in females. Arterial and venous bloods differ in the amount of SH-groups. The SH-content is decreased on aeration and entirely destroyed by H₂O₂. Reduction of Folin-Wu blood filtrates by nascent H increases the SH-content, whereas there is no such increase if the filtrate has been previously oxidised by H₂O₂. Hence substances other than oxidised glutathione are reduced by nascent H and are determined in the method used.

F. O. HOWITT.

Physico-chemical differences between α -, β -, and γ -hæmoglobins. II. T. TADOKORO, M. ABE, and K. YOSHIMURA (J. Biochem. Japan, 1932, 15, 197—204).—Horse oxyhæmoglobin was separated into three fractions by differences in solubility in H₂O. The globins from these three fractions differed in isoelectric point, sp. rotation, and distribution of the constituent NH₂-acids (cf. this vol., 292).

F. O. HOWITT.

Denatured globin. N. U. MELDRUM (Biochem. J., 1932, 26, 162—164).—Meldrum and Dixon's observation (A., 1930, 803) that denatured globin gives no nitroprusside test for SH or S-S groups is confirmed. The colour reaction observed by Anson

and Mirsky (A., 1931, 972) is due to COMe_2 used in the prep. of globin. A. COHEN.

Amide-nitrogen in the blood of children. A. BERNHARD and J. S. LEOPOLD (Amer. J. Dis. Children, 1931, 42, 1100—1102).—The val. (98—132 mg. per 100 c.c.) appears to be independent of the lactic acid concn. and CO_2 -combining power of the blood. CHEMICAL ABSTRACTS.

Amide-nitrogen of blood. VI. S. BLISS (J. Pharm. Exp. Ther., 1932, 44, 397—407; cf. A., 1931, 110).—A reply to Nash and Williams (this vol., 295). H. DAVSON.

Determination of residual nitrogen in blood. L. N. LAPIN and W. E. KILL (Z. klin. Med., 1931, 148, 278—285; Chem. Zentr., 1932, i, 261).—The blood is deproteinised with ZnSO_4 and NaOH , ashed by Kjeldahl's method, and treated with Nessler's and Fehling's reagents, when a green colour appears. The colour is compared with that similarly obtained from NH_4Cl . A. A. ELDRIDGE.

Residual nitrogen and its determination. Y. JADERHOLM (Erip. Aikakaus. Duodecim, 1930, 417—434; Chem. Zentr., 1932, i, 261).—A discussion. A. A. ELDRIDGE.

Changes in blood-chlorine and -water with oxygen-deficient air. D. ADLERSBERG and J. GLASS (Arch. exp. Path. Pharm., 1932, 165, 383—400).—Fasting rabbits exposed for 72 hr. to air at a pressure equiv. to that at a height of 6000 m. experience a decrease in the alkali reserve of the blood, an increase of plasma-Cl, and a decrease of plasma- H_2O . The corpuscles show irregular variations in Cl content and, on the average, an increase in H_2O , the val. of the ratio corpuscular-Cl/corpuscular- H_2O : plasma-Cl/plasma- H_2O decreasing in each instance. Control fasting animals show an increase in this ratio. The changes due to deficiency of O_2 are, to a certain degree, similar to those occurring with decrease of CO_2 tension of blood *in vitro* or with hyperventilation alkalosis *in vivo*. F. O. HOWITT.

Iodometric determination of iron in blood. J. H. BLACKWOOD and J. D. STERLING (Biochem. J., 1932, 26, 353—356).—The method is based on the liberation of I from KI by Fe^{+++} at $[\text{H}^+]$ on the acid side of neutrality, when the reaction is quant. Results accurate to about 2% are obtained with 2 c.c. of blood. S. S. ZILVA.

Application of Winterstein's micro-electrode to determination of blood- p_{H} . W. LAUBENDER (Arch. exp. Path. Pharm., 1932, 165, 1—4).—The Winterstein micro-electrode cannot in general be applied for the determination of the p_{H} of blood because of the uncontrollable loss of CO_2 . W. O. KERMACK.

Effect of bile acids on the hydrogen-ion concentration of the blood. T. IROO (Arb. Med. Univ. Okayama, 1931, 2, 572—578).—Injection of bile salts increases the alkali reserve of dog's blood but does not affect the p_{H} . Removal of bile from the gall-bladder diminishes the p_{H} and alkali reserve; injection of bile acids produces normal or supernormal vals. CHEMICAL ABSTRACTS.

Variations of serum-calcium in the rabbit. M. C. BOURNE and D. A. CAMPBELL (Biochem. J., 1932, 26, 183—195).—The wide variation of serum-Ca in normal rabbits is decreased by fasting. A cabbage diet results in increased serum-Ca (14.3—19.3 mg. per 100 c.c.), decreased inorg. serum-P, and a large vol. of alkaline urine rich in Ca, poor in P. Oats cause decreased serum-Ca (11—15.8 mg. per 100 c.c.), increased serum-P, and a small vol. of acid urine rich in P, poor in Ca. A. COHEN.

Osmotic behaviour of the water of blood-serum. F. W. SUNDERMAN (J. Biol. Chem., 1932, 96, 271—283).—The addition of sucrose (0.06—0.98M) to NaCl solutions and to serum, and the addition of NaCl to serum, all produce the theoretical f.-p. depression, calc. on the basis of total H_2O ; the effects of urea on serum and on solutions of NaCl and sucrose are slightly less than theoretical. It is concluded that the total H_2O of serum is osmotically "free." J. B. BATEMAN.

Physical method for following changes produced in serum by dilution. A. BOUTARIC and M. DOLADILHE (Compt. rend., 1932, 194, 1385—1387).—To characterise the behaviour of serum diluted with distilled H_2O the following magnitudes are important: (1) the degree of dilution, L , at which the pptn. is a max.; (2) the val. at this dilution of the product LH (where H is the optical density). W. O. KERMACK.

[Determination of serum-]alkali reserve. J. MULLER (Klin. Woch., 1931, 10, 2038—2040; Chem. Zentr., 1932, i, 262).—Ellinger's method (*ibid.*, 1931, 10, 2036) is acceptable, but not the expression of the results in vol.-% of CO_2 . The method is inapplicable to hæmolytic, icteric, turbid, or lipæmic sera. A. A. ELDRIDGE.

Diffusible and non-diffusible serum-calcium following intravenous injection of calcium salts. R. G. SMITH and H. R. STERNBERGER (J. Biol. Chem., 1932, 96, 245—257).—When serum-Ca of dogs is increased by intravenous injection of Ca chloride, lactate, or gluconate, both diffusible and non-diffusible parts in the serum rise, so that the normal relation is approx. maintained. This is not explainable by a rise in serum-protein or by exchange between blood and tissues, since the same result is obtained *in vitro*. Diffusible Ca tends to be adsorbed on collodion sacs during ultrafiltration. J. B. BATEMAN.

Mineral constituents of the blood-serum and survival of tissue from *Vipera aspis*. P. DODEL and P. FEBURE (Bull. Soc. Chim. biol., 1932, 14, 272—274).—The blood-serum of *V. aspis* contains Na 3.9, K 0.30, Ca 0.19, glucose 0.1 g. per litre. The striated muscle survived for 50 hr. in a solution containing NaCl 8.4, KCl 0.5, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 0.68, glucose 0.5, NaHCO_3 1 g. per litre, and smooth muscle for 7—8 hr. in a solution containing NaCl 9, KCl 0.5, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 0.67, glucose 0.5, MgCl_2 0.01, NaHCO_3 0.5 g. per litre of H_2O . The addition of 3 c.c. of human blood-serum to 250 c.c. of the second solution prolonged the survival of the muscle. A. LAWSON.

Refractometric investigation of serum-proteins. IX. Ultrafiltration of serum under high

pressure. D. VON DESEÖ and E. LAMOTH (Biochem. Z., 1932, 247, 322—328; cf. this vol., 412).—When horse-serum is subjected to fractional ultrafiltration under pressure (up to 120 atm.) gradual increase in n of the fractions is observed, the last fraction having the highest n . The amounts of the org. and inorg. constituents of the serum increase to equal extents, since their n does not change during the process. Removal of bound H_2O by the pptd. protein may be the cause of the increase in n of the ultrafiltrates. For the determination of n the first ultrafiltrate only should be used. W. MCCARTNEY.

Transformation of serum-albumin into serum-globulins. A. FISCHER (Science, 1932, 75, 443).—Albumin-antiprothrombin compounds behave as globulins and must be regarded as identical with them. The addition of small amounts of antiprothrombin (heparin) results in an increased amount of globulin in the serum. Antiprothrombin is the only substance, normally found in the body, which can form globulins, and the amount of globulins present in blood-serum is determined by the amount of antiprothrombin. L. S. THEOBALD.

Determination of serum-carotene. F. D. WHITE (J. Lab. Clin. Med., 1931, 17, 53—59).—Palmer's method is modified. The normal serum-carotene is 0.063, and diabetic 0.072—0.379, mg. per 100 c.c. CHEMICAL ABSTRACTS.

Specificity and chemical structure. H. BIERRY (Compt. rend., 1932, 194, 1271—1273).—Amongst the carbohydrates present in the products of hydrolysis of the proteins of dog's plasma, galactose, mannose, and glucosamine are identified, the percentage of the last two constituents being much less than in the case of the horse. W. O. KERMAK.

Determination of cholesterol in blood-serum or -plasma. A. BERNHARD and I. J. DREKTER (J. Lab. Clin. Med., 1931, 16, 1225—1229).—Modifications are proposed (cf. A., 1918, ii, 336). A mixture of equal parts of $EtOH$ and Et_2O is the most efficient agent for extracting cholesterol when filter-paper is used as the absorbent. CHEMICAL ABSTRACTS.

Plasma-lipins and stability of blood-suspensions. B. ÖHLSON and O. RUNDQVIST (Biochem. Z., 1932, 247, 249—256).—Removal of the lipins from blood-plasma (without denaturation of the proteins) causes no change in the rate of sinking of red corpuscles in the plasma. The increased stability of normal blood-suspensions produced by heat is not found in the lipin-free plasma. W. MCCARTNEY.

Method of immunisation with carbohydrate haptens adsorbed on collodion particles. J. FREUND (Science, 1932, 75, 418).—Rabbits injected with collodion particles coated with the sp. substance from pneumococcus type III did not produce agglutinins or precipitins. A faintly positive precipitin reaction was obtained in the case of 1 out of 3 rabbits injected with anthrax-carbohydrate coated on collodion. L. S. THEOBALD.

Inorganic constituents of cerebrospinal fluid. II. Ultrafiltration of calcium and magnesium from human sera. E. WATCHORN and R. A.

MCCANCE (Biochem. J., 1932, 26, 54—64).—The ratios of ultrafiltrable $Ca(Mg)$: total serum- Ca and - Mg are nearly const. in normal and pathological cases, and are 57 and 75%, respectively. In pregnancy total serum- Mg and - Ca tend to fall and the ultrafiltrable fractions to increase. "Parathormone" administration caused a fall in the ultrafiltrable Ca :total serum- Ca ratio. A. COHEN.

Cuprous glutathione. N. W. PIRIE Crystallography of glutathione. J. D. BERNAL (Biochem. J., 1932, 26, 75—79).—The Cu^+ compound has $+45.1^\circ$ and $+45.4—45.8^\circ$ when prepared from reduced and oxidised glutathione, respectively. Analytical data do not verify the existence of a Cu^+ derivative of oxidised glutathione of the type $Cu_2GS \cdot SG$ (Kozlowski, this vol., 77). Crystallographic data for glutathione are given. A. COHEN.

Phosphorus and glutathione contents of the atrioventricular bundle. G. DEL GUERRA (Arch. Ital. Biol., 1931, 85, 182—189; Chem. Zentr., 1931, ii, 2628).—The atrioventricular bundle contains 1% of total P and 0.36% of org. P. The iodometric method gives a glutathione content of 123 mg. per 100 g. of muscle tissue. L. S. THEOBALD.

Chemical nature of unsaponifiable fraction of fish-liver oils. II. Cod-liver oil. G. WEIDEMANN and F. ENDER (Biochem. J., 1932, 26, 264—268).—The unsaponifiable matter of cod-liver oil was treated with phthalic anhydride in C_5H_5N , and the alkyl H phthalates were fractionated. In addition to cholesterol, two dihydric aliphatic alcohols (I vals. 64 and 160), a monohydric cyclic alcohol, m. p. 144° , a dihydric cyclic alcohol, and a hydrocarbon giving an $SbCl_3$ colour reaction 250 times as intense as that of cod-liver oil were obtained. A. COHEN.

Oil of the moon-fish; modifications due to parasites; abnormal content of cholesterol. H. MARCELET (Compt. rend., 1932, 194, 1392—1393).—The oil extracted from the liver of a "moon fish" (*Orthogoriscus mola*) strongly infested with parasites (*Anthocephalus gigas*) differed from that of a healthy specimen in being less in amount (2.7 g. instead of 31.0 g. per 100 g. of liver) and containing less cholesterol (20.0% instead of 35.5%). W. O. KERMAK.

Swelling of single collagen fibre-bundles. R. H. MARRIOTT (Biochem. J., 1931, 26, 46—53).—A technique for the microscopical measurement of fibre-bundles is described. They are rendered less sensitive to the swelling action of acid by repeated use. The combined effects of "plumping" and "opening out" of the fibres determine the extent of the swelling. This is max. at p_H 1.9 for pure collagen and at p_H 2.8 for fresh ox-hide fibre-bundles which undergo more opening out, a process occurring at higher p_H . A. COHEN.

Phosphatides. IV. Unsaturated fatty acids of the ether-soluble phosphatides of brain. E. KLENK (Z. physiol. Chem., 1932, 206, 25—40; cf. A., 1931, 1321).—Fractions of highly and weakly unsaturated acids were obtained with the aid of the Li salt- $COMe_2$ and of the Pb salt- $EtOH$ methods. The esters were then further fractionated by distillation. The C_{18} fraction consisted principally of oleic

acid. The C_{20} group contained an acid, $C_{20}H_{38}O_2$, m. p. 20° , probably identical with gadoleic acid, and an acid, $C_{20}H_{32}O_2$, probably arachidonic acid. The C_{22} fraction contained mainly an acid, $C_{22}H_{34}O_2$, probably elupanodonic and smaller amounts of acids with <5 double linkings. J. H. BIRKINSHAW.

Enzymes in the intestines of *Haliotus giganteus*, Gm. K. OSHIMA (J. Agric. Chem. Soc. Japan, 1931, 7, 328—331).—Cellulase, amylase, gelase, and rennin were present; *alginate* hydrolysed alginic acid from brown seaweeds. Weak reactions for invertase, maltase, and protease were obtained; tyrosinase, amygdalase, and esterase were not found.

CHEMICAL ABSTRACTS.

Presence of an acid-soluble organic phosphorus compound in the submaxillary gland of the dog. A. ROSSI and G. SCOZ (Atti R. Accad. Lincei, 1931, [vi], 14, 582—585).—The gland contains about 0.14 g. of P per 100 g. of the fresh tissue, about 0.04 g. of this being in the form of an acid-sol. compound. The fact that part at least of the latter is determinable only after incubation at 37° indicates it to be a labile org. P compound the behaviour of which recalls that of phosphagen. T. H. POPE.

Reaction of the thiol group. A. GIROUD and H. BULLIARD (Bull. Soc. Chim. biol., 1932, 14, 278—279).—The presence of the SH group may be shown by treatment of the material with 5% aq. $Zn(OAc)_2$ and washing with H_2O before carrying out the nitroprusside reaction. A lasting red coloration is obtained. Creatinine, $COMe_3$, and substances containing the $\cdot S \cdot S \cdot$ group do not give the reaction.

A. LAWSON.

Total and thyroxine iodine in the thyroid of the horse. L. BLANCHARD and H. SIMONNET (Bull. Soc. Chim. biol., 1932, 14, 229—237).—In nine cases the normal thyroid tissue of the horse contained 0.031—0.177 g. of total I, and 0.009—0.086 g. of thyroxine-I per 100 g. of fresh material. In three cases, the total I was 0.260—0.334 g., and the thyroxine-I 0.128—0.189 g. per 100 g. of dry material. In four cases the foetal thyroid contained 0—0.0133 g. of total I per 100 g. of fresh tissue, and in the one case examined, the foetal thyroid at birth showed the same I content as that of the mother. Putrefaction caused complete disappearance of thyroid-I only when continued for 12 days. The total I and thyroxine-I content of several pathological thyroids were in general below the normal vals.

A. LAWSON.

Amino-acid content of ox-horn. Detection of *l*(+)-norvaline. E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1932, 206, 137—145).—The fraction of the hydrolysis products analysing to amino-valeric acid was converted into the corresponding α -bromovaleric acids with $NOBr$ and these were separated by their different rates of amination. The hydantoins obtained by means of $PhNCO$ were identical with those from *d*(-)-norvaline [*d*(+)-3-phenyl-5-n-propylhydantoin, m. p. 112° , $[\alpha]_D^{20} +73.4^\circ$ (in EtOH)], and *l*(+)-valine [*l*(-)-3-phenyl-5-isopropylhydantoin, m. p. 133° , $[\alpha]_D^{20} -92.3^\circ$ (in EtOH)]. Ox-horn keratin therefore contains *l*(+)-norvaline (Walden inversion on bromination and amination)

and *l*(+)-valine. In addition *l*(-)-histidine and 15% of glutamic acid were detected.

J. H. BIRKINSHAW.

Vital staining of trout eggs. P. ADLER (Proto-plasma, 1932, 15, 15—23).—The capsule of fertile and unfertilised (but surviving) trout eggs is equally permeable to acidic and to basic stains dissolved in 0.8% NaCl solution. The penetration of Congo-red is somewhat limited. Dyes do not enter the interior portion of the egg while the latter is still alive. Injury to the egg by the dye is least when applied in 0.8% (isotonic) NaCl solution. The primary injury is associated with an increased permeability of the surface of contact.

A. G. POLLARD.

Isolation of pure, anhydrous ethyl alcohol from non-alcoholic human and animal tissues. A. O. GETTLER, J. B. NIEDERL, and A. A. BENEDETTI-PICHLER (J. Amer. Chem. Soc., 1932, 54, 1476—1485).—Micro-apparatus for the isolation of pure anhyd. EtOH from extremely dil. solutions (0.0025% or less, as found in tissues) is described. The average quantity of EtOH normally present in body tissues is: human brain, 0.0004%; human liver, 0.00256%; human blood, 0.004%; dog brain, 0.003%; dog liver, 0.0007%; dog blood, 0.0013%; pig brain, 0.00007%.

C. J. WEST (b).

Relationship between sugar in blood and lactic acid in brain. E. G. HOLMES and M. A. F. SHERIF (Biochem. J., 1932, 26, 381—387).—The lactic acid content of mouse brains fixed rapidly in liquid air is invariably low. The amount formed on anaerobic incubation depends on the blood-sugar level at death up to blood-sugar vals. of some 200 mg. per 100 c.c. At higher levels there is a smaller increase in lactic acid in proportion to the increase in blood-sugar which is due to a corresponding failure of the brain tissue to take up carbohydrate. At blood levels at which hypoglycæmic symptoms occur the "resting" brain-lactic acid level is decreased.

S. S. ZILVA.

Amino-acids of tissues. VI. Determination of basic amino-acids in small quantities of proteins. J. L. ROSEDALE and G. A. DA SILVA (Biochem. J., 1931, 26, 369—376).—Separate samples are hydrolysed with acid and with alkali. Histidine is pptd. by $HgSO_4$ from the alkaline hydrolysate. The remaining data obtained from the material yielded by the acid hydrolysis offer information which is ordinarily given by Van Slyke's method. Gelatin, caseinogen, oysters, and *Torula utilis* were analysed by this method and the results are given. Prolonged hydrolysis of proteins with acid is required completely to destroy tryptophan.

S. S. ZILVA.

Amino-acids. V. T. YAGINUMA, G. ARAI, and K. HAYAKAWA (Proc. Imp. Acad. Tokyo, 1932, 8, 91—93).—From 5 kg. of spinal cord from cattle 2 g. of pure cryst. norleucine (m. p. $276-278^\circ$) were isolated. Crystal consts. of formyl-*l*-leucine, m. p. $142-144^\circ$, and of the formyl derivative, m. p. $115-116^\circ$, of the synthesised *d*-norleucine are given.

W. R. ANGUS.

Body-fats of the pig. Formation of animal depot fats. A. BANKS and T. P. HILDITCH (Biochem. J., 1932, 26, 298—308).—The outer back, inner

back, and leaf fats from pigs receiving fish-meal in their diet were investigated. The different component acids of each of these groups showed a numerical relationship similar to that previously observed (this vol., 189). The united molar percentages of stearic, oleic, and linoleic acids were approx. 70%. The increase in stearic acid was again mainly at the expense of oleic and not of linoleic acid. The relationship between the molar percentage of fully-saturated glycerides and the total molar content of saturated acids was very similar to that observed in the cases of tallows and butter-fat (A., 1931, 757, 1178). Fish-meal diets lead to the production of extremely soft fat due to the general increase in unsaturated components, especially to unusually large proportions of linoleic acid. S. S. ZILVA.

Determination of the hydrogen-ion concentration of the tissues in living animals. C. VOEGTLIN and H. KAHLER (Science, 1932, 75, 362—364).—A method using a capillary glass electrode is described. L. S. THEOBALD.

Formation of ammonia in the kidney. H. WASSERMAYER (Arch. exp. Path. Pharm., 1932, 165, 420—431).—Adenosinephosphoric acid, which occurs in the dog's or rabbit's kidney in amounts equiv. to approx. 10 mg. of NH_3 , serves as a source of NH_3 . Analysis of the efferent and afferent blood-streams of the kidney indicates a synthesis of adeninephosphoric acid. The *post-mortem* liberation of NH_3 from kidney pulp is, however, greater than can be accounted for by the content of the acid. The normal content of NH_3 in the kidney is $< 0.001\%$. To a smaller extent the presence of adenosinephosphoric acid and the formation of NH_3 are also observed in the blood, submaxillary and parotid glands, stomach, spleen, lungs, and liver. F. O. HOWITT.

Adrenal cortex and muscle chemistry. K. LANG (Pflüger's Archiv, 1931, 229, 60—85; Chem. Zentr., 1932, i, 830).—In the muscle of adrenalectomised cats the NH_3 content is double the normal; the phosphagen content falls to 33%. Other values were normal. A. A. ELDRIDGE.

Actual acidity of the hæmolymph of *Bombyx mori*. L. I. Metabolism of silkworms. S. DEMJANOVSKI, R. GALZOVA, and V. ROSHDESTVENSKA (Biochem. Z., 1932, 247, 386—405).—During the caterpillar and pupal stages the hæmolymph of *B. mori* has p_{H} 6.7—6.8. At each of the five sheddings of skin the acidity undergoes considerable reduction. Differences in the acidity occur at various stages of growth (egg to butterfly, winter rest period included) and there are also differences due to sex. W. MCCARTNEY.

Magaki (*Ostrea gigas*, Thunberg). I. Difference in composition according to sex. B. MASUMOTO, M. MASUMOTO, and M. HIBINO (J. Sci. Hiroshima Univ., 1932, 2, 155—158).—The female oysters have a heavier shell and more soft tissue than the male. A similar difference exists in the abs. and % contents of H_2O , total N, fat, and glycogen. F. O. HOWITT.

Effect of diet rich in phosphatides on the phosphatide content of milk. A. TRAUTMANN and H. KIRCHHOF (Biochem. Z., 1932, 247, 275—296).—The

phosphatide content of goat's milk is only occasionally and temporarily increased and the composition of the milk is but little affected as a result of administration of lecithin. W. MCCARTNEY.

Absorption of milk precursors by the mammary gland. I. Kaufmann-Magne technique. II. Relation of blood-sugar absorption to lactose secretion. J. H. BLACKWOOD and J. D. STIRLING (Biochem. J., 1932, 26, 357—361, 362—368).—I. The corpuscular vol. and the Fe content of the blood from the radial artery and the jugular and abdominal subcutaneous (mammary) veins of lactating and non-lactating cows have been determined. The differences in the contents of indiffusible constituents are alike in lactating and non-lactating animals. The content of the indiffusible constituents of the jugular blood is higher than that of arterial or mammary blood. There therefore appears to be a withdrawal of H_2O from the arterial blood by the salivary glands.

II. In non-lactating cows the sugar content of the jugular blood is lower than that of the mammary venous blood, which is itself lower than that of arterial blood. In lactating animals the sugar content of the jugular blood is higher than that of mammary venous blood, but lower than that of arterial blood. The great lowering of mammary venous blood-sugar in lactating animals is partly due to the increased energy requirements of the active gland and partly to lactose secretion. S. S. ZILVA.

Determination of zinc in milk. M. SATO and K. MURATA (Trans. Tottori Soc. Agric. Sci., 1931, 2, 206—223).—Milk ash is dissolved in 2N-HCl, diluted with H_2O , and heated to boiling; Fe is pptd. with aq. NH_3 and Mn with $(\text{NH}_4)_2\text{S}$. The cold filtrate is acidified with HCl; Na_2CO_3 is added to alkalinity (Me-orange), then 50% HCO_2H to acidity. ZnS is pptd. with H_2S from the boiling solution, the gas being passed until the solution is cool. The ZnS is dissolved in 15% HCl (6 c.c.), Zn being determined nephelometrically as $\text{Zn}_2\text{Fe}(\text{CN})_6$. The Zn content was highest immediately after parturition; it decreased gradually and then slightly increased towards the end of lactation. Human milk contained (average) 7.35, 1.23, and 3.89 mg. per litre 3, 25, and 360 days after parturition, respectively. Cow's milk contained 13.57 mg. immediately after parturition, 2.35—2.12 mg. in the 2nd or 3rd month, and 4.58 mg. at the end of lactation. The average Zn content of market milk was 3.3 mg. Ewe's milk contained 13.78 mg. immediately after parturition, 2.45—2.90 mg. during 1—7 months, and 3.5 mg. at the end of lactation.

CHEMICAL ABSTRACTS.

Peptic degradation of caseinogen. H. HOLTER, K. LINDERSTRÖM-LANG, and J. B. FUNDER (Z. physiol. Chem., 1932, 206, 85—115).—Samples of caseinogen obtained by fractionation with HCl in EtOH, also commercial preps., were subjected to peptic digestion, and the hydrolysis was followed by the changes in viscosity of the substrate. Marked differences were observed. The characteristic of peptic caseinogen hydrolysis is the separation of an intermediate product containing P. The ratio P/N and hence probably the composition of this product for the various caseinogen preps. is approx. const. This phospho-

peptone is not identical with that obtained by tryptic digestion of caseinogen. Both the viscosity changes and the velocity of the titratable proteolytic fission depend on the P content of the original substrate.

J. H. BIRKINSHAW.

Determination of salivary urea. A. M. CEN-
TENO (Presna med. Argentina, 1931, 17, 1751—1754).—Saliva is equal, or nearly equal, to blood-urea. In pathological conditions the increase in the saliva-urea is proportional to that of blood-urea.

CHEMICAL ABSTRACTS.

Urea-excreting function of the liver. I. M. SAKAI (Japan. J. Gastroenterol., 1931, 3, 316—328).—Liver-bile of rabbits contains 9, whilst bladder-bile contains 19, mg. of urea per 100 c.c. Intravenous injection of urea increases excretion by both liver and kidneys. Kidney injury is partly compensated by urea excretion by the liver. CHEMICAL ABSTRACTS.

Bile acid of wild pig's bile. S. SHIBUYA and T. MIKI (Z. physiol. Chem., 1932, 206, 279—281).—From the hydrolysed extract of the dried gall-bladder of the wild pig α -hyodeoxycholic acid and glycine were isolated, indicating the presence of glycohyodeoxycholic acid in the original material.

J. H. BIRKINSHAW.

Bile acid metabolism. V. Atophan chloro-
rrhœa. I. SAKAMOTO and S. NAKAGAWA. VI. Bile acid secretion and blockage of the reticulo-
endothelial system. H. MIKAMI and S. NAKAGAWA (J. Biochem. Japan, 1932, 15, 115—128, 129—149).—V. In dogs with fistulæ of the bile-duct or -bladder the proportion of bilirubin and bile acid is fairly steady, whilst that of NaCl remains const. Following administration of atophan the amounts of bilirubin and bile acid secreted are unchanged despite the increased flow of bile. The action of atophan is not dependent on the autonomic nervous system, but is probably due to direct stimulation of the liver cells.

VI. Blockage of the reticulo-endothelial system by colloids produces a marked fall in the secretion of bile, whilst the change in bilirubin depends on the type of colloid used. The NaCl content is unchanged, the abs. amount being dependent on the amount of bile secreted.

F. O. HOWITT.

Bile acids and carbohydrate metabolism. XII. Influence of bile acids and the autonomic nervous system on liver-glycogenesis. T. MIKI. XIII. Influence of bile acids and internal secretions on liver-glycogenesis. K. FUGIWARA (J. Biochem. Japan, 1932, 15, 167—179, 181—192).—XII. The synergising action of Na cholate on liver-glycogenesis in starved rabbits is inhibited by section of the splanchnics or of the vagi, the inhibition being subsequently removed by administration of ergot-amine. Thus the stimulating action of bile acids on liver-glycogenesis is related to the autonomic nervous system.

XIII. Na cholate antagonises the glycogenolytic action of adrenaline or phloridzin and synergises the glycogenetic influence of insulin. F. O. HOWITT.

Bile acid formation. V. Influence of feeding on the bile acid content of bile. T. FUKASE and K. FUGIWARA (J. Biochem. Japan, 1932, 15, 193—196).—In rabbits fed with "okara" (soya-bean oil?)

the bile is richer in glycocholic acid than in those fed on clover.

F. O. HOWITT.

Bilirubin and the van den Bergh reaction. F. S. FOWWEATHER (Biochem. J., 1932, 26, 165—182).—Cryst. bilirubin from gallstones, and its Na and NH₄ salts, give delayed van den Bergh reactions in serum. The pigment pptd. from the mother-liquor gives a direct reaction, as also do pigments obtained from fresh bile with and without acidification. These are regarded as free acid and salt. Directly reacting salts of bilirubin are pptd. from dil. alkaline solutions of cryst. bilirubin by alkaline salts. Bilirubin is regarded as existing in two forms, giving rise to two series of salts.

A. COHEN.

**Poison of the skin-glands of the marble sala-
mander (*Molge marmorata*).** O. GESSNER (Arch. exp. Path. Pharm., 1932, 165, 350—374).—The secretion consists of a volatile, strongly irritating substance and two non-volatile constituents, one of which possesses agglutinating activity, the other being the main toxic element and having the following properties. It induces local irritation on superficial application, whilst parenteral administration causes intense hæmolysis, contraction of striped and smooth muscle, and finally death, the min. lethal dose for mice being 0.0054 mg. per g. The physical properties of this substance indicate a "sapotoxin."

F. O. HOWITT.

Mucoprotein as a normal constituent of gastric juice. D. R. WEBSTER and S. A. KOMAROV (J. Biol. Chem., 1932, 96, 133—142).—Gastric juice from dogs with gastric fistulæ contains a mucoprotein which has a higher N content and a lower reducing val. after hydrolysis than mucoproteins such as mucin from the submaxillary gland. Its non-identity with the mucin from the mucus of the gastric surface epithelium indicates a secretory product of the gastric glands. The relation of the mucin to pepsin is discussed.

F. O. HOWITT.

Gastric acidity in normal individuals. J. LERMAN, F. D. PIERCE, and A. J. BROGAN (J. Clin. Invest., 1932, 11, 155—165).—The average free acidity (after stimulation with histamine and EtOH) was 40.4 c.c. of 0.1N-acid, and the average total acidity 50.1, with no correlation between acidity and age. An acidity was correlated with basal metabolism.

CHEMICAL ABSTRACTS.

Does wool-fat contain "hydroxycholesterol"? I. LIFSCHUTZ (Arch. Pharm., 1932, 270, 205—207).—Substances described as "hydroxycholesterol" and the "saturated cyclic alcohol" (Frick, G.P. 458,198) are isocholesterol and the (aliphatic) derivative of lanoceric acid (A., 1896, i, 522), respectively.

R. S. CAHN.

**Urinary protein excretion as a physico-
chemical problem.** F. MAINZER (Naturwiss., 1932, 20, 264—268).—The selective permeability of the human kidney to serum-albumin and -globulin, hæmoglobin, and Bence-Jones protein is discussed with reference to their physico-chemical properties and also to those which possibly function in the living membrane.

F. O. HOWITT.

Bromide retention. K. O. MOLLER (Arch. exp. Path. Pharm., 1932, 165, 244—260).—The urinary

Cl: Br ratio in rabbits is identical with the corresponding serum val. Depression of the Cl' storage produces a marked retention of injected Br' in order to normalise the osmotic pressure and halogen level of the serum. Up to 75% of the serum-Cl' in the rabbit can be replaced by Br' without causing death. Administration of theophylline to Br'-treated animals results in an increased excretion of Br' and, to an equal degree, of Cl', whereas with I'-treated animals no increased excretion of I' occurs.

F. O. HOWITT.

Determination of dialkylbarbituric acids in urine. M. KLINGENFUSS and M. REINERT (Arch. exp. Path. Pharm., 1932, 165, 416—419).—The urine is pptd. by basic Pb acetate, excess of Pb removed by CO_2 , and the Et_2O extract extracted with 0.1N-NaOH, the aq. extract being saturated with CO_2 and re-extracted with Et_2O . The second Et_2O extract is boiled with C, and the filtrate evaporated in presence of C_6H_6 , yielding a cryst. residue which is weighed and identified by its m. p. Amounts of 10—100 mg. per litre are accurately determined by this method.

F. O. HOWITT.

Determination of urea in urine by means of hydrolysis. S. L. LEIBOFF and B. S. KAHN (J. Lab. Clin. Med., 1931, 17, 77—78).—The urine is treated with permutoite to remove NH_3 , acidified, and digested under pressure for 10 min.; the N content is then determined by direct nesslerisation.

CHEMICAL ABSTRACTS.

Determination of [urinary] acetone by a steam-distillation method. L. DE SAINT-RAT and T. MENA (Bull. Soc. Chim. biol., 1932, 14, 317—326).—The apparatus and technique of the method are described. The method consists in treating the urine with basic Pb acetate and aq. NH_3 , filtering, and passing steam through 5 c.c. of the filtrate for several min. The COMe_2 is collected in H_2O and determined iodometrically. β -Hydroxybutyric acid is determined by double treatment with $\text{K}_2\text{Cr}_2\text{O}_7$ of the solution left after the COMe_2 is removed, the COMe_2 formed being determined as before.

A. LAWSON.

Determination of 8-hydroxyquinoline in urine in presence of phenol. F. LUTHER (Deut. med. Woch., 1931, 57, 1739; Chem. Zentr., 1932, i, 108).—Fission of 8-hydroxyquinoline takes place and part is eliminated as PhOH . An analytical method is described.

A. A. ELDRIDGE.

Determination of glycuronic acid in urine and blood. M. HAENDEL (Rev. asoc. med. Argentina, 1929; 42, 215—220).—The glycuronic acid is pptd. from urine or deproteinised (Seegen) blood with ammoniacal $\text{Pb}(\text{OAc})_2$; the ppt. is treated with HCl and the furfuraldehyde distilled in steam. KHSO_3 is added to the distillate and the excess determined iodometrically.

CHEMICAL ABSTRACTS.

Bromine reaction of pregnancy urine. A. R. ARMSTRONG and E. WALKER (Biochem. J., 1932, 26, 143—146).—The isolation of the substance in the urine of pregnancy giving Knoop's Br-water test is described. It is identified as histidine. The test is regarded as sp. for histidine and *N*-methylhistidine.

A. COHEN.

Detection of diastase in urine. J. WOHLGEMUTH (Biochem. Z., 1932, 247, 465).—The objection raised by Herzfeld (this vol., 79) can be overcome by the use of excess of I. There is no need to prepare an osazone, but the buffer solution must be prepared exactly as originally (A., 1930, 1207) described.

W. MCCARTNEY.

Effect of intensive function of sweat glands on the excretion of uric acid and phosphate in the urine. J. MELKA (Pflüger's Archiv, 1931, 228, 666—670; Chem. Zentr., 1932, i, 544).—Activity of the sweat glands is accompanied by increase in urinary uric acid and PO_4''' .

A. A. ELDRIDGE.

Spectrophotometric determination of urobilin and urobilinogen. L. HEILMEYER (Z. ges. exp. Med., 1931, 76, 220—235; Chem. Zentr., 1932, i, 108).—Urobilin is not a chemical individual. Its determination is possible only by way of urobilinogen by Terwen's method. The quant. absorption spectrum of the urobilinogen-MeCHO condensation product is const. A method for the determination of urobilinogen and the sum urobilin + urobilinogen is described.

A. A. ELDRIDGE.

Excretory function of the liver. I. Uric acid. T. MATSUDA (Japan. J. Gastroenterol., 1931, 3, 293—307).—Of rabbits, the blood contains 1.2—1.5, urine 9—13, and bile 0.7—1.1 mg. of uric acid per 100 c.c. After intravenous injection of uric acid the rises in blood and bile are parallel. Kidney failure is incompletely compensated by increased elimination of uric acid by the liver.

CHEMICAL ABSTRACTS.

Physiology of excretion in a blood-sucking insect, *Rhodnius prolixus* (Hemiptera, Reduviidae). I. Composition of the urine. III. Mechanism of uric acid excretion. V. B. WIGGLESWORTH (J. Exp. Biol., 1931, 8, 411—427, 443—451).—I. The urine is alkaline and contains large quantities of NaCl and KCl , with traces of urea, HCO_3' , SO_4''' , and uric acid; after the first day it becomes semi-solid and contains urates, Ca , Mg , SO_4''' , PO_4''' , and creatine. All of the N is excreted as uric acid.

CHEMICAL ABSTRACTS.

Phospholipins in the blood of infants and children. I. N. KUGELMASS and E. GREENWALD (Amer. J. Dis. Children, 1931, 42, 1134—1136).—The average val. (2.5 mg. per 100 c.c.) tends to remain const. irrespective of changes in tissue-phospholipin in disease. The val. may decrease in marasmus.

CHEMICAL ABSTRACTS.

Alkalosis in the vomiting of infancy. M. MAIZELS (Arch. Dis. Childhood, 1931, 6, 293—302).—The obstructive vomiting of infancy is unaccompanied by alkalosis or marked reduction in blood-Cl'. An increase in plasma- HCO_3' and a decrease in plasma- and cell-Cl' may accompany pyloric obstruction.

CHEMICAL ABSTRACTS.

Glutathione content of anti-anæmic substances used in the treatment of pernicious anæmia. R. FLEMING (Biochem. J., 1932, 26, 461—463).—Commercial anti-anæmic products contain glutathione mostly in the oxidised form, whilst in fresh tissue (gastric mucosa of the pig) it is present more in the reduced form.

S. S. ZILVA.

Certain metals in the prevention of nutritional anæmia in the rat. J. M. ORTEN, F. A. UNDERHILL, and R. C. LEWIS (J. Biol. Chem., 1932, 96, 1—9).—Cu, but not Mn, Co, Ni, or Zn, either alone or admixed, has the power of preventing nutritional anæmia in rats fed a milk diet supplemented by inorg. Fe. F. O. HOWITT.

Action of cinchophen on the liver tract. E. P. C. WHITE (J. Lab. Clin. Med., 1931, 17, 17—21).—Normal vals. were obtained for blood-non-protein-N, -uric acid, and -creatinine, icterus index, van den Bergh reaction, glucose and fructose tolerance test during continuous administration of cinchophen to arthritic patients who had no liver or pancreatic dysfunction. CHEMICAL ABSTRACTS.

Cholesterol content of lipins of carcinomas. R. WILLHEIM and G. FUCHS (Biochem. Z., 1932, 247, 297—305).—Lipin from carcinoma cells (chiefly from liver) contains more cholesterol than does that from cells of normal parenchymatous organs. The difference is due to the sp. chemical composition of the cells. The connective tissue of tumours likewise has a high cholesterol content. W. MCCARTNEY.

Hyperplastic reaction of the skin to thiol and its significance in neoplasia. S. P. REIMANN (Amer. J. Cancer, 1931, 15, 2149—2168).—The SH-SO₂ equilibrium forces cells to divide beyond their normal division levels. Malignancy is discussed in relation to stimulus by -SH and the chemical groups of chromosomes. CHEMICAL ABSTRACTS.

Analysis of tumour resistance. I. Enzymes. N. WATERMAN (Z. Krebsforsch., 1931, 34, 313—326; Chem. Zentr., 1932, i, 251).—Inactive pancreatic lipase is activated by serum at 60°. The activity of the substance in the serum is diminished by reduction with HSO₃', but increased by oxidation with H₂O₂. A. A. ELDRIDGE.

Modifying the respiration of tumours. I. By amino-acids. B. KIRSCH (Biochem. Z., 1932, 247, 354—364; cf. this vol., 420, 643).—The respiration of fresh and old tissue from Jensen rat sarcoma and Ehrlich mouse carcinoma is sometimes increased by serine and by α -aminobutyric acid, whilst valine also occasionally increases slightly the respiration of the sarcoma tissue. Other NH₂-acids (and sarcosine) which increase respiration in healthy tissue (kidney, retina) have no effect on that of the diseased tissue. W. MCCARTNEY.

Proteins of the lens in cataract. T. TSUJI (J. Biochem. Japan, 1932, 15, 33—64).—The proteins of the lens of the ox increase with increasing age. Experimental cataract in rabbits is accompanied by a decrease in total proteins and in β -crystallin (A., 1893, ii, 424) and by an increase in the "albumoid" and α -crystallin. In such animals and also in human cases the cysteine content is decreased and cystine, which normally is absent, appears. Other changes in the physico-chemical character of the lens-proteins are described. F. O. HOWITT.

Iodine content of food and incidence of goitre. L. SCHEFFER (Biochem. Z., 1932, 247, 418—423).—Although goitre is prevalent (10% of the population suffer) in Pécs (Hungary) the food and H₂O consumed

by the inhabitants contain more I than is required to prevent the onset of the disease. Hence doubt is cast on the validity of the theory that goitre is caused by lack of I. W. MCCARTNEY.

Biological value, iodine content, histological, structural, and clinical picture of goitre. A. JORDI (Arch. Int. Med., 1932, 49, 541—577).—26 cases of goitre in California are described. Adenomas with hyperfunction differ biologically from diffuse goitre of primary Basedow's disease, the relation between biological activity and I content being const. only in the former. A. LAWSON.

Gastric secretion in exophthalmic goitre and myxoedema. J. LERMAN and J. H. MEANS (J. Clin. Invest., 1932, 11, 167—182).—The frequency of anacidity is out of proportion to the lowered average acidities, suggesting a threshold of gastric secretion. In exophthalmic goitre there is correlation between the incidence of achlorhydria, but not between gastric acidity and other factors. CHEMICAL ABSTRACTS.

Congestive heart failure. XIII. Relation of dyspnoea of exertion to oxygen saturation and acid-base condition of the blood. G. E. CULLEN, T. R. HARRISON, J. A. CALHOUN, W. E. WILKINS, and M. M. TIMS. XIV. Orthopnoea; relation to ventilation, vital capacity, oxygen saturation, and acid-base condition of arterial and jugular blood. J. A. CALHOUN, G. E. CULLEN, T. R. HARRISON, W. L. WILKINS, and M. M. TIMS (J. Clin. Invest., 1931, 10, 807—831, 833—855).—XIII. With mild exercise in congestive heart failure there are no significant changes in blood-p_H, CO₂ content and tension. Administration of NH₄Cl caused a large decrease in p_H and slight increase in ventilation. Max. exertion in normal subjects caused reduction in p_H and CO₂ content.

XIV. The increased respiratory rate is not due to changes in oxidation or acid-base balance.

CHEMICAL ABSTRACTS.

Physiology, correlations, and technique of the van den Bergh reaction, icterus index, and quantitative serum-bilirubin. N. W. ELTON (J. Lab. Clin. Med., 1931, 17, 1—13).—A direct positive van den Bergh reaction is obtained when the suspensoid colloid and the unstable crystalloid form of bilirubin are both present in the blood-serum. Minute quantities of the crystalloid form suffice. The lengths of the delay periods indicate intermediate stages in the transition nascent \rightarrow crystalloid bilirubin. The icterus index is not directly proportional to the serum-bilirubin. At an icterus index of 16.6, colloidal bilirubin may accumulate in the bloodstream; this causes no increase in colour intensity until the physical change indicated by development of the immediate type of van den Bergh reaction occurs. Methods for carrying out the three determinations in continuity with a small quantity of serum are described. CHEMICAL ABSTRACTS.

Ketosis. I. Sexual variation in starvation ketosis. H. J. DEUEL, jun., and M. GULICK (J. Biol. Chem., 1932, 96, 25—34).—During fasting a greater degree of ketosis is developed in the female than in the male, as indicated by the excretion of ketones in the

urine and by the fall in CO_2 -combining power of the blood. The decrease and subsequent increase in N excretion are due to the sparing action of the residual tissue-glycogen and, whilst occurring in both sexes, are more prolonged in the male. F. O. HOWITT.

Chemistry of the blood of dairy cows before and after parturition and its relation to milk-fever. L. T. WILSON and E. B. HART (J. Dairy Sci., 1932, 15, 116—131).—The Ca and P of cows' blood falls slightly within the first 3 days of calving, the effect being more definite in the case of second and later calves. The essential factor in milk-fever is a deficiency of blood-Ca. Plasma-phosphatase varies considerably about the time of calving. Phosphatase activity in milk is normally higher than that of plasma and in heavily milking cows is greater at the end than at the beginning of lactation. A. G. POLLARD.

Potassium and chronaxie in experimental muscular degeneration. A. LEULIER, B. POMME, and A. RICHARD (Compt. rend., 1932, 194, 1280—1282).—The degeneration in the muscles of rabbits which follows section of the sciatic is accompanied by an increase in chronaxie and a simultaneous but proportionately smaller decrease in K content. W. O. KERMACK.

Plasma-proteins in relation to blood hydration. VI. Serum-proteins in nephritic oedema. VII. Proteins in acute nephritis. J. P. PETERS, F. S. BRUCKMAN, A. J. EISENMAN, P. N. HALD, and A. M. WAKEMAN. VIII. Serum-proteins in heart disease. S. A. PAYNE and J. P. PETERS. IX. Serum-proteins in the terminal stages of renal disease. J. P. PETERS, F. S. BRUCKMAN, A. J. EISENMAN, P. N. HALD, and A. M. WAKEMAN (J. Clin. Invest., 1931, 10, 941—973; 1932, 11, 97—102, 103—112, 113—122).—VI. Reduction of serum-protein at the expense of the albumin fraction is common in nephritis with non-cardiac oedema, but not in idiopathic nephrosis. The chief causes of serum-protein deficiency are albuminuria and depletion of protein stores in the body.

VII. Lowering of serum-albumin is referable to leakage of albumin into the urine or to malnutrition. High serum-globulin is frequently found.

VIII. Oedema is generally associated with albumin deficiency referable to malnutrition.

IX. Reduction of serum-proteins, particularly the albumin fraction, is common, without correlation between albumin deficiency and oedema.

CHEMICAL ABSTRACTS.

Comparison of the racemisation curves for urinary, oedema fluid, and blood-plasma proteins. J. W. CAVETT and R. B. GIBSON (J. Clin. Invest., 1931, 10, 857—867).—The rate of racemisation of albumins and pseudoglobulins of nephritic urines is the same as that of the corresponding serum-proteins. Blood-pseudoglobulin of a nephritic patient gave a rate identical with that of normal blood.

CHEMICAL ABSTRACTS.

Nutritional oedema. Relation of the serum-proteins to the occurrence of oedema and to the effect of certain inorganic salts. A. A. WEECH and S. W. LING (J. Clin. Invest., 1931, 10, 869—888).—Oedema appeared at serum-albumin levels below

2.5, but not above 2.9, g. per 100 c.c.; there was no relation between globulin and oedema. Administration of NaCl and NaHCO_3 depressed Cl' excretion; Na is more nearly related than Cl' to the cause of oedema. CHEMICAL ABSTRACTS.

Variations in serum-calcium, -protein, and -inorganic phosphorus in early and late pregnancy, during parturition and the puerperium, and in non-pregnant women. W. F. OBERST and E. D. PLASS (J. Clin. Invest., 1932, 11, 123—127).—Correlation between serum-Ca and -protein in pregnant and puerperal women disappears in late pregnancy and parturition. No correlation between serum-Ca and -P was observed.

CHEMICAL ABSTRACTS.

Mineral exchanges in man. III. Mineral metabolism during treatment of polycythaemia vera. S. H. BASSETT, T. KILLIP, and W. S. MCCANN (J. Clin. Invest., 1931, 10, 771—785).—Administration of acetylphenylhydrazine reduced the blood vol., cell vol., haemoglobin, and red cells. The large increase in endogenous Fe metabolism did not result in loss of body-Fe. During increased Fe excretion (probably haemoglobinuria) there is a decrease in faecal Fe which more than compensates for that found in the urine. Marked loss of N accompanies blood destruction. No significant changes in P, Mg, and Ca could be demonstrated. CHEMICAL ABSTRACTS.

Experimental hypotrophic rickets. G. MOURIQUAND, A. LEULIER, and L. WEILL (Compt. rend., 1932, 194, 1201—1202).—Hypotrophic rickets may be produced experimentally in animals placed on Pappenheimer diet, no. 85, if a "defixing" agent such as Sr or Mg is administered. This results in a loss of Ca from the animals and a retardation of growth or actual loss of wt. Rickets may thus be produced in the absence of rapid growth. W. O. KERMACK.

Calcium and phosphorus metabolism in late rickets. G. C. LINDER and D. G. M. VADAS (Lancet, 1931, 221, 1124—1126).—In a case of late rickets with a partial hyperparathyroid syndrome excision of the parathyroid relieved pain without affecting the Ca-P metabolism. L. S. THEOBALD.

Phosphorus and rickets. I. Sources of inorganic phosphorus in the treatment of experimental rickets. R. LECOQ and F. VILLUIS (J. Pharm. Chim., 1932, [viii], 15, 393—397).—With rats, the antirachitic activity of CaHPO_4 , Na_2HPO_4 , $\text{Ca}_2(\text{HPO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2$, NaH_2PO_4 , and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ falls in this order, the last two salts being inactive even in the highest concn. studied (3% of diet). $\text{Zn}_3(\text{PO}_4)_2$, in so far as it can be tolerated by the animals, is inactive. A. LAWSON.

Calcium and phosphorus studies. I. Effect of calcium and phosphorus of the diet on tetany, serum-calcium, and food intake of parathyroidectomised rats. II. Effect of diet and of viosterol on the tetany and on the serum-calcium of parathyroidectomised rats. III. The source of excess serum-calcium in viosterol hypercalcaemia. D. H. SHELLING (J. Biol. Chem., 1932, 96, 195—214, 215—228, 229—243).—I. In parathyroidectomised rats low-Ca and high-P diets produce

tetany, whilst high-Ca and low-P diets relieve it and the accompanying anorexia. Serum-Ca depends on Ca and P intake and on severity of tetany. Excess P, administered as Na_2HPO_4 or $\text{Na}_2\text{P}_2\text{O}_7$, causes anorexia, but is ineffective as NaPO_3 or NaH_2PO_2 .

II. With low-Ca diets, parathyroid tetany is relieved by fairly large doses of viosterol, and such doses can raise serum-Ca from tetanic to hypercalcaemic levels even when no Ca or P is ingested. The activity of viosterol may therefore be independent of the parathyroid. Injection of parathormone into rachitic rats causes further bone decalcification.

III. Viosterol hypercalcaemia may be induced in rats fed on Ca-free diets, and more readily if P is also absent. It is accompanied by excess Ca excretion by the kidney in the latter case and as phosphate in the faeces if excess P is fed. The animals show histological and X-ray evidence of bone decalcification.

J. B. BATEMAN.

Calcium and phosphorus metabolism. VI. In hypoparathyroidism and chronic steatorrhoea with tetany. J. C. AUB, F. ALBRIGHT, W. BAUER, and E. ROSSMEISL. XV. In various metabolic diseases. J. C. AUB and R. F. FARQUHARSON (J. Clin. Invest., 1932, 11, 211—234, 235—248).—VI. In tetany associated with chronic steatorrhoea there is low serum-P and high partition of P in the urine as compared with the faeces; disordered Ca and P metabolism is due to decreased Ca absorption. Thyroid medication in hypoparathyroidism causes a rise in serum-Ca and increased urinary excretion of Ca and P. In hypoparathyroidism the Ca on being removed from the bones by the thyroid hormone is below the level necessary for excretion.

XV. Ca and P may be liberated in one part and deposited in another part of a bone. In chronic bone diseases and jaundice the variations from normal in Ca and P excretion were slight.

CHEMICAL ABSTRACTS.

Accumulation of iron in tuberculous areas. II. V. MENKIN (J. Exp. Med., 1932, 55, 101—108).—Repeated intravenous injection of FeCl_3 increases the survival time of tuberculous rabbits.

CHEMICAL ABSTRACTS.

Metabolism of the Chinese. I. Body surface. H. NECHELES and C. T. LOO. II. Basal metabolism. H. NECHELES. III. Specific dynamic action. H. NECHELES and C. T. LOO. IV. Basal metabolism and methods. H. NECHELES (Chinese J. Physiol., 1932, 6, 129—152, 153—174, 175—200, 201—224).

Technique for studying metabolism of rats. V. KORENCHESKY and M. DENISON (Biochem. J., 1932, 26, 147—150).

Food requirements of pregnancy in swine. H. H. MITCHELL, W. E. CARROLL, T. S. HAMILTON, and G. E. HUNT (Illinois Agric. Exp. Sta. Bull., 1931, no. 375, 467—504).—The rate of deposition of nutrients in the contents of the uterus with the advancing time of gestation is expressed mathematically. In the gilts examined no tendency was indicated for the retention of nutrients in the body increase as the period of gestation advanced. A. G. POLLARD.

Effect of amino-acids on respiration of tissues. V. β -Aminopropionic acid and α -aminobutyric acid. B. KISCH (Biochem. Z., 1932, 247, 365—370; cf. this vol., 420).—The respiration of tissue from the kidney, liver, and retina of the rat, guinea-pig, rabbit, cat, and ox is increased by β -aminopropionic and α -aminobutyric acid. The former acid is less active than is alanine, especially in the case of old tissue from rat kidney. In general, butyric acid is less active than is its α - NH_2 -derivative. W. MCCARTNEY.

Change of reaction of muscle in relation to development of tension and chemical change. O. MEYERHOF, W. MOHLE, and W. SCHULZ (Biochem. Z., 1932, 246, 285—318).—At a given pressure of CO_2 muscle tissue is not isohydric with a Ringer's solution containing an equiv. amount of HCO_3^- . The deviation from Hasselbalch's equation is due to a change of p_K (CO_2) caused by the presence of buffers. The large CO_2 -uptake of iodoacetic acid-poisoned muscle in rigor from HCO_3^- -Ringer's solution is due to the diffusion of the buffer-substances into the surrounding fluid. H. W. DUDLEY.

Yeast and casein supplements to corn and soya-bean rations for rats and swine. C. L. SHREWSBURY, C. M. VESTAL, and S. M. HAUGE (J. Agric. Res., 1932, 44, 267—274).—Casein supplements a maize but not a soya-bean ration, whilst dried yeast does not supplement either to an economic extent. Cooked beans are of greater nutritive val. than raw beans. P. G. MARSHALL.

Feeding experiments with decomposition products of proteins. S. MAYEDA (Proc. Imp. Acad. Tokyo, 1932, 8, 98—101).—Normal growth was obtained for 6 months in rats fed on a diet containing 8% of H_2SO_4 -hydrolytic product of fish protein and 8% of $\text{Ba}(\text{OH})_2$ -hydrolytic product, but devoid of protein. Oryzanin or EtOH extract of yeast was used as the source of vitamin-B. Growth was also maintained for 50 days with acid decomp. products alone, provided that 3% of *r*-tryptophan was added. P. G. MARSHALL.

Optimum protein content of rations for growing chicks. R. W. SWIFT, A. BLACK, L. VORIS, and E. M. FUNK (Poultry Sci., 1931, 10, 288—298).—The digestibility of protein was not markedly influenced by the level of protein intake. When the ration contained 14.74—15.31% of protein the protein, but not the whole ration, was most efficiently utilised. With 14.74—24.83% of protein the feed was most efficiently utilised to produce gain in wt., whereas greatest total gain in wt. was produced by rations containing 20—22% of protein. Data on N-retention, digestibility, and composition of feed are tabulated. P. G. MARSHALL.

CHEMICAL ABSTRACTS.

Metabolism of phospholipins. V. Relationship between the amount of fat ingested and the degree of unsaturation of the phospholipins and neutral fat in the tissues of the rat. R. G. SINCLAIR (J. Biol. Chem., 1932, 96, 103—125).—The addition of cod-liver oil to the diet of rats on a fat-free diet results in a marked and proportional increase in the I val. of the phospholipin fatty acids, especially of those of the liver, but in only a slight increase in that of the neutral fatty acids. This phenomenon also

occurs with lard and, to a smaller extent, with coconut oil. The bearing of this unsaturation on growth and fat metabolism is discussed. F. O. HOWITT.

Autolysis and production of acetaldehyde in adrenalectomised cats. A. SIMON and B. KOLONITS (Biochem. Z., 1932, 247, 476—481).—In the livers of the cats autolysis is more extensive and in their muscles the production of MeCHO from glycogen is less pronounced than with normal cats.

W. MCCARTNEY.

Micro-electric investigation of intestinal resorption. Transport of sugar in the portal vein and in the lymph. R. KELLER (Biochem. Z., 1932, 247, 466—473).—The importance of the liver-glycogen as a source of energy has been overestimated, since the lymph is also concerned, sometimes to a greater extent than is the portal vein, in the transport of sugar from the intestine.

W. MCCARTNEY.

Nutritional value of bread. III. Assimilation of the carbohydrate of various kinds of bread in the animal body. I. ABELIN and A. BIERBOHR (Biochem. Z., 1932, 247, 429—444; cf. A., 1931, 648).—As regards the resorption by rats of the carbohydrate which they contain white and wholemeal breads do not differ. In those breads about 99% and in other kinds of bread (rye etc.) 93—97% of the carbohydrate is resorbed. No matter which kind of bread is consumed, the resulting storage of glycogen in the rats is about the same, but differences are observed in the resulting changes in the amounts of glycogen in the liver. The causes of these differences are unknown. W. MCCARTNEY.

Metabolism of normal and tumour tissue. V. Carbon dioxide retention of serum: its use in the measurement of tissue glycolysis. F. DICKENS and F. ŠMER (Biochem. J., 1932, 26, 90—98).—The CO₂ retention of normal and dialysed serum and of Warburg's "serum-model" is approx. linearly related to p_H change between p_H 7.0 and 7.7. This result is applicable to the measurement of production or consumption of org. acids by tissues in serum.

A. COHEN.

Carbohydrate metabolism in birds. Site of the biochemical lesion in avian polyneuritis. N. GAVRILESCU, A. P. MEIKLEJOHN, R. PASSMORE, and R. A. PETERS (Proc. Roy. Soc., 1932, B, 110, 431—447).—Various parts of the brain of normal pigeons and of pigeons suffering from advanced B₁-avitaminosis were examined for O₂-uptake in Ringer-PO₄ solution alone and in presence of glucose, lactate, or succinate. No significant differences between normal and avitaminosis brain-tissue occur in the residual oxidation, the val. of which varies somewhat, due to varying amounts of unknown substances present as substrate in addition to the greater proportion of preformed lactic acid. The O₂-uptake for both normal and avitaminosis brain attains a max. with approx. 0.037*M*-lactate, whilst with succinate the max. is at approx. 0.18*M*. Its val. in 0.037*M*-lactate is decreased in avitaminosis both for cerebral and optic lobe tissue, a return to normal occurring on addition of vitamin-B₁ concentrates. Similar phenomena occur with glucose

but not with succinate. Addition of B₁ concentrates to normal tissue in presence of lactate results in only a slight increase of O₂-uptake. Hence in the pathological condition of avian polyneuritis there occurs a lesion not affecting all oxidase systems, but associated with lactate. The vitamin cannot be considered as part of the respiratory enzyme or cytochrome system, although it forms an integral part of an oxidase system and constitutes a true factor in the intermediary metabolism of carbohydrate.

F. O. HOWITT.

Bile acids and carbohydrate metabolism. XIV. Production of glycogen in the liver by bile acids given together with adrenaline or insulin. Influence of the vegetative nervous system. XV. Production of glycogen in muscle by bile acids following section of the splanchnic nerves. T. MIKI (Biochem. Z., 1932, 247, 445—458, 459—464; cf. this vol., 639).—XIV. In rabbits administration of adrenaline increases and that of insulin decreases the production of glycogen in the liver if the splanchnic nerves are cut. Cholic acid, administered at the same time, causes increase in both cases, but the increase with adrenaline is much greater than is that with insulin and exceeds that due to cholic acid alone. The results of section of the vagus nerves are similar but much less pronounced. It follows that, in the liver, mobilisation of glycogen is dependent on increased sympathetic tonus and synthesis of glycogen on decreased sympathetic tonus. Possibly the effect produced by insulin is due to increased peripheral oxidation of sugar resulting from over-stimulation of the vagus nerves which increases the secretion of insulin in the pancreas. The stimulating action of cholic acid and of adrenaline depends more on the tonus of the sympathetic than on that of the vagus nerves, whilst the opposite is true for the action of insulin. Moreover, there is synergy between the actions of cholic acid and adrenaline, but antagonism between those of the acid and insulin.

XV. Production of glycogen in the muscles of rabbits is increased by administration of small amounts of adrenaline or of cholic acid if the splanchnic nerves are cut. Simultaneous administration of the two substances with section of these nerves results in a production of glycogen in the muscles which is greater than that due to adrenaline alone but less than that due to cholic acid alone.

W. MCCARTNEY.

Ligation of the parotid duct and carbohydrate metabolism. L. M. ZIMMERMAN and S. SOSKIN (Arch. Int. Med., 1932, 49, 663—665).—Ligation of the parotid ducts of totally depancreatized dogs has no effect on the carbohydrate metabolism as indicated by the N and glucose content of the urine.

A. LAWSON.

Carbohydrate changes during anaerobiosis of mammalian muscle. G. T. CORI (J. Biol. Chem., 1932, 96, 259—269).—Analyses on extirpated gastrocnemii of rats before and after anaerobiosis in N₂ 37° showed that glycogen breakdown is nearly balanced by formation of lactic acid and hexose-phosphate. There was no accumulation of hexose-diphosphate during anaerobiosis. J. B. BATEMAN.

Glycogenesis. F. RATHERY, S. GIBERT, and Y. LAURENT (Bull. Soc. Chim. biol., 1932, 14, 327—368).—In dogs fed on normal diets, in starved animals, and in those in which hepatic glycogen has almost completely disappeared, the administration of large amounts of glucose causes in most cases an increase in hepatic glycogen, but sometimes a decrease. The glucose content of the portal vein shows the liver to be receiving glucose, but a comparison of the glucose content of the portal vein with the amounts of hepatic and muscle-glycogen shows that complete transformation of the glucose into glycogen does not take place. There are probably sources of stored carbohydrate in the liver other than glycogen.

A. LAWSON.

Physiological behaviour of the trioses and of related compounds. I. Increase of liver-glycogen after feeding methylglyoxal and pyruvic acid. II. Increase of liver-glycogen after feeding glyceraldehyde. R. STOHR (Z. physiol. Chem., 1932, 206, 15—24, 211—216).—I. COMe-CHO fed to fasting rats in doses of 100 mg. per 100 g. body-wt. produces an increase in liver-glycogen; with 150—200 mg. glycogen is strongly diminished, probably owing to lactic acid formation. In general COMe-CHO was absent from the blood 3 hr. after the dose; the blood-sugar did not vary to any extent.

II. The feeding of 0.2—0.3 g. of glyceraldehyde per 100 g. of body-wt. to fasting rats produced an increase in liver-glycogen (from 0.051 to 0.792 g. per 100 g. of liver). The blood-sugar was either unchanged or showed a large increase; glyceraldehyde had disappeared from the blood in 3 hr. The phosphoric-molybdic acid reagent of Folin gives a blue colour with glyceraldehyde, which can then be determined by titration with KMnO_4 to disappearance of the colour.

J. H. BIRKINSHAW.

Action of methylglyoxal on acetoacetic acid. III. The ketol ($\text{C}_6\text{H}_{10}\text{O}_3$) as glycogen-former. R. STOHR and M. HENZE (Z. physiol. Chem., 1932, 206, 1—14; cf. A., 1931, 69).—After administration of the ketol $\text{C}_6\text{H}_{10}\text{O}_3$ to fasting rats the liver-glycogen increased considerably; the glycogen storage was independent of the quantity resorbed. Higher doses of the ketol, by their toxic action, lowered the glycogen content. The ketol is probably first oxidised to the triketone COMe-CO-CH₂-COMe, which breaks up into two 3-C units both capable of producing glycogen. The ketol produces a slight increase in the blood-sugar. A method was evolved for the determination of the ketol in blood in presence of blood-sugar.

J. H. BIRKINSHAW.

Behaviour of the carbohydrates and lactic acid of the muscle of haddock (*Gadus aeglefinus*) after death. N. L. MACPHERSON (Biochem. J., 1932, 26, 80—87).—Immediately after death the glycogen content of haddock muscle is 0.4—0.6%. This rapidly falls in a few hr. and then more slowly to <0.1 of the original val. in 24 hr. The sugar content is 0.05% if extracted with aq. EtOH, and 0.01% if determined by adsorption on CuSO_4 and CaO, or extracted with $\text{CCl}_3\text{CO}_2\text{H}$. Acid hydrolysis doubles the reducing power of EtOH extracts. The lactic acid content is 0.08%, which increases to 0.17% in

40 hr. The lag in lactic acid production during glycogen disappearance indicates an intermediate which is not a polysaccharide, since no increase in the original vals. of free sugar before and after hydrolysis is observed.

A. COHEN.

Lactic acid production in isolated rabbit's intestine. M. TAKAHASHI (Sci-i-kwai Med. J., 1931, 50, No. 2, 24—85).—Drugs which stimulate intestinal movement produce more lactic acid than those which depress it; in both cases the amount was subnormal. Except with acetylcholine and adrenaline, the intestinal movement and lactic acid production are parallel. Except with acetylcholine the p_H of the liquid is proportional to the amount of lactic acid found. The lactic acid content of the small intestine varies with the locality; the average is 92.18 mg. per 100 g.

CHEMICAL ABSTRACTS.

Lactic acid metabolism. II. Lactic acid content of the blood of different animals. F. MATAKAS (Arch. exp. Path. Pharm., 1932, 165, 221—229).—Rabbits, pigeons, and fowls show a greater variation in the resting blood-lactic acid level than do cats, dogs, goats, or sheep. The variations are not due to the experimental conditions, but are characteristic of the animal. Hence these three animals are unsuitable for the study of lactic acid metabolism.

F. O. HOWITT.

Relationship between chemical structure and physiological response. I. Conjugation of substituted benzoic acids. A. J. QUICK and M. A. COOPER (J. Biol. Chem., 1932, 96, 83—101).—Various derivatives of BzOH, α -naphthoic acid, and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ were neutralised, fed to dogs, and the conjugation of the compounds excreted in the urine was determined. Substitution of BzOH in the *o*-position greatly inhibits its conjugation with glycine, the effect being independent of the nature of the group, whereas for conjugation with glycuronic acid an acidic group diminishes and a basic group increases the excretion, whilst a neutral group has little effect. An opposite but less marked effect occurs with *m*-substitution, whilst *p*-substitution more closely resembles the *o*-. The dissociation const. of the substituted BzOH is related to the rate at which it is excreted combined with glycuronic acid.

F. O. HOWITT.

Site of the synthesis of hippuric acid and phenylacetic acid in the dog. A. J. QUICK (J. Biol. Chem., 1932, 96, 73—81).—Hippuric acid is synthesised by the action of an enzyme ("hippuricase"), which in the dog is present only in the kidney but in the rabbit occurs in other organs. "Phenylaceturicase," the enzyme which produces phenylacetic acid, occurs in the kidney and also in other organs of the dog. Injection of hippuric acid into nephrectomised dogs is followed by a gradual disappearance of the acid from the blood and replacement by BzOH and glycuronic acid monobenzoate. Hence there exists a separate enzyme ("histozyme") for the hydrolysis of hippuric acid.

F. O. HOWITT.

Behaviour of lactacidogen in muscular work. G. KRAFT (Z. physiol. Chem., 1932, 206, 155—167).—In confirmation of previous results (this vol., 188),

exhaustive stimulation of isolated frog's gastrocnemius in summer decreases, and in winter increases the lactacidogen. In the living frog, exhaustive stimulation always decreases the lactacidogen. After short stimulation of the living frog there is an increase in lactacidogen accompanied by lactic acid accumulation and fatigue. With continued stimulation the lactic acid again decreases and the fatigue passes off.

J. H. BIRKINSHAW.

Vital need of the body for certain unsaturated fatty acids. I. Experiments with fat-free diets in which sucrose furnishes the sole source of energy. H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1932, 96, 143—156; cf. A., 1929, 853).—Production of a sp. deficiency disease on rigidly fat-free diets is confirmed, characterised by impairment of growth, dermatitis, disturbed H₂O metabolism, and hæmaturia. The condition is cured by maize starch and rice starch, by the fatty acids extracted from them, and by linoleic acid. Vitamin-B-deficiency as cause is definitely excluded. Potato starch and glycogen are ineffective.

J. B. BATEMAN.

Physiological action of phytosteryl esters. J. NIKUNI (J. Agric. Chem. Soc. Japan, 1931, 7, 827—838).—The growth responses of mice fed with cholesteryl and phytosteryl acetate and palmitate were compared. When large quantities of sterols were fed, only small quantities were deposited in the body. Cholesteryl esters are stored to a greater extent than phytosteryl esters.

CHEMICAL ABSTRACTS.

Cystine metabolism. G. SCOZ (Atti R. Accad. Lincei, 1931, [vi], 14, 586—589).—Feeding experiments with rats and puppies show that cystine has a distinct positive influence on general body and on hair-growth.

T. H. POPE.

Metabolism of *i*-cystine in the rat. N. R. LAWRIE (Biochem. J., 1932, 26, 435—440).—The rat can oxidise *i*-cystine as rapidly and completely as *l*-cystine. The val. of *i*-cystine for tissue-building purposes in the rat is $\frac{1}{3}$ — $\frac{2}{3}$ of that of *l*-cystine.

S. S. ZILVA.

Is preformed cystine essential to sheep for wool production? C. RIMINGTON and J. G. BEKKER (Nature, 1932, 129, 687—688).—A discussion.

L. S. THEOBALD.

Sulphur metabolism. R. SATO (Sei-i-kwai Med. J., 1930, 49, No. 8, 1—51).—The average S distribution in the urine of normal rabbits was: total S 0.6002, neutral S 0.1881, total SO₄ 0.4117, inorg. SO₄ 0.3796, ethereal SO₄ 0.0338 g.; increases following experimental icterus are recorded. The average total S contents for normal rabbits were: liver 1.30, lung 1.33, heart 1.43, kidney 1.30, testicles 0.85, spleen 1.33, adrenals 0.88, muscles 1.16%. The effects of injection of glucose and insulin are recorded.

CHEMICAL ABSTRACTS.

Growth reaction of embryonic marine forms to thiol and sulphoxide. D. M. HAMMETT and F. S. HAMMETT (Protoplasma, 1932, 15, 59—70).—The embryonic development of 5 species of marine organisms is accelerated by the SH group and retarded by the S'O group.

A. G. POLLARD.

Calcium and phosphorus requirements of dairy cows. I. Weekly balances through lactation

and gestation periods. H. B. ELLENBERGER, J. A. NEWLANDER, and C. H. JONES (Vermont Agric. Exp. Sta. Bull., 1931, No. 331, 27 pp.).—Negative Ca and P balances appear to be normal during the early stages of lactation and are compensated by rapid storage as the lactation and gestation periods advance. Feeding of mineral supplements reduced the periods of negative balance.

A. G. POLLARD.

Calcium and phosphorus metabolism of infants receiving undiluted milk. M. VAN K. NELSON (Amer. J. Dis. Children, 1931, 42, 1090—1099).—More Ca and P is retained than by infants receiving diluted milk or undernourished.

CHEMICAL ABSTRACTS.

Calcium and phosphorus requirements for growing chicks. I. Salt mixtures under rachitic conditions. II. Natural minerals. W. C. TULLY, S. M. HAGUE, C. W. CARRICK, and R. E. ROBERTS (Poultry Sci., 1931, 10, 299—309, 310—318).—I. Variations of McCollum's mineral diet no. 185 with a wide Ca : P ratio variation produced satisfactory growth and bone formation only when vitamin-D was present.

II. Mixtures of steamed bone meal with oyster shell or limestone were superior to mixtures of CaCO₃ and Ca₃(PO₄)₂ as sources of Ca and P in the absence of vitamin-D.

CHEMICAL ABSTRACTS.

Avertin. H. J. STANDER (Amer. J. Obstet. Gynecol., 1931, 22, 219—224).—Avertin (100 mg. per kg.) produced no change in (women's) blood-non-protein-N, -urea-N, -uric acid, -lactic acid, -creatinine, -Cl, or -CO₂ combining power, and only a slight increase in -sugar. In dogs, 500 mg. per kg. produced no significant blood changes.

CHEMICAL ABSTRACTS.

Partition of chloroform in the hen's egg during intoxication of the embryo by this anæsthetic. Order of magnitude of the toxic cellular dose. S. LALLEMAND (Compt. rend., 1932, 194, 1396—1397).—When hens' eggs are kept for several days in an atm. of CHCl₃ saturated at 18°, the concn. of CHCl₃ in the white and yolk is 6 mg. and 65 mg. per g., respectively. At the time of the death of the embryo the concn. of CHCl₃ in the latter is probably about 2.4—2.7 mg. per g., which corresponds with an amount of 3×10^{-9} mg. of CHCl₃ per cell.

W. O. KERMACK.

Influence of homatropine, hyoscyamine, and scopalamine on the sugar mobilisation in the toad's liver produced by adrenaline. M. NAKANO (Folia Pharmacol. Japon., 1931, 13, No. 1, 42—77).—The alkaloids act on the sugar stores in the liver and behave like atropine towards glycogenolysis and glycogen mobilisation caused by adrenaline.

CHEMICAL ABSTRACTS.

Influence of the Δ^2 -cyclopentyl radical in the hyponotics of the barbituric acid series. Pharmacodynamics of Δ^2 -cyclopentylallylbarbituric acid. R. CHAUX (Compt. rend., 1932, 194, 1193—1195).—A second substituent in the 5-position of 5- Δ^2 -cyclopentylbarbituric acid increases the hypnotic activity on rabbits of the resulting compounds in the order Ph < Bu^a < Pr^a < β -bromoallyl, Et < Δ^2 -cyclopentyl < allyl, all the compounds being more active than veronal (5:5-diethylbarbituric acid) except the first.

W. O. KERMACK.

Combustion of alcohol in homeotherms. M. NICLOUX (Compt. rend., 1932, 194, 1390—1391).—In white mice at 30° to which EtOH has been administered subcutaneously the rate at which the EtOH is combusted in each animal is const. and independent of the quantity administered, but proportional to the wt. of the animal. The average quantity of EtOH burnt per g. animal per hr. is 0.65 mg., which it is proposed to name the const. of Et oxidation.

W. O. KERMACK.

Influence of various drugs on sugar mobilisation in the liver. Y. KAGAWA (Japan. J. Med. Sci., 1931, 5, No. 3, 113—138).—Alcohols, chloral hydrate, and Na barbital (1—5%) increase the sugar production of toads' livers; quinine, HgCl₂, and H₃AsO₃ in low concn. cause no increase. PrOH (0.3%) inhibits sugar mobilisation by adrenaline; EtOH, Et₂O, quinine, HgCl₂, and H₃AsO₃ do so only at certain concns., and increase the effect at other concns.

CHEMICAL ABSTRACTS.

Effect of alcohol on the oxygen uptake of brain tissue. J. D. ROBERTSON and C. P. STEWART (Biochem. J., 1932, 26, 65—74).—Following EtOH administration to rabbits the O₂ uptake of brain tissue increases (more in grey matter than in white) for about 1 hr. and then falls slightly below normal.

A. COHEN.

Effect of irradiated amino-acids on the vascular action of adrenaline. S. FREYTAG (Pflüger's Archiv, 1931, 229, 226—235; Chem. Zentr., 1932, i, 830—831).—Irradiation of alanine increases its depressant action on the vascular action of adrenaline; with arginine the depressant substance is produced only when the irradiated solution is evaporated. Glutamic acid is unchanged.

A. A. ELDRIDGE.

Can the sympathicolytic poisons transform, into a vaso-dilator action, the vaso-constrictor action of amines of which they do not reverse the pressor action? RAYMOND-HAMET (Compt. rend., 1932, 194, 1529—1532).—A sec.-amine such as *p*-OH·C₆H₄·CH(OH)·CH₂·NHMe which has normally a vaso-constrictor action produces vaso-dilatation in presence of yohimbine methosulphate, although ergotamine or yohimbine does not reverse but only decreases the pressor action. Reversal of pressor action such as occurs with adrenaline is dependent on the vaso-dilator action being sufficiently powerful.

W. O. KERMACK.

Absorption of *Digitalis* preparations from the intestine. A. VON NYARY (Arch. exp. Path. Pharm., 1932, 165, 432—442).—Digitoxin is absorbed from the intestine of the cat twice as rapidly as digiclarin or strophanthin and three times as rapidly as *Digitalis* infusion. Digitonin or saponin antagonises the absorption of digiclarin and digitoxin but accelerates that of strophanthin. The residual, saponin-containing, "ballast-substance" from the purification of the digiclarin exhibits a marked inhibitory action on the absorption of digiclarin, digitoxin, and strophanthin.

F. O. HOWITT.

Fate of salicylic acid introduced into the body. II. C. W. MYUNG (Folia Pharmacol. Japon., 1931, 12, No. 3, 428—433).—In normal rabbits the blood-salicylic acid is max. 1 hr. after subcutaneous injection

of Na salicylate; in 24 hr. it is zero. After previous treatment with HCl or NaHCO₃ the max. was reached in 2—4 hr. or 20 min., respectively.

CHEMICAL ABSTRACTS.

Currosaponin. C. A. SAGASTUME and L. P. PONCE (Semana méd., 1931, II, 227—228).—The hæmolytic power of the saponin of *Colletia cruciata*, Gill and Hook, is destroyed by large, but not by small, doses of sugars. The min. lethal subcutaneous dose for rats is 0.6 mg. per g. Certain bacteria destroy the hæmolytic power of saponin solutions, leaving the toxicity and foam-producing qualities unchanged; hence hæmolytic tests for the detection of saponin in beverages may be untrustworthy.

CHEMICAL ABSTRACTS.

Mechanism of the uric acid excretory action of cinchophen preparations. I, II. P. H. RI (Folia Pharmacol. Japon., 1931, 13, No. 1, 1—12, 13—21).—I. Increase in urinary and blood-uric acid in dogs follows subcutaneous injection of erycon (2-*p*-methoxyphenylquinoline-4-carboxylic acid). The intestine or liver forms uric acid faster than muscle, and muscle faster than the brain. The uric acid contents of portal and femoral blood, liver, etc. are compared.

II. Subcutaneous injection of erycon produces a greater difference in concn. between hepatic and portal blood in splachnectomised than in normal rabbits. Vagotomy does not depress the action of erycon on the transport of uric acid retained in the liver.

CHEMICAL ABSTRACTS.

Pharmacology of thebaine and its derivatives. II. **Influence on nitrogen metabolism.** Y. TAKEUCHI (Sei-i-kwai Med. J., 1930, 49, No. 9, 74—87).—Quant. changes in blood- and urinary N exhibited by rabbits on subcutaneous injection of thebaine, dihydrothebaine, oxycodone, and dihydrohydroxycodone hydrochlorides are recorded.

CHEMICAL ABSTRACTS.

Effect of India ink and of tolylenediamine on the augmenting properties of bile salts on glycogen synthesis by the liver. S. FUJITA (Arb. Med. Univ. Okayama, 1931, 2, 557—565).—Small amounts of C₇H₆(NH₂)₂ are slightly synergistic, but larger amounts, or India ink, are antagonistic, to the augmenting influence of bile salts on the glycogen-synthesising property of the liver.

CHEMICAL ABSTRACTS.

Pharmacological actions of some alkyl derivatives of harmol. II. Propylharmol. G. K. ELPHICK and J. A. GUNN. III. Butylharmol. J. A. GUNN and M. H. MACKEITH. IV. Amylharmol. V. Nonylharmol. G. K. ELPHICK and J. A. GUNN (Quart. J. Pharm., 1932, 5, 37—47, 48—55, 56—62, 63—71).—With increasing length of side-chain, general symptoms in the frog appear more slowly; increased motor excitability in mammals is decreased, with correspondingly earlier onset of paralysis; contracture of voluntary muscle occurs less readily; stimulation of uterus decreases and inhibition becomes more marked. In small doses, all except the Bu compound cause pressor effects, and in larger doses all produce a fall in blood-pressure. Respiration is depressed in the order Pr > Et, whilst Bu, amyl, and nonyl compounds always cause acceleration, nonyl being much slower in action than the

others. Mammalian coronaries are dilated and heart-muscle is depressed in the order $\text{amyl} \gg \text{Pr} > \text{Et} > \text{Bu} \gg \text{nonyl}$. The isolated intestine is relaxed by moderate doses of amyl, Bu, Pr, Et ($\text{Pr} > \text{Et}$) and stimulated by minute doses. Nonylharmol is by far the most toxic to protozoa and slowest in action.

J. B. BATEMAN.

Pharmacological action of new choline derivatives in relation to their chemical constitution. W. F. VON OETTINGEN and D. F. EVELETH (J. Pharm. Exp. Ther., 1932, 44, 465—477).—Substitution of the alcoholic OH group by Cl or the quaternary trimethylammonium chloride radical reinforces the characteristic choline actions, whereas substitution by NH_2 - and NHMe -groups increases the depressant action on muscular tissue; hence it follows that the $\cdot\text{NMe}_3\cdot\text{C}_2\text{H}_4\cdot$ nucleus is pharmacologically the essential part of the choline molecule. H. DAVSON.

Neutralisation of toxic properties of strychnine sulphate. A. C. MARIE (Ann. Inst. Pasteur, 1932, 48, 449—456).— KMnO_4 will neutralise the toxicity of about an equal wt. of strychnine sulphate. Neither adrenaline nor blood alone shows any effect, but together they detoxicate strychnine sulphate; the blood may be replaced by bile. The alkaloid is non-toxic even when extracted from the mixture by Et_2O , but regains its toxicity on reduction by $\text{Na}_2\text{S}_2\text{O}_4$. The effect is due to a preferential oxidation of strychnine in presence of adrenaline.

P. G. MARSHALL.

Spermicidal activity of quinones and quinols. J. M. GULLAND (Biochem. J., 1932, 26, 32—45).—The toxicities to spermatozoa of many phenols, quinols, and *o*- and *p*-quinones have been determined. The greater toxicity of *p*-quinones and quinols is related to their greater chemical reactivity. Introduction of an alkyl group into *p*-benzoquinone enhances activity, but further alkylation decreases the toxicity. Aromatic *o*-hydroxyaldehydes are more spermicidal than the *m*- or *p*-derivatives. The following are new: 2:5-dihydroxyphenyl *Pr* ketone, m. p. 87—89°; 2:5-dihydroxybutylbenzene, m. p. 89°; butyl-1:4-benzoquinone, m. p. 32°. A. COHEN.

Calcium therapy. M. BUFANO (Clin. méd., 1928, No. 6; Rev. sud-amér. endocrinol., 1931, 14, 705—706).—After intramuscular injection of CaCl_2 (0.15 g.) the blood-Ca is increased for 24 hr.; the increase in K is slower. The use of Ca gluconate does not always cause higher calcæmia; the ratio K:Ca is always low.

CHEMICAL ABSTRACTS.

Formation of wheals. IV. Influences of calcium concentration on histamine wheals. W. K. WEAVER, H. L. ALEXANDER, and F. S. McCONNELL (J. Clin. Invest., 1932, 11, 195—209).—Ingestion of NH_4Cl decreases, and of NaHCO_3 increases, histamine wheals; an explanation involves change in Ca concn.

CHEMICAL ABSTRACTS.

Cadmium poisoning. I. History of cadmium poisoning and uses of cadmium. L. PRODAM (J. Ind. Hygiene, 1932, 14, 132—155).

Effect of phosphate and hydrogen carbonate buffers on ionisation of calcium salts in physiological salt solutions. W. F. VON OETTINGEN and R. E. PICKETT (J. Pharm. Exp. Ther., 1932, 44,

435—443).—Ca ions are determined by measuring their effect on a drop of castor oil floating on H_2O in presence of soap. Concn. of the order of 0.03% of NaHCO_3 and 0.008—0.048% phosphate buffers cause association of the Ca ions. The effect of phosphate buffers is modified by the addition of 0.008—0.015% of NaHCO_3 . H. DAVSON.

Influence of light-rays on the total cholesterol content of the skin. S. KAWAGUCHI (J. Biochem. Japan, 1932, 15, 111—114).—Artificial irradiation of the rabbit results in an increase of cholesterol and its esters in the skin. The H_2O content is also increased. F. O. HOWITT.

Synthesising action of enzymes. R. AMMON (Angew. Chem., 1932, 45, 357—359).—A review.

Laws of combination of enzymes with substrates. H. FISCHGOLD and R. AMMON (Biochem. Z., 1932, 247, 338—353).—All enzymic processes which can be explained on the basis of the law of mass action (Michaelis and Menten) can also be based on Langmuir's adsorption theory. The lack of conformity to the theories at high substrate concn. is a consequence of elimination of H_2O from the surface of reaction. The reversal of the direction of optical rotation produced by some esterases when the concn. of the substrate is high may be due, if the adsorption theory is assumed, to differing sensitivity of the two diastereoisomeric enzyme-substrate compounds, to the decreased concn. of H_2O in the region of reaction, or to alteration in the proportions of the two antipodes resulting from change in the concn. of the substrate. A third possibility is that the enzyme undergoes irreversible alteration when this concn. becomes high.

W. MCCARTNEY.

Determination of oxidase. T. HANAZAWA (Trans. Tottori Soc. Agric. Sci., 1931, 3, 187—194).—The neck of the flask containing the sample is provided with side-tubes and containers for *N*-NaOH (25 c.c.) and 1% pyrocatechol solution (10 c.c.) and with a mineral-oil manometer. The O_2 absorption for 100 c.c. of potato juice was about 40 mg.

CHEMICAL ABSTRACTS.

Milk-peroxidase. Preparation, properties, and action with hydrogen peroxide on metabolites. Determination of small amounts of hydrogen peroxide in complex mixtures. K. A. C. ELLIOTT (Biochem. J., 1932, 26, 10—24).—A crude conc. peroxidase free from catalase is obtained from milk by fractional pptn. with $(\text{NH}_4)_2\text{SO}_4$. The prep. loses activity very slowly at 0—5°, and is active between p_{H} 4 and 10. Thiol compounds interfere with peroxidase tests using benzidine, guaiacum, and *p*-phenylenediamine. H_2O_2 is determined by measuring the O_2 liberated by MnO_2 . Under conditions suitable for the complete oxidation of NaNO_2 by H_2O_2 in the presence of peroxidase, no oxidation of formate, acetate, oleate, stearate, triolein, EtOH , glucose, glycerol, MeCHO , β -hydroxybutyrate, lactate, glycine, phenylalanine, or histidine was observed, whilst tyrosine and tryptophan were oxidised to coloured products. Dihydroxyacetone and phenylglyoxal were oxidised by dil. H_2O_2 without peroxidase.

A. COHEN.

Accelerating action of uric acid on the xanthine-oxidase system. D. C. HARRISON (Biochem. J., 1932, 26, 472—475).—The inhibiting action of uric acid on the oxidation of hypoxanthine in presence of xanthine-oxidase and methylene-blue may be converted into an acceleration either by increasing the hypoxanthine or decreasing the enzyme concn. The accelerating effect appears to be due to the replacement on the enzyme surface of the inhibitor hypoxanthine by the less powerful inhibitor uric acid.

S. S. ZILVA.

Tyrosinase and pseudo-peroxidase. S. BERENSTEIN (Arch. Sci. phys. nat., 1932, [v], 14, 24—54).—The various types of oxidising enzymes are discussed and classified. Pseudo-peroxidase, a dehydrogenase, occurs in *Cyperus esculentus*, L., and other plants, but is isolated from these sources only with difficulty. Sweet almonds, however, readily yield the enzyme on aq. extraction. The extract is pptd. by EtOH, yielding an active ppt. In presence of NaHCO₃ and H₂O₂ the enzyme forms a red pigment from *p*-cresol. The additional presence of an NH₂-acid, indole, or phloroglucinol results in the formation of characteristic pigments. The pigment yielded by an NH₂-acid is identical with that produced by tyrosinase in presence of the NH₂-acid; the presence of H₂O₂ is essential for pseudo-peroxidase to react in this way. The accelerating influence of H₂O₂ on the *p*-cresol-tyrosinase reaction is not confirmed (cf. A., 1930, 1474). "Cresol-azure," the blue pigment from *p*-cresol, is prepared by the action of potato-oxidase in presence of glycine; it is identical with the product from 3:4-toluquinone (A., 1911, i, 728) and glycine. Solutions of this pigment show absorption bands at 530—610, 588, and 555 mμ. The pigments from phloroglucinol ("cresol-rubin") and indole ("indocresol") are similarly synthesised and examined.

F. O. HOWITT.

α- and β-Amylase in malt and barley. E. WALDSCHMIDT-LEITZ, M. REICHEL, and A. PURR (Naturwiss., 1932, 20, 254).—Treatment of a green-malt extract at *p*_H 3·8 with Al₂O₃ gives in the mother-liquor the pure α-component, whilst in the alkaline washings of the adsorbate the β is found. In this method they may be separated from the natural activator of amylase, *amylokinase*. Barley contains both α- and β-amylase, the α being in its inactive form; α-amylase seems necessary for the rapid conversion of starch into sugars.

H. DAVSON.

Action of cellulase and hemicellulase on plant materials *in vitro*. K. SILBERSCHMIDT (Münch. med. Woch., 1931, 78, 1819—1824; Chem. Zentr., 1931, ii, 3499).—Loss of sensitivity to cellulose dyes is followed by loss of sensitivity to pectin dyes, the effects being parallel with the softening of the cell membrane.

A. A. ELDRIDGE.

Dilatometric investigation of enzymic processes. II. Di- and tri-saccharides. P. RONA, N. NEUENSCHWANDER-LEMMER, and H. FISCHGOLD (Biochem. Z., 1932, 247, 257—274; cf. A., 1931, 983).—During the hydrolysis of lactose, cellobiose, and raffinose with enzymes (emulsin, invertase) and with dil. H₂SO₄, vol. decreases proportional to the changes in optical rotation and similar to those

x x *

previously found with sucrose and maltose are observed. When more conc. acids are employed with cellobiose and lactose the decreases in vol. differ from those found with enzymes and dil. acids, whilst with maltose and glucose there is a vol. increase irregular for the former, regular for the latter. The mutarotations of glucose, galactose, and fructose are accompanied by vol. changes related to the changes of form which occur during the process. In the case of glucose and galactose the vol. changes which accompany the complete change of one modification into the other are equal.

W. MCCARTNEY.

Action of the alkaloids and carbon monoxide on the enzymic activity of plants. M. PADOA (Nature, 1932, 129, 686).—The addition of small amounts of strychnine nitrate increases the amylase activity of barley during germination, and the activities of lipase, amylase, protease, and oxidase in castor-oil seeds germinating in H₂O, but not the enzymic extracts of seeds. *Ricinus* seedlings are improved by additions of strychnine nitrate and caffeine, but the latter is toxic towards barley, flax, and other plants. Small amounts of CO stop the assimilatory activity of green plants in light but not the respiration; CO slightly increases the lipase activity but decreases the amylase activity of barley and of *Ricinus*. Wheat, lupins, and peas germinate in an atm. rich in CO, cabbage and hemp germinate with difficulty, whilst flax and tomato fail. N assimilation in leguminous plants appears to be due, but not exclusively, to the stimulating action of N bacteria; it is also related to enzymic activities latent in the plants.

L. S. THEOBALD.

Directive influences in biological systems. I. Specificities of lipase actions. K. G. FALK (J. Biol. Chem., 1932, 96, 53—71).—The action of pancreatic lipase on various simple esters alone and in presence of inactive proteins or of lipolytically active normal tissue- and tumour-extracts was investigated. In addition to the protective action by the added material there occurred interaction which resulted in selectively increasing certain of the hydrolyses. It is suggested that lipase or ester-hydrolysing actions are due to a definite grouping on the enzyme and that the sp. action of the added tissue extracts or proteins is due to certain characteristics of the added substance.

F. O. HOWITT.

Isolation of asparagine from an enzymic digest of edestin. M. DAMODARAN (Biochem. J., 1932, 26, 235—247).—Edestin was digested by the successive action of pepsin, trypsin, and yeast-di-peptidase with only slight splitting of amide-N, and asparagine was isolated from the digest. The presence of glutamine was also indicated by the method of Chibnall and Westall (cf. this vol., 660).

A. COHEN.

Proteolytic enzymes of the pancreas and intestine. (MLLE.) E. LE BRETON (Bull. Soc. Chim. biol., 1932, 14, 417—506).—A lecture.

Proteolytic degradation of crystalline urease. E. WALDSCHMIDT-LEITZ and F. STEIGERWALDT (Z. physiol. Chem., 1932, 206, 133—136).—It is reaffirmed that by the action of proteinase up to 80% of the substance in cryst. urease precipitable by

sulphosalicylic acid is destroyed without affecting the urease activity (cf. Sumner and Kirk, this vol., 544).

J. H. BIRKINSHAW.

Crystalline urease. Preparation of meal from jack-beans. J. S. KIRK and J. B. SUMNER (Ind. Eng. Chem., 1932, 24, 454—455).—A special grinder is described.

P. G. MARSHALL.

Uricase and its action. V. Ox-kidney uricase. R. TRUSZKOWSKI (Biochem. J., 1932, 26, 285—291).—Ox-kidney uricase suspensions do not yield fractions of different activity on sedimentation. Both medullary and cortical tissues are active, the action of the latter being, however, about 25% greater than that of the former. Uricase is irreversibly inactivated in solutions of p_H 2—6.56, but not of p_H 7.59, by neutral solutions of KCN, I (0.01—0.1N), H_2O_2 , $FeSO_4$, and $HgCl_2$, but not by $CuSO_4$. The enzyme is completely inactivated by heating for 5 min. above 70° and almost completely at 70°, partly at 60°, and not at all at 50° or less. KCN completely inhibits uricolysis by ox-kidney uricase, whilst $Na_4P_2O_7$ has no effect. Dog, rabbit, and cat kidneys do not contain uricase.

S. S. ZILVA.

Action of phosphatase on various substrates. Y. IMANISHI (Biochem. Z., 1932, 247, 406—417).—Na fructosemonophosphate is hydrolysed to the extent of 80—97% (according to experimental conditions) by phosphatase from *Aspergillus oryzae* and from top and bottom yeast. K diphenylorthophosphate is hydrolysed by takaphosphatase to the extent of 44.5—62.0% and by phosphatase of animal origin (rabbit kidney and liver) to the extent of 35—63%.

W. MCCARTNEY.

Phospho-monoesterase and -diesterase. S. UZAWA (J. Biochem. Japan, 1932, 15, 19—28).—Adsorption methods applied to aq. extracts of rice-bran or to solutions of takadiastase yield an enzyme solution which hydrolyses mono-esters but not di-esters of H_3PO_4 . The venom of the snake *Trimeresurus flavoviridis* contains a di-esterase with a p_H optimum of 8.6. This enzyme admixed with the mono-esterase from takadiastase hydrolyses completely a di-ester of H_3PO_4 , the optimum being at p_H 5.6.

F. O. HOWITT.

Phosphatase from bran. I, II. S. UZAWA (J. Biochem. Japan, 1932, 15, 1—10, 11—17).—I. Rice-bran is extracted with H_2O , the extract dialysed, treated with kaolin, and the adsorption complex eluted with phosphate buffer to yield a solution of the enzyme which, following dialysis for removal of PO_4^{3-} , is further purified by electrodialysis. This solution contains a phosphatase which hydrolyses various types of mono-esters of H_3PO_4 at an optimum reaction of p_H 5.4—5.6. Hence there exist three types of monophosphatases with p_H optima at 3, 5.5, and 9, respectively (cf. A., 1929, 847; 1930, 372).

II. The solution also contains an enzyme hydrolysing di-esters of H_3PO_4 with p_H optima varying from 3.0 to 5.1 according to the concn. of the substrate.

F. O. HOWITT.

Hydrolysis of glucose-sulphuric acid and sucrose-sulphuric acid by sulphatase from bacteria. B. TANKÓ (Biochem. Z., 1932, 247, 486—

490).—Chondrosulphatase from bacteria hydrolyses these acids to the extents of 53 and 29%, respectively.

W. MCCARTNEY.

Dehydrogenating enzymes. H. WIELAND (Helv. Chim. Acta, 1932, 15, 521—532).—A lecture.

H. A. PIGGOTT.

Preparation of succinodehydrogenase free from fumarase. N. ALWALL and J. LEHMANN (Skand. Arch. Physiol., 1931, 61, 159—160; Chem. Zentr., 1931, ii, 3498).—Fumarase is not decomposed by heating at 50°. Fumarase can be washed out of muscle, whereas succinodehydrogenase remains and can be extracted with phosphate.

A. A. ELDRIDGE.

Arginase. VII. Activation and inhibition experiments. S. EDLBACHER, J. KRAUS, and G. WALTER. **VIII. Thyroxine and arginine metabolism.** S. EDLBACHER and B. SCHULER (Z. physiol. Chem., 1932, 206, 65—77, 78—83; cf. A., 1931, 393).—VII. Arginase changes its solubility in COMe, or EtOH preps., becoming almost insol. in glycerol and H_2O , sol. in buffers of p_H 6.4—9.4. Liver COMe, extract evaporated in vac. does not activate arginase. HCN, cysteine, and glutathione inhibit arginase at neutrality even at 0.001M. At p_H 9.4 cysteine produces weak activation. The statement that arginase acts only in presence of natural activator (glutathione etc.) was not confirmed. O_2 inactivates arginase at 40°, particularly at alkaline reaction, N_2 only slightly; such a partly inactivated product is inhibited by cysteine at p_H 6.8 in the same way as native arginase, but there is no reactivation at p_H 9.4. Frothing produces strong inactivation.

VIII. Injection of arginine into guinea-pigs increases the arginase val. of the muscle (fourfold) and kidneys; the max. vals. are attained in 5 hr. If thyroxine is injected 1 hr. before the arginine, no increase of muscle-arginase is observed. Surviving cat's liver perfused with erythrocytes in Ringer solution hydrolyses only 60—70% of the amount of arginine hydrolysed without thyroxine.

J. H. BIRKINSHAW.

Iron in relation to tyrosinase. C. E. M. PUGH (Biochem. J., 1932, 26, 106—117).—The activity of tyrosinase preps. from mealworms and fungi, as free from extraneous Fe as possible, is not related to the Fe content of the enzyme prep. There is no evidence, however, that tyrosinase does not contain Fe. The hastening of the coloration of tyrosine and *p*-cresol by tyrosinase on addition of Fe^{++} salts indicates the formation of H_2O_2 . The oxidation of phenols by H_2O_2 and Fe^{++} salts is not as sp. as the tyrosinase action. Dialysis causes loss of activity of tyrosinase which is prevented by dialysing into a medium at p_H 8.5.

A. COHEN.

Properties of glyoxalase. J. O. GERŠAVICIUS (Biochem. J., 1932, 26, 155—161).—PhMe inhibits the action of glyoxalase. Borate buffer has little effect, but phosphate and diethylbarbiturate have increasing inhibiting effect. The optimum p_H for glyoxalase is 6—7.

A. COHEN.

Baicalinase, an enzyme which hydrolyses flavone glycuronides. I. T. MIWA (Acta Phytochim., 1932, 6, 155—175).—Baicalinase (I) (A., 1931,

493; modified prep.) hydrolyses baicalin (II) and scutellarin (III), but not rutin, robinin, myricitrin, k  mferitrin, acaciin, salicin, or amygdalin. It is thus different from emulsin, takadiastase, and rhamno-diastase, which do not hydrolyse (II) or (III). Menthylglycuronic acid was not hydrolysed by Kahlbaum's emulsin nor by (I). A table of Cu equivs. is given for determination of glycuronic acid [K salt does not mutarotate in H_2O (cf. A., 1929, 541)] by Bertrand's method. (I) is most active at p_H 5.9—6.0.

R. S. CAHN.

Plastein. S. J. FOLLEY (Biochem. J., 1932, 26, 99—105).—The mol. wt. of plastein, determined by the ultra-centrifugal method, is <1000. The amide-N is less, and the NH_2 -acid-N greater, than in the parent ovalbumin. The $PhNCO$ derivative yields two fractions with equivs. of the same order as that of proteose. Plastein is not regarded as a product of enzyme synthesis.

A. COHEN.

Respiratory processes in pea and cereal seeds. IX. Role of boiled yeast-juice. Oxidised carotene as hydrogen acceptor. A. FODOR and L. FRANKENTHAL (Biochem. Z., 1932, 246, 414—430).—The dehydrogenating activities of various meals are studied in relation to various hydrogen acceptors. Boiled yeast juice is essential to the reaction in some cases, and under certain conditions methylglyoxal and also oxidised carotene retard the process. Their effect on the respiration is also studied.

H. W. DUDLEY.

Selective fermentation of glucose and fructose by yeast. E. R. DAWSON (Biochem. J., 1931, 26, 531—535).—Theoretical.

S. S. ZILVA.

Mechanism of the formation of organic acids by mould fungi. I. Action of *Aspergillus niger* on sodium hexosediphosphate in the presence of toluene. A. J. SUTHERS and T. K. WALKER (Biochem. J., 1932, 26, 317—322).—*A. niger* forms methylglyoxal from Na hexosediphosphate.

S. S. ZILVA.

Effect of acid on the growth of moulds. A. JURACEC (Bull. Acad. Sci. Roumaine, 1932, 15, 47—50).—The optimum reaction for the germination of spores of *Aspergillus niger* in Raulin's medium is p_H 3.45. The reaction is varied by addition of tartaric acid or K_2CO_3 . When tartaric acid is replaced by H_3PO_4 the optimum p_H is 3.7. A p_H >8 inhibits growth.

P. G. MARSHALL.

Relation between the sugars of *Aspergillus niger* and those serving as nutrients. OBATON (Compt. rend. Soc. Biol., 1930, 105, 673—674; Chem. Zentr., 1931, ii, 3501).—Addition of glucose to the nutrient solution leads to a high yield of trehalose in the mycelium; mannitol is formed to only a small extent. With invert sugar or fructose the reverse holds.

A. A. ELDRIDGE.

Metabolic physiology of *Aspergillus oryzae*. IV. Utilisation of various carbon compounds [for growth and respiration] of moulds. H. TAMURA (Acta Phytochim., 1932, 6, 1—129; cf. A., 1929, 958).—By the use of a semi-quant. technique, described in detail, it is shown that *A. oryzae* grown from cultures can utilise 51 (mostly alcohols and

acids) out of 123 org. compounds examined for growth and respiration, and 8 for respiration only, whilst 17 were without effect and 47 were deleterious. When grown from spores, the mould utilises only 47 for good growth, 7 for slight growth, and 69 not at all. Certain groups, e.g., CO, CHO, ether, inhibited growth (in the concns. used), but in general the presence of one sp. group was not sufficient for growth. The two series of experiments gave approx. parallel results for different substances. *A. oryzae* utilises many sugars and $AcCO_2H$, but not alcohols, acids, aldehydes, ketones, or ethers, for anaerobic fermentation, which is similar in nature to fermentation by yeast. Kojic acid is formed from many compounds containing from 3 to 6 C atoms. From a comparison of the formulae of the compounds examined it is concluded that certain pairs of groups [e.g., $CHMe(OH)$, $\cdot CH \cdot C(OH) \cdot$, $\cdot CH_2(OH) \cdot CH_2 \cdot$, etc. (termed "chief radicals")] must be present in an utilisable compound, joined at least once (in a ring or a straight chain) to another group (termed "residual radical"), such that β -degradation does not lead to fission of the "chief radical." Fission of di- and poly-saccharides and of glucosides precedes their utilisation by the mould, and the nascent fission products can usually be utilised better than the preformed substance.

R. S. CAHN.

Biochemistry of micro-organisms. Puberulic acid, $C_8H_6O_6$, and an acid, $C_8H_4O_6$, new products of the metabolism of glucose by *Penicillium puberulum*, Bainier, and *Penicillium aurantio-virens*, Biourge. Certain dihydroxybenzenedicarboxylic acids. J. H. BIRKINSHAW and H. RAISTRICK (Biochem. J., 1932, 26, 441—453).—Each of these acids is produced by *P. puberulum* and *P. aurantio-virens* when grown in a synthetic medium containing glucose as sole source of C. Puberulic acid (I), $C_8H_6O_6$, m. p. 316° (decomp.) (Ac_2 derivative, m. p. 212° ; Me , m. p. 272 — 276° , decomp. 320 — 330° , Me_2 , m. p. 271 — 272° , and Me_4 , m. p. 112 — 113° , derivatives; diacetyldimethyl derivative, m. p. 102°), and the acid $C_8H_4O_6$ (II), m. p. 296° (decomp.), are pptd. from the neutralised filtered metabolic solutions as the Ni salts. The acids are separated by treating the mixed salts with Ac_2O and $NaOAc$; (II) is pptd., whilst (I) remains in solution as the Ac_2 compound. (I) is probably a dihydroxybenzenedicarboxylic acid. (I) and (II) may form an oxidation-reduction system.

S. S. ZILVA.

Supposed production of maclurin from acacatechin. M. HEALEY (Biochem. J., 1932, 26, 388—391).—No maclurin is formed from Gambier catechin or acacatechin by the action of *Penicillium solitum* (cf. Hazleton and Nierenstein, A., 1924, i, 1218).

S. S. ZILVA.

Production of acetoin by Linder's *Thermobacterium mobile*. B. TANK   (Biochem. Z., 1932, 247, 482—485).—In solutions containing glucose (or glucose and sucrose) and $MeCHO$ the bacterium produces acetoin in yields equiv. to about 40% or more of the aldehyde originally present.

W. MCCARTNEY.

Factors influencing the formation of products in the thermophilic fermentation of cellulose.

W. B. SARLES, E. B. FRED, and W. H. PETERSEN (Zentr. Bakt. Par., 1932, II, 85, 401—415).—Differences in acid production by crude and purified cultures under varied cultural conditions are recorded. A pure culture produced volatile acids consisting of 71% of AcOH and 29% of butyric acid. A. G. POLLARD.

Biochemistry of light-producing bacteria. I. Influence of sodium and potassium chlorides and bromides on the generation of light by *Photobacillus radians*. F. FUHRMANN (Monatsh., 1932, 60, 69—105).—The isolation of *P. radians* from North Sea codfish or haddock and its characterisation are described; it can develop under anaerobic conditions but glows only in presence of O₂, best at p_H 7.1—7.4. The effect on growth of the bacteria and the amount of light produced of NaCl, NaBr, KCl, and KBr is studied in presence and absence of glycerol in a fish bouillon-peptone medium. With the same cation, which may be either Na⁺ or K⁺, the effect on the glow produced by the anions Cl⁻ and Br⁻ differs, and they cannot replace each other in isotonic solution; the same is true of the cations combined with the same anion. KCl and KBr tend to cause agglomeration of the individual cells, an effect observed with Na salts only in high concn. The production of light and the multiplication of cells do not seem to be related. H. A. PIGGOTT.

Influence of the medium on production of bacterial gelatinase. R. B. HAINES (Biochem. J., 1932, 26, 323—336; cf. this vol., 197).—The change in viscosity of a mixture of gelatin and sterile centrifugate from the medium in which the organism (*proteus* or *Pseudomonas*) had been grown indicated that a certain amount of gelatinase is present whatever the medium used, providing adequate growth occurred. In a synthetic medium containing no Mg or Ca salts no single NH₂-acid is markedly superior to any other or to NH₄Cl in its effect on gelatinase production, although rather better growth is obtained with some than with others. In all cases salts of Ca and Mg together greatly stimulate the production of gelatinase. In some cases salts of Mg alone while stimulating growth partly inhibit gelatinase formation. Salts of Ca alone have little or no growth-stimulating action, but in most cases greatly stimulate gelatinase production. In a medium containing NH₄Cl, glucose, or phosphates together with salts of Ca and Mg, gelatinase is produced to the same extent as in broth. S. S. ZILVA.

Physiology of amoeboid movement. VIII. Action of certain non-electrolytes. Isoelectric point of the proteins of a marine amoeba. C. F. A. PANTIN (J. Exp. Biol., 1931, 8, 365—378).—Movement in 1.05*M*-sucrose, -glucose, -glycerol, or -urea was studied. The isoelectric point is p_H 4.6—5.

CHEMICAL ABSTRACTS.

(i) Presence of a principle lysing Yersin's bacillus in the blood of a plague convalescent. M. ADVIER. (ii) Existence in a bubo of a plague convalescent of an agent producing transmissible lysis, apart from its presence in the intestine. R. PONS and C. DURIEUX (Compt. rend., 1932, 194, 1397—1399, 1399—1400).—(i) From the serum of a

convalescent recovering from plague a bacteriophage has been obtained which produces transmissible lysis in cultures of Yersin's bacillus (*B. pestis*).

(ii) The bacteriophage was also isolated from a bubo. W. O. KERMAK.

***Bacillus coagulans*.** W. B. SARLES and B. W. HAMMER (J. Bact., 1932, 23, 301—314).—Evaporated milk coagulated by *B. coagulans* contained abnormally high proportions of total and volatile acids. The latter consisted mainly of AcOH and EtCO₂H. The non-volatile acid was *D*-lactic acid. Coagulated evaporated milk shows no evidence of proteolysis, but in coagulated skim-milk there was an increase in sol. and NH₂-N. Gas from tins of normal or coagulated, evaporated milk contained no O₂, but with coagulated samples the CO₂ content was above normal. A. G. POLLARD.

Reaction regulators for bacteriological cultures. (a) A. BERTHELOT. (b) A. BERTHELOT and G. AMOUREUX. (c) A. BERTHELOT, F. VAN DEINSE, and G. AMOUREUX (Bull. Soc. Chim. biol., 1932, 14, 280—285, 286—289, 290—293).—(a) (b) The p_H of cultures of *B. aminophilus* on meat peptone media with and without addition of glucose and each containing quantities of the K or Na salt of one of the following acids, HCO₂H, AcOH, EtCO₂H, pyruvic, lactic, malonic, butyric, malic, fumaric, etc., is found to change at definite rates according to the acid used and as the media contain or do not contain glucose. It is suggested therefore that such acids can be used as buffers.

(c) The Na salts of acyclic acids known to be attacked by *B. tuberculosis* can be used to regulate the p_H of cultures of this bacillus, but the choice of the acid depends on the nature of the medium.

A. LAWSON.

Origin of acetylmethylcarbinol in the degradation of sucrose by *B. subtilis*. LAFON (Bull. Soc. Chim. biol., 1932, 14, 263—271).—In the products of fermentation of both glucose and fructose by *B. subtilis*, acetylmethylcarbinol is formed. Using glucose as substrate, negative results attended attempts to isolate pyruvic acid and MeCHO in the production of acetylmethylcarbinol, nor could the last-named substance be isolated using pyruvic acid and MeCHO as substrate. *B. subtilis*, unlike yeast, attacks MeCHO very slowly. It is suggested that the production of acetylmethylcarbinol by *B. subtilis* from glycerol is due to the intermediate synthesis of a hexose from which it is then produced directly.

A. LAWSON.

Relation of p_H to the absorption of dyes by bacteria. S. J. FRENCH and W. H. WRIGHT (Proc. Indiana Acad. Sci., 1931, 40, 175—177).—*Pseudomonas tumefaciens* and *Radiobacter*, when grown in presence of Congo-red, did not (as Stearn supposes) adsorb acid dyes in media of low p_H and basic dyes in those of high p_H , possibly owing to the amphoteric nature of Congo-red. CHEMICAL ABSTRACTS.

Influence of carbohydrates on the pigment production of *Azotobacter*. S. ARAKAWA (Tottori Agric. Coll. Sci. Papers (10th Anniv.), 24—31; Proc. Internat. Soc. Soil Sci., 1932, 7, 21—22).—Pigmentation of *A. chroococcum* occurred in simple media

containing raffinose, inulin, dextrin, or starch. *A. vinelandii* produced pigment in glycerol media but not in those containing polysaccharides. Both organisms showed pigmentation in 1% KNO_3 media containing glucose, fructose, maltose, sucrose, or mannitol. KNO_3 as a N-source intensified pigmentation.

A. G. POLLARD.

Nodule bacteria and production of phosphatides in *Soja hispida*. B. REWALD and W. RIEDE (Biochem. Z., 1932, 247, 424—428).—The phosphatide and oil contents of soya beans and plants are not affected at any stage of growth by the presence or absence of nodule bacteria, although these cause increase in the protein content. W. MCCARTNEY.

Biochemical characters of human and animal strains of hæmolytic streptococci. P. R. EDWARDS (J. Bact., 1932, 23, 259—266).—Animal strains produce greater acidity in glucose media than do human strains, and are further differentiated by the production of acid from sorbitol and failure to ferment trehalose. Human strains ferment trehalose but do not attack sorbitol.

A. G. POLLARD.

Atypical (slow) lactose-fermenting *B. coli*. F. S. JONES, M. ORCUTT, and R. B. LITTLE (J. Bact., 1932, 23, 267—279).—During the fermentation of lactose by colon bacilli from cow fæces, there is a phase in which the sugar is utilised without acid production.

A. G. POLLARD.

Growth of *Aspergillus versicolor* on higher paraffins. S. J. HOPKINS and A. C. CHIBNALL (Biochem. J., 1932, 26, 133—142).—A strain of *A. versicolor* will grow on odd and even no. paraffins up to $\text{C}_{34}\text{H}_{70}$ as sole source of C. Apart from CO_2 and mycelium no metabolic products were obtained from a culture on $\text{C}_{27}\text{H}_{56}$. The mould grows well on the higher ketones but not on sec. alcohols. In the oxidation of paraffins, therefore, a ketone appears to be the initial product, which is further metabolised to shorter fatty acids.

A. COHEN.

Antibodies. IV. Carbohydrate content as a criterion of the suitability of a broth for the culture of pneumococci. G. MCGUIRE, E. VALENTINE, E. WHITNEY, and K. G. FALK (J. Bact., 1932, 23, 223—234).—Good broth should have 0.5 mg. of fermentable reducing substance per c.c. With the growth of the organism p_{H} changes in the medium correspond with acid produced from fermentable reducing substances.

A. G. POLLARD.

Bacterial metabolism. II. Glucose breakdown by pneumococcus variants and the effect of phosphate thereon. L. F. HEWITT (Biochem. J., 1932, 26, 464—471).—Of the glucose disappearing from cultures of pneumococci about 78% is recovered as lactic acid. The ratio of the latter to the broken-down glucose is unaffected by altering a variety of cultural conditions; this was previously observed in the case of hæmolytic streptococci. There is more glucose breakdown in growing cultures with certain forms of pneumococcus than with others. The presence of inorg. phosphate appears to play an essential part in bacterial growth and glucose breakdown and not merely that of a buffer salt.

S. S. ZILVA.

Rôle of the soluble specific substances in oral immunisation against pneumococcus types II and III. V. ROSS (J. Exp. Med., 1932, 55, 1—12).

CHEMICAL ABSTRACTS.

Fate of orally administered soluble specific substance of pneumococcus types I, II, and III. V. ROSS (J. Exp. Med., 1932, 55, 13—25).—The substance was excreted by rats largely in the fæces; none was detected in the serum or urine. The recovered polysaccharide of type I is active.

CHEMICAL ABSTRACTS.

Identity of the mechanisms of type-specific agglutinin and precipitation reactions with pneumococcus. T. FRANCIS (J. Exp. Med., 1932, 55, 55—62).—The essential mechanism is the same; the active agents are the capsular polysaccharides.

CHEMICAL ABSTRACTS.

Biology of the tubercle bacillus. II. Asparagine and glycerol metabolism of the tubercle bacillus. J. H. DINGLE and J. WEINZIRL (J. Bact., 1932, 23, 281—299).—The metabolism of virulent and avirulent strains of the organism was similar except that the former produced a final acidity and the latter a final alkalinity in the medium. The NH_3 content of the medium was greatest at the max. growth period and declined later. Alkalinity produced in media was probably not due to NH_3 . All the N of asparagine was utilised by the organism, the NH-N being more readily attacked than $\text{NH}_2\text{-N}$. Glycerol was almost completely utilised, and partial oxidation to org. acids did not occur.

A. G. POLLARD.

Specific carbohydrate of the tubercle bacillus. G. A. C. GOUGH (Biochem. J., 1932, 26, 248—254).—Mild hydrolysis of the carbohydrate with 2.5% H_2SO_4 or $\text{H}_2\text{C}_2\text{O}_4$ yields in addition to mannose, *d*-arabinose, and galactose, a mixture of acidic substances which have been investigated. Ca salts containing 2.5—10% Ca have been obtained by fractional pptn. Further hydrolysis destroys the acidity with production of mannose. Acetylation of the carbohydrate gives a H_2O -insol. substance converted by alkaline hydrolysis into the carbohydrate with the original pptg. power.

A. COHEN.

Bacterial metabolism. I. Lactic acid production by hæmolytic streptococci. L. F. HEWITT (Biochem. J., 1932, 26, 208—217).—Good cultures were obtained with a glucose-salt solution buffered with NaHCO_3 and containing 10% of meat broth. The lactic acid formed averaged about 75% of the glucose which disappeared under varying conditions. Matt virulent streptococci caused much more rapid breakdown of glucose than did glossy variants.

A. COHEN.

Decomposition of caseinogen by lactic streptococci under aerobic and anaerobic conditions. C. BARTHEL (Orla-Jensen Festschr., 1931, 60—62; Chem. Zentr., 1932, i, 153).—The yields of sol. and NH_2 -acid N were practically zero with *S. cremoris*, and little different with *S. lactis*.

A. A. ELDRIDGE.

Effect of various yeasts on the growth and physiological properties of lactic acid bacteria and moulds. O. K. PALLADINA and V. A. MASJUKOVITSCH (Orla-Jensen Festschr., 1931, 89—93; Chem. Zentr., 1932, i, 153).—Culture of lactic acid bacteria

with yeast is not a substitute for addition of yeast autolysate and does not promote the formation of acid. The growth of moulds is not markedly arrested by culturing with yeast; the proteolytic power of *Oidium lactis* in milk is even promoted and the production of acid in cream is arrested. A. A. ELDRIDGE.

Inhibition of bacterial lactic fermentation by the halogeno-aliphatic acids. L. GENEVOIS and T. NICOLAIEV (Compt. rend., 1932, 194, 1270—1271).—The lactic acid fermentation of bacteria is inhibited by bromo- and iodo-acetic acid and by their esters and homologues, as is the formation of lactic acid by muscle or EtOH by yeast. The inhibition is practically complete within several min. when the concn. of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ or $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ is $N/2000$; the corresponding concns. for $\text{CHMeBr}\cdot\text{CO}_2\text{H}$ or $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ are $N/100$, the respiration remaining unaffected for several hr. The inhibiting action is less marked in a medium poor than in one rich in phosphate. This supports the view that the effect of the acid is to inhibit the initial esterification of the phosphate. It is suggested that $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ or $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ may be used to prevent the souring of milk. W. O. KERMAK.

Respiratory processes of lactic acid bacteria. A. BERTHO and H. GLÜCK (Annalen, 1932, 494, 159—191).—Partly a more detailed account of work previously reviewed (A., 1931, 394). The following is new. Glucose is dehydrogenated by benzoquinone (I) in presence of *B. Delbrückii* or *B. acidophilus*; HCN ($M/625$ — $M/5000$) has no influence on the reaction, CO causes a slight activation, but $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ ($M/500$) has a considerable retarding action (more pronounced with *B. Delbrückii*). With methylene-blue (II) in place of (I), dehydrogenation is accelerated slightly by $M/500$ -HCN, retarded slightly by 0.05% ethylurethane and considerably by $M/500$ - $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$. The ratio of the activities of O_2 , (I), and (II) as acceptors is 1:4:2.5; the dehydrogenations with these substances are all catalysed by the same dehydrogenase. With mixtures of O_2 and (I), no O_2 is consumed in the initial stages of the reaction, but the amount absorbed increases with the disappearance of (I). With (II) + O_2 , a large (250%) increase in O_2 -uptake occurs initially; (II) probably functions as the H-acceptor, the resulting leuco-compound being re-oxidised by O_2 . The respiratory quotients of *B. acidophilus* and *B. Delbrückii* are 0.45—0.59 and 0.33, respectively, in contrast to the val. of 0.5 calc. from the equation $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + 12\text{O}_2 = 6\text{CO}_2 + 12\text{H}_2\text{O}_2$. The formation of lactic acid from glucose by *B. acidophilus* is completely inhibited by $M/500$ - $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$; respiration continues but is retarded. Dihydroxyacetone and glyceraldehyde are as efficient donors as glucose; AcCHO causes a diminished O_2 -consumption and H_2O_2 is never detected. Systems (such as the above) unaffected by HCN contain no Fe-porphyrin complexes. H. BURTON.

Vegetable peptone agars for quantitative work with *Lactobacillus acidophilus*. F. M. BACHMANN and W. D. FROST (Science, 1932, 75, 440—441). L. S. THEOBALD.

Propionic acid bacteria. I. Classification and nomenclature. C. H. WERKMAN and S. E.

KENDALL (Iowa State Coll. J. Sci., 1931, 6, No. 1, 17—32).—Nine species are recognised and their effects on 32 carbohydrates are recorded.

CHEMICAL ABSTRACTS.

Symbiosis of *Vibrio cholerae* with bacteriophage, and variations of its biological characteristics. W. DOORENBOS (Ann. Inst. Pasteur, 1932, 48, 457—469).—Details are given of the factors influencing the agglutination of sheep erythrocytes by cultures of *V. cholerae*. The variability of the haemolytic power is due to the development of antihaemolysins in the older cultures. Modifications of most of the biological characteristics are dependent on the presence of bacteriophage. P. G. MARSHALL.

Bacterial antagonism and bacteriophage. A. GRATIA (Ann. Inst. Pasteur, 1932, 48, 413—437).—A strain of *B. coli* (V) was obtained which produced a toxin antagonistic to the growth of *B. coli* (ϕ) and to a smaller extent of *B. dysenteriae* (Shiga). The two strains are able to develop a resistance to the toxin as they can to bacteriophage. The active principle is pptd. by COMe_2 but inactivated by EtOH; unlike bacteriophage it is not destroyed by quinine hydrochloride. Other points of difference from bacteriophage are mentioned. P. G. MARSHALL.

Effects of various carbohydrates on production of diphtheria toxin with special reference to its flocculating titre and final p_H . E. L. HAZEN and G. HELLER (J. Bact., 1932, 23, 195—209).—Carbohydrates are essential to the production of toxic filtrates from *C. diphtheriae*. Glucose is more effective than maltose or glycerol in this respect. Dextrin is without action. The toxicity of the filtrates is largely dependent on the final p_H of the culture and is greater at p_H 7.1 than at the commonly accepted range (7.8—8.2). A. G. POLLARD.

Cryptotoxins. L. VELLUZ (J. Pharm. Chim., 1932, [viii], 15, 400—409).—A review.

Oligodynamic action of metals. A. J. MARKVOORT and K. T. WIERINGA (Chem. Weekblad, 1932, 29, 242—247).—The opposing dissolution and radiation theories regarding the bactericidal action of metals are discussed, and experiments on sterilisation by means of active Ag described. The Ag must first dissolve to be effective; some bacteria, especially those forming spores, are more resistant, and after repeated use the surface loses its sterilising power. The action is stronger if air has access to the solution, and with rise of temp. Dil. AgNO_3 solution exhibits properties similar to those of H_2O which has been in contact with an active Ag surface. S. I. LEVY.

Action of ether and chloroform on *Actinomyces* of the asteroid type. J. DUCHÉ (Compt. rend., 1932, 194, 1509—1510).— Et_2O has little effect on *A. asteroides*, but CHCl_3 is toxic and removes a wax-like substance. W. O. KERLACK.

Natural and acquired resistance of certain strains of *Escherichia coli* to the bacteriostatic and germicidal effects of cations. E. K. BORMAN (J. Bact., 1932, 23, 315—329).—The bacteriostatic and germicidal efficiencies of Na, Mg, Ba, Ca, Fe, Cu, and Hg salts were of the same order for different strains of the organism. A. G. POLLARD.

Bactericidal activity of silver. G. LAKHOVSKY (Compt. rend., 1932, 194, 1200).—Polemical (cf. this vol., 546).
W. O. KERMACK.

Bactericidal action of metals. P. LASSEUR, M. PIERRET, A. DUPAIX, G. MAGUITOT (Compt. rend., 1932, 194, 1401).—A reply to the above.

W. O. KERMACK.

Bactericidal action of silver on typhoid and colon bacilli. A. KLING (Compt. rend., 1932, 194, 1402—1404).—The bactericidal action of Ag on *B. coli* and typhoid bacilli is accounted for by the solubility of Ag in distilled H₂O.
W. O. KERMACK.

Effect of the parathyroid hormone on the calcium content of human milk. F. ADAMCSIK and A. VON BEZNAK (Klin. Woch., 1931, 10, 2219—2220; Chem. Zentr., 1932, i, 407).—The Ca content of human milk is lowest in the morning. Injection of parathyroid hormone prevents the normal increase during the day.
A. A. ELDRIDGE.

Hormothylin, the thyroid-stimulating hormone of the anterior pituitary lobe. H. PAAL (Klin. Woch., 1931, 10, 2172—2174; Chem. Zentr., 1932, i, 405).—"Prahormon" from urine of pregnancy partly protects mice against MeCN; this is attributed to the hormothylin component. The same agent is present in the anterior pituitary lobe. It is thermostable and may be administered orally.

A. A. ELDRIDGE.

Existence of an extra-pancreatic (or cellular) insulin in the dog after pancreatectomy. S. SOSKIN (Science, 1932, 75, 382).—A criticism (cf. Tuttle, New Eng. Med., 1932, 8, 206).

L. S. THEOBALD.

Insulin action of pure pancreatic secretion. F. L. SOLER (Rev. farm., 1931, 74, 1—7).—Pancreatic secretion, when injected intravenously, has an insulin effect. Gastric secretion increases the blood-sugar.
CHEMICAL ABSTRACTS.

Effect of digestive fluids on the activity of insulin. A. A. SCHMIDT and K. TULJTSCHINSKAJA (Z. ges. exp. Med., 1931, 77, 58—66; Chem. Zentr., 1931, ii, 3223).—Gastric juice of the dog destroys insulin in 30 min. at 37°; the pancreatic juice does not completely inactivate it in 2 hr., whilst the intestinal fluids have scarcely any effect in 2 hr.

L. S. THEOBALD.

Cure of cachexia following hypophysectomy by administration of the growth hormone and its relation to the resulting adrenocortical repair. H. M. EVANS, K. MEYER, R. PENCHARZ, and M. E. SIMPSON (Science, 1932, 75, 442—443).—The growth rate of hypophysectomised rats receiving purified preps. of the growth hormone free from gonad-stimulating effect exceeded that of normal animals similarly treated. Prompt and uniform relief from the cachectic state follows administration of the growth hormone extracts, whilst the growth-free, gonad-stimulating hormone has no influence on the cachexia. The growth, but not the gonad, hormone also partly repairs the thyroids and the adrenals. Atrophy of the adrenals and the cachectic state are probably related causally.
L. S. THEOBALD.

Oxytocic principle of the posterior lobe of pituitary gland. I. J. M. GULLAND and W. H. NEWTON (Biochem. J., 1932, 26, 337—348).—"Norit" adsorbs the oxytocic principle between p_H 1 and 13. The active substance can be eluted by glacial AcOH. The oxytocic activity which is recovered from the adsorbent when freshly-prepared partly-purified extracts are used varies from 50 to 75% of that of the same solution 3 weeks later even when kept at p_H 3 and 0°. In the case of the more mature solution the amount of activity recoverable is about 80% of the total. [H⁺] has no influence on the amount of activity adsorbed from fresh or more mature solutions. The most active prep. contains 225 international oxytocic units per mg.

S. S. ZILVA.

Pituitary. VIII. Relation of the pituitary gland to calcium metabolism and ovarian function in *Xenopus*. L. HOGBEN, E. CHARLES, and D. SLOME (J. Exp. Biol., 1931, 8, 345—354).—Removal of the pituitary or the anterior lobe alone lowers serum-Ca in *Xenopus laevis*.

CHEMICAL ABSTRACTS.

Œstrin. V. Mechanism of the conversion of trihydroxyœstrin into ketohydroxyœstrin. G. F. MARRIAN and G. A. D. HASLEWOOD (Biochem. J., 1932, 26, 25—31).—Trihydroxyœstrin (I), m. p. 279.5—280.5°, $[\alpha]_{5461} +41.9^\circ$ in C₅H₅N, +76° in EtOH, yields Butenandt's ketohydroxyœstrin (II), m. p. 242—246°, $[\alpha]_{5461} +188^\circ$ in EtOH, by dehydration with KHSO₄, and, with alkaline Me₂SO₄, a *Me ether* (III), m. p. 162.5—164°, $[\alpha]_{5461} +29.9^\circ$ in C₅H₅N, +65.3° in EtOH. (II) gives a *Me ether*, m. p. 164—167°, $[\alpha]_{5461} +171^\circ$ in CHCl₃, identical with the dehydration product of (III). The identity is confirmed by prep. of the *oxime*, m. p. 182—187°. H₂O is therefore eliminated between the non-acidic OH groups of (I) in its conversion into (II). The acidity of the latter is due to a phenolic OH group.

A. COHEN.

Active substances in testicles. G. PERITZ (Endokrinol., 1931, 9, 355—362; Chem. Zentr., 1932, i, 539).—Three active substances were found in the testicular extract of castrated and castrated rats: (1) increasing the sugar combustion in the organism, (2) causing the development of secondary sexual characteristics, (3) providing for spermiogenesis. Possibly a fourth accelerates testicular growth.

A. A. ELDRIDGE.

Physiology and pathology of urinary excretion of prolan in children and adolescents. F. SCHORCHER (Klin. Woch., 1931, 10, 2221—2222; Chem. Zentr., 1932, i, 539).—The sexual hormone of the anterior lobe could not be found; all the hormone formed at this period appears to be utilised by the generative glands.
A. A. ELDRIDGE.

Influence of the freshness of the testes and of desiccation of the testicular tissue on the yield of testicular hormone. V. KORENCHESKY, R. SCHALIT, and D. GRAETZ (Biochem. J., 1932, 26, 423—428).—Freshness plays an important part in the yield of the hormone. It is possible to dry at 37° testicular tissue without appreciably decreasing the yield of the hormone after boiling the tissue in H₂O.

acidified with AcOH to p_H 4.6—4.8. Besides causing oxidation, the autolytic enzymes present in testicular tissue are probably the most destructive agents of the hormone. S. S. ZILVA.

Assay of testicular hormone preparations. V. KORENCHESKY (Biochem. J., 1932, 26, 413—422).—The wt. of the prostate with the seminal vesicles of castrated rats injected and uninjected with the hormone is compared. An increase of 40% in wt. after 6 days' injection is taken as the criterion for the activity and strength of the prep.

S. S. ZILVA.

Influence of gonads on protein metabolism. I. Urinary creatinine after castration. I. SCHRIRE and H. ZWARENSTEIN (Biochem. J., 1932, 26, 118—121).—Castration causes a 25—50% increase in the urinary creatinine of adult male rabbits. The normal excretion is re-established in a few weeks by a graft of testes. Removal of the graft again increases creatinine excretion. A. COHEN.

Exact evaluation of the specific hormone of the corpus luteum. C. CLAUBERG (Klin. Woch., 1931, 10, 1949—1952; Chem. Zentr., 1931, ii, 3222).—If much follicular hormone is present together with the luteohormone there is an increase in the growth of the uterine muscle. Limiting vals. are given.

A. A. ELDRIDGE.

Function of the endocrine glands on the sugar-excretion threshold. S. YOKOTA (J. Biochem. Japan, 1932, 15, 65—110).—The sugar threshold val., which in the rabbit is normally 0.17—0.20%, is lowered by, transplantation of suprarenal cortex whilst the assimilation is increased. Destruction of the cortical substance is generally accompanied by a rise in the leak-point, whilst the assimilation is unchanged. The leak-point is also increased in adrenalectomy and lowered by destruction of the adrenal medulla. Orally administered thyroid gland or injected thyroxine induces an increase in the threshold val. and a decrease in the assimilation, whilst thyroidectomy has the opposite effect. Injection of pituitrin results in a temporary decrease followed by an increase in the threshold val. and in the sugar tolerance whilst the assimilation is significantly decreased. Subcutaneous administration of anterior pituitary lobe extracts produces a significant fall both in threshold val. and sugar tolerance frequently accompanied by an increase in the assimilation; unlike pituitrin, no increase in the fasting blood-sugar is effected. F. O. HOWITT.

Influence of cryptorchidism on the gaseous and nitrogenous metabolism of rats. V. KORENCHESKY and M. DENNISON (Biochem. J., 1932, 26, 429—434).—The max. increase of gaseous metabolism occurs during the period of greatest resorption of the seminiferous cells. After this period the wt. of the animals returns towards or reaches normal and even in some cases increases. There is a deposition of N in the body, in some rats remaining at or exceeding the normal level even during the period of increased gaseous metabolism. S. S. ZILVA.

Hormone-like diuresis-promoting and -inhibiting substances in human and animal urine.

J. OLIVET (Z. ges. exp. Med., 1931, 78, 650—694; Chem. Zentr., 1931, ii, 2630).—Serum of rabbits suffering diuresis owing to injury of the vermiform process, when injected into other animals, causes polyuria. Extracts having a diuretic action can be obtained from the urine of man and animals.

A. A. ELDRIDGE.

Lovibond value of liver oils of animals and promotion of growth by vitamin preparations. P. KARRER, H. VON EULER, and K. SCHOPP (Helv. Chim. Acta, 1932, 15, 493—495).—The Carr-Price reaction for vitamin-A is applied to the liver oils from a variety of animals, and numerous vitamin-A preps. from such are tested biologically.

H. A. PIGGOTT.

Calcium-phosphorus metabolism in the chicken. III. Influence of cereals and vitamins-A and -D. E. J. KING and G. E. HALL (Poultry Sci., 1931, 10, 332—352).—The anticalcifying action of oatmeal was increased by boiling the meal with 1% HCl followed by neutralisation with NaOH. Data concerning the ash, Ca, P, and phosphatase content of the bones and the Ca and P content of the blood-serum are tabulated.

CHEMICAL ABSTRACTS.

Halibut-liver oil as a source of vitamin-A. J. A. LOVERN (Nature, 1932, 129, 726).—The vitamin-A content of halibut-liver oil varies irregularly from 30 to 1600 blue units in 0.2 c.c. of 20% solution.

L. S. THEOBALD.

Photochemistry of vitamins-A, -B, -C, and -D. F. P. BOWDEN and C. P. SNOW (Nature, 1932, 129, 720—721).—The absorption spectrum of β -carotene contains an additional weak band at 2700 Å. A solution of carotene in cyclohexane, irradiated in an atm. of N_2 by the Hg line 2650 Å., shows the band at 3280 Å. associated with vitamin-A. The solution gives a blue colour with $SbCl_3$ in $CHCl_3$. Vitamin-A is destroyed by light of wave-length 3130 Å. which eliminates the 3280 Å. band in a few hr. Vitamin- B_1 shows 3 bands at 2600, 2400, and 2100 Å. Irradiation by the Hg line 2537 Å. reduces the intensity of the 2600 Å. band and destroys the B_1 activity towards rats. Vitamin- B_1 deactivated by heating with alkali shows a similar absorption spectrum with the 2600 Å. band again missing. Hexuronic acid gives at 2650 Å. a strong band which is practically unaffected by irradiation. Light of wave-length 3000 and 2850 Å. has no effect on the absorption spectrum of narcotine, but a wave-length of 2400 Å. produces a complete change in the spectrum which, after irradiation, consists of a single band at 2900 Å. The 2967 Å. Hg line produces a strong absorption in the calciferol region when used to irradiate ergosterol. Calciferol is completely destroyed by irradiation for 1 hr. with the Hg lines 2650 or 2537 Å.; a slow destruction occurs with the line 3130 Å. L. S. THEOBALD.

Interpretation of the colour match in the anti-mony trichloride test for vitamin-A. R. S. MORGAN (Biochem. J., 1932, 26, 377—380).—The blue reading in the Lovibond match of $CuSO_4$ solution varies widely as the quality of the light from the solution is varied by interposition of red glasses. The variation obtained is similar to that given in the colour matches on a wide range of oils and concen-

trates. The "blue minus yellow" val., however, remains const. and is independent of the interposition of red. This val. is therefore recommended as a criterion for vitamin-A. S. S. ZILVA.

Absorption and elimination of lipins during vitamin-A deficiency. L. EMERIQUE (Bull. Soc. Chim. biol., 1932, 14, 305—312).—Ingestion of different amounts of fat by rats fed on diets lacking in vitamin-A has no effect on the time required for the symptoms of the deficiency to appear. The utilisation of factor-A is not influenced by the fat content of the diet, and there is no decrease with time in the absorption of fat from the diet during the deficiency.

A. LAWSON.

Pecan nut as source of vitamin-A. H. LEVINE (J. Home Econ., 1932, 24, 49—53).—The nut contains about 3—6 (Sherman and Smith) units per g.

CHEMICAL ABSTRACTS.

Absorption spectrum of vitamin-A concentrates. J. W. WOODROW and J. B. PHILIPSON (Proc. Iowa Acad. Sci., 1930, 37, 310).—Prominent bands occur at 310 and 328 m μ , and minor bands at 323 and 340 m μ .

CHEMICAL ABSTRACTS.

Vitamin-A and carotene. IX. Conversion of carotene into vitamin-A in the cow. T. MOORE (Biochem. J., 1932, 26, 1—9).—Small quantities of carotene are found in the body-fat of cows but vitamin-A accumulates in the liver- and milk-fats. In spite of the large amount of carotene available during pasture feeding, the output of carotene and vitamin-A is restricted by liver-storage of reserves which are depleted during stall-feeding. At the end of winter, addition of carotene to the diet increases the carotene and vitamin-A content of the butter-fat. Carotene therefore appears to be converted into vitamin-A as in the rat (A., 1930, 962). Jersey cows yield a butter-fat more highly pigmented than that of shorthorns.

A. COHEN.

Sparing action of fat on vitamin-B. II. Rôle played by m. p. and degree of unsaturation of various fats. III. Rôle of glycerides of single fatty acids. H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1932, 96, 165—177; cf. A., 1929, 852, 1203).—II. The effect of fats in diminishing the dose of vitamin-B necessary for a definite growth performance is independent of their degree of saturation and of their m. p., provided it is low enough for absorption. The effect is unchanged by hydrogenation at 170°, or under pressure, by saponification, distillation, or esterification with glycerol at 230°.

III. In presence of vitamin-B, natural fat is superior in effect on growth to any single glyceride; in absence of vitamin-B some pure glycerides are better, especially myristin and caprylin. The most favourable fatty acids do not necessarily resemble each other in m. p. or length of chain.

J. B. BATEMAN.

Rôle of the vitamin-B complex and alimentary balance in the utilisation of protein. R. LECOQ (Compt. rend., 1932, 194, 1267—1269).—Pigeons fed on various diets deficient in vitamins-B never fail to develop symptoms of avitaminosis even when the diet is rich in protein and poor in carbohydrate,

but under the latter condition the development of symptoms tends to be delayed. With diet lacking vitamins-B and containing various proportions of fat, carbohydrates, and proteins, the addition of brewer's yeast is always beneficial, but even in the presence of vitamins-B the best results are obtained when the constituents of the diet are present in proportion similar to that existing in cow's milk.

W. O. KERMAK.

Isolation of crystalline oryzanin. I. S. OTAKE (J. Agric. Chem. Soc. Japan, 1931, 7, 775—808).—Active (antineuritic) oryzanin (33 g.), obtained from rice bran (100 kg.), was dissolved in H₂O and H₂SO₄ added to p_H 2.6; AgNO₃ was added, and adenine and hypoxanthine were isolated from the ppt. The filtrate was treated with Ba(OH)₂ to p_H 2.5—4.5; nicotinic acid and adenine were isolated from the ppt. The ppt. obtained on further addition of Ba(OH)₂ to p_H 4.5—6.8 afforded nicotinic acid, a base, C₃H₆N₂ (hydrochloride, m. p. 262°), and oryzanin hydrochloride, C₆H₈O₂N₂·HCl, m. p. 250°, resembling Jansen's cryst. vitamin-B. The AgNO₃-Ba(OH)₂ ppt. at p_H 6.8—9.0 afforded nicotinic acid; the filtrate on treatment with phosphotungstic acid yielded choline and a base, C₈H₁₀O₃N (hydrochloride, m. p. 204—205°).

CHEMICAL ABSTRACTS.

Antineuritic vitamin. II. Removal of impurities by oxidising agents. R. J. BLOCK and G. R. COWGILL (J. Biol. Chem., 1932, 96, 127—132).—The action of various oxidising agents on vitamin-B₁ concentrates was investigated. Modification of the CCl₄ process for the purification of the vitamin (this vol., 309) to include the use of H₂O₂ for oxidation of carbohydrate impurities results in a considerable purification without loss of the antineuritic factor.

F. O. HOWITT.

Vitamin-C in goat's and cow's milk. J. C. DE R. DE WILDT and E. BROUWER (Vereen. Expl. Proofzuiv. Hoorn, 1930, 11—20; Chem. Zentr., 1932, i, 412).—The vitamin-C content is the same for both milks; also the vals. for summer and winter milk are very closely similar.

A. A. ELDRIDGE.

Chemical nature of vitamin-C. C. G. KING and W. A. WAUGH (Science, 1932, 75, 357—358).—Vitamin-C, conc. from lemon juice and recryst. from org. solvents, corresponds with a hexuronic acid (cf. this vol., 548). In daily doses of 0.5 mg. it protects growing guinea-pigs from scurvy and permits normal vitality in animals fed on a vitamin-C-free diet.

L. S. THEOBALD.

Hexuronic acid as the antiscorbutic factor. J. L. SVIRBELY and A. SZENT-GYORGYI (Nature, 1932, 129, 690).—The animals treated with hexuronic acid (cf. this vol., 548) showed no scurvy after 90 days. Vitamin-C is therefore concluded to be a single substance identical with hexuronic acid. Other claims (see above) appear to need the support of a chemical analysis and a specification of the test period.

L. S. THEOBALD.

Hexuronic acid as the antiscorbutic factor. S. S. ZILVA (Nature, 1932, 129, 690).—Critical (cf. preceding abstract). Hexuronic acid and the antiscorbutic factor may not be identical.

L. S. THEOBALD.

Reduction capacity of plant foodstuffs and its relation to vitamin-*C*. III. Quantities of reducing substance in various fruits and vegetables. J. TILLMANS, P. HIRSCH, and J. JACKISCH. IV. Reversibility of the oxidation of the reducing substances in lemon-juice. J. TILLMANS, P. HIRSCH, and H. DICK. V. Antiscorbutic action of various extracts of cucumber. J. TILLMANS, P. HIRSCH, and J. JACKISCH (Z. Unters. Lebensm., 1932, 63, 241—267, 267—275, 276—283).—III. The authors' method (this vol., 310) gives results parallel with animal experiments if the samples are extracted with a 4-fold vol. of 3% H_2SO_4 for 4 min., H_2O or cold acid giving lower results; coloured liquids are first extracted with PhNO_2 . Exceptions (e.g., preserves) were due to the presence of metallic salts. Titration with $\text{Na}_2\text{S}_2\text{O}_3$ of the excess of 0.001*N*-I unabsorbed after 1 min. is less sp., and often gives high results, particularly for old solutions. The ratios, max. no. of c.c. of 0.001*N*-indicator equiv. to 100 g. of sample/Hahn's guinea-pig unit, are calc., and the 130 samples are classified. The high vals. from leaf vegetables cannot be attributed to reducing substances other than those associated with vitamin-*C*.

IV. The reducing substances associated with vitamin-*C* (see above, also this vol., 310) may be oxidised by 2:6-dichlorophenol-indophenol by atm. O_2 or H_2O_2 in the warm, or by Cl or I . This oxidation may be reversed (except for O_2 and only partly for Cl) by the action of H_2S for 24 hr., excess being then removed in N_2 ; Pd-H_2 is without effect. The reversal is less rapid at low temp., and is incomplete if the juice is not fresh or if the H_2S is not added soon after the oxidising agent.

V. Animal experiments with hot and cold extracts of cucumber indicate that for aq. extracts the reducing substance associated with vitamin-*C* activity (see above) is more easily oxidised by atm. O_2 than that obtained from lemon-juice. It is also concluded that the oxidation product is not present originally in the cucumber. The titration val. of a H_2SO_4 extract is not raised by the action of H_2S for 1 hr. followed by removal of the excess in a vac., but that of 5 c.c. of juice from a ripe cucumber fell from 2.2 to 0.25 c.c. after 24 hr. in CO_2 , but was raised to 3.9 c.c. by subsequent treatment with H_2S .

J. GRANT.

Properties and structures of crystalline vitamins. J. D. BERNAL (Nature, 1932, 129, 721).—The changes produced in solutions of ergosterol and calciferol by irradiation in monochromatic ultra-violet light can be produced in the crystals and can be observed by the progressive alteration from anisotropic to isotropic material. Ergosterol is changed, presumably to calciferol, by light of 2967 Å., but scarcely at all in 3650, 3130, and 2537 Å. Calciferol is stable at 3650 and 2537 Å. but is destroyed at 3130 Å. Ring mols. are indicated for the structures of vitamin-*B* and hexuronic acid, whilst crystals of β -carotene and α -crocin do not show the long spacings expected from their constitution.

L. S. THEOBALD.

Crystalline vitamin-*D*. C. E. BILLS and F. G. MACDONALD (J. Biol. Chem., 1932, 96, 189—194).—Impure resins, potency 25,000 units per mg., stored

at 0° in CO_2 , crystallised slowly after several weeks. Irradiated ergosterol preps. have marked tendency to form mixed crystals, suggesting that all the cryst. products hitherto described are isomorphous mixtures, containing much inert material. These products show wide variation in antirachitic val.

J. B. BATEMAN.

Vitamin-*D* deficiency and anæmia. H. HAUSS (Z. Vitaminforsch., 1932, 1, 26—38).—Anæmia in rickets is not due to vitamin-*D* deficiency.

H. DAVSON.

Action of vitamin preparations on bactericidal powers of blood. T. HOLSEN (Z. Vitaminforsch., 1932, 1, 3—25).—A daily dose of 60 c.c. of a 1% "vigantol" solution increases the resistance of the rabbit's blood to *Staphylococci*; hypervitaminosis decreases this resistance, an effect which may be counteracted by simultaneous administration of yeast. The latter seems to neutralise the poisonous action of "vigantol." "Pro Ossa," containing vitamins-*A* and -*D*, increases the resistance to *Staphylococci*.

H. DAVSON.

Photographic records of vitamin-*D* line tests. H. STEVENS and E. M. NELSON (Ind. Eng. Chem. [Anal.], 1932, 4, 200—201).—A staining procedure and a photomicrographic apparatus are described.

E. S. HEDGES.

Mode of action of irradiated ergosterol. I. Effect on the calcium, phosphorus, and nitrogen metabolism of normal individuals. W. BAUER, A. MARBLE, and D. CLAFLIN. II. Effect on the calcium and phosphorus metabolism of individuals with calcium-deficiency diseases. III. Effect on formation of bone trabeculae. W. BAUER and A. MARBLE. IV. Hyperparathyroidism. W. BAUER, A. MARBLE, and D. CLAFLIN (J. Clin. Invest., 1932, 11, 1—19, 21—35, 37—45, 47—62).—I. Small doses produced no const. change in Ca or P metabolism; 30 mg. per day caused an increase in faecal and a decrease in urinary Ca and P, the quantities being reversed later. The Ca and P balances and the serum-Ca, -P, and -N were only slightly affected.

II. When there is a deficiency of Ca in the serum or bones, ergosterol therapy produces Ca retention.

IV. The beneficial results are directly related to the Ca intake. On a high Ca intake, with ergosterol, there were: decreased faecal Ca, increased urinary Ca, positive Ca balance, serum-Ca, faecal and urinary P; a fall in positive P balance and serum-P; and a rise in the product of serum-Ca and -P.

CHEMICAL ABSTRACTS.

Photochemistry of ergosterol. E. H. REERINK and A. VAN WIJK.—See this vol., 480.

Hormones and ergosterol intoxication. M. HAENDEL and J. MALET (Rev. assoc. méd. Argentina, 1929, 42, 295—324).—The toxic effects on rabbits of large doses of irradiated ergosterol are diminished by concurrent administration of insulin or sexual hormone, and increased by that of adrenaline, thyroïdin, or hypophysin.

CHEMICAL ABSTRACTS.

Vitamin-*D* content of red palm oil. W. J. DANN (Biochem. J., 1932, 26, 151—154).—Four samples of red palm oil showed very little antirachitic

activity, 100 mg. daily of the richest (native) oil being insufficient to protect rats from rickets. The oil is recommended as a source of vitamin-A free from vitamin-D.

A. COHEN.

Determination of vitamin-D. K. M. KEY and B. G. E. MORGAN (Biochem. J., 1932, 26, 196—207).—The curative effect on rats of graded doses of vitamin-D has been determined by reference to Dyer's scale of healing (cf. this vol., 97). Curves relating degree of healing to dosage are similar to those of Dyer, give similar results for the vitamin-D val. of unknown substances, and agree with results of prophylactic tests in which ash content of fat-free bone is determined. A change in the Ca:P ratio in Steenbock's rachitogenic diet from 4:1 to 2:1 is equiv. to the antirachitic effect of a daily dose of 0.7 unit of vitamin-D.

A. COHEN.

Determination of vitamin-D. I. Relationship between graded doses of a standard solution of vitamin-D, administered to young rats on a rachitogenic diet, and the ash content of their bones. E. M. HUME, M. PICKERSGILL, and M. M. GAFFIKIN (Biochem. J., 1932, 26, 488—505).—With groups of animals of the same litter composition on different doses with 10—20 animals per dose, smooth curves are obtained. When the vals. for the percentage ash are plotted against the logarithms of the doses (with the exception of the lowest and the highest) a linear relationship between the two variables is revealed. For assaying purposes two groups of 8—10 young rats receive suitable doses of irradiated ergosterol, whilst two other groups of animals similarly constituted as regards litter and sex receive two doses of the unknown substance. The average result of the groups receiving the unknown dose is then read from curves which have been constructed to correlate doses of a standard solution of irradiated ergosterol administered prophylactically with the percentage of ash in the bones of young rats on a rachitogenic diet. If the resulting vals. for the doses of the standard do not fall directly on one of the curves, the experiment is repeated. If they do not fall on any of the curves, a graph in which the ash vals. are plotted against logarithms of the doses is employed, since these graphs are straight lines, and a knowledge of two points is sufficient to construct the whole graph.

S. S. ZILVA.

Determination of vitamin-D. II. Comparison of radiography and bone analysis in the estimation of vitamin-D. III. Stability of preparations of vitamin-D. R. B. BOURDELLON, H. M. BRUCE, and T. A. WEBSTER (Biochem. J., 1932, 26, 506—521, 522—530).—II. A radiographic scale is described showing various degrees of development of rickets for use in determination of vitamin-D by measurement of its prophylactic effect. The error in the determination of the resultant effect is considerably greater with the radiographic scale than with bone analysis. The chief variations in the sensitivity of a stock of rats fed on a supposedly const. diet are probably due to some factor other than vitamin-D. The prophylactic radiographic scale is less satisfactory than the curative scale.

III. Vitamin-D in solution in olive oil may de-

teriorate seriously if kept at room temp. for periods of a year or more. Deterioration at 0° has not been detected in the time available. Extrapolation from results at higher temp. suggests that preps. at 0° may lose half their activity in about 3 years, but there is some reason to think that the solidification of the oil has a preservative effect and that the stability at 0° may be greater than the experiments suggest. The addition of various common substances likely to be present as impurities has no very great effect with the exception of S which causes deterioration.

S. S. ZILVA.

Apparatus for determination of carbon dioxide and oxygen of respiration [of fruit]. M. H. HALLER and D. H. ROSE (Science, 1932, 75, 439—440).

L. S. THEOBALD.

Biological effect of associated water molecules. H. T. BARNES and T. C. BARNES (Nature, 1932, 129, 691).—H₂O from recently condensed steam, containing less trihydrol, causes filaments of *Spirogyra* to assume a colourless mass occupying less vol. than the filaments in trihydrol H₂O which maintains the rigidity and turgor of the cells.

L. S. THEOBALD.

Biological degradation of chlorophyll. II. Phyllobombycin and probophorbide. H. FISCHER and A. HENDSCHEL (Z. physiol. Chem., 1932, 206, 255—273; cf. A., 1931, 966).—Hydrolysis of phyllobombycin with KOH in MeOH or PrOH gives a mixture of uncrystallisable chlorins, including chlorin *e*. Treatment with HBr in AcOH at 170° or with HCO₂H at 140° gives small amounts of deoxyphylloerythrin and rhodoporphyrin ester. With HBr-AcOH at 50° phylloerythrin was produced and identified spectroscopically. Reduction with HI after treatment with O₂ led to the isolation of phaeoporphyrin *a*₅ ester. Phyllobombycin, treated with diazomethane without crystallisation, gave the cryst. Me₃ ester (I), m. p. 264° (Fe, Zn, and Cu salts), identical with phaeopurpurin 18 Me₃ ester. Reduction of (I) with HI in AcOH gave an ester, m. p. 224°, spectroscopically resembling chloroporphyrin *e*₄ ester. HBr and AcOH at 170° produced isophaeoporphyrin *a*₄. At 50°, traces of phylloerythrin together with chloroporphyrin *e*₆ were obtained. When treated with pyridine and Na₂CO₃, (I) gave pseudoverdoporphyrin. Phyllobombycin must contain a nucleus with a propionic acid, a nuclear CO₂H, and an OAc radical (the two last from the reductive hydrolytic fission of the isocyclic ring of chlorophyll).

Phylloerythrin was obtained from sheep faeces. Coproporphyrin was also detected and four probophorbides were isolated as the esters: *a* (Me ester, m. p. 226°; oxime; Fe salt); *b* (Me ester, m. p. 207°); *c* (Me ester, m. p. 233°); *d* (Me ester, m. p. 230°). These probophorbides are divided spectroscopically into two groups: (i) *a*, *c*, *d* and (ii) *b*. The analysis of *b* gives the constitution C₃₆H₄₀O₆N₄; with HI *b* yields chloroporphyrin *e*₆ and traces of phylloerythrin. It is closely related to phyllobombycin. Probophorbide *a* resembles phylloerythrin and is converted into the latter by HI in AcOH. Probophorbides *c* and *d* contain more H and OMe than *a* but are easily converted into phylloerythrin.

Winter faeces of rabbits contained phylloerythrin

and a chlorin, isolated as the *Me* ester (diazomethane), m. p. 221°. The crude Et_2O extract after 3 min. with HI in AcOH at 65° gave rhodoporphyrin. Treatment of phaeophytin with HI in AcOH for 2 min. gave phaeoporphyrin α_5 , which when heated for 24 hr. with HBr in AcOH at 50–55° gave phylloerythrin.

J. H. BIRKINSHAW.

Formation of chlorophyll in roots exposed to light, especially in the roots of barley. R. J. GAUTHERET (Compt. rend., 1932, 194, 1510–1513).—The roots of barley may develop a green colour due to chlorophyll when placed in light, the most marked results being obtained with isolated roots detached from the plant. Glucose or fructose added to the medium has a favourable effect.

W. O. KERMACK.

Absorption and migration of nitrogen in the leaves of *Salix fragilis*, L. N. T. DELEANO and M. ANDRESCO (Bul. Soc. Stiinte Cluj, 1931, 6, 209–220; Chem. Zentr., 1932, i, 537).—Three stages in the life cycle are: growth (25%), assimilation period (50%), N-migration (25%). In the last period the N is present chiefly as NH_3 and NH_2 -acids; the quantity of albumin-N falls.

A. A. ELDRIDGE.

Stimulation of growth and metabolism in wheat tissue. A. RADOEFF (Compt. rend., 1932, 194, 1527–1529).—The stimulation of the growth of wheat embryos which is produced by Mg and Mn and to only a very slight extent by Zn, Fe, and Cu, is not accompanied by any significant increase in the metabolic rate measured by the O_2 and CO_2 exchange.

W. O. KERMACK.

Wax metabolism in the leaves of Brussels sprout. P. N. SAHAI and A. C. CHIBNALL (Biochem. J., 1931, 26, 403–412).—The following constituents were identified in the leaf-wax: *n*-nonacosane, 15-nonacosanone, 15-nonacosanol, ceryl alcohol, cerotic acid, and probably *n*-hentriacontane. Olefines were absent. The seeds contain no wax, but synthesis takes place rapidly in all parts of the embryo and proceeds continuously in the leaf throughout the life-history of the plant. The composition of the wax does not alter throughout this period and there is no evidence that the paraffin is formed by reduction of the ketone. All the components of the wax are probably end-products of metabolism.

S. S. ZILVA.

Synthesis and metabolism in cultivated plants. S. ODÉN and K. SJÖBERG (Medd. Centr. Försöksvas. Jordbruk., 1931, No. 386, 3–56; Chem. Zentr., 1931, ii, 3109).—The increase in N and mineral constituents is most marked during the first half of the vegetative period. The carbohydrate content undergoes large variations.

A. A. ELDRIDGE.

Utilisation of excess mineral matter in the leaf in relation to growth of the plant. H. LEGATU and L. MAUME (Compt. rend., 1932, 194, 933–935).—An increased K content of the leaves of the potato is no criterion of the wt. of fresh tubers obtained.

P. G. MARSHALL.

Rôle of plastids and of the cytoplasm in amylogenic condensation. A. MAIGE (Compt. rend., 1932, 194, 1376–1378).—A discussion of the formation of starch in plant cells. The plastids are prob-

ably concerned with the conversion of the proenzyme into the active amylogenase which effects condensation.

W. O. KERMACK.

Absorption of salts by plant tissues. G. E. BRIGGS (Ann. Bot., 1932, 46, 301–322).—Recent work is discussed and evidence advanced to show that the mechanism of salt intake by plants from dil. solutions is by an exchange of anions between solution and cell-sap and of cations between solution and cytoplasm. From more conc. solutions of single salts both anions and cations pass into the sap. In very dil. solutions leaching of ions from cytoplasm and sap is significant.

A. G. POLLARD.

Plant nutrition. III. Effect of potash deficiency on the rate and respiration in leaves of barley. F. J. RICHARDS (Ann. Bot., 1932, 46, 367–388).—Differences in the ratio of dry wt. to leaf area in barley plants grown with varying proportions of K are almost entirely attributable to differences in H_2O content. Leaf-to-leaf variations in the same plant result from differences in anatomical structure. With decreasing proportions of K in the nutrient, respiration rates increase up to a max., subsequently falling with further dilution of the nutrient. These facts are discussed in relation to the carbohydrate and NH_2 -acid content of the leaves. The K content of leaves varies with that of the nutrient, but the relationship is not linear. From leaves rich in K leaching of the element by rain is probable, but no leaching occurs from K-deficient plants.

A. G. POLLARD.

Reserve polysaccharide of the seeds of fennugreek. Digestibility and fate during germination. K. M. DAOUD (Biochem. J., 1932, 26, 255–263).—Acid hydrolysis of the polysaccharide yields equiv. amounts of mannose and galactose. The polysaccharide, which is a salt of a silicophosphoric ester of mannogalactan, is not hydrolysed by saliva or pancreatic extract, and does not alter the blood-sugar after ingestion. During germination of the seeds the mannose and galactose are converted into glucose, fructose, and sucrose.

A. COHEN.

Determination of glutamine in presence of asparagine. A. C. CHIBNALL and R. G. WESTALL (Biochem. J., 1932, 26, 122–132).—In the reaction with HNO_3 in the Van Slyke determination 92% of the total N of glutamine appears as NH_2 -N. After heating glutamine 3 hr. at 100° at p_{H} 8, the amide-N and NH_2 -N are 35.5% and 8.5% of the total N, respectively. Asparagine is stable and gives normal vals. The results are employed to determine the glutamine and asparagine contents of mixtures of these substances and of plant extracts, several cases of which are quoted.

A. COHEN.

Relations between the physiological and geological characters of a forest of *Cryptomeria japonica* and soil conditions. K. MORIKAWA (Bull. Coll. Agric. Kyushu Fukuoka, 1931, 4, No. 4; Proc. Internat. Soc. Soil Sci., 1932, 7, 31).—Transpiration rates and the H_2O and ash contents of leaves varied in parallel with growth rates.

A. G. POLLARD.

Fat, lecithin, and protein of the soya bean. H. KÜHL (Pharm. Zentr., 1932, 73, 243–248).—A review.

Separation of growth-promoting substances. N. NIELSEN and V. HARTELUS (Compt. rend. Lab. Carlsberg, 1932, 19, No. 8, 17 pp.; cf. A., 1931, 1091, 1334).—*Rhizopus suinus* forms two growth-promoting substances when grown in a NH_4 tartrate-glucose medium. One, substance A, is sol. in Et_2O , is readily destroyed on oxidation by H_2O_2 , and promotes the growth of *Avena* coleoptiles as shown by the bending reaction. The other, substance B, is insol. in Et_2O , is not oxidised by H_2O_2 , and promotes the growth of *Aspergillus niger*. Both substances are stable to heat.

F. O. HOWITT.

Chemistry of the plant growth-promoting substance. F. KOGL and R. J. HAAGEN-SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1411—1416).—A unit is defined as the least quantity of active substance which, under standard conditions, will cause a bending of 10° in the decapitate coleoptile of *Avena sativa* within 2 hr. The activity of products from various sources is given. The active principle is obtained as a by-product in the prep. of oestrin from pregnancy urine. A NaHCO_3 extract of the urine is acidified and extracted with Et_2O . Inactive impurity is removed by boiling light petroleum, the insol. residue having an activity of 130,000 units per mg. It is dissolved in aq. EtOH and the solution extracted with C_6H_6 , the hormone remaining in the former. Further purification *via* the Pb salt yields a product of 10^6 units per mg. The active principle after distillation at $125\text{--}130^\circ/0.1$ mm. has an activity of 5×10^6 units per mg. Two crystallisations from aq. COMe_2 yield a product, m. p. 172° (uncorr.) (C 68.62, H 10.18%), with an activity of 30×10^6 units per mg. The name *auxin* is suggested. Theelin (Parke Davis, 50 R.U. per c.c.) is inactive as regards growth effect in contrast to some preps. of progynon.

P. G. MARSHALL.

Flow of sap in plants. B. HUBER (Ber. deut. bot. Ges., 1932, 50, 89—109).—The rate of flow of sap is determined by the rate of transmission of heat from a locally warmed stem area to a thermocouple. Radioactive substances (e.g., Th-B) are successful indicators of sap flow.

A. G. POLLARD.

Relations between the growth of various parts of the melon seedling and the quantity of reserves left for the embryo. P. CHOUARD and G. TEISSIER (Compt. rend., 1932, 194, 1513—1515).—Removal of part of the food reserves from the seeds of *Cucumis melo* results in a general decrease in size of the resulting embryo, but the relative size of the parts is not significantly altered.

W. O. KERMACK.

Stomatal movement and hydrogen-ion concentration. E. P. SMITH and M. S. JOLLY (Nature, 1932, 129, 544).—The p_{H} vals. at which the stomata of the guard-cells of *Tulipa*, *Scilla*, *Iris*, and *Tradescantia* are open in solutions of CO_2 , and in B.D.H. "universal buffer mixture," are recorded.

L. S. THEOBALD.

Radioactivity and the germination of bulbs. D. MONTET (Compt. rend., 1932, 194, 1093—1095).—With the hyacinth and tulip a more fully developed foliage is obtained under the influence of radioactivity, whether supplied in the form of Ra emanation

or U_2O_5 . The optimum quantity of the latter for increased growth of the tulip is 0.5 g. per 1500 g. of soil.

P. G. MARSHALL.

Action of Italian radioactive soils on germination of seeds and on growth of plants. G. MEZZADROLI and E. VARETON (Atti R. Accad. Lincei, 1931, [vi], 14, 443—447).—With plants grown in Knopp's nutrient solution, addition of finely ground radioactive soil showing 4.2×10^{-9} g. of Ra per g. causes marked increases in the root and plant growth. In field experiments, the use of the soil as fertiliser results in greener and stronger plants and in increase of the crop by at least 20%.

T. H. POPE.

Direct versus indirect effects on potato-amylase by chemicals which induce sprouting of dormant tubers. F. E. DENNY (Contr. Boyce Thompson Inst., 1932, 4, 53—63).—The effect of certain chemicals (e.g., ethylene chlorohydrin, NaCNS, and KCNS) on the amylase activity of expressed potato juice (direct effect) was not related to their action in stimulating the sprouting of the tubers, nor to changes in amylase activity produced subsequent to treatment of the whole tissue with these substances (indirect effect). Sprouting response was more nearly related to the indirect amylase effect. KNO_3 and KCl were not markedly active in inducing sprouting and had little effect on amylase activity. The sprouting response to chemical treatment is indirect and is not dependent on the development of high amylase activity in treated tubers.

A. G. POLLARD.

Development and ripening of peaches as correlated with physical characteristics, chemical composition, and histological structure of the fruit flesh. I. Physical measurements of growth and flesh texture in relation to the market and edible qualities of the fruit. M. A. BLAKE, O. W. DAVIDSON, R. M. ADDOMS, and G. T. NIGHTINGALE (New Jersey Agric. Exp. Sta. Bull., 1931, No. 525, 35 pp.; cf. A., 1931, 273).—The increased vegetative activity and production of tender growth resulting from high N feeding occurs independently of the nature of the N source. Repeated treatment with N fertilisers or certain systems of cultural operations produce a high N-low carbohydrate type of tree. Treatments of an opposite character produce a low N-high carbohydrate type.

A. G. POLLARD.

Origin of the uronic acids in the humus of soil, peat, and composts. S. A. WAKSMAN and H. W. REUSZER (Soil Sci., 1932, 33, 135—151).—During the biological decomp. of plant residues, true pentosans are attacked more readily than uronic acid complexes. In different plant materials the relative proportions of various hemicelluloses and the relative ease of decomp. varies considerably. Manuring of soil causes an increase in pentosan content. Prolonged cultivation without the addition of org. matter results in a decreased humus content and a relative increase in uronic acids.

A. G. POLLARD.

Apparatus for continuous extraction of plant materials with ether under tropical conditions. W. J. BLACKIE (J.S.C.I., 1932, 51, 129—130r).—The apparatus is designed to extract 100 g. of material.

Vapour and siphon tubes are carried by a glass connecting piece which is attached at each end by long ground-glass joints to boiling flask (1500 c.c.) and extractor (7×30 cm.). The latter is connected by a ground-glass joint with Hg seal to a worm condenser.

C. W. DAVIES.

Lignin-like complexes in fungi. C. THOM and M. PHILLIPS (J. Wash. Acad. Sci., 1932, 22, 237—239).—Brown-walled moulds such as *Cladosporium* and *Alternaria* contain 17—29% of lignin-like substances, and brown-walled bracket fungi such as *Trametes pini* and *Fomes igniarius* larger proportions. Light-coloured bracket fungi contain very little.

C. W. GIBBY.

Composition of the cell membrane of the alder (*Alnus glutinosa*). K. NEVROS (Praktika, 1931, 6, 270—274; Chem. Zentr., 1932, i, 536).—Schmidt's improved ClO_2 method was employed in the determination of the cellulose:xylan ratio. 0.01—0.2% NaOH removed the carboxyl substances consisting of 2 acids and xylan; with >0.2% the pentosan begins to dissolve, and with 9% max. solubility occurs, with dissolution of cellulose constituents. Attack by 5—7% NaOH on the cellulose is diminished by addition of 3% NaCl without diminution of the solubility of the skeletal substance. The acid-free substance remaining after treatment of the latter with 0.05N-NaOH contains $3\text{C}_6\text{H}_{10}\text{O}_5 : 1\text{C}_5\text{H}_8\text{O}_4$. Hence the cellulose and the H_2O -sol. xylan are chemically combined.

A. A. ELDRIDGE.

Juice of the Maguey plant (*Manso fino*). I. H. D. JONES (J. Amer. Pharm. Assoc., 1932, 21, 354—356).—The composition, properties, and reactions of "aguamiel," the fresh juice of *Agave atrovirens*, Karw, and of the syrup are given.

E. H. SHARPLES.

New vegetable constituent: uric acid. R. FOSSE, P. DE GRAEVE, and P. E. THOMAS (Compt. rend., 1932, 194, 1408—1413).—Uric acid exists in many plants and especially in grains, and has been isolated in a pure form from the seeds of *Melilotus officinalis*.

W. O. KERMAK.

Non-alkaloidal fraction of ergot. H. LANG-ECKER (Arch. exp. Path. Pharm., 1932, 165, 299—324).—The separation of the alkaloids from the amines in extracts of ergot and the standardisation of the latter by comparison with histamine in their action on the small intestine and uterus of the guinea-pig were investigated. The "intestine val." is less than the "uterus val.," but with increasing purity the vals. tend to agree, indicating that the intestine method is sp. for the amine fraction. In ergot preps. the average amine content is lower than the alkaloid content, but the former exhibits a greater stability. Ergotamine (1:40,000) suppresses the tonus action of histamine in the surviving guinea-pig intestine. CO_2 , H_2S , or increased acidity greatly diminishes this action to an extent which is not influenced by the age of the extract. Bacterial infection of the extracts occasionally leads to increased action on the intestine and uterus. Thus following bacterial fermentation a material can be separated which closely resembles, but is not identical with, histamine, although traces of the latter are present.

F. O. HOWITT.

Glucoside fractions of *Digitalis* leaves. M. GUGGENHEIM, K. FROMHERZ, and W. KARRER (Arch. exp. Path. Pharm., 1932, 165, 412—415).—The work of Hoekstra (A., 1931, 1453) is criticised on the grounds that the fractions of *Digitalis* glucosides prepared, e.g., digitoxin, gitalin, and bigitalin, neither were identical with the pure glucosides nor even represented specimens in which the respective glucoside predominated. Hence the quant. fractionation method employed is erroneous. Also digalen occurs in *D. purpurea* and not in *D. lutea*.

F. O. HOWITT.

New glucoside, citronin, from peel of *Citrus limon*. Burm. f. *ponderosa* Hort. R. YAMAMOTO and Y. OSHIMA (J. Agric. Chem. Soc. Japan, 1931, 7, 312—319).—Citronin, $\text{C}_{28}\text{H}_{34}\text{O}_{14}$, m. p. 235° (Ac derivative, m. p. 132°), (yield 0.13%), when heated in a sealed tube with EtOH and H_3PO_4 , afforded citronetin, $\text{C}_{16}\text{H}_{14}\text{O}_5$, m. p. 204° (Me, ether, m. p. 125°), the sugar fraction of which contains rhamnose and glucose (equimol.). Citronin is 5-hydroxy-2'-methoxy-flavanone-7-rhamnoglucoside.

CHEMICAL ABSTRACTS.

Glucoside from Portuguese laurel, *Cerasus lusitanica*, Lois. H. HÉRISSEY and J. LAFOREST (Compt. rend., 1932, 194, 1095—1097).—*Lusitanicoside* crystallises from EtOAc in needles (m. p. 187—188°, $[\alpha]_D^{20}$ —74.69°) and does not contain N. It is hydrolysed by 2.5 wt.-% H_2SO_4 at 100° in 3½ hr. to give a dextrorotatory substance, but only slowly by emulsin. An enzyme prep. from laurel leaves hydrolyses it at room temp. in 5 days, giving a levorotatory saccharide. Pentoses are not formed either by acid or enzymic hydrolysis.

P. G. MARSHALL.

Proteins of grasses. I. E. J. MILLER and A. C. CHIBNALL (Biochem. J., 1932, 26, 392—402).—The protein preps. have a low N content (12.3—14%) and contain varying amounts of N-free impurities which are difficult to remove. The NH_2 -acid composition of a prep. containing 14% N was very similar to that of other leaf-proteins; cystine could not be demonstrated, although the protein contained 1.0% S. Another prep. containing 0.75% S gave only small amounts of inorg. S, suggesting the presence of a non-basic S-containing NH_2 -acid.

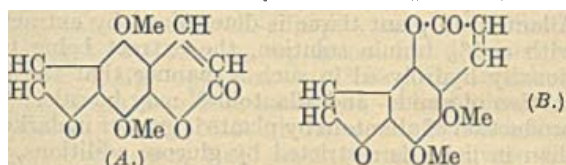
S. S. ZILVA.

Glyceride fatty acids of forage grasses. I. Cocksfoot and perennial ryegrass. J. A. B. SMITH and A. C. CHIBNALL (Biochem. J., 1932, 26, 218—234).—The fatty acids from cocksfoot and ryegrass are mainly unsaturated, saturated acids (palmitic and stearic) being present to the extent of 6 and 12% of the mixed acids, respectively. The presence of α -linolenic and α -linoleic acids is shown by Br addition and oxidation to OH-acids, but no oleic acid is found. Thiocyanometric analysis, which indicates the presence of oleic acid, is discussed critically.

A. COHEN.

Constituents of the root of *Pimpinella saxifraga*. I. F. WESSELY and F. KALLAB (Monatsh., 1932, 59, 161—174).—The light petroleum extract of the root contains pimpinellin (I) (cf. A., 1898, i, 598; 1908, i, 905), $\text{C}_{13}\text{H}_{10}\text{O}_5$, m. p. 119° (sinters at 117°), isopimpinellin (II), m. p. 151° (sinters at 148°), and a substance (still being investigated) closely allied to

(I) and (II). (I) and (II) both contain a lactone and two OMe groups. Reduction of (I) with Na-Hg gives (after distillation) *dihydropimpinellin* (III), m. p. 87—88° (slight previous sintering), converted by Me_2SO_4 and aq. KOH into an *acid* (IV), $\text{C}_{10}\text{H}_6\text{O}(\text{OMe})_3\text{CO}_2\text{H}$, m. p. 119°. Similar reduction of (II) affords a *hydroxy-acid*, m. p. 141° (sinters from 130°), converted by distillation into *dihydroisopimpinellin*, m. p. 99.5°, and by treatment with diazomethane (and subsequent hydrolysis) into (IV). Me_2SO_4 and alkali transform (I) and (II) into the same *acid*, $\text{C}_{10}\text{H}_6\text{O}(\text{OMe})_3\text{CO}_2\text{H}$, m. p. 162° (sinters at 143—156°), reduced by Na-Hg to (IV). Oxidation of (III) with HNO_3 gives $(\text{CH}_2\text{CO}_2\text{H})_2$, whilst (I), (II), (III), bergapten, and xanthotoxin are all oxidised by alkaline H_2O_2 to furan-2:3-dicarboxylic acid. Reduction of the quinone obtained by Thoms (A., 1912, i, 40; 1913, i, 192) from aminobergapten, with SO_2 in H_2O at 90—95° and methylation of the resultant quinol with Et_2O -MeOH diazomethane gives (II), indicating that it is probably (A); (I) is probably (B).



H. BURTON.

Plant chemistry. XXIII. Chemistry of barks. VIII. C. G. DANOFF and J. ZELLNER (Monatsh., 1932, 59, 307—313).—The unsaponifiable matter of the material (2.75% of dry matter) extracted by light petroleum from the bark of the mountain ash (*Sorbus aucuparia*, L.) contains ceryl alcohol (I) and a substance (II), $\text{C}_{35}\text{H}_{69}\text{O}$ (termed *sorbicortol* I), m. p. 193°; the hydrolysate contains stearic acid. The unsaponifiable matter of the Et_2O -sol. matter (7.12%) consists of (I), (II), and *sorbicortol* II, $\text{C}_{16}\text{H}_{30}\text{O}_2$, m. p. 263°, α —28.9° in EtOH (crystallographic data given) (*benzoate*, m. p. 145°); amorphous resin acids are isolated from the hydrolysate. The EtOH extract contains phlobaphens, tannin, invert sugar, and (probably) choline. The dry material contains H_2O -sol. material (18.26%), sol. polysaccharide (0.37%), invert sugar (0.41%), tannin (4.47%), total N (1.55%), crude protein (9.72%), ash (4.62%), crude fibre (42.27%), pentosans (11.24%), and methyl-pentosans (1.16%).

The Et_2O -sol. material from the chestnut (*Castanea sativa*, Mill.) gives (on hydrolysis) phytosterol and higher fatty acids; the EtOH extract contains phlobaphens, tannin, and an unusually large amount of invert sugar.

H. BURTON.

Chemistry of lichens. I. *Peltigera canina*. J. ZELLNER (Monatsh., 1932, 59, 300—304).—The unsaponifiable matter of the light petroleum-sol. fraction of the residue from the COMe_2 extract of the lichen consists mainly of ergosterol. The petroleum-insol. material is separated by Et_2O and aq. KHCO_3 into (a) Et_2O -sol., (b) aq. extract, and (c) an insol. ppt., from which the following are isolated: (a) ergosterol, (b) a trace of an acid, and (c) a phenolic compound, m. p. 158° (sinters at about 150°), which may be identical with peltigerin (Zopf, A., 1909, i, 237).

Further extraction of the COMe_2 -treated material with EtOH affords mannitol and (after hydrolysis) ergosterol as the only recognisable products. The aq. extract of the lichen contains the K derivative of a substance similar to viscotin, small amounts of amorphous polysaccharides, H_2SO_4 , H_3PO_4 , and $\text{H}_2\text{C}_2\text{O}_4$, but no tannin.

H. BURTON.

Chemistry of halophytes. III. J. ZELLNER (Monatsh., 1932, 59, 305—306).—Details are given for the separation of betaine and a pectin-like carbohydrate from the aq. extract of *Suaeda salsa*, Pall.; tannins and a little invert sugar are also present.

H. BURTON.

Process of accumulation of oil and other principal nutritious substances in the grain of flax for fibre and for seed. M. P. ARCHANGELSKI and V. N. SUCHKINA (Bull. Appl. Bot., Russia, 1931, 25, 199—219).—During ripening the daily increase in org. matter and the wt. finally reached are greater in flax grown for seed than in that grown for fibre. The composition of the oil is the same, but is different from that of the oil of immature seed.

CHEMICAL ABSTRACTS.

Properties of plant substances in relation to climate and habitat—volatile oils, saponins, cyanogenetic glucosides, and carbohydrates. J. B. McNAIR (Amer. J. Bot., 1932, 19, 168—193).—Acids, alcohols, esters, and hydrocarbon constituents of volatile oils, saponins, and carbohydrates in plants from temperate regions have higher mol. wts. than those of tropical origin. *d*-Compounds predominate in temperate oils and *l*-compounds in tropical oils. Tropical saponins are less toxic to mice and to trypanosomes than those from temperate areas. Among the hydrolytic products of cyanogenetic glucosides COMe_2 is more general in those of temperate climates and PhCHO in tropical plants. Starches from temperate plants are very reactive, have a wide range of polarisation vals., higher gelatinisation temp., and are less "saturated" towards I than tropical plant starches.

A. G. POLLARD.

Composition of the seed of oleiferous plants in relation to geographical distribution. N. N. IVANOV, M. N. LAVROVA, and M. P. GAPOCHKO (Bull. Appl. Bot., Russia, 1931, 25, 1—86).—In general the oil content of a particular plant decreases from northerly to southerly latitudes. Increasing soil- H_2O increases the oil content and, for flax, the I val. of the oil.

CHEMICAL ABSTRACTS.

Constituents of essential oil in *Asarum*, Sieboldi, var. *seoulensis*, Nakai. T. KAKU, T. KONDO, C. CHO, and T. ORITA (Keijo J. Med., 1931, 2, 566—572).—The oil obtained by steam-distillation (yield 2.21%) had d_4^{25} 0.9988, $[\alpha]_D^{25}$ —0.75°, n_D^{25} 1.5141, sap. val. 28.4 (after acetylation 56.1), and acid val. 28.4. Constituents included palmitic acid, a phenol, $\text{C}_{10}\text{H}_{10}\text{O}_4$ (0.51%), *l*- β -pinene, saffrole, methyleugenol (47%), and eucaryone.

F. O. HOWITT.

Occurrence of iodine in fruits of *Feijoa sellowiana*, Berg. L. V. SERGEEV (Bull. Appl. Bot., Russia, 1931, 25, 279—288).—An irregularly high H_2O -sol. I content is recorded.

CHEMICAL ABSTRACTS.

Physiological effects of boron on wheat. H. S. MORRIS (Bull. Torrey Bot. Club, 1931, 58, 1—30).— $\text{Na}_2\text{B}_4\text{O}_7$, H_3BO_3 , or $\text{K}_2\text{B}_4\text{O}_7$ was toxic in concns. >0.005 g. of B per litre: except at high concns. of FeSO_4 neither Ca nor Fe reduced the toxicity. The alkali borates, but not H_3BO_3 , stimulate growth at concns. between 0.003 and 0.0005 g. of B per litre. With $\text{Na}_2\text{B}_4\text{O}_7$ and H_3BO_3 on wheat, differences attributed to p_{H} were observed.

CHEMICAL ABSTRACTS.

Rauwolfia serpentina, Benth. L. VAN ITALLIE and A. J. STEENHAUER (Pharm. Weekblad, 1932, 69, 334—348).—Three alkaloids have been isolated from the root; that present in greatest quantity (*rauwolfine*) resembles in properties and reactions the ajmaline of Siddiqui (this vol., 203), but has the formula $\text{C}_{21}\text{H}_{25}\text{O}_2\text{N}_2$, m. p. 160° , $[\alpha]_{\text{D}} +13.1^\circ$ (hydrochloride, m. p. 130 — 140° , $[\alpha]_{\text{D}} +96.6^\circ$). The other two alkaloids (not characterised) have m. p. 262° and m. p. 177° , $[\alpha]_{\text{D}} -76.4^\circ$, respectively.

S. I. LEVY.

Millet proteins. H. ITO (Res. Bull. Gifu Imp. Coll. Agric., 1931, No. 17, 1—68).—The albumin, globulin, glutelin, and prolamine were isolated from *Panicum miliaceum*, *P. Crus-galli* var. *frumentaceum*, and *Setaria italica*; the properties and NH_2 -acid-N distribution were compared. CHEMICAL ABSTRACTS.

Influence of ageing on the alkaloid content of poppy capsules. C. BRAGA (Arch. Farm. sperim., 1931, 53, 255—260).—Ripe capsules of *Papaver somniferum* do not lose in alkaloid content during ageing. During ripening, the alkaloids of the narcotine and codeine group increase in amount at the expense of the morphine. Incision of the capsule does not influence the alkaloid content. T. H. POPE.

Fluctuations in the alkaloid content of the lupin. N. N. IVANOV and M. N. LAVROVA (Bull. Appl. Bot., Russia, 1931, 25, 291—302).—The total N content varied from 4.0 to 6.1% for *Lupinus angustifolius* and from 5.4 to 7.3% for *L. luteus*; the alkaloid content was parallel to the N content.

CHEMICAL ABSTRACTS.

Alkaloids of *Archangelisia flava* (L.), Merr. A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1931, 1, 153—161).—The principal alkaloid is berberine; small quantities of jatrorrhizine, columbamine, and shobakunine were isolated.

CHEMICAL ABSTRACTS.

Alkaloids of *Pheanthus ebracteolatus* (Presl), Merrill. Pheanthine. I. A. C. SANTOS (Rev. Filipina Med. Farm., 1931, 22, No. 9, 11 pp.).—At least 2 alkaloids are present. Pheanthine, $\text{C}_{34}\text{H}_{38}\text{O}_6\text{N}_2$, m. p. 210° , $[\alpha]_{\text{D}}^{20} -278^\circ$ in CHCl_3 [hydriodide, m. p. 268° ; picrate, m. p. 263° ; chloroaurate, m. p. 170 — 171° ; chloroplatinate, m. p. 280° (decomp.)], contains 3 OMe and 2 NMe groups, but no OH, CO, or CH_2O , groups or lactone structure. The structure is probably based on a tetrahydroisoquinoline ring system. (See this vol., 472.) CHEMICAL ABSTRACTS.

Alkaloids of *Argemone alba*, Lestib. P. A. FOOTE (J. Amer. Pharm. Assoc., 1932, 21, 246—248).—The dried overground portions of the flowering plant contain 2.63% (stems 3.25%) of alkaloid consisting principally of berberine. A small quantity of

an alkaloid giving a picrate, m. p. 232 — 235° , was isolated. Berberine was the only alkaloid found in the root. E. H. SHARPLES.

Isolation of sparteine from *Lupinus barbiger* (Watson). J. F. COUCH (J. Amer. Chem. Soc., 1932, 54, 1691—1692).—The light petroleum-sol. alkaloids from the leaves and stems of *L. barbiger* contain sparteine, isolated as the mercurichloride. Evidence for the presence of lupmine is not obtained. Two or three other alkaloids are present. C. J. WEST (b).

Fats of brown sea-weeds. B. RUSSELL-WELLS (Nature, 1932, 129, 654—655).—In the series *Pelvetia libera*, *P. canaliculata*, *Fucus vesiculosus*, and *Laminaria digitata* which grow at increasing depths, the fat content decreases with an increase in depth of immersion whilst that of the unsaponifiable residue increases; the general character of the fats is approx. the same. L. S. THEOBALD.

Origin of allantoin in plants. H. PURUCKER (Planta [Z. wiss. Biol.], 1932, 16, 277—331).—Allantoin in plant tissue is determined by extraction with a 4% tannin solution, the extract being fractionally hydrolysed in such a manner that the proportion of amide- and allantoin-N may be calc. The production of allantoin by plants is greater in darkness than in light, is restricted by glucose additions, but not appreciably affected by CHCl_3 narcosis. Allantoin is produced by the oxidation of purines and uric acid. The latter is not an intermediate product of purine oxidation, but is itself oxidised in several stages, one of which involves the formation of urea. Plants containing allantoin are characterised by cell-sap contents of high p_{H} in which purine degradation ceases with the formation of allantoin. The function of allantoin in plants is not that of counteracting NH_3 -poisoning. A. G. POLLARD.

Relation of life to electricity. VII. Stainability and electromotive forces in tissues which do not depend on acid-base combination. R. BEUTNER (Protoplasma, 1932, 15, 1—14).—Differential staining of cuticular and parenchymatous tissue, e.g., in the apple, is not related to acid-base combinations previously described (A., 1931, 1451) but to differences in partition coeffs. and other factors.

A. G. POLLARD.

Absorption and accumulation of solutes by living plant cells. I. Conditions which determine salt absorption by storage tissue. F. C. STEWARD (Protoplasma, 1932, 15, 29—58).—The accumulation of Br' in the sap of sliced potato tubers during immersion in aq. KBr is dependent on the maintenance of a high O_2 and low CO_2 concn. in the medium. Accumulation ceases at 5 — 6° . The extent of the accumulation is unaffected by illumination, but is markedly influenced by agitation. A logarithmic relationship exists between the internal and external Br' concns. Br' does not replace Cl' in the tissue to any appreciable extent. Absorption of both K and Br' was considerable, but over any given time interval that of K was the greater. Freshly cut tissue immersed in salt solutions rapidly loses relatively large proportions of K and Mg and smaller amounts of Ca. These appear to be combined with org. anions. Dur-

ing the subsequent accumulation of K^+ and Br^- the internal concn. of Ca and Mg changed but little. The absorbed Br^- is in true solution in the cell-sap. In aerated solutions the time required to attain equilibrium between KBr solution and cell-sap may exceed 100 hr.

A. G. POLLARD.

Genetical and biochemical aspects of anthocyan pigments. M. W. ONSLOW (Nature, 1932, 129, 601—604).—A review. L. S. THEOBALD.

Tormentol in several species of *Potentilla*, L. P. GILLOT and H. WIOLAND (Bull. Soc. Chim. biol., 1932, 14, 313—316).—Tormentol found in *P. tormentilla* (A., 1915, i, 83) occurs also in *P. anserina* and *P. reptans*, but not in *P. verna*. A. LAWSON.

**Enzyme and salt-ions. III. Saccharogen-
amylase of the leaves of differently nourished
potatoes.** G. VON DOBY and E. SZLADITS (Z. physiol. Chem., 1932, 206, 177—186; cf. A., 1931, 876).—The saccharogen-amylase of the leaves of potatoes grown on differently fertilised soil, viz., (a) unfertilised, (b) K-fertilised, and (c) K^+ , PO_4^{3-} , and Ca-fertilised, was compared. The pH optimum for amylase is 6.75, the temp. optimum is 38.8°. The amylase concn. always decreases with age; it is highest on (a). Salts (NaCl, NaF, KCl) activate according to the fertilisation, NaF most strongly in case (a) at 0.001M; in case (c) at 0.1M it inhibits. Autolysis in case (a) increases the amylase activity up to 40% above normal on the 4th day; in the other cases the amylase activity falls from the 1st day. Salts, particularly NaF, augment the action of autolysis.

J. H. BIRKINSHAW.

Constituents of gums. I. Gum arabic. E. PFAU (Apoth.-Ztg., 1931, 46, 724—725; Chem. Zentr., 1931, ii, 3218).—Gum arabic consists of 0.8% of NH_2 -acid (as salt), 2.6% of ash, a small quantity of carbohydrate, and a substance which is regarded as a connecting link between cellulose and carbohydrate (approx. 21% of galactose + 75% of arabinose).

L. S. THEOBALD.

Oil from the fruit of *Melia azedarach*, L. L. E. HARRIS and R. M. WILSON (J. Amer. Pharm. Assoc., 1932, 21, 242—244).—Extraction of the ground fruit with light petroleum gave 7.38% of oil having d_{25}^{25} 0.9218, I val. (Hanus) 73.1, sap. val. 188.3, acid val. 3.5, and unsaponifiable matter 1.1%. The fatty acids contained oleic, linoleic, linolenic, and probably myristic and lauric or palmitic acids.

E. S. SHARPLES.

Interrelation between substances in plants: essential oils and resins, cyanogen and oxalate. J. B. MCNAIR (Amer. J. Bot., 1932, 19, 255—271).—Essential oils, resins, and CaC_2O_4 occur in twice as many species of tropical plants as in temperate ones. Essential oils and resins are found in similar anatomical structures and the constituents of the oils form resins by polymerisation or condensation. In plants CaC_2O_4 occurs in both mono- and tri-hydrated crystals, the latter predominating in temperate climates. Plants containing cyanogenetic glucosides also produce CaC_2O_4 in practically all instances.

A. G. POLLARD.

Resin of *Ipomoea*. L. E. WARREN (J. Amer. Pharm. Assoc., 1932, 21, 217—223).—The charac-

teristics of 15 specimens of resin from *I. orizabensis*, Ledenois, ranged between the following limits: H_2O 0.65—5.25%, ash 0.07—1.03%, acid val. 8—18, sap. val. 171—195, ester val. 160—190, H_2O -sol. 0.22—7.49%, Et_2O -sol. 58—96%, $EtOH$ -insol. 0.015—2.76% (13 < 1%), light petroleum-sol. 1.70—3.48%.

E. H. SHARPLES.

Croton-seed. II. Vesicant principle. E. CHERBULIEZ, E. EHNINGER, and K. BERNHARD (Helv. Chim. Acta, 1932, 15, 658—670).—The vesicant principle is obtained as a pale-coloured resin by extraction of croton-seed oil or of a MeOH extract of the seed with a mixture of Et_2O or light petroleum (b. p. 65—70°) with aq. MeOH (90%) or C_5H_5N ; 0.05—0.1% is thus obtained from the oil and 1—2.8% from the total seed. No loss of the vesicant properties occurs during its isolation. The product is unsaturated and has alcoholic properties; its vesicant properties are destroyed by bromination and considerably lessened by acetylation in the cold. Measurements of $[\alpha]_D$, I val., and Ac val. indicate that it is a mixture. It is not the cause of the purgative properties of the oil.

H. A. PIGGOTT.

Significance of the occurrence of saponins for the systematic botany of varieties of *Clematis*. E. GILG and P. N. SCHURHOFF (Arch. Pharm., 1932, 270, 217—223).—Prantl's subdivision of the genus *Clematis* is in the main supported by the presence or absence of saponins.

R. S. CAHN.

Poisonous constituent of *Coriaria intermedia*, Matsumura. J. MARANON (Philippine J. Sci., 1932, 47, 359—367).—The poisonous constituent of this shrub (which contains also gallic acid) is coriamyrtin. This substance, $C_{15}H_{18}O_5$, m. p. 218°, $[\alpha]_D^{25}$ —42.68° (in $EtOH$) (colour reactions described), reduces Fehling's solution after hydrolysis by acid, but is not a glucoside.

R. S. CAHN.

Iron content of vegetables and fruits. H. K. STIEBELING (U.S. Dept. Agric., Circ. No. 205, 1932, 19 pp.).—Many original and published analyses of 110 different parts and varieties of vegetables and fruit show that most Fe is contained in potatoes and chlorophyll-containing parts of plants, but fruits on the whole are poor sources of this metal.

E. B. HUGHES.

Unequal manganese contents of green and of etiolated leaves. G. BERTRAND and (ALME.) M. ROSENBLATT (Compt. rend., 1932, 194, 1405—1408).—In a no. of vegetables examined, etiolated leaves contained less Mn than green leaves of the same species and variety.

W. O. KERMACK.

Membranes of spores and pollens. VI. Determination of the polyimide-bitumens of brown and mineral coals. VIII. Pollenin from a brown coal. F. ZETTSCHKE and O. KALIN (Helv. Chim. Acta, 1932, 15, 412—431, 457—464).—VI. Sporin is estimated by measuring the increase in wt. on bromination, nitration, and oxidation. Lange-sporin, treated thus, is stable at room temp. and very sensitive to bases, by which it is debrominated. Fusin was determined by measuring its increase in wt. on conversion from its NO_2 - into its bromonitro-form. The polyimide-bitumens of

substances of varying stages of carbonisation, ranging from peat to mineral coal, were determined by treatment with Br and HNO_3 , washing the residue with HNO_3 , EtOH, and Et_2O , and, after drying over P_2O_5 , weighing. If the coal contains cellulose, treatment with H_3PO_4 is necessary. The stages in the natural carbonisation of the raw materials cellulose, lignin, fat, etc. are discussed.

VIII. Comparison of the empirical formulæ of pollenin, obtained from a brown coal and from *Pinus sylvestris*, bothrodendrin, obtained from a later brown coal, Lange-sporonin from a mineral coal, and tasmanin from an oil shale, shows that the process of carbonisation is accompanied by dehydration which may be followed by the addition of H_2 or S; in the former case an oil-shale results, in the latter a brown coal which loses H_2S to form an older brown coal. This loses H_2O , H_2S , and H_2 to form a mineral coal. A high S and OH-group content corresponds with easy oxidation by conc. HNO_3 . H. DAVSON.

Changes in root-tips of wheat and maize grown in mutual solutions deficient in calcium. R. BAMFORD (Bull. Torrey Bot. Club, 1931, 58, 149—178).—The injury is described. In the absence of Ca, other constituents of the culture solution, and especially Mg, are highly toxic to the root cells.

CHEMICAL ABSTRACTS.

Growth and variability of wheat seedlings in magnesium sulphate solutions. J. CARMIN (Bull. Torrey Bot. Club, 1931, 58, 179—190).—

CHEMICAL ABSTRACTS.

Magnesium injury of wheat. S. F. TRELEASE and H. M. TRELEASE (Bull. Torrey Bot. Club, 1931, 58, 127—148).—Injury of wheat, oats, rye, or barley seedlings grown in culture solutions containing 0.01—0.0025M-MgCl₂ is decreased or suppressed by addition of Ca or Sr.

CHEMICAL ABSTRACTS.

Action of arsenic on leaves. I. A. PARFENTIEF and W. K. DEVRIENT (J. Pharm. Exp. Ther., 1932, 44, 171—189).—A cut bean-leaf, after immersion in H_2O , loses aq. vapour at the same rate as an uncut one immersed in 0.1% aq. As_2O_3 , showing that the toxic action of As is due to the prevention of utilisation of H_2O by the cells. The conductivity to H_2O of the vessels and the plasmolytic activity of the cells are unimpaired by treatment with As. The extracts obtained by immersing leaves in As solutions contain a hexose which is believed to be combined with As_2O_3 . The toxic action of As on leaves is ascribed to the decomp. of glucosides to form a complex with As. H. DAVSON.

Toxicity of sodium nitrate for a species of moss. A. B. BEAUMONT (Science, 1932, 75, 312—313).—Chilean NaNO_3 is toxic to *Polytrichum commune*. KNO_3 , KCl, and NaCl are also toxic but not $\text{Ca}(\text{NO}_3)_2$, urea, $(\text{NH}_4)_2\text{SO}_4$, or Ca cyanamide.

L. S. THEOBALD.

Toxic substance in mulberry leaves damaged by tobacco. T. YABUTA and T. KOZU (J. Agric. Chem. Soc. Japan, 1931, 7, 932—941).—Leaves of mulberry, growing near tobacco, were toxic for the silk-worm owing to the presence of nicotine (1 in 10⁵).

CHEMICAL ABSTRACTS.

Assimilation of potato plants infected with leaf-roll. D. MULLER (Planta, [Z. wiss. Biol.], 1932, 16, 10—16).—The reduced dry matter production of diseased plants is partly or wholly the outcome of reduced assimilation intensity. A. G. POLLARD.

Use of celloidin in botanical technique. R. H. WETMORE (Stain Tech., 1932, 7, 37—62).

Titration of sugar with de Jong's reagent. N. SCHOORL (Pharm. Weekblad, 1932, 69, 253—255).—De Jong's method (this vol., 295) is accurate to within 5% if air is prevented from reaching the solution by keeping the liquid boiling. S. I. LEVY.

Determination of sugars in plant extracts. T. G. PHILLIPS (J. Biol. Chem., 1932, 95, 735—742).—EtOH extracts of plants were freed from EtOH, the aq. suspensions cleared with neutral $\text{Pb}(\text{OAc})_2$, and excess of Pb was removed by $\text{Na}_2\text{C}_2\text{O}_4$. The sugar contents of the resulting solutions were determined by methods employing reduction of Cu salts. For amounts of glucose less than 5 mg. a modified Fehling's method (A., 1922, ii, 92) is not satisfactory. No one reagent of those used is suitable for every type of plant extract. The corrections for sucrose vals. as given by glucose determinations before and after inversion were investigated. F. O. HOWITT.

Determination of amides in presence of carbohydrates. F. BAERTS and P. DELVAUX (Bull. Soc. Chim. biol., 1932, 14, 224—228).—The method of Schulze for the determination of amide-N does not give accurate results due to the partial decomp. of glutamine and asparagine in the $\text{NH}_2\text{-N}$ determination, and to the combination of fructose with the liberated NH_3 in the total-N determination. The loss of N in the second case increases as the duration of hydrolysis and the amounts of sugar and acid present increase. A. LAWSON.

Nephelometric micro-method for determination of cholesterol. O. MUHLBOCK, C. KAUFMANN and H. WOLFF (Biochem. Z., 1932, 246, 229—246).—Bloor's method is recommended as being most trustworthy. A nephelometric micro-method for the determination of free and combined cholesterol in serum, blood, and organs is described.

P. W. CLUTTERBUCK.

Sero-diagnosis in foodstuff investigations. C. GRIEBEL and H. MAASS (Z. Unters. Lebensm., 1932, 63, 166—176).—Sp. anti-sera were prepared by defatting ground seeds with Et_2O and removing sugars in EtOH, followed by extraction of the residue with physiological saline. The filtered and diluted extract was then injected into dogs (2—5 c.c. in 2—4 days) and the anti-serum collected. Almond or apricot stones yielded sera which were sp. for both of these substances, but it was not possible either by means of the precipitin test itself or by fractional pptn. of the resulting deposits to distinguish between them. Sp. sera were obtained for hazelnut and groundnut and for anacardium (cashew nut) and pine seeds but not for walnut. The method has been applied successfully to the detection of ground hazels, pine, and anacardium seeds among hazels in chocolate. J. GRANT.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1932.

General, Physical, and Inorganic Chemistry.

Theoretical intensities in the spectrum of H_α. W. C. PRICE (Proc. Roy. Soc., 1932, A, 136, 264—271).—The calc. intensities agree with experiment.

L. L. B.

Isotope effect in the band spectrum of LiH. G. NAKAMURA and T. SHIDEI (Japan. J. Phys., 1931, 7, 33—46).—Full data for bands previously reported (cf. this vol., 1) are tabulated. Intensities indicate a relative abundance Li⁷ : Li⁶ varying from 5 : 2 to 8 : 1.

N. M. B.

Quantum mechanics of lithium hydride. E. HUTCHISSON and M. MUSKAT (Physical Rev., 1932, [ii], 40, 340—344).—Mathematical.

N. M. B.

Electric arc between carbon and substances which are insulators at ordinary temperatures. M. PIERUCCI (Nature, 1932, 129, 724).—The chief characteristics of electric arcs formed between C and heated glass, chalk, or porcelain are described.

L. S. T.

Quantum analysis of the rotational structure of the first positive bands of nitrogen. S. M. NAUDE (Proc. Roy. Soc., 1932, A, 136, 114—144).—An analysis has been made of the 5 → 2 (6705 Å.) and 6 → 3 (6623 Å.) bands of N₂. The structure agrees with a ³Π → ³Σ transition. The results indicate that the N₂ nucleus has unit internal angular momentum. The mol. consts. have been evaluated.

L. L. B.

Decrease in intensity in forbidden series. S. SAMBURSKY (Z. Physik, 1932, 76, 132—134).—The abnormally slow decrease in intensity in the forbidden Na series is explained on the assumption of forced dipole radiation.

A. B. D. C.

Ultra-violet absorption bands of sodium vapour. M. KIMURA and Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 109—118).—The absorption and emission spectra of Na vapour have been investigated in the ultra-violet region. Six band systems were detected in the former and two in the latter and the vibrational structures analysed. Energy levels of the Na atoms produced by dissociation of excited Na₂ mols. have been determined.

J. W. S.

Emission of the yellow-red band spectrum of sodium. M. KIMURA and Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 119—129).—The emission band spectrum of heated Na vapour excited by a high-tension discharge is identical with certain parts of the absorption spectrum of Na₂.

Magnetic rotation spectrum and heat of dissociation of the sodium molecule. F. W. LOOMIS and R. E. NUSBAUM (Physical Rev., 1932, [ii], 40, 380—386; cf. A., 1928, 460).—Wood's magnetic rotation spectrum of Na₂ has been extended by the method used with Li₂ and K₂ (cf. this vol., 207) to higher vibrational levels. The energy of dissociation of the normal mol. is, by extrapolation, 0.76 ± 0.02 volt, in good agreement with experimental data.

N. M. B.

Heat of dissociation of sodium molecule. W. H. RODEBUSH (J. Amer. Chem. Soc., 1932, 54, 2123).—Recent data lead to a val. of 0.76—0.78 volt.

C. J. W. (c)

Nuclear spin of phosphorus from the band spectrum. F. A. JENKINS and M. ASHLEY (Nature, 1932, 129, 829—830).—High-dispersion spectrograms of the P₂ bands show that the intensities alternate in a manner to be expected from a mol. composed of two like atoms. The intensities alternate in the ratio 3 : 1 and the nuclear spin of the P atom is $\frac{1}{2}$. The deduced val. of the moment of inertia of P₂ in its normal state is 90.8 × 10⁻⁴⁰ g.-cm.², and the internuclear distance 1.88 × 10⁻⁸ cm.

L. S. T.

Spectra of inert gases. II. E. RASMUSSEN (Z. Physik, 1932, 75, 695—704; cf. this vol., 208).—The arc spectrum of A is completed by addition of a new term.

A. B. D. C.

Stark effect for argon. N. RYDE (Nature, 1932, 129, 758—759).—The Stark effect for A has been observed; the displacements of the energy levels of A in electrical fields are much smaller than those of Ne.

L. S. T.

Estimation of temperature of exploded aluminium vapour by means of an aluminium hydride emission band. H. NAGASHIMA (Sci. Rep. Tokyo Bunrika Daigaku, 1932, 1, 219—225).—The intensity of the AlH band at 4241 Å. when an Al wire was exploded by passing a heavy electric current through it in H₂ was determined, and the temp. of the mols. in the vapour was calc. to be 2500°.

A. J. M.

Nuclear moment of potassium and silver. S. FRISCH (Physikal. Z. Soviet Union, 1932, 1, 302—303).—A series of K II lines in the visible region, generated in a discharge tube, has been investigated. The magnetic moment of the K nucleus is small compared with that of the Na nucleus, and the Ag has a smaller magnetic moment than Cu.

J. W. S.

Anomalous dispersion of calcium vapour. A. FILIPPOV and N. KREMENEVSKY (Physikal. Z. Soviet Union, 1932, 1, 299—301).—The relative intensities of the lines in the $1S-mP$ series in the absorption spectrum of Ca vapour have been determined, and the corresponding transition probabilities calc. These indicate that Ca vapour is not monat. J. W. S.

Zeeman effect in the arc spectrum of nickel. C. J. BAKKER (Proc. R. Akad. Wetensch. Amsterdam, 1932, 35, 82—91). J. W. S.

Anomalous dispersion of zinc and cadmium vapours. A. FILIPPOV (Physikal. Z. Soviet Union, 1932, 1, 289—296).—The anomalous dispersion of Zn and Cd resonance lines has been measured with a Jamin-Mach interferometer. J. W. S.

First spark spectrum of arsenic (As II). A. S. RAO (Proc. Physical Soc., 1932, 44, 343—348; cf. A., 1929, 733).—Combinations between the deep terms of the singlet and triplet system of As II were discovered, and about 70 lines classified. A provisional term scheme is set up, the largest term leading to an ionisation potential of about 20.1 volts. N. M. B.

Term values in the arc spectrum of selenium. R. C. GIBBS and J. E. RUEDY (Physical Rev., 1932, [ii], 40, 204—206).—The region λ 1000—10,000 was photographed. Classified ultra-violet and new classified lines and all known terms are tabulated. The first ionising potential of the Se atom in its lowest energy state is $78,659 \pm 2$ cm.⁻¹ or 9.70 volts. N. M. B.

Fluorescence spectrum of iodine. J. J. AGAR-BICEANU (Compt. rend., 1932, 194, 1913—1914; cf. this vol., 552).—A revised table of the fluorescence spectrum of I₂ as excited by λ 5461, 5770, and 5791 is given, including new anti-Stokes terms (—4), (—5), and (—6) of the series excited by λ 5770 and 5791. The quantum levels $v''=0$ now become $v''=4$ (cf. A., 1922, ii, 178; 1923, ii, 669). C. A. S.

Isotope displacement effects for mercury, thallium, and lead. H. SCHULER and E. G. JONES (Z. Physik, 1932, 76, 14—18).—Hg I and Hg II have isotope displacements in the same direction; Pb I and Pb II are also in one direction, but opposite to the Hg displacements, whilst Tl II are opposite to Tl I. Isotope displacements have been spectroscopically observed only for light and heavy elements. A. B. D. C.

Absorption spectrum of mercury vapour. H. KUHN and K. FREUDENBERG (Z. Physik, 1932, 76, 38—54).—The heat of dissociation of Hg₂ is 1.6 kg.-cal., and that of the initial state of the 3300 Å. emission band 17 kg.-cal. A. B. D. C.

Hyperfine structure of lead lines between 5000 and 8000 Å. Proof of existence of the lead isotope 204. H. SCHULER and E. G. JONES (Z. Physik, 1932, 75, 563—569). A. B. D. C.

Pressure shift and broadening of spectral lines. H. MARGENAU (Physical Rev., 1932, [ii], 40, 387—408).—Theoretical. An analysis directly applicable to absorption lines, but qualitatively correct for emission lines, is presented, and compared with data for the shift of λ 2537 (Hg) in foreign gases. The shift is proportional to the density of the perturbing

gas, and is usually to the red, with a slight dependence on temp. N. M. B.

Hyperfine structure and selective absorption. B. VENKATESACHAR (Z. Physik, 1932, 75, 676—678).—Polemical against Lau and Reichenheim (this vol., 208). A. B. D. C.

Isotopic displacement and hyperfine structure. G. RACAH (Nature, 1932, 129, 723—724).—Theoretical. L. S. T.

Complex spectra. G. H. SHORTLEY (Physical Rev., 1932, [ii], 40, 185—203).—Theoretical. N. M. B.

Validity of the Schwarzschild relation as applied to the use of the logarithmic sector. F. TWYMAN and A. HARVEY (Trans. Opt. Soc., 1932, 33, 1—8).—The relation is valid within the limits of an experiment for an intensity range of 150 : 1, obtained by varying the distance from the source of the slit, with exposures of 2 min. for a condensed spark between Sn electrodes, the relation being applied to the logarithmic sector used in conjunction with a quartz spectrograph. The length of a spectral line on the plate is proportional to the log. of its intensity. N. M. B.

Emission of the auroral green light in the night sky. M. KIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 166—176).—Of the four processes by which atm. O₂ can be excited to ¹S state atoms, ready for the emission of the auroral green 5577 Å. line, the principal will be the collision of ¹D state O atoms with ²D state N atoms. Both these atoms are produced by the action of solar radiation during the day. J. W. S.

Auroral spectrum in the infra-red. W. JEVONS (Nature, 1932, 129, 759—760).—A discussion of Vegard's numeration (cf. this vol., 441). L. S. T.

Visual spectroscopic method for heterochromatic photometry. L. S. ORNSTEIN, J. G. EYMERS, and D. VERMEULEN (Z. Physik, 1932, 75, 575—583).—A double monochromator may readily be adapted for visual comparison of intensities at different wave-lengths, and eliminates error due to uncertainty in the effective wave-length of filters. A. B. D. C.

New mass spectrometer. W. R. SMYTHE and J. MATTAUCH (Physical Rev., 1932, [ii], 40, 429—433; cf. A., 1927, 85).—A design to avoid the presence of particles of velocities other than those desired, and to eliminate contamination by Hg from the pumps, is described. N. M. B.

Use of a large Rowland grating, and its defects. P. LACROUTE (Compt. rend., 1932, 194, 1803—1805).—By interposing a cylindrical lens, preferably of quartz, with the axis horizontal, between the slit and the grating, the luminosity attainable when using a concave Rowland grating can be increased 5—10 times. The production of "ghosts" is discussed. S.

Optical experiments on the accommodation coefficients for molecular rotations of rarefied gases. W. R. VAN WIJK (Z. Physik, 1932, 75, 584—596).—The distribution of intensity in the band lines was used to determine the change in rotational

energy of mols. on collision with walls in the containing vessel. H_2 gave uncertain results, but N_2 showed that the ordinary condensation and re-evaporation theory is incomplete; as the rate of rotation increases the probability of condensation decreases.

A. B. D. C.

Light absorption by crystals and an optical method of determining the heat of sublimation. M. KIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 129—140).—It is deduced theoretically that the difference between the crystal absorption frequency and the corresponding vapour absorption frequency gives an approx. measure of the heat of sublimation of the substance. This relation is shown to be valid for Tl, Ag, and alkali halides, and enables the position of the first crystal absorption frequency to be estimated when the heat of sublimation of the substance and heat of dissociation of the mol. are known.

J. W. S.

Linear dependence of energy levels on the valency of elements. V. KUNZL (Coll. Czech. Chem. Comm., 1932, 4, 213—224).—The influence of chemical combination with O on the character of the X-ray spectra (K energy levels of elements of at. no. 10—28 and L_{III} energy levels of elements of at. no. 47—53) is independent of at. no., but depends on valency. Differences between the energy levels of the elements combined with O and in the free state increase linearly with the positive valency.

E. S. H.

Satellites accompanying the X-ray diagram line $K\beta_1$. F. R. HIRSH, jun. (Physical Rev., 1932, [ii], 40, 151—155).

N. M. B.

Refractive index of liquids for X-rays. S. W. SMITH (Physical Rev., 1932, [ii], 40, 156—164).—Data obtained $\times 10^6$ for $\delta = 1 - n$ using the Cu $K\alpha_1$ line ($\lambda = 1.537 \text{ \AA.}$) and a total reflexion method are: H_2O 3.69, Bu phthalate 3.57, ethylene glycol 4.08, $N(CH_2CH_2OH)_3$ 3.86, glycerol 4.41, and glass 8.19, in good agreement with calc. vals.

N. M. B.

M series in the ultra-soft X-ray region. J. A. PRINS and A. J. TAKENS (Z. Physik, 1932, 75, 741—745).—This series was observed for elements between Zr and Sb, and only one intense line ($M_{\gamma}N_{III}$) appeared.

A. B. D. C.

Temperature and the Compton effect of sylvine. G. E. M. JAUNCEY and G. C. HARVEY (Physical Rev., 1932, [ii], 40, 329—334).—The ratio of the intensity of the incoherent to that of the total scattering for X-rays of wave-length 0.4 \AA. scattered from sylvine at 300° and 90° abs. increased with fall of temp.

N. M. B.

Atomic scattering power of iron for various X-ray wave-lengths. A. J. BRADLEY and R. A. H. HORE (Proc. Roy. Soc., 1932, A, 136, 272—288).—Powder photographs of FeAl were made with Mo, Cu, Co, Fe, and Cr radiations, from which the at. scattering factor of Fe for different wave-lengths was determined.

L. L. B.

Anomaly in absorption of X-rays by lead at 210 kv. M. E. NAHMIAS (Compt. rend., 1932, 194, 1911—1912).—On plotting the coeff. of absorption of Pb against the voltage the anomalous increase for 204 and 210 kv. is confirmed. It is attributed to a

level in the Pb nucleus excited directly or by resonance with radiation about 210 kv.

C. A. S.

Elastic reflexion of atoms from crystals. C. ZENER (Physical Rev., 1932, [ii], 40, 178—184).—Theoretical.

N. M. B.

Double crystal X-ray spectrometer. P. A. ROSS (Rev. Sci. Instr., 1932, [ii], 3, 253—260).

X-Ray investigation of elastic and plastic deformation of polycrystalline metals. F. REGLER (Physikal. Z., 1932, 33, 435—438).—The method of conical reflexion with monochromatic X-rays is used.

A. J. M.

Comparison of the multiplex interference spectroscopy with other interference spectroscopes. E. LAU and E. RITTER (Z. Physik, 1932, 76, 190—200).

Multiplex interference spectroscopy. E. PAULS (Physikal. Z., 1932, 33, 405—410).—A method of increasing the efficiency of the spectroscopy by the use of an arrangement of several plates is described.

A. J. M.

Photo-electric properties of thin films of alkali metals. S. ASAO (Physics, 1932, 2, 12—20).—A composite surface of R-Ag-R₂O-Ag has a higher sensitivity over a wider range of λ than R-R₂O-Ag and has 2 peaks: one at 330—370 m μ and one at about 500 m μ (R-K), 550 m μ (Rb), or 700—800 m μ (Cs).

CH. ABS.

Effect of adsorbed gases on photo-electric emissivity of Fe and Pt. A. K. BREWER (J. Amer. Chem. Soc., 1932, 54, 1888—1900).—In presence of various gases Fe and Pt have the photo-electric properties characteristic of composite surfaces. The degree of dissociation of the gases is estimated from curves of known ion density as a standard. Threshold measurements on surfaces of known ion density show the field of influence about an ion to extend to many times its normal radius. The observed ionisation of N_2 , H_2 , and NH_3 on Fe and Pt surfaces accords with an ionic mechanism for surface catalysis and with the results of activation in the glow discharge.

R. H. C. (c)

Photo-electric cells with thin film alkali cathodes. R. SEWIG (Z. Physik, 1932, 76, 91—105).—Improvements in making cells with unimol. alkali layers are described, and the mechanism of increased efficiency is discussed.

A. B. D. C.

Ionisation at high gas pressures. R. M. SIEVERT (Nature, 1932, 129, 792—793).

L. S. T.

Properties of ionised gases in high-frequency fields. A. ROSTAGNI (Compt. rend., 1932, 194, 1906—1908).—Along the negatively-charged wall of a discharge tube there is, by reason of the superior mobility of electrons compared with positive ions, a layer of positive ions the thickness, δ , of which at const. pressure is $\propto \sqrt{n}$, where n is the no. of electrons per c.c. in the central (uniform) region and α a const. (cf. A., 1931, 139).

C. A. S.

Atoms and electrons. (SIR) J. J. THOMSON (Mem. Manchester Lit. Phil. Soc., 1930—1931, 75, 77—93).—A lecture.

Magnetism of free electrons. L. POSNER (Z. Physik, 1932, 75, 809—811).—Theoretical. The paramagnetic susceptibility of an electron gas is $2/3$ that of pure spin magnetism. A. B. D. C.

Collisional friction experienced by vibrating electrons in ionised air. E. V. APPLETON and F. W. CHAPMAN (Proc. Physical Soc., 1932, 44, 246—254).

Electrons and light quanta. (SIR) A. FLEMING (Proc. Physical Soc., 1932, 44, 281—294).

Search for preferentially directed electron velocities in crystalline graphite with the multi-crystal spectrograph. J. W. M. DUMOND, H. A. KIRKPATRICK, and L. ALDEN (Physical Rev., 1932, [ii], 40, 165—177). N. M. B.

Electron diffraction and molecular structure. II. R. WIERL (Ann. Physik, 1932, [v], 13, 453—482; cf. A., 1931, 665).—Previous methods of measuring the electron diffraction are applied to more complicated mols. The constancy of at. separations is the basis on which structural discussion is made. Experimental results on C_2H_6 , C_2H_4 , C_3H_4 , C_2H_2 , C_3H_8 , C_4H_{10} , C_5H_{12} , C_6H_{14} , butadiene, cyclopentane, diacetylene, C_2N_2 , ethylene oxide, $\alpha\alpha$ - and $\alpha\beta$ -dichloro- and -dibromo-ethane, and the dichloroethylenes are given and the structures of these mols. discussed. W. R. A.

Electron diffraction by single crystals. J. J. TRILLAT and T. VON HIRSCH (Z. Physik, 1932, 75, 784—803).—Diffraction of 40-kv. electrons by beaten Au and Pt foil showed single-crystal diffraction as well as Debye-Scherrer rings. The patterns obtained are due to gratings in three dimensions, and not to crossed plane gratings. A. B. D. C.

Emission of negative electricity from nickel when bombarded by positive lithium ions. W. S. STEIN (Physical Rev., 1932, [ii], 40, 425—428).—The emission of the cold Ni target showed a max. for bombarding ions of energies between 10,000 and 11,000 volts, and for a red-hot outgassed target increased almost linearly from 1000 to 20,000 volts. N. M. B.

Collision of slow electrons with atoms. I. General theory and elastic collisions. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1932, A, 136, 289—311).—Mathematical. The elastic scattering of slow electrons in H_2 and He is investigated and the effect of electron exchange considered. L. L. B.

Dissociation by collision with positive ions. A. SCHECHTER (Z. Physik, 1932, 75, 671—675).—A crit. potential in the "clean up" process is confirmed. A. B. D. C.

"Electrical diffusion" of ions in unipolar charged gases. N. VOLODKEVITSCH (Z. Physik, 1932, 75, 680—686).—Theoretical. A. B. D. C.

Origin of fast molecular rays at the cathode of a luminous arc. R. RISCH and F. LÜDI (Z. Physik, 1932, 75, 812—822).—These rays are due to mols. multiply ionised by the intense electron stream at the cathode. A. B. D. C.

Mobility of positive alkali ions in argon, neon, and helium. A. M. TYNDALL and C. F. POWELL (Proc. Roy. Soc., 1932, A, 136, 145—152).—The

mobilities of positive ions of Na, K, Rb, and Cs decrease with increase in the mass of the ion in A, Ne, and He. In A the mobilities range from 3.21 cm./sec./volt/cm. for Na ions to 2.23 for Cs. Corresponding figures for Ne are 8.87 and 6.49, and for He 23.1 and 19.2. The relation $K \propto (1+m/M)^{1/2}$, where K is the mobility, M the mass of the ion, and m the mass of the A atom, gives the variation of the mobility in A. In Ne the fall of mobility with increase in mass of the ion is slightly greater, and the deviation is still more marked in He. L. L. B.

Collision of slow electrons in gases. III. Formation of multiply-charged molecular ions. E. FRIEDLANDER, H. KALLMANN, V. LASAREV, and B. ROSEN (Z. Physik, 1932, 76, 70—79).—The potentials at which doubly-charged ions appear in CO, CO₂, NO, and NO₂ have been determined. Doubly-charged ions were not observed in N₂ and O₂. A. B. D. C.

Dissociation of molecular ions by collision. E. FRIEDLANDER, H. KALLMANN, V. LASAREV, and B. ROSEN (Z. Physik, 1932, 76, 60—69).—A mass spectrograph revealed that CO⁺⁺ spontaneously decomposes into C⁺ and O⁺, and on collision CO⁺ dissociates into C⁺ and O, CO⁺⁺ into C and O⁺, NO⁺ into N and O⁺, NO₂⁺ into NO⁺ and O, and NO₂⁺⁺ into NO⁺⁺ and O. A. B. D. C.

Disruptive processes produced by ultra-radiation. W. HEISENBERG (Naturwiss., 1932, 20, 365—366).—A discussion of the work of Steinke and Schindler (this vol., 556) from the point of view of new quantum mechanics. The no. of impacts per cm. and the effective cross-section for the impacts are considered. W. R. A.

Detection and isolation of element 91. A. VON GROSSE (Naturwiss., 1932, 20, 362—363).—A criticism of the work of Hahn and Meitner (A., 1931, 1208). W. R. A.

[Detection and isolation of element 91.] O. HAHN and L. MEITNER (Naturwiss., 1932, 20, 363).—A reply (cf. preceding abstract). W. R. A.

At. wt. of fluorine. H. S. PATTERSON and W. CAWOOD (Nature, 1932, 129, 794).—MeF prepared by Collie's method and by the Me₂SO₄-KF method has t_c 44.55°, 58.0 ± 0.2 atm., and v_c 3.33 c.c. per g. The p - v isothermal of MeF made by the second method is linear: at 0° the val. for the compressibility over 1 atm. is 1.0115. The compressibility at 21° is 1.0087 and both vals. are in satisfactory agreement with those obtained from microbalance data. The correct val., 1.0087, still gives 19.01 for the at. wt. of F (cf. this vol., 106, 209, 317). Moles and Batuecas' vals. for the normal density and compressibility of MeF are incorrect. L. S. T.

Isotopic constitution of lead. H. SCHULER and E. G. JONES (Nature, 1932, 129, 833—834).—Aston's data for Pb²⁰⁴ (this vol., 554) are in good agreement with those obtained by the authors from the hyperfine structure of the Pb spectrum (this vol., 442). No indications of Pb²⁰⁹ were observed with this method, and since Tl was always present in all the samples of ordinary Pb used, the possibility of contamination

by traces of Tl should be examined before the mass nos. 203 and 205 are finally attributed to Pb.

L. S. T.

Ionisation produced by radon in spherical vessels. G. GLOCKLER and G. B. HEISIG (J. Physical Chem., 1932, 36, 769—779; cf. A., 1931, 1208).—In order that the Geiger law may hold for ionisation by α -particles from Ra-Em it is necessary to use empirically defined ranges, which are calc. The vals. of the const. in Geiger's $2/3$ power law for α -particles from Ra-C, Ra-A, and Ra-Em are calc.

J. W. S.

Effect of α -rays on the passage of electricity through crystals. G. JAFFE (Physikal. Z., 1932, 33, 393—399).—There is a definite effect, greater for quartz than for mica.

A. J. M.

Resonance penetration of α -particles into aluminium nuclei. K. DIEBNER and H. POSE (Z. Physik, 1932, 75, 753—762).—The short-range H -rays emitted by Al vary in intensity with the energy of the primary α -ray beam, and long-range H -particles are obtained only at characteristic α -ray energies.

A. B. D. C.

Diminution of velocity of α -particles in air and Bethe's theory. G. MANO (Compt. rend., 1932, 194, 1813—1815; cf. this vol., 555).—Bethe's formula (cf. A., 1930, 972) for the diminution in velocity of an α -particle after travelling a distance p , $-dv/dp = [4-e^2z^2NZ \log(2mv^2/E)]/mMv^3$, where m and e are mass and charge of an electron, M and eZ the same of an α -particle, N is the no. of atoms per c.c., Z the no. of electrons per atom, and E a const., gives a satisfactory result if $E=92$ electron-volts, instead of Bethe's 35.

C. A. S.

Absolute velocities of principal groups of α -particles. S. ROSENBLUM and G. DUPOUY (Compt. rend., 1932, 194, 1919—1922).—Using an improved focus method (cf. A., 1931, 16, 280) the following velocities (in cm. $\times 10^{-9}$ /sec.) of α -particles have been determined: from Th-C' 2.054₄, Ra-C' 1.921₈, Ac-C α 1.784₈, Ac-C α ., 1.737₃, Th-C α 1.705₈, Po 1.596₁, Ra-A 1.698₈.

C. A. S.

γ -Rays from actinium emanation and their origin. (LORD) RUTHERFORD and B. V. BOWDEN (Proc. Roy. Soc., 1932, A, 136, 407—412).—Evidence has been obtained that the transformation actinon \rightarrow actinium-A is accompanied by weak β -rays and strong γ -rays. From a measurement of the penetrating power of the γ -rays it is estimated that the energy of transformation of the γ -rays from the emanation is approx. 350,000 volts, about the magnitude to be expected from the observed difference in energy of disintegration of the two groups of α -particles (356,000 volts). This supports Gamow's view that γ -rays must accompany all transformations where more than one group of α -particles is emitted.

L. L. B.

Ranges of the α -particles from the radioactive emanations and "A" products and from polonium. W. B. LEWIS and C. E. WYNN-WILLIAMS (Proc. Roy. Soc., 1932, A, 136, 349—363).—The mean ranges in air of the α -particles emitted by radon, Ra-A, thoron, Th-A, actinon, Ac-A, and Po have been measured by the new counting methods. All these

elements, with the exception of actinon, emit a single homogeneous group of α -rays. The α -rays from actinon consist of two groups, analogous both in relative nos. and in energy difference to the two groups emitted by Ac-C.

L. L. B.

γ -Radiation of boron and beryllium. H. BECKER and W. BOTHE (Naturwiss., 1932, 20, 349).—The γ -radiation of B and Be has been studied by the coincidence method and the results are discussed.

W. R. A.

Dependence of ionisation by γ -rays on temperature. K. WOLFF (Z. Physik, 1932, 75, 570—574).—The ionisation current due to γ -rays was increased by 1% when CO₂ and N₂ at 21.5 atm. were raised in temp. by 4° and 7°, respectively.

A. B. D. C.

Scattering of short-wave γ -radiation by heavy elements. L. MEITNER and H. H. HUFFELD (Z. Physik, 1932, 75, 705—715).—Ra-C γ -radiation scattered at right angles to the incident beam by Pb has 4% of wave-length coincident with that of the primary beam; this must be scattered by Pb nuclei, and explains deviations from the Klein-Nishina formula.

A. B. D. C.

Photographic measurement of the absorption coefficients of γ -rays from radium-B+C. J. S. ROGERS (Proc. Physical Soc., 1932, 44, 349—367; cf. A., 1931, 281).—The absorption per electron for the lighter elements of γ -rays filtered by 1.6 cm. of Pb was const. in accordance with the Klein-Nishina formula, and led to a wave-length of 7.0 Å. The increase of absorption for the heavier elements varied as Z^3 , the additional absorption being assumed to be due to the photo-electric effect.

N. M. B.

Compton effect of very hard γ -rays of thorium-C'. D. SKOBELZYN (Compt. rend., 1932, 194, 1914—1917; cf. A., 1931, 16; this vol., 556).—Numerous observations with γ -rays of Th-C' filtered through 30 mm. of Pb give a curve showing fair agreement with that deduced from the Klein-Nishina formula, but the same excessive max. for deviations of 8—10°, inexplicable by the theory.

C. A. S.

Artificial production of nuclear γ -radiation. H. C. WEBSTER (Proc. Roy. Soc., 1932, A, 136, 428—453).—The production of nuclear γ -radiation by bombardment with α -particles has been observed for the elements Li, Be, B, F, Na, Mg, Al, using two methods of measurement, Geiger-Müller tube-counters and high-pressure ionisation chambers. By measurements of the absorption coeffs. in Pb the quantum energies of the radiations are deduced from the Klein-Nishina formula. These range from about 8 million electron-volts for B to 0.5 million for Na. In some cases the radiations can be connected with the artificial disintegration of the nucleus accompanied by the release of a proton, whilst in others they appear to be due to the capture of an α -particle by a nucleus without proton emission.

L. L. B.

Association of γ -rays with the α -particle groups of thorium-C. C. D. ELLIS (Proc. Roy. Soc., 1932, A, 136, 396—406).—Experiments have been made to decide whether certain γ -rays, known to be emitted as the result of the disintegration of

Th-C or -C'', actually arise from Th-C, as predicted by Gamow (A., 1930, 1339). The fact that the γ -rays are found to be emitted directly after the disintegration of Th-C, in agreement with theory, provides a further proof of the association of γ -rays with excited nuclear α -particle states. Probably all the γ -rays of radioactive substance arise in this way. L. L. B.

Selection rule for nuclear γ -radiation. K. BECHERT (Naturwiss., 1932, 20, 266).—The selection rule for nuclear γ -radiation is probably $\Delta i=0, \pm 1$ (and eventually ± 2). Energy levels are represented. W. R. A.

Radioactive phenomena of second order and artificial origin. G. REBOUL (Compt. rend., 1932, 194, 1733—1735; cf. this vol., 321, 446).—It is suggested that the atoms of the activated substances are out of electrical equilibrium, returning thereto slowly, the more so as the substance is less conducting. C. A. S.

Investigations with a Wilson chamber. II. Photography of artificial disintegration collisions. II. Accuracy of the angle determinations. P. M. S. BLACKETT and D. S. LEES (Proc. Roy. Soc., 1932, A, 136, 325—338, 338—348).—I. 750,000 tracks in an A-O₂-H₂ mixture and 350,000 in a N₂-O₂-H₂ mixture were photographed. Four capture disintegration collisions were observed, two in each group. The two in the A mixture are attributed to N₂, assumed to be present as an impurity.

II. The accuracy of the angular measurements of forked tracks is estimated by studying various types of collision. The probable errors of the angles ψ and ω of a N₂ disintegration track are about 30 and 60 min. of arc. Exact methods are given for calculating the angles from the photograph and for obtaining the reduced lengths of the tracks. L. L. B.

Disintegration of atomic nuclei. H. S. ALLEN (Nature, 1932, 129, 830).—The Al nucleus may yield neon on disruption in accord with $\text{Al}^{27} + \text{H}^1 \rightarrow 2\text{He}^4 + \text{Ne}^{20}$ (cf. this vol., 556). The particles of mass unity in Be radiation (this vol., 443) may not be the ultimate neutron, but may be composed of two neutrons. L. S. T.

Nature of the penetrating beryllium radiation. F. RASSETTI (Naturwiss., 1932, 20, 350; cf. this vol., 556). W. R. A.

Dispersion of neutrons from beryllium and production of recoil nuclei from lithium. M. DE BROGLIE and L. LEPRINCE-RINGUET (Compt. rend., 1932, 194, 1616—1617).—Neutrons resulting from the action of α -particles from Rn on Be are strongly dispersed on passing through matter, e.g., Pb, paraffin, or KCl, resulting in the production of strongly ionising nuclei, but with no preferential production of one kind of recoil nuclei rather than another. Neutrons are also produced, though in much smaller number, by the action of α -particles from Rn on Li (cf. this vol., 194, 210). C. A. S.

Penetrating power of radiation (neutrons) produced from beryllium by α -particles. J. THIBAUD and F. D. LA TOUR (Compt. rend., 1932, 194, 1647—1649; cf. this vol., 210).—The absorption in Pb of neutrons projected by α -particles of Rn from

Be is complex. The curve $\log I_x/x$ (x =thickness) is strongly convex to the axis of x . The coeff. of absorption, μ_x , decreases from 0.20 for $x=1$ cm. to 0.065 for $x=20$ cm., indicating the probability of still further decrease in μ_x , and that some neutrons can penetrate 50 cm. of Pb. Similar progressive filtration is indicated where neutrons, after passing through 4.4 cm. of Pb, traverse Al, Si, S, Fe, Zn, Sn, Sb, Hg, Pb, ZnO, KNO₃, or KBr. The thicknesses absorbing half of such neutrons are: of Al 5.5, Si 8, S 10, Fe 6—9, Hg 6, and Pb 5.5 cm. Light elements, e.g., Si, S, Fe, absorb per atom slightly less than Pb. These results point to neutrons being projected with varying velocities, and colliding with at. nuclei only when very close, e.g., within 5×10^{-13} cm. for Pb. C. A. S.

Theory of diffusion of neutrons, coefficient of absorption and ionisation. J. L. DESTOUCHES (Compt. rend., 1932, 194, 1909—1911).—Expressions are deduced by aid of Schrodinger's equation for the scattering of neutrons by a heavy nucleus, their coeff. of absorption, and hence of k , the coeff. of field, $= 0.8-1.7 \times 10^{13}$ (cf. this vol., 318, and preceding abstract), loss of energy after traversing a given path (cf. this vol., 443), and the ionisation, showing this last to be negligible. Results agree satisfactorily with those of experiment. C. A. S.

Neutron hypothesis. D. IWANENKO (Nature, 1932, 129, 798).—A suggestion that neutrons play an important role in the structure of nuclei, the nuclear electrons being all packed in α -particles or neutrons. L. S. T.

Theory of atomic disintegration by resonance. H. KALLMANN (Naturwiss., 1932, 20, 393—396).—Mathematical. A. R. P.

Existence of neutrons in atomic nucleus. W. M. LATIMER (J. Amer. Chem. Soc., 1932, 54, 2125—2126).—A discussion (cf. A., 1931, 544). C. J. W. (c)

Periodic properties of atomic nuclei. G. POKROVSKI (J. Phys. Radium, 1932, [vii], 3, 150—154).—Theoretical. From simple hypotheses periodic properties of at. nuclei are derived. W. R. A.

Cosmic-ray energies and their bearing on the photon and neutron hypotheses. R. A. MILLIKAN and C. D. ANDERSON (Physical Rev., 1932, [ii], 40, 325—328).—A summary of deductions from cosmic-ray track photographs. N. M. B.

Characteristic oscillations of an ionised gas from wave mechanics. (MLLE.) J. J. PLACINTEANU (J. Phys. Radium, 1932, [vii], 3, 155—159).—Mathematical. W. R. A.

Sir A. S. Eddington's recent theories. W. N. BOND (Proc. Physical Soc., 1932, 44, 374—382).—Evidence for the correctness of Eddington's vals. for the fine-structure const., the ratio of masses of proton and electron, and the cosmical const. is discussed. The val. of e is probably $(4.777_5 \pm 0.001) \times 10^{-10}$ e.s.u. N. M. B.

Probable values of e , h , c/m , and α . R. T. BIRGE (Physical Rev., 1932, [ii], 40, 228—261).—A method for the simultaneous evaluation of e and h from several known functional relations between these

two consts. is developed (cf. Bond, A., 1931, 1207). All available data are discussed. Vals. deduced are $h=6.5443\pm0.0091$, $e=4.7688\pm0.0040$, $1/\alpha=137.307\pm0.048$, and $e/m=1.7611\pm0.0009$. N. M. B.

Relations between fundamental physical constants. J. E. MILLS (J. Physical Chem., 1932, 36, 1039—1107).—A no. of numerical relations between certain physical consts. have been discovered.

G. M. M. (c)

Absorption measurements on glasses with the thorium and Uviol lamps, and the hydrogen spectrum. W. M. COHN and C. ANDRESEN-KRAFT (Z. tech. Physik, 1931, 12, 428—433; Chem. Zentr., 1931, ii, 3574).—The ultra-violet continuous spectra from these sources are compared. The Th lamp consists of Th bombarded by cathode rays and has the advantage that the visible and heat rays either are missing or can be suppressed. Data for FeO and Fe₂O₃ glasses are given. L. S. T.

Absorption spectra at high pressures and at low temperatures. Transparency of argon and methane. B. J. EISEMAN, jun. (J. Amer. Chem. Soc., 1932, 54, 1778—1782).—A and CH₄ are transparent at high pressure between 2100 and 6900 Å.

H. S. H. (c)

Transmission of liquid carbon dioxide. B. J. EISEMAN, jun., and L. HARRIS (J. Amer. Chem. Soc., 1932, 54, 1782—1784; cf. preceding abstract).—Liquid CO₂ at -51° is transparent to the visible and ultra-violet (cf. A., 1929, 236). At room temp. it is transparent except perhaps for a slight continuous absorption below 2500 Å.

H. S. H. (c)

Absorption spectra of carbon dioxide, carbon monoxide, and water vapour in the range 600—900 Å. H. J. HENNING (Ann. Physik, 1932, [v], 13, 599—620).

A. J. M.

Absorption spectra of solid bodies. R. PEIERLS (Physikal. Z. Soviet Union, 1932, 1, 297—298).—The dependence of the absorption spectrum of a crystal on the thermal vibration of the crystal lattice and its coupling with the electronic motion is discussed.

J. W. S.

Ultra-violet absorption of nitrates and chromates at 20° abs. H. SCHAUMANN (Z. Physik, 1932, 76, 106—131).—Absorption spectra were determined between 4200 and 2400 Å. for Na, K, and Ba nitrates, K chromates, and NH₄Cl.

A. B. D. C.

Molecular spectra and spectroscopic analysis.
III. Detection of yttrium. G. PICCARDI and A. SBERNA (Atti R. Accad. Lincei, 1932, [vi], 15, 309—312).—Small amounts of Y can be detected conveniently by means of the brilliant band spectrum of YO, which is obtained readily when any Y compound is volatilised at high temp. in air or O₂. The spectrum of YO is described. A variation of 5% of the total concn. can be detected in the concn. range 1:10 to 1:10⁵.

O. J. W.

Absorption spectra of certain triatomic molecules and their dissociation products. M. KIMURA (Sci. Papers Inst. Phys. Chem. Tokyo, 1932, 18, 150—156).—The energies required to dissociate the mols. CO, NO, N₂O, and H₂O in various

excited states are compared with the absorption frequencies of these mols. in the extreme ultra-violet region, and dissociation products resulting from the absorption by these mols. are suggested. J. W. S.

Absorption spectra and certain thermo-chemical constants of lead halides. M. KIMURA and Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 157—165; cf. preceding abstract).—The absorption frequencies of PbI₂, PbBr₂, and PbCl₂ vapours have been measured and dissociation products for the various electronic excited states of the mol. are suggested. The heat of sublimation of PbCl₂ and the energies of dissociation into PbX+X (X=halogen) and into Pb+2X are calc.

J. W. S.

Band spectrum of nitrogen sulphide. A. FOWLER and C. J. BAKKER (Proc. Roy. Soc., 1932, A, 136, 28—36).—By passing uncondensed discharges through tubes containing N₂ and S vapour a band spectrum, attributed to NS, is obtained. This is very similar to that of NO, and appears in almost the same ultra-violet region.

L. L. B.

Absorption band spectra of germanous sulphide: isotopic constitution of germanium. C. V. SHAPIRO, R. C. GIBBS, and A. W. LAUBENGAYER (Physical Rev., 1932, [ii], 40, 354—365).—Full data for the ultra-violet absorption spectra of GeS, showing bands in the regions 3358—2709 Å. and 2782—2464 Å., are tabulated. In the former the vibrational isotope effect was resolved; isotopes 74, 72, 70, and 76 were recognised. Energies of dissociation are 5.65 volts for the normal state, and 2.84 and 2.17 volts for the excited states.

N. M. B.

Absorption spectrum of iodine monochloride in the near infra-red. O. DARBYSHIRE (Physical Rev., 1932, [ii], 40, 366—379; cf. Wilson, A., 1928, 1306).—The absorption spectrum for the region 6750—8770 Å. was photographed and consists of portions of 7 progressions. Bands of 3 progressions of the ICl³⁷ spectrum were identified. Revised vals. for the vibrational and related consts. are deduced.

N. M. B.

Absorption spectra of photochemically coloured alkali halide crystals. E. MOLLWO (Nachr. Ges. Wiss. Gottingen, 1931, 97—99; Chem. Zentr., 1932, i, 492).—For LiF, LiCl, NaF, NaCl, NaBr, KF, KCl, KBr, KI, RbCl, and RbBr the characteristic frequency of the colour centres in the photographic elementary process is inversely proportional to the square of the lattice const.

A. A. E.

Modified residual-ray method for the visible and ultra-violet. C. SCHAEFER (Z. Physik, 1932, 75, 687—694).—Residual rays from a liquid were enhanced by placing on its surface a plate of which the refractive index is approx. that of the liquid, except for regions of anomalous dispersion. Characteristic frequencies between 200 and 700 mμ were determined by this method for solutions of fuchsin, for NMe₂·C₆H₄·NO, furfuraldehyde, CH₂I₂, PhNO₂, PhCHO, PhAc, NH₂Ph, and PhI.

A. B. D. C.

Absorption of light by substances which form liquid crystals. J. FISCHER (Z. physikal. Chem., 1932, 160, 101—115).—Examination of substances

of this type has shown that phase changes of solid crystals, liquid crystals, and isotropic liquids cause discontinuous changes in the absorption const. for monochromatic light. In respect of their absorbent properties liquid crystals resemble the isotropic liquids rather than the corresponding solid crystals. The absorption const. of a solution of a substance which forms liquid crystals approximates to that of the solute in the form of an isotropic liquid when the val. for the solution is calc. for a layer of equal thickness free from solvent.

R. C.

Absorption spectra of crystals of aromatic compounds at low temperatures. I. OBREIMOV and A. PRICHOTJKO (Physikal. Z. Soviet Union, 1932, 1, 203—214).—The absorption spectra of $C_{10}H_8$, anthracene, and phenanthrene have been investigated over the temp. range 20° to -190° .

J. W. S.

Absorption measurements in the ultra-violet of short wave-length. I. Carboxylic acids, amines, and amino-acids. H. LEY and B. ARENDS (Z. physikal. Chem., 1932, B, 17, 177—219).—Measurements have been made down to about 180 m μ . Saturated mono- and di-carboxylic aliphatic acids have an absorption band at 204—207 m μ , which also appears with their chlorides and anhydrides and is ascribed to the CO group. The acids probably have another band at a shorter wave-length. The character of the absorption curve of fatty acids is not affected by ester formation, but is totally changed by salt formation. With $H_2C_2O_4$ the long-wave max. is at about 250 m μ . The characteristic frequency of H_2CO_3 , as $CO(OMe)_2$, lies below 180 m μ . Dissolved in hexane, NH_3 has a band at 192 m μ , which is displaced towards shorter wave-lengths in aq. solution, the transparency increasing at the same time. Other amines exhibit similar medium effects. Introduction of alkyl groups into NH_3 widens the band, probably through damping action. The latter increases with the no. of alkyl groups, but may be counteracted by the introduction of an H nucleus into the amine to produce a state of higher saturation, as when NH_3 is converted into NH_4^+ . The absorption relations of aq. solutions of aliphatic NH_2 -acids and the effect of salt formation agree with the theory that in solution the acids are present almost exclusively as dipoles, such as $'NH_3 \cdot CH_2 \cdot CO_2'$. The absorption curves of solid glycine and α -aminoisobutyric acid between 225 and 242 m μ are the same as for solutions.

R. C.

Effect of temperature on the absorption bands of benzene and some of its derivatives at low temperatures. A. H. CROUP (Physical Rev., 1932, [ii], 40, 345—353).—The temp.-frequency curves for the ultra-violet absorption spectra of C_6H_6 and *o*-, *m*-, and *p*- $C_6H_4Cl_2$ in the range -190° to 20° are plotted and discussed. Both the frequency and intensity of the bands increase with fall of temp.

N. M. B.

Absorption spectra in solution at low temperatures. L. B. ARNOLD, jun., and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1932, 54, 1713—1722).—Absorption spectra have been obtained of solutions in a mixture of C_3H_8 and C_5H_{12} of $CH_2Ph \cdot CHO$, *o*-

phenylpropaldehyde, C_6H_6 , cyclohexadiene, $PhCHO$, $MeCHO$, $PrCHO$, $PhCl$, $BzCl$, ω -phenyl-butyl-, -ethyl-, -propyl-, and -heptyl chlorides. The compounds having aromatic rings show narrow absorption bands, whilst those containing aliphatic groups have diffuse spectra.

G. M. M. (c)

Absorption spectra of cyanogen and the cyanogen halides. R. B. MOONEY and H. G. REID (Proc. Roy. Soc. Edin., 1932, 52, 152—158; cf. A., 1931, 1110).—Details are given of results already reported. Measurements of the band edges of the $(CN)_2$ absorption spectrum are given. The influence of temp. on their relative intensities has been investigated.

J. W. S.

Some organic solutions of iodine. M. CHATELET (Compt. rend., 1932, 194, 1809—1810).—The absorption spectrum of I dissolved in mixtures of C_6H_6 with $COMe_2$, $EtOAc$, or $CHCl_3$ is an additive function of the spectra in the two solvents separately, the I being distributed proportionately to the amounts of the solvents. In mixtures of CCl_4 with C_6H_6 , $COMe_2$, $EtOH$, or $CHCl_3$ this is not the case.

C. A. S.

Absorption of ultra-violet light by organic substances. XXVI. W. GOSŁAWSKI and L. MARCZLEWSKI. XXVII. A. BORYNIEC and L. MARCZLEWSKI (Bull. Acad. Polonaise, 1931, A, 383—391, 392—399).—XXVI. Extinction coeffs. are given for the three $C_6H_5(OH)_3$ and their Ac_3 derivatives in $EtOH$, and for chloral in H_2O , $EtOH$, and $CHCl_3$.

XXVII. Extinction coeffs. are given for pyrrole, furan, indole, and 2-, 3-, and 7-methylindole in $EtOH$.

D. R. D.

Transmission spectra of dyes in the solid state. W. C. HOLMES and A. R. PETERSON (J. Physical Chem., 1932, 36, 1248—1254).—Spectra of 32 azo-, $CHPh_3$, and xanthen dyes are reproduced. Dissolution displaces the absorption bands towards shorter wave-lengths. The dry dyes consist of large mol. aggregates. Evidence of tautomerism is given.

S. L. (c)

Application of study of ultra-violet absorption spectra of alkaloids to the determination of their structure, and to analytical chemistry, pharmacy, and toxicology. V. BRUSTIER (Chim. et Ind., 1932, 27, 1007—1016).—The Bz grouping in alkaloids produces a min. at 2612 Å. Atropine, hyoscyamine, homatropine, cocaine, novocaine, strychnine, brucine, and aconitine have been studied and a no. of analytical and toxicological experiments are described.

W. S.

Absorption spectra of lignin solutions. A. J. STAMM, J. SEMB, and E. E. HARRIS (J. Physical Chem., 1932, 36, 1574—1584).—Hardwood and softwood lignin preps. gave characteristic absorption max. at 2740—2760 and 2810—2760 Å., respectively. Lignin solutions from partly chlorinated wood gave bands of smaller extinction coeffs. than those prepared from completely chlorinated wood.

F. U. (c)

Rotation-vibration spectrum of ammonia. P. LUEG and K. HEDFELD (Z. Physik, 1932, 75, 599—612).—The rotation-vibration bands at 8800 and 10,230 Å. were photographed with high dis-

persion, and give H—H distance as 1.72 Å. and the height of the pyramid as 0.3 Å. A. B. D. C.

Infra-red characteristic frequencies of alkali halide crystals. R. B. BARNES (Z. Physik, 1932, 75, 723—734).—Characteristic infra-red frequencies were observed by absorption of films 0.2—0.3 μ thick between 20 and 125 μ , for Li, Na, Tl fluoride, Na, K, Rb, Cs, Tl chloride, Na, K, Rb, Cs bromide, and for Na, K, and Rb iodide. A small unexplained max. appears on the short-wave side of the characteristic max. A. B. D. C.

Intensity of infra-red water absorption bands of concentrated solutions of lithium chloride or nitrate. M. NEUNHOEFFER (Physikal. Z., 1932, 33, 439—443).—The absorption bands of H₂O at 1.47 μ and 1.98 μ were investigated. LiNO₃ causes displacement towards the shorter waves, the amount depending on concn. LiCl displaces the 1.98 μ band towards the longer waves, but leaves the other unaltered. A. J. M.

Raman effect in gases. III. Comparison of theory and experiment. S. BHAGAVANTAM (Indian J. Physics, 1932, 6, 557—562; cf. this vol., 108).—Calculation of the intensity of vibrational Raman scattering for some simple mols. yields results of the same order of magnitude as that observed experimentally. Discrepancies occur between the calc. and observed states of polarisation of these lines. J. W. S.

Raman effect in inorganic compounds. J. C. GHOSH and S. K. DAS (J. Physical Chem., 1932, 36, 586—594; cf. A., 1931, 146, 668).—Raman lines for H₃PO₃, (NH₄)₂MoO₄, and various Na salts have been obtained. The relation between Raman lines, at. no., and ionic composition is discussed. J. H. H. (c)

Raman effect in crystals. Water of crystallisation. H. NISI (Japan. J. Physics, 1931, 7, 1—32).—Full data are tabulated for the following substances: the hydrated cryst. sulphates of Li, Na, K, Rb, NH₄, Be, Mg, Zn, Cd, Ca, Sr and Ba (anhyd), Fe, Fe(NH₄), Mn, Ni, Cu; alum, Na₂S₂O₃, K Na tartrate, and citric acid. Paramagnetic sulphate crystals give at least one inactive line. N. M. B.

Raman effect in molecules of the types XY₆ and XY₅. O. REDLICH (Naturwiss., 1932, 20, 365).—Intense Raman lines have been found for the anions of HSbCl₆ and H₂SnCl₆ in agreement with theoretical deductions assuming an octahedral model. SbCl₅ has also been studied. W. R. A.

Raman spectra of aqueous solutions of sodium and potassium hydroxides. J. R. NIELSEN (Z. Physik, 1932, 76, 55—59).—A displacement of 3603 cm.⁻¹ is ascribed to the OH ion. A. B. D. C.

Valency- and deformation-oscillations of polyatomic molecules. III. Methane, acetylene, ethylene, and their halogen derivatives. R. MECKE (Z. physikal. Chem., 1932, B, 17, 1—20).—The Raman and infra-red spectra of the above compounds are interpreted by the methods previously detailed (this vol., 559). R. C.

Raman effect. III. G. EISEN (Chem. Weekblad, 1932, 29, 298—306).—A review of work with

cryst. substances, and a discussion of circular polarisation in relation to the structure of org. compounds. H. F. G.

Nature of the continuous background in the Raman effect in liquids. R. BAE (Helv. phys. Acta, 1931, 4, 369—371; Chem. Zentr., 1932, i, 352).—With glycerol, conc. H₂SO₄, and 65% HNO₃ the continuous background is due to fluorescence. A. A. E.

Oscillations of the methane molecule. S. BHAGAVANTAM (Nature, 1932, 129, 830).—The Raman line 2918 cm.⁻¹ of CH₄ is almost completely polarised, whilst the line 3019 is practically unpolarised. This supports the view that the fundamental frequencies of CH₄ are 1304, 1520, 2918, and 3019. L. S. T.

Raman spectra of the simpler hydrocarbons. S. BHAGAVANTAM (Indian J. Physics, 1932, 6, 595—604).—The Raman spectra of gaseous CH₄ and C₂H₆ and of liquid C₃H₈, *n*- and *iso*-butane are described and compared with the infra-red absorption spectra. The fundamental frequencies of the CH₄ mol. chosen are 1304, 1520, 2918, and 3018 cm.⁻¹, of which only the last two occur in the Raman spectrum. The frequency 2918 is not observed in infra-red absorption, but is strong in the Raman spectrum and so is attributed to the symmetrical expansion of the mol. The 3018 frequency occurs in both series. Dennison's fundamental 4217 is attributed to a combination of 1304 and 2918. The strong frequency 993 cm.⁻¹ in C₂H₆ is attributed to symmetrical vibration of the Me groups. Frequencies at 2900 and 2955 coincide with an infra-red band. 377 cm.⁻¹ occurring with C₃H₈ is in accordance with the triangular structure of the mol. C₃H₈, *n*- and *iso*-butane show a strong Raman frequency 1453 arising from transverse oscillation of the H atoms. This does not occur with CH₄, C₂H₆, C₂H₂, and C₂H₄. The spectrum of *isobutane* is very similar to those of CHCl₃ and CHBr₃, indicating similar structures. J. W. S.

Complete Raman spectrum in relation to infra-red absorption. II. Benzene, cyclohexane, and octane. P. KRISHNAMURTI (Indian J. Physics, 1932, 6, 543—556; cf. this vol., 213).—New lines have been observed in the Raman spectra of C₆H₆, cyclohexane, and C₈H₁₈. The Raman frequency 992 cm.⁻¹ for C₆H₆ is inactive. The line 1025 cm.⁻¹ is just detectable. It becomes stronger in substituted C₆H₆ derivatives. Faint lines and bands below 1100 cm.⁻¹ appear to be due to the long-chain character of the octane mol. The continuous spectrum between 2852 and 2938 cm.⁻¹ observed with both C₈H₁₈ and cyclohexane is attributed to the vibrations of the H atoms as influenced by their free rotation about certain axes. Most of the more prominent infra-red absorption maxima are represented by Raman lines of corresponding frequency. J. W. S.

Chemical constitution and Raman effect. *cuclo*Propanes. R. LESPIEAU, M. BOURGUEL, and R. WAKEMAN (Bull. Soc. chim., 1932, [iv], 51, 400—413).—The Raman frequencies are tabulated for *cyclo*-propane, methyl-, 1:2-dimethyl-, 1-methyl-2-ethyl-, 1-methyl-2-propyl-, phenyl-, and 1:2-diphenyl-*cyclo*-propane. The line 1188 characterises the kernel C₃, but the frequency varies slightly, being augmented

when H attached to the kernel is replaced by substituents. With apparatus of sufficient precision the Raman spectra may be used to determine impurities with an accuracy of 1%.
E. S. H.

Modification of light quanta by elastic heat oscillations in scattering media. E. GROSS (Nature, 1932, 129, 722—723; cf. A., 1930, 1498).—Results with CS₂ and PhCl confirm those previously obtained (*ibid.*, 1237); the modified and unmodified components in these two liquids are very diffuse. No displacement of scattered lines towards the red (cf. A., 1929, 489; 1930, 15) could be observed in any of the liquids as yet investigated or with styrene.
L. S. T.

Influence of substitution on vibration frequencies of ethylenic compounds: a method for classifying radicals. M. BOURGUEL (Compt. rend., 1932, 194, 1736—1739; cf. this vol., 7).—The Raman spectra of CH₂:CHR (R=Me, CH₂:OH, CHMe:OH, Et, CH₂Ph, CO₂H, CH₂Br, Ph, CHO, or Br) are given. Variations in the line near 1600 cm.⁻¹ in these and similarly constituted substances show that as compared with most alkyl radicals, Me and the alcohol increase, whilst negative radicals decrease, the strength of the linking.
C. A. S.

Raman spectrum of diethyl ether and its variation at low temperature. R. BÄR (Helv. phys. Acta, 1931, 4, 366—368; Chem. Zentr., 1932, i, 352).—At -95° to -110° the intensities, but not the wave-lengths, of the Raman lines were altered; new lines were not observed.
A. A. E.

Increasing of interference colours of thin oxide layers. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 75, 597—598).—A thin transparent and reflecting layer of Au condensed on oxide layers greatly increases the brilliance of their interference colours.
A. B. D. C.

Chemiluminescence of amarine. S. S. BHATNAGAR and K. G. MATHUR (Z. physikal. Chem., 1932, 159, 454—458; cf. A., 1918, ii, 283).—When amarine reacts in EtOH solution with Br, Cl₂, or H₂O₂, the same continuous luminescence spectrum appears to be produced in each case, the short-wave limit being at about 4500 Å. Since this val. gives 63 kg.-cal. for the heat of oxidation of amarine, in good agreement with the directly determined figure, it must be concluded that luminescence occurs only during oxidation.
R. C.

Electrical conductivity and high-tension polarisation in sodium nitrate crystals. II. B. HOCHBERG and V. JOFFE (Physikal. Z. Soviet Union, 1932, 1, 237—254; cf. A., 1931, 286).—The polarisation of NaNO₃ crystals produces a space charge in the vicinity of each electrode which gradually reaches to the parts of the crystal lying further from the electrodes. The scattering of the space charge by discharge follows the reverse process. The density of the space charge in the polarisation layer, and the effect of impurities diffusing from the electrodes to the crystal, have been investigated.
J. W. S.

Variation of electrical conductivity of liquid metals in magnetic fields. I. FAKIDOV and I. KIKOIN (Z. Physik, 1932, 75, 679).—A linear relation

exists between applied magnetic field and electrical resistance of the liquid alloy KNa from 0.5 to 12 kilogauss.
A. B. D. C.

Theory of change in electrical resistance of metals with hydrostatic pressure. K. HONDA, T. NISHINA, and T. HIRONE (Z. Physik, 1932, 76, 80—90).
A. B. D. C.

Conductivity of oils at low temperatures. A. GEMANT (Z. Physik, 1932, 75, 613—621).—The conductivity of transformer, car, and cylinder oils was determined between room temp. and -60°. The viscous oils have a negative temp. coeff. between -20° and -40°.
A. B. D. C.

Unidirectional layer in lead sulphide. F. HEINECK (Naturwiss., 1932, 20, 365).—Pure PbS was prepared; the detector effect was measured in atm. of different gases and vapours. It is concluded that PbS has a unidirectional layer like Cu₂O. W. R. A.

Calculation of dipole moments of molecules with several axes of free rotation. C. T. ZAHN (Physikal. Z., 1932, 33, 400—405).—Mathematical. The mean square of the dipole moment of a mol. with several axes of free rotation is calc. by a vector method for an ideal case.
A. J. M.

Clausius-Mossotti law. P. VAN RYSELBERGHE (J. Physical Chem., 1932, 36, 1152—1155).—A general expression of the Clausius-Mossotti law is derived for the dielectric const. of any perfect, homogeneous, and isotropic dielectric, which is independent of the system of units.
H. F. J. (c)

Inorganic halides and their molecular compounds. V. Dipole moments and constitution of molecular compounds of titanium and tin tetrachlorides in benzene solution. H. ULICH, E. HERTEL, and W. NESPITAL (Z. physikal. Chem., 1932, B, 17, 21—45; cf. this vol., 447).—Mol. wt. determinations with C₆H₆ solutions of mol. compounds of SnCl₄ and TiCl₄ with org. substances show that in solution all the compounds SnCl₄.2X and TiCl₄.2X dissociate more or less into 2, or even 3, mols. Some of the compounds with co-ordination no. 5 thus formed are more stable in solution than the compounds with co-ordination no. 6. Sn^{IV} compounds enter into the composition of hexa-co-ordinated compounds more readily than Ti^{IV} compounds, and similarly with ketones as compared with nitriles and Et₂O. With either co-ordination no. the dipole moment is high, showing that the compounds with co-ordination no. 6 have the *cis* configuration; the existence of *trans*-isomerides is unlikely. In the above compounds the partial moments of the SnCl₄ and TiCl₄ groups are less than those of BeCl₂ and AlCl₃ in similar compounds. The compounds TiCl₄.EtCN, m. p. 106°, and TiCl₄.PhCN, m. p. 178°, have been prepared.
R. C.

Dipole moments and molecular structure. I. Simple resonance method for the measurement of dielectric constants. II. Trichlorides of the elements of group V. J. W. SMITH (Proc. Roy. Soc., 1932, A, 136, 251—255, 256—263).—I. Details of the construction and operation of the apparatus are given.

II. The dielectric consts. and densities of a series of

dil. solutions of PCl_3 , AsCl_3 , and SbCl_3 in C_6H_6 at 25° and 40° have been measured, and the electric moments of the mols. calc. The vals. increase with increasing at. wt. of the central atom (PCl_3 0.90, AsCl_3 2.15, SbCl_3 3.75×10^{-18}); this is the reverse of the progression observed with the corresponding hydrides.

L. L. B.

Dielectric constant of water and its temperature coefficient as determined by a resonance method. II. E. P. LINTON and O. MAASS (J. Amer. Chem. Soc., 1932, 54, 1863—1865).—Dielectric consts. of H_2O at 0 — 50° and of PhNO_2 , $\text{C}_2\text{H}_4\text{Cl}_2$, Et_2O , and C_6H_6 at 25° have been determined. The vals. for H_2O agree with the Debye-Huckel theory. A variable condenser which can be adjusted with a precision of 0.1% is described.

R. H. C. (c)

Dielectric constant of ethylene dichloride and dibromide, chlorobromoethane, and diacetyl, and the phenomenon of free rotation. C. T. ZAHN (Physical Rev., 1932, [ii], 40, 291—298).—A temp. variation similar to that previously observed for ethylene dichloride (cf. A., 1931, 1113) was found, and is attributed to the possibility of free rotation around the C—C linking, and a simultaneous dipole interaction between the two mutually rotating parts of the mol. Evidence for free rotation in C_2H_6 obtained from the sp. heats of C_2H_4 and C_2H_6 is discussed.

N. M. B.

Dipole moments of di- and tri-phenylmethane derivatives. E. BERGMANN, L. ENGEL, and H. A. WOLFF (Z. physikal. Chem., 1932, B, 17, 81—91).—Moments have been determined from measurements with solutions in indifferent solvents. Discrepancies between the observed vals. for the moments of the above and other CH_3 derivatives and those calc. from group moments by vectorial addition, assuming a regular tetrahedral arrangement of the central C linkings, are, in general, solely attributable to spreading of the valencies by the substituents. The valency angle required to account for the observed moment agrees for several compounds with that obtained by X-rays, but with the methylene halides there are deviations, suggesting that here the group moments are reduced by mutual polarisation.

R. C.

Dipole moments of fluorene derivatives. E. BERGMANN, L. ENGEL, and H. HOFFMANN (Z. physikal. Chem., 1932, B, 17, 92—99).—Moments derived from measurements with solutions in indifferent solvents indicate that the fluorene system has a uniplanar structure and that when two o-positions in Ph_2 are linked by a CO group to give fluorenone the other two o-C atoms are displaced away from each other.

Dipole moments of certain organic nitrogen compounds. E. BERGMANN and M. TSCHUDNOVSKI (Z. physikal. Chem., 1932, B, 17, 100—106).—Dipole moment measurements with *p*-monohalogenoanilines and similar derivatives of PhNCS have shown that the NH_2 group is an irregular substituent with a characteristic angle of about 42° , whilst the NCS group is linear. Raman spectra suggest that some at least of the mols. of PhNCS may have the structure

$\text{Ph}:\text{N}::\text{C}::\text{S}$.

R. C.

Dipole moments of some aromatic oxygen and sulphur compounds. E. BERGMANN and M. TSCHUDNOVSKI (Z. physikal. Chem., 1932, B, 17, 107—115).—New and existing data for the moments of *p*-substituted anisoles show the characteristic angle of the OMe group to have always approx. the same val. With *p*-substituted derivatives of Ph_2O and Ph_2S the angle for the OPh or SPh group varies from one compound to another, perhaps owing to mutual repulsion of *p*-substituents.

R. C.

Dipole moments of some compounds containing a triple linking. E. BERGMANN and M. TSCHUDNOVSKI (Z. physikal. Chem., 1932, B, 17, 116—119).—The moments of *p*-chloro- and -iodobenzonitrile indicate that the linking by which the CN is attached to the ring makes an angle with the line joining the C to the N. CPh-CH and its *p*- NO_2 -derivative have the moments 0.66 and 3.63×10^{-18} , respectively.

R. C.

Dipole moments of aromatic nitriles and isonitriles. H. POLTZ, O. STEIL, and O. STRASSER (Z. physikal. Chem., 1932, B, 17, 155—160).—Dipole moment measurements with PhMe, PhCN, PhNC, and simple substituted derivatives of the two latter show that the angle between the moments of the $\cdot\text{CN}$ and $\cdot\text{NC}$ groups and the corresponding diameter of the ring cannot exceed 15° , and that the moments have the same sense.

R. C.

Dipole moment of caoutchouc. W. OSTWALD and R. RIEDEL (Kolloid-Z., 1932, 59, 150).—Vals. between 3.75×10^{-18} and 33×10^{-18} are obtained; these are at least 3—4 times those determined for the most highly polymerised styrenes.

E. S. H.

Polarity of chemical compounds. I. K. HIGASHI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 729—740).—From the densities and dielectric consts. of dil. solutions in C_6H_6 or in C_6H_{14} , the following dipole moments have been calc.; amyl alcohol 1.66, BzOH 1.69, *i*-borneol 1.65, thiophen, 0.53—0.54, *d*-camphor 3.05, 1-nitroso- β -naphthol 4.39, 2-nitroso- α -naphthol 4.36, cobalti-1-nitroso- β -naphthol 3.8, ferri-1-nitroso- β -naphthol 3.1, and 8-hydroxyquinoline 2.70 (all $\times 10^{-18}$ e.s.u.). The relations of the dipole moments to the chemical structures are discussed.

J. W. S.

Existence of polythiochlorides [of sulphur]. Refractive index of solutions of sulphur in sulphur chlorides. A. BARONI (Atti R. Accad. Lincei, 1932, [vi], 15, 305—309).—Measurements of n for solutions of S in SCl_2 and in S_2Cl_2 at 100° , 150° , and 200° , and also after ageing for about six months, are recorded. The results indicate the existence of the compound S_3Cl_2 , but not of compounds containing greater proportions of S.

O. J. W.

Anisotropic liquids ("liquid crystals") in electric fields. II. W. KAST (Z. Physik, 1932, 76, 19—23; cf. A., 1931, 1116).—The effect of azoanisole on the crit. frequency at which the anisotropy of *p*-azoxyanisole vanishes was investigated for several samples.

A. B. D. C.

New type of magnetic birefringence. S. W. CHINCHALKAR (Indian J. Physics, 1932, 6, 581—594).

—A detailed account of results already reported (A., 1931, 1355). With some simplifying assumptions, Langevin's theory gives the right order of magnitude for the magnetic birefringence of $\text{Ce}(\text{NO}_3)_3$ solution. The solutions which show negative birefringence show also a negative Faraday effect. J. W. S.

Magnetic birefringence and molecular anisotropy. S. W. CHINCHALKAR (Indian J. Physics, 1932, 6, 563—572).—The magnetic anisotropy of mols. of a no. of org. liquids has been calc. on Langevin's theory from the Cotton-Mouton const. of magnetic birefringence and the depolarisation factor for light scattered by the liquids. The results are compared with the optical anisotropies for the same mols. in the gaseous state. J. W. S.

Photographic method for measuring the retardation of a weakly double refracting plate in the ultra-violet. G. SZIVESSY and A. DIERKESMANN (Z. Krist., 1932, 82, 258—270; cf. A., 1929, 628).

C. A. S.

Faraday effect in liquid mixtures. K. SCHARF (Ann. Physik, 1932, [vi], 13, 377—408).—Investigations of the Faraday effects for $\text{EtOH-H}_2\text{O}$, $\text{Me}_2\text{O-H}_2\text{O}$, $\text{PhNO}_2\text{-EtOH}$, $\text{EtOH-C}_6\text{H}_6$, and $\text{PhNO}_2\text{-C}_6\text{H}_6$ have been made by a special apparatus. The trustworthiness of the Verdet-Schönrock law for mixtures is discussed. Measurements for Na light show deviations from calc. vals. assuming additivity. These deviations are discussed. W. R. A.

Thermal variation of Faraday rotation. P. K. PILLAI (Indian J. Physics, 1932, 6, 573—579).—For most aq. solutions of paramagnetic salts the Faraday rotation is nearly inversely proportional to the abs. temp. A few show no change with temp., whilst $\text{Fe}(\text{NO}_3)_3$ and FeCl_3 show an increase of rotation with rise in temp. There is no general relation between the changes of susceptibility and of Faraday rotation with temp. J. W. S.

Stroboscopic method of measuring electric birefringence. R. LUCAS and M. SCHWOB (Compt. rend., 1932, 194, 1729—1731).

C. A. S.

Variation with thickness of magneto-optic effects due to transmission through thin layers of iron. M. CAU (Compt. rend., 1932, 194, 1642—1644; cf. A., 1929, 633).

C. A. S.

Magnetic behaviour of complexes. IV. Ferric NN-dipropyldithiocarbamates. L. CAMBI, L. SZEGO, and A. CAGNASSO (Atti R. Accad. Lincei, 1932, [vi], 15, 266—271; cf. A., 1931, 1382).—Magnetic susceptibility measurements are recorded for the three Pr_2 isomerides of $(\text{NPr}_2\text{CS}_2)_3\text{Fe}$. The susceptibility of these three compounds does not vary with the temp. according to the simple Curie-Weiss law. O. J. W.

Diamagnetism of liquid mixtures. S. R. RAO and G. SIVARAMAKRISHNAN (Indian J. Physics, 1932, 6, 509—526; cf. this vol., 10).—Details are given of results previously reported. Mixtures of C_6H_6 and CS_2 and of C_6H_{14} and PhCl also follow the additivity rule. The results are discussed from the point of view of X-ray scattering by liquid mixtures. J. W. S.

Diamagnetic susceptibilities of inorganic compounds. I. Acids and alkali and alkaline-earth salts. K. KIDO (Sci. Rep. Tohoku, 1932, 21, 149—170).—Measurements with alkali and alkaline-earth hydroxides, halides, nitrates, sulphates, carbonates, and acetates, and with the corresponding acids, are described. The ionic susceptibilities χ of the ions present have been calc. on the assumption of an additive law, and found to conform to the equation $\chi = cn \times 10^{-6}$, where n is the no. of electrons in the ion; c is 0.98 for the anions, 0.80 for alkali ions, and 0.45 for alkaline-earth ions. H. F. G.

Ferromagnetic moments and the periodic system. P. WEISS (Anal. Fis. Quim., 1932, 30, 237—243).—The variation of the magnetic moment of a no. of binary alloys with the composition is discussed. The moments of the elements in any column of the periodic table are of the same val., whilst those of the elements forming a series rise to a max. and then decrease with increase of at. no. H. F. G.

Magnetic susceptibilities of some nickel compounds. R. A. FEREDAY (Proc. Physical Soc., 1932, 44, 274—280).—Vals. were obtained at room temp. for the following Ni compounds: formate, cyanide, borate, citrate, sulphate, ammonio-sulphate, benzoate, K sulphate, $(\text{NH}_4)_2$ sulphate, phosphate, acetate, ferrocyanide, ferricyanide, fluoride, oxalate, carbonate, chromate, and dioxime compounds. The at. susceptibility of combined Ni remained const. except for the anhyd. cyanide and the dioxime compounds. Some of the latter are diamagnetic. N. M. B.

Optical rotation of liquids, its variation with wave-length, temperature, solvent, and concentration. T. M. LOWRY (U.S. Bur. Stand. Miscell. Publ., 1932, No. 118, 1—104).—A record of the available rotation data for substances classified as follows: the asymmetric C atom does not form part of a ring; at least one asymmetric C atom forms part of a ring; no asymmetric C atom, or containing an asymmetric or a dissymmetric atom of some other element; substances of unknown, doubtful, or complex structure, such as alkaloids etc. Sugars are not included. Data are also given for the influence of salts and other substances on rotatory power. M. S. B.

Solvent action. III. Rotatory powers of *l*-menthyl methyl naphthalate in mixtures of alcohols with benzene or hexane. IV. Optical rotation of *l*-menthyl hydrogen naphthalate in polar and non-polar solvents. H. G. RULE and A. McLEAN (J.C.S., 1932, 1400—1409, 1409—1415).—III. The mol. rotation of *l*-menthyl Me naphthalate has been determined in mixtures of varying concn. of C_6H_6 with EtOH , PrOH , *n*- and *iso*- BuOH , and *iso*- and *tert*-amyl alcohol, respectively, and of C_6H_{14} with PrOH , Bu^OH , and *iso*amyl alcohol. On comparing the changes in polarisation of the alcohol with the changes in rotatory power of the ester, calc. as due to the alcohol present, the latter shows a pronounced min. corresponding with the max. in the polarisation curves for the first four alcohols in C_6H_6 . The two polarisation max. of *iso*amyl alcohol correspond with the two min. of

the rotatory powers, but *tert.*-amyl alcohol gives for both polarisation and rotatory power diagrams approx. straight lines which tend in opposite directions at low concns. of alcohol, but are practically parallel at higher concns. With C_6H_{14} as diluent the rotation min. are more pronounced than with C_6H_6 . In pure alcohols the rotatory power of the ester increases, in general, with increase in mol. wt. of the solvent. Among isomeric alcohols the lowest val. is given in the *n*-derivatives, whilst in the *tert.*-derivatives the rotatory powers approx. to those in C_6H_6 or C_6H_{14} . These differences are probably due to the greater capacity of the *n*-alcohols to enter into dipole association with the ester, thus lowering the internal mol. field and reducing the rotatory power.

IV. The mol. rotation of *l*-menthyl H naphthalate has been determined in two series of solvents of CH_4 derivatives and C_6H_6 derivatives, respectively. As with the corresponding menthyl Me ester, the rotatory power of the acid ester tends to vary with the polarity of the medium, but in the opposite direction. The results confirm the conclusion that, in general, the rotatory power most characteristic of an optically active solute is exhibited when the substance is dissolved in a non-polar solvent, whereas a polar solvent enters into dipole association with the optically active solute and shifts the rotatory power towards that of the unsubstituted *l*-menthyl naphthoate.

M. S. B.

Properties of nicotine and its derivatives. IV. Refractive dispersion. V. Magnetic rotatory dispersion. T. M. LOWRY and C. B. ALLSOPP (J.C.S., 1932, 1613—1622).—IV. By a modified Pulfrich refractometer vals. have been obtained for the refractive indices of nicotine at 20° for 28 wave-lengths between 7685 and 4341 Å. A further series of 63 wave-lengths, extending to 2863 Å., has been obtained by photographic readings with an etalon refractometer. The refractive dispersion is simple in the visible region, where it is controlled almost entirely by a single absorption band. Its real complexity is shown by the ultra-violet data. The refractive indices can be represented throughout the whole range by a Ketteler-Helmholtz expression with 6 consts. and 2 variable terms representing the influence of characteristic frequencies in the Schumann region at λ 1326 Å. and in the middle ultra-violet at 2586 Å. In the visible the low-frequency term is 0.01 of the high-frequency term.

V. Verdet's consts. for the magnetic rotatory power of nicotine have been determined for 12 wave-lengths between 6708 and 4358 Å. The relation between magnetic rotatory power and other optical properties of nicotine is discussed.

M. S. B.

Influence of solvents and temperature on rotatory power and dispersion of active substances. R. LUCAS and (MLLE.) D. BIGNARD (Compt. rend., 1932, 194, 1805—1806).—Vals. of $[\alpha]_{5780}$, $[\alpha]_{5460}$, and $[\alpha]_{4358}$ and the dispersions between 5780 and 4358 of *d*-phenyl-lactic and -succinic and *d*-diphenyl-succinic acids, and of Me_2 *d*-phenylsuccinate in various solvents, and of the ester at 21° , 120° , and 155° are tabulated. There are indications of the existence

of two active forms in all, and that *d*-phenyl-lactic acid is an equilibrium mixture of *l*- and *d*-forms.

C. A. S.

Magnetic properties of manganese and chromium in dilute solid solutions. L. NEEL (J. Phys. Radium, 1932, [vii], 3, 160—171).—Dilute solid solutions of Mn in Cu and in Ag, and of Cr in Au are paramagnetic and obey Weiss' law. Curie consts. depend on the quantities of Mn or Cr present. The moment of Cr under these conditions is 23.47 Weiss magnetons. An explanation of the data is developed.

W. R. A.

Ferromagnetic moments of the elements and the periodic system. C. SADRON (Ann. Physique, 1932, [x], 17, 371—452).—Magnetic measurements with the alloys of Ni and of Co have led to the determination of the at. moments of Cr, Mo, W, Pt, Pd, Ru, V, Sb, Si, Sn, Al, Zn, Cu, and Au. The at. moment is const. for elements in the same vertical group of the periodic table; in the horizontal series containing Fe the at. moment is a linear function of the at. no.

E. S. H.

Paramagnetism of crystalline and gaseous ferric chloride, and its constitution. A. LALLEMAND (Compt. rend., 1932, 194, 1726—1727).—Fe in cryst. $FeCl_3$ has a magnetic moment of 27.99 Weiss magnetons. $\chi_m (\times 10^3)$ falls from 9.98 at 125° to 4.59 at 327° , is const. to 430° , and then decreases again. The change above 125° is due to formation of gaseous Fe_2Cl_6 , that at 430° to dissociation to $FeCl_3$. In Fe_2Cl_6 mols. the two atoms of Fe are of the same valency, coupled directly and anti-parallel (cf. A., 1923, ii, 123).

C. A. S.

Multiple reflexions in the Kerr effect of thin layers of iron. M. CAU (Compt. rend., 1932, 194, 1807—1809).

C. A. S.

Constitution of abnormal ammonium salts. W. H. HUNTER and G. D. BYRKIT (J. Amer. Chem. Soc., 1932, 54, 1948—1957).—Di- and tri-hydrochlorides of NMe_3 do not exist. The m.-p. curve for the system $NHPhMe-HCl$ shows the existence of a dihydrochloride. An explanation of the absorption of HCl by the normal NH_4 salts with and without the formation of stoichiometric compounds is suggested. A classification of mol. compounds of higher orders according to the definiteness of the no. and positions of the groups about the central atom, and the firmness with which they are held, is discussed.

C. J. W. (c)

Compact molecules. H. J. BACKER (Natuurwetensch. Tijds., 1932, 14, 73—82).—Org. mols. may be classified as being of open or compact structure. The latter type arises from factors such as excessive branched chain formation and the crowding together of large groups; examples are CMe_4 and camphor. Compact mols., as compared with the open type, are characterised by small cohesion between the mols., characterised by low b. p., small latent heat of evaporation, large coeff. of expansion, and small surface tension, and by great stability of the cryst. phase, resulting in high m. p., high crystallisation velocity, slight solubility; especially characteristic is the small temp. range throughout which the compound is liquid.

H. F. G.

Grating energies of the alkaline-earth oxides and sulphides and the electron affinity of oxygen and sulphur. J. E. MAYER and (Miss) M. McC. MALTBY (Z. Physik, 1932, 75, 748—752).—The method of Born and Mayer (cf. this vol., 564) was applied to these crystals, and shows that O and S have both negative electron affinities for two electrons.

A. B. D. C.

New octet equations for chemical formulæ. A. CALANDRA (Chem. News, 1932, 144, 327).—Various equations resulting from the octet rule are applied to org. compounds.

D. R. D.

Structure and unimolecular decomposition of nitrous oxide and carbon dioxide molecules. G. HERZBERG (Z. physikal. Chem., 1932, B, 17, 68—80).—The diamagnetism of N_2O points to a singlet ground state, whereas triplet states would result from the products of decomp., normal $NO+N$ or N_2+O . Hence N_2O cannot dissociate into these substances adiabatically, i.e., without electron transition, and the unimol. thermal decomp. must be interpreted as a predissociation. Similar considerations apply to CO_2 . It is probable that in N_2O and CO_2 the strength of either linking is affected by the presence of the third atom. The structure $N\cdot N\cdot O$ is advocated for N_2O .

R. C.

Calculation of space displacements of terminal carbon atoms in ring formation. K. R. GUNJIKAR and T. S. WHEELER (J. Indian Chem. Soc., 1932, 9, 87—89).—The "approach val." for a uniplanar polymethylene chain forming a ring is expressed by the general formula $\sin(n-1)(90-\theta)/2 \cos \theta - 0.5$, in which n is the no. of CH_2 groups and 2θ is the valency angle. The formula yields vals. agreeing with those given by Ingold and by Short.

F. L. U.

Surface chemistry of hydrates. II. Decomposition without lattice rearrangement. V. R. DAMERELL, F. HOVORKA, and W. E. WHITE (J. Physical Chem., 1932, 36, 1255—1267).— $Al_2O_3 \cdot 3H_2O$ loses H_2O superficially at room temp. without the lattice structure being appreciably rearranged. A theory of dehydration applicable to all classes of hydrate decomp. is advanced.

S. L. (c)

Interchange of energy in collisions between gas atoms and solid surfaces. J. K. ROBERTS (Trans. Faraday Soc., 1932, 28, 395—398).—A summary of previous work (see A., 1930, 1340; this vol., 316).

J. G. A. G.

Highly attenuated flames of sodium vapour with cadmium halides and zinc chloride. E. HORN, M. POLANYI, and H. SATTLER (Z. physikal. Chem., 1932, B, 17, 220—232).—The light- and ppt.-distribution curves, which are of the same form as for the Hg halides, show that the flames are of type 2 (cf. A., 1928, 1339) and that almost every collision results in reaction. The curves representing the fall in the light yield as the partial pressure of the halide increases and that of Na in the flame decreases, i.e., as the flames burning at a nozzle change into simple flames, are similar to that for $HgCl_2$, but the yields for the flame at the nozzle are much smaller. Raising the temp. of the reaction zone does not affect the light emission. The energies of combination of

the first and second halogen atoms in the halides have been deduced.

R. C.

Energy levels of the cadmium iodide molecule and the relation between the absorption frequencies of the substance in the states of vapour and crystal. M. KIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 141—149).—The dissociation products of excited CdI_2 mols. at various energy levels have been determined. The heat of sublimation of the compound is calc. from thermochemical data, and hence the absorption frequencies of the crystal estimated (cf. this vol., 673). These are in good agreement with the observations of Fesefeldt (A., 1930, 1497) and indicate that light absorption by the crystal dissociates it into CdI and I .

J. W. S.

Electron affinity of free radicals. III. Free radicals containing diphenyl and naphthyl groups. H. E. BENT and M. DORFMAN (J. Amer. Chem. Soc., 1932, 54, 1393—1401).—The free energies of addition of Na to phenyldiphenylmethyl, triphenylmethyl, α -naphthyldiphenylmethyl, and β -naphthyldiphenylmethyl fall within narrow limits about 2.5 kg.-cal. Within these limits the effects produced by the various groups are additive.

R. H. F. (c)

Rectilinear diameter of carbon monoxide. E. MATHIAS, W. J. BIJLEVELD, and P. P. GRIGG (Compt. rend., 1932, 194, 1708—1710).—Using methods previously described (cf. A., 1922, ii, 561) the density of liquid CO and of its saturated vapour have been determined from -141.63° to -204.97° ; the ordinate of the diameter is given by $\eta = 0.03290 - 0.0019120\eta$; the crit. temp. is -140.21° , crit. density 0.3010, crit. coeff. 3.395. The max. deviation of the diameter is about 1%, as in the case of N_2 and C_2H_4 (cf. A., 1915, ii, 143; 1928, 574).

C. A. S.

Parachor and chemical constitution. XVIII. Additive compounds of boron trifluoride. S. SUGDEN and M. WALOFF (J.C.S., 1932, 1492—1496).—Determinations of the parachor of the additive compounds of BF_3 with HCO_2Me , HCO_2Et , $MeOAc$, $EtOAc$, Me_2O , Et_2O , and $NAcPhMe$ give the following vals.: 228.4, 262.7, 269.8, 303.1, 220.6, 294.6, and 453.2, respectively. These are in satisfactory agreement with the vals. calc. on the assumption that the

substances can all be formulated as $(R_1R_2)O \cdot BF_3$, the linking between B and O being a co-ordinate linking or semi-polar double linking, for which an allowance of -1.6 units is made (this vol., 449). In these compounds two more than the normal no. of electrons are shared and the valency shell of the B atom increases from 6 to 8 electrons. The results show that neither condition causes a contraction, contrary to other hypotheses. The hypothesis of singlet linkings remains the only one which accounts in a simple manner for the negative parachor anomalies found in higher halides etc. The action of BF_3 on a no. of amines and amides has been investigated. Many of the compounds formed are hygroscopic and decompose when melted.

M. S. B.

Germanium. XXXVIII. Parachors of certain compounds of germanium, and atomic con-

stant for germanium. N. V. SIDGWICK and A. W. LAUBENGAYER (J. Amer. Chem. Soc., 1932, 54, 948—952).—From surface tension measurements with GeCl_4 , GeBr_4 , and GeEt_4 , the average at. parachor of Ge is 37.4. $\text{Ge}(\text{OEt})_4$ gives a divergent val., due to difference in type of compound. M. M. (c).

Use of convergent light for rapid production of layer-line diagrams. O. KRATKY (Z. Krist., 1932, 82, 152—154). C. A. S.

Cross lattice spectra. M. VON LAUE (Z. Krist., 1932, 82, 127—141).—By applying the methods valid for space lattice spectra to cross lattices the effects analogous to Debye-Scherrer rings obtained by Sugiura (cf. A., 1931, 1107) by the diffraction of protons are at least qualitatively explained as interference phenomena in non-transparent cross lattices. C. A. S.

Structure determination by means of Weissenberg photographs. F. HALLA (Z. Krist., 1932, 82, 316—323). C. A. S.

Physical properties of single-crystal magnesium. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1932, 67, 29—41).—Vals. for thermal e.m.f. with respect to Cu, Cauchy elastic moduli, and linear thermal expansion are recorded. CH. ABS.

Crystal lattice distortion in stretched wire. W. A. WOOD (Nature, 1932, 129, 760—761). L. S. T.

Fibrous structure of cold-worked metals. K. YAMAGUCHI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 741—760).—Theoretical. J. W. S.

Structure of the surface of polished metal crystals. W. BOAS and E. SCHMID (Naturwiss., 1932, 20, 416—419).—From Laue reflexion diagrams of the polished surface of metals immediately after polishing and after subsequent etching to different depths it is shown that grinding and polishing produce two layers on the surface of the metal, the outer consisting of a finely cryst. zone 0.005—0.03 mm. thick and the inner of a deformed zone forming a union between the outer zone and the undistorted original structure. A. R. P.

X-Ray studies on Bi single crystals. A. GOETZ and R. C. HERGENROTHER (Physical Rev., 1932, [ii], 40, 137—150; cf. A., 1930, 792).—An X-ray analysis of different types of Bi single crystals grown within or outside a transverse magnetic field showed no change in lattice structure or parameter, and indicated that the difference in density, electric conductivity, and thermal e.m.f. which distinguishes the two types of crystals can exist in spite of the unchanged conditions for the existence and distribution of the free electrons as given by the geometric configuration of the atoms in the lattice. The effects are ascribed to changes of certain variations in the lattice, indicating very large mean free paths for the electrons in a crystal. N. M. B.

Crystal structure of praseodymium. A. ROSSI (Atti R. Accad. Lincei, 1932, [vi], 15, 298—300).—X-Ray measurements show that Pr has a hexagonal structure: a 3.657 Å., c/a 1.62, d_{obs} 6.765 \pm 0.008, d_{calc} 6.777. O. J. W.

Crystal chemistry. V. M. GOLDSCHMIDT (Fortschr. Min. Kryst. Petr., 1931, 15, 73—146; Chem. Zentr., 1932, i, 486).—A discussion. A. A. E.

Crystal-chemical relationships of gallium and aluminium, germanium, and silicon. V. M. GOLDSCHMIDT (Norsk geol. Tidsskr., 1931, 12, 247—264; Chem. Zentr., 1932, i, 486).

Crystal-chemistry of germanium. V. M. GOLDSCHMIDT (Nachr. Ges. Wiss. Göttingen, 1931, 184—190; Chem. Zentr., 1932, i, 369).—The lattice const. of Mg_2GeO_4 are about 2% greater than those of Mg_2SiO_4 . $\text{Sc}_2\text{Ge}_2\text{O}_7$ gives a powder diagram similar to that of $\text{Sc}_2\text{Si}_2\text{O}_7$. $\text{BaTiGe}_3\text{O}_9$ has a 6.72 \pm 0.01, c 9.70 \pm 0.02 Å. $\text{CaMg}(\text{GeO}_3)_2$ is similar in crystal structure to diopside. Zn_2GeO_4 has a 8.74 Å., α 107° 45'. Ba_2GeO_4 has a approx. 7.82 Å., α approx. 108°. Ni_3GeO_4 has a 8.20 Å. A. A. E.

Rutile modification of germanium dioxide. V. M. GOLDSCHMIDT (Z. physikal. Chem., 1932, B, 17, 172—176; cf. this vol., 117).—X-Ray examination gives a 4.390 \pm 0.006, c 2.895 \pm 0.004 Å., u 0.3, and d 6.27. R. C.

Growth and dissolution of crystals of the sodium chloride type. I. N. STRANSKI (Z. physikal. Chem., 1932, B, 17, 127—154).—The growth of NaCl crystals, in particular when ground into a spherical or cylindrical shape, has been interpreted on the lines of the theory previously described (A., 1928, 1178; 1931, 1115). R. C.

Mixed crystals of alkaline-earth nitrates. H. T. RINGDAL (Z. Krist., 1932, 82, 50—58).—X-Ray examination of mixed crystals of nitrates of Ca, Sr, and Ba shows that Vegard's additive law (cf. A., 1917, ii, 243; 1921, ii, 627; 1927, 815) is accurately followed for the dimensions of the unit cells. C. A. S.

Crystal habit of potassium chlorate: effect of other ions: formation of very thin plates. H. E. BUCKLEY (Z. Krist., 1932, 82, 31—49). C. A. S.

Crystal structure of silver sulphate. W. H. ZACHARIASEN and K. HERRMANN (Z. Krist., 1932, 82, 161—162).—Revised calculation of Herrmann and Ilge's data (cf. this vol., 12) gives an almost regular tetrahedral arrangement for the O atoms in the SO_4 group. C. A. S.

Crystal structure of lead fluobromide. W. NIEUWENKAMP and J. M. BIJVOET (Z. Krist., 1932, 82, 157—160; cf. this vol., 450).— PbFBr is pptd. as tetragonal tables, d 7.52, on treating excess of aq. PbBr_2 with KF . The unit cell has a 4.18, c 7.59 Å., and contains 2 mols. Its structure closely resembles that of PbFCl . C. A. S.

Structure of Tutton's salts. W. HOFMANN (Z. Krist., 1932, 82, 323—324; cf. A., 1931, 1001).—A correction of the dimensions of unit cells as deduced from Tutton's topic axial ratios, due to the use of revised at. wts. C. A. S.

Crystal structure of beryllium sulphate tetrahydrate. C. A. BEEVERS and H. LIPSON (Z. Krist., 1932, 82, 297—308; cf. A., 1929, 463; 1931, 1218).—The space-group is ; the structure consists of tetrahedral groups of 4 O around a S, and of 4 H_2O around a Be, each of either group being surrounded

by 8 equidistant groups of the other kind. At. distances are S-O 1.5, O-O 2.6, Be-H₂O 1.65, H₂O-H₂O 2.75, O-H₂O 2.6 Å. C. A. S.

Effects of ionic impurities on crystal habit of potassium chromate. H. E. BUCKLEY (Z. Krist., 1932, 82, 285—296; cf. this vol., 450).—K₂CrO₄, although isomorphous with K₂SO₄, is much more susceptible to the influence of other ions. C. A. S.

Symmetry of potassium dichromate crystals. A. SCHÖEP (Natuurwetensch. Tijds., 1932, 14, 86—90).—Previous views are discussed. Study of the etching of K₂Cr₂O₇ crystals by H₂O indicates that the crystals belong to the holohedral class of the triclinic system. H. F. G.

Morphological signification of the method of attachment of accessory minerals to crystal faces. R. L. PARKER (Z. Krist., 1932, 82, 239—257). C. A. S.

Stereochemistry of crystal compounds. VII. SiO₂ structures and structure-principles of the chief rock-forming silicates. P. NIGGLI and E. BRANDENBERGER (Z. Krist., 1932, 82, 210—238; cf. A., 1930, 411, 1215).—The bearing of the relative quantities of the constituent elements, their at. radii, interat. distances, and co-ordination nos. on the structure and consequent nature and relative quantities of the magmatic, rock-forming anhyd. silicates is discussed. C. A. S.

Classification of silicates. F. LAVES (Z. Krist., 1932, 82, 1—14; cf. A., 1929, 749; 1930, 1241).—Assuming that each Si atom is surrounded by four O atoms arranged in equal regular tetrahedra, at least one O being common to two tetrahedra, it is shown that for silicates in which the Si:O ratios are respectively 1:4, 1:3, 2:5, and 1:2, the possible dimensions of the corresponding unions of tetrahedra are: 0; 0 and 1; 0, 1, 2, and 3; and 1, 2, and 3. Diagrams of such unions, and of unions in which the ratios are intermediate, are given. C. A. S.

Crystal structure of malachite. H. BRASSEUR (Z. Krist., 1932, 82, 111—126).—Malachite is monoclinic; the unit cell has *a* 9.38, *b* 11.95, *c* 3.18 Å., β 91° 3', and contains 4 mols. CuCO₃·Cu(OH)₂, space-group *C*_{2h}²-*P*2/*a*. C. A. S.

Crystal structure of lewisite. F. MACHATSCHKI and O. ZEDLITZ (Z. Krist., 1932, 82, 72—76).—The type specimen of lewisite (cf. A., 1895, ii, 58) has *a* 10.269 Å. and is a member of the isomorphous romeite-pyrochlore series (cf. this vol., 450), in which Sb is partly replaced by Ti, its composition corresponding with (Ca,Fe,Na)₃(Sb,Ti)₃(O,OH)₇. C. A. S.

Oriented intergrowths of pyrrhotite and pentlandite. H. EHRENBERG (Z. Krist., 1932, 82, 309—315).—These are described as exhibited by crystals from Miggiandone (Piedmont) and Sudbury (Ontario). In view of the X-ray structures (pentlandite has *a* 10.02 Å., space-group *O*³ or *O*_h³) the metal planes are most probably the faces of intergrowth, a trigonal axis of pentlandite coinciding in direction with the *c*-axis of pyrrhotite. Pyrrhotite from Miggiandone contains about 0.5% Co (cf. A., 1883, 1061). C. A. S.

Crystal structure of chalcopyrite. L. PAULING and L. O. BROCKWAY (Z. Krist., 1932, 82, 188—194).—Chalcopyrite has *a* 5.24, *c* 10.30 Å. the unit cell contains 4CuFeS₂, space-group *D*_{2h}¹²—*I*42*d*. The least interat. distances are Cu-S 2.32, Fe-S 2.20 Å., indicating that the atoms probably have no fixed valencies, but fluctuate between Cu^IFe^{III}S₂ and Cu^{II}Fe^{II}S₂ (cf. A., 1918, ii, 46). C. A. S.

Crystal structure of lollingite. M. J. BUERGER (Z. Krist., 1932, 82, 165—187).—Lollingite from Franklin (N.J.) has *d* 7.53, and contains As 69.80, S 0.21, Fe 29.40%, total 99.41, the deficiency being due to CaCO₃. This corresponds with FeAs₂ with 4% (at.) As replaced by Fe, which is in solid solution. The unit cell has *a* 2.85, *b* 5.25, *c* 5.92 Å., and contains 2 mols., space-group *V*_h¹²; at. radius of Fe 1.12, of As 1.24 Å., distance Fe-As 2.35 Å.; neither Fe nor As is ionised. C. A. S.

Structure of chessylite. H. BRASSEUR (Z. Krist., 1932, 82, 195—209; cf. A., 1931, 707).—Chessylite has *a* 4.96, *b* 5.83, *c* 10.27 Å. The unit cell contains 2 mols. of 2CuCO₃·Cu(OH)₂; space-group *C*_{2h}²; interat. distances Cu-O 2.05, Cu-OH 2.4 Å. C. A. S.

X-Ray investigation of the *n*-monoalkylmalonic acids. D. COSTER and A. V. D. ZIEL (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 91—98).—The higher *n*-monoalkylmalonic acids show an alteration in the grating const. with increasing size of the alkyl group, but the lower members (up to *n*-amylmalonic acid) show a progressive increase with no alternations. The vals. for the lower members are continuous with neither the odd nor the even series of the higher members. J. W. S.

Crystallography of the simpler quinones. W. A. CASPARI (Proc. Roy. Soc., 1932, A., 136, 82—94).—X-Ray spectrograms with Cu radiation, using both the rotational and oscillation methods, gave: benzoquinone, *a* 7.08, *b* 6.79, *c* 5.80 Å., β 101° 0', *d*_{calc.} 1.310, 2 mols. to unit cell; 1:2-naphthoquinone, *a* 3.84, *b* 8.10, *c* 13.40 Å., β 118° 40', *d*_{calc.} 1.450, 2 mols. to unit cell; 1:4-naphthoquinone, *a* 13.50, *b* 7.74, *c* 8.25 Å., β 121° 10', *d*_{calc.} 1.422, 4 mols. to unit cell; 1:2-anthraquinone, *a* 11.41, *b* 11.56, *c* 9.30 Å., β 130° 30', *d*_{calc.} 1.480, 4 mols. to unit cell; 1:4-anthraquinone *a* 4.19, *b* 5.81, *c* 19.62 Å., β 101° 30', *d* 1.477, 2 mols. to unit cell; meso-anthraquinone, *a* 19.65, *b* 24.57, *c* 4.00 Å., *d*_{calc.} 1.432, 8 mols. to unit cell. L. L. B.

Methylbixin. H. WALDMANN and E. BRANDENBERGER (Z. Krist., 1932, 82, 77—86; cf. A., 1931, 415).—Methylbixin is holohedral monoclinic, *a*/*b*—0.78(9), β 120° 54'; the ψ -rhombic symmetry is due to twinning. The unit cell has *a* 10.36, *b* 13.40, *c* 20.62 Å., β 121°, and contains 4 mols. (C₂₀H₃₂O₄); length of mol. 27—28 Å.; space-group (probable) *C*_{2h}²-*P*2₁/*a*. Double refraction very strong, *n*^v 1.44, 1.649, *n*^D 2.63 (approx., but ? 1.92); dispersion, *n* for λ 6500, 5890, and 5700 Å., respectively, 1.630, 1.649, and 1.660; pleochroism strong, pale yellow, orange-red, black. These data are consistent with the close similarity of the proposed structure of its

mol. with that of the diphenylpolyenes (cf. A., 1929, 1453; 1931, 551). C. A. S.

Structural changes of cellulose nitrate films on drying. J. J. TRILLAT (Compt. rend., 1932, 194, 1922—1924).—X-Ray examination of films prepared from an COMe_2 solution of cellulose nitrate (12.9% N) and dried for periods of 0.25—100 hr. shows a cryst. structure, reverting gradually, with contraction, to the structure of the original nitrate. This is due to an additive compound which gradually disappears as the solvent evaporates (cf. A., 1930, 750, 1519). The contraction occurring on drying is in the direction perpendicular to the main valency chains (cf. A., 1931, 1276). Less highly nitrated cellulose shows progressively less cryst. structure. C. A. S.

Cry of tin. H. O'NEILL (Nature, 1932, 129, 833).—Attention is directed to similar observations by other workers (cf. this vol., 563). L. S. T.

Torsion modulus of nickel at high temperatures and simultaneous magnetisation. W. MORIUS (Physikal. Z., 1932, 33, 411—417).—The unsteady variation of the elastic consts. of ferromagnetic crystals in the neighbourhood of the Curie point was tested for the torsion modulus of Ni wire. This behaviour is probably connected with magnetostriction and not with valency coupling as has been supposed by Heisenberg. A. J. M.

Temperature variation of plasticity and tensile strength of rock-salt crystals. W. THEILE (Z. Physik, 1932, 75, 763—776).—Max. strain rapidly increases with rise of temp. above 200° , and the breaking stress is approximately 10 kg. per mm. at 600° . A. B. D. C.

Tempering of rock-salt crystals. E. REXER (Z. Physik, 1932, 73, 777—783).—When rock-salt crystals have been tempered for periods up to 24 hr. at 780° , the surface and inner crystals behave differently. A. B. D. C.

Allotropy in liquids. II. A. SMITS (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 186—193; cf. A., 1931, 416).—The available data for the variation of the dielectric const. and d of Et_2O with temp. are discussed with reference to the existence of allotropic forms. The effect of impurity on the results is also considered. M. S. B.

Piezo-electric modulus of zinc blende. K. S. KNOL (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 99—106).—A redetermination of the piezo-electric modulus of Zn blende leads to a val. 9.80, almost double the figure quoted in the literature. J. W. S.

Velocity of sound in solutions of benzene and *n*-butyl alcohol in *n*-heptane. E. B. WILSON, jun., and W. T. RICHARDS (J. Physical Chem., 1932, 36, 1268—1270; cf. A., 1928, 828; 1929, 637).—The velocities in *n*-heptane, C_6H_6 , and BuOH are 1130, 1302, and 1245, respectively, at 25° , and 1025, 1187, and 1156 metres per sec. at 50° . With addition of solute the velocity, v , progressively increased in both solutions. No connexion of v with any thermodynamic coeff. was discovered; in particular there are no irregularities corresponding with those in the polarisation-composition-temp. relations of solutions of BuOH in *n*-heptane. F. E. B. (c)

Sound velocity in reactive mixtures of real gases. D. G. C. LUCK (Physical Rev., 1932, [ii], 40, 440—444).—Mathematical. N. M. B.

Electrical resistance of carbon. Z. NISHIYAMA (Sci. Rep. Tohoku, 1932, 21, 171—192).—The electrical resistance of graphite over the interval 0 — 2000° and its decrease on heating the specimen at 2500 — 3000° have been studied. X-Ray measurements show that grain growth occurs at 2500 — 3000° , and it is suggested that C has a conductivity of essentially the same order as that of metals; the low vals. for ordinary specimens are a result of the fine-grain structure. H. F. G.

Determinations with the aid of liquid helium. XIV. Systematic investigation of some alloys in connexion with superconductivity. XV. Resistance of barium, indium, thallium, graphite, and titanium at low temperatures. W. MEISSNER, H. FRANZ, and H. WESTERHOFF (Ann. Physik, 1932, [v], 13, 505—554, 555—563).—XIV. Alloys with two superconductors as components were investigated. The resistance of the following series of alloys at low temp. was found: In-Pb, Tl-Sn, Tl-In, Pb-Hg, and Mo-C.

XV. The temp. at which the above elements become superconducting were determined. Ba and C do not show superconduction. A. J. M.

Theory of electrical resistance and of superconductivity of metals. E. KRETSCHMANN (Ann. Physik, 1932, [v], 13, 564—598).—The dependence of electrical resistance and superconductivity on temp., magnetic field, and pressure is discussed. A. J. M.

Establishment of an absolute scale for the thermo-electric force. G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON, and J. O. LINDE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 10—14).—The Thomson theory and the Nernst theorem give an expression $e_{\text{abs.}} = \int_0^T (\sigma/T) dT$ (where σ = the Thomson heat) for the thermo-electric force per degree of a metal in the abs. thermo-electric scale. Assuming also that $\sigma = 0$ for the superconducting state, this function is calc. for Sn, Pb, and a Ag alloy. J. W. S.

Thermo-electric forces down to temperatures obtainable with liquid or solid hydrogen. G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON, and J. O. LINDE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 15—24; cf. this vol., 453).—Thermo-electric forces have been measured down to liquid or solid H temp. for Ag, a Ag-Au alloy, and for Au containing small amounts of Fe, Co, Ni, Mn, Cr, or Ti, each against a Ag alloy normal. At low temp. traces of Fe or Co in Au lead to very high thermo-electric forces against the pure metal. J. W. S.

Thermo-electric forces down to temperatures obtainable with liquid helium. G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON, and J. O. LINDE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 25—33; cf. preceding abstract).—Thermo-electric forces against a Ag alloy normal have been measured down to liquid helium temp. for Pt and for Cu containing 0.004—0.87 at.-% of Fe. For the Cu-Fe alloys the thermo-electric force per degree near 0° abs. is

proportional to the abs. temp. With rising temp. it reaches a max. and then decreases. Increasing concn. of Fe displaces this max. towards higher temp. The combination Au containing about 1 at.-% Co against Ag containing about 1 at.-% Au is recommended as a sensitive thermo-element for liquid H_2 and liquid He temp. J. W. S.

Phenomena of superconductivity with alternating currents of high frequency. J. C. McLENNAN, A. C. BURTON, A. PITT, and J. O. WILHELM (Proc. Roy. Soc., 1932, A, 136, 52—76).—A coil of Pb wire shows an abrupt considerable loss of resistance with currents of frequency 1.1×10^7 per sec. at a temp. slightly lower than the crit. temp. 7.2° abs., which is characteristic of the transition to superconductivity when using direct current. With Sn wires the resistance began to decrease abruptly at 3.76° abs. and disappeared completely at 3.70° abs. With currents of the above frequency the corresponding temp. were 3.67° and 3.61° abs. Similar results were obtained with Ta wires. The depression of the transition temp. is a function of the frequency of the current and is not a direct function of the skin effect. Polarisation and orientation phenomena are probably involved in the production of the superconducting state in metals. L. L. B.

Complexity of aluminium chloride. A. SMITS, J. L. MEYERING, and M. A. KAMERMANS (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 193—196).—Further data are given in support of the former conclusions (cf. this vol., 453). The triple point temp. is 0.1° higher and the triple point pressure 1 cm. lower than previously found. The sublimation temp. is 180.2° , and more accurate vals. are also given for heats of dissolution, sublimation, etc. M. S. B.

Thermal conductivity of indium at low temperatures. W. J. DE HAAS and H. BREMMER (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 131—136).—The same method was employed as for Pb and Sn (A., 1931, 792) and the general behaviour is the same, but the min. val. for the thermal resistance of In is at a higher temp., 18° abs., than for Pb and Sn. The influence of a longitudinal magnetic field on the thermal resistance below the transition point is very nearly equal to that of a transverse field. The resistance-temp. curves show a discontinuity at the transition point, due to a decrease of the thermal resistance at that point as the temp. falls. For lower temp. the thermal resistance in the superconductive state is proportional to $T^{-1.7}$ and in the non-superconductive state to $T^{-1.2}$. M. S. B.

Thermal conductivity of normal primary saturated alcohols. M. DANILOFF (J. Amer. Chem. Soc., 1932, 54, 1328—1332).—Conductivities have been determined at 30° , 75° , and 100° . The conductivity decreases with rise in temp., and for a given temp. is a min. for the alcohol with 6 C atoms. The conductivity-temp. curves for alcohols with up to 6 C atoms are linear and parallel to each other. F. E. B. (c)

Heat of sublimation of carbon. W. E. VAUGHAN and G. B. KISTIAKOWSKY (Physical Rev., 1932, [ii], 40, 457—462).—In saturated C vapour from 4150° to

4700° abs. the partial pressures of both atoms and mols. are of the same order of magnitude. The heats of sublimation at 0° abs. into atoms and mols. are 161 and 176 g.-cal. and 195 and 189 g.-cal., respectively, for the 5.5- and 7.0-volt dissociation energies. N. M. B.

Specific heats of solids at the temperature of liquid helium. IV. Atomic heats of tin and zinc. W. H. KEESOM and J. N. VAN DEN ENDE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 143—155).—At. heat data for Sn and Zn between 1.3° and 21° abs. are recorded. The at. heat of Sn at approx. 3.7° abs. rises abruptly so that the at. heat just below this temp. is larger than immediately above. Since the temp. practically coincides with the transition point the phenomenon appears to be connected with the superconductivity of Sn. M. S. B.

Atomic heat of bismuth at higher temperatures. L. G. CARPENTER and T. F. HARLE (Proc. Roy. Soc., 1932, A, 136, 243—250).—The thermal capacity of Bi was measured with a vac. calorimeter from 30° to 370° . C_p exceeds the Debye max. of $3R$ at all temp. above 260° abs., and at the m. p. this excess is $>10\%$. For solid Bi C_p varies inversely with the temp. above 300° abs., but in the liquid state C_p diminishes with rise of temp. L. L. B.

Vibrational specific heat of carbon dioxide. H. O. KNESER (Nature, 1932, 129, 798).—Theoretical. L. S. T.

Calculation of normal vapour pressures from the data of the gas current method, particularly in the case of iodine. H. T. GERRY and L. J. GILLESPIE (Physical Rev., 1932, [ii], 40, 269—280).—A method involving the thermodynamic treatment of mixtures of real gases is developed, and applied to the case of the v. p. of solid I from 0° to 100° . N. M. B.

General vapour-pressure apparatus. R. MOHR (Physikal. Z., 1932, 33, 419—420).—The construction of an apparatus suitable for demonstrating the usual v.-p. laws is described. A. J. M.

Simple derivation of general equations of energy and entropy of gases. T. HUANG (J. Amer. Chem. Soc., 1932, 54, 1024).—Cf. A., 1931, 1362. R. H. C. (c)

Pressure-volume-temperature relations of paraffin hydrocarbons. G. G. BROWN, M. SOUTHERS, jun., and R. L. SMITH (Ind. Eng. Chem., 1932, 24, 513—515).—The available experimental data of the pressure-vol.-temp. relationships of the hydrocarbons CH_4 to $n-C_8H_{18}$ have been correlated by means of an empirical reduced equation of state which reproduces them with sufficient exactness for engineering work. H. I.

Volume-temperature-pressure relations for several non-volatile liquids. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1932, 7, 1—27).—In order of compressibility, mono->di->tri-hydric alcohols. No liquid less compressible than glycerol was found; tri-*o*-tolyl phosphate is near to glycerol. Many liquids were examined at pressures up to 12,000 kg. per sq. cm. at 0° , 50° , and 95° . CH. ABS.

Vapour pressures and latent heats of vaporisation of hydrocarbons. J. B. MAXWELL (Ind. Eng. Chem., 1932, 24, 502—505).—Theoretical. The v.-p. data for paraffin hydrocarbons (C_2 — C_{19}) are correlated with those for C_6H_6 . Data for the latent heats of a no. of hydrocarbons are also given. H. I.

Proportionality of van der Waals' constants a and b . I. TRAUBE (Kolloid-Z., 1932, 59, 136).—A claim for priority (cf. A., 1931, 1117). The "constancy" of a/b for liquids is illustrated. E. S. H.

Heat capacity and entropy of thallos nitrate from 17° to 300° abs. Entropy and free energy of nitrate ion. W. M. LATIMER and J. E. AHLBERG (J. Amer. Chem. Soc., 1932, 54, 1900—1904).—From new and existing data the following vals. have been calc. at 298.1° abs. for entropy in the standard state: solid $TiNO_3$, 38.1; aq. ($H^+ + NO_3^-$) at hypothetical 1M, 36.9 (free energy of formation in standard state, -26,700 g.-cal.); solid $AgNO_3$, 27.7; aq. ($H^+ + NO_3^-$) at hypothetical 1M, 24.0. F. D. R. (c)

Salts of low m. p. V. Preparation, density, conductivity, and viscosity of alkylated ammonium picrates. VI. Density, conductivity, and viscosity of alkylated ammonium iodides and perchlorates in the molten state. P. WALDEN and E. J. BIRR (Z. physikal. Chem., 1932, 160, 45—56, 57—68; cf. A., 1928, 112).—V. The determinations have been made with the molten salts. Comparison of isomeric picrates either at a fixed temp., or at the m. p. (abs.), T , shows that for the picrates of primary, sec., and tert. bases the mol. vol., the coeff. of expansion, α , and the val. of αT are greater than for picrates of quaternary NH_4 bases. The effect of the degree of substitution of the cation on the conductivity and viscosity is examined. The conductivity of molten $C_{10}H_8$ picrate shows that it is not a salt-like compound. NH_4Bu^2 picrate, m. p. 98—99°, *di-n-cetyl*ammonium picrate, m. p. 55—10°, $NHBu^3$ picrate, m. p. 105.6°, and NBu^4 picrate, m. p. 90.3°, have been prepared.

VI. Tri- and tetra-alkylammonium salts have been examined. The viscosities and conductivities show that the degree of dissociation of these compounds and of mono- and di-alkylammonium nitrates in the molten state is determined primarily by the degree of substitution of the cation, the influence of the anion being negligible. Molten mono- and di-alkyl compounds contain products of association, as well as simple ions, the tendency to association being the greater with the monoalkyl compounds. R. C.

Variation of the vapour viscosities of n - and iso-pentane with pressure by the rotating-cylinder method. R. K. DAY (Physical Rev., 1932, [ii], 40, 281—290).—Measurements from a few mm. to the saturated v. p. at 25° show a linear decrease with pressure. Vals. for n - and iso-pentane are $(677.2 - 0.0084p) \times 10^{-7}$, and $(696.5 - 0.0077p) \times 10^{-7}$, respectively, where p is the v. p. in mm. Hg.

N. M. B.

Viscosity of gases over a large temperature range. B. P. SUTHERLAND and O. MAASS (Canad. J. Res., 1932, 6, 428—443).—An oscillating-disc apparatus is described for temp. down to -200°.

The apparatus was calibrated with air. Viscosity-temp. curves for air and H_2 were slightly concave towards the temp. axis, the viscosities falling to 551.1×10^{-7} at -194.2° and 336.0×10^{-7} at -198.4°, respectively. The curve for CO_2 was convex and the viscosity fell to 906.0×10^{-7} at -95.4°, the lowest temp. used. At the lowest temp. viscosity was independent of the pressure down to 2 cm., below which it diminished slightly. A. G.

Coefficient of viscosity of sulphur dioxide over a low temperature range. W. W. STEWART and O. MAASS (Canad. J. Res., 1932, 6, 453—457).—The viscosity of SO_2 over the range 30—75° is a linear function of temp. E. S. H.

Diffusion of hydrogen through palladium. V. LOMBARD and C. EICHNER (Compt. rend., 1932, 194, 1929—1931).—At a pressure of 770 mm. the rate of diffusion varies more or less linearly with the temp. between 400° and 600°. At 372° for pressures of 40—770 mm. the rate of diffusion is proportional to $p^{0.8}$. C. A. S.

Formation of superlattices in alloys of iron and aluminium. A. J. BRADLEY and A. H. JAY (Proc. Roy. Soc., 1932, A, 136, 210—232).—X-Ray examination by the powder method of alloys of Fe and Al in the range Fe-FeAl shows that all the structures are primarily based on a simple body-centred cubic lattice like α -iron. Alloys quenched from above 600° show a random distribution up to 25 at.-% Al. At 25—26% there is an abrupt change of structure and cube centres differ in composition from cube corners. Annealed alloys with <18% Al have a random distribution, and from 40 to 50% Al they have the FeAl type of structure like the quenched alloys of this range. Intermediate compositions have the Fe_3Al type, where the Al atoms lie on a face-centred cubic lattice forming a superlattice with dimensions twice those of the small body-centred cube. L. L. B.

Binary systems, aluminium-cadmium, -lead, and -bismuth. M. HANSEN and B. BLUMENTHAL (Metall.-Wirt., 1931, 10, 925—927; Chem. Zentr., 1932, i, 866).—The above metals exhibit limited solubility in liquid Al. Max. depression of f. p. is reached as follows: Cd 11°, Pb 1.5°, Bi 3.5°. The solubility of Al in the molten heavy metal is practically zero. The solubility of Cd in solid Al is <0.97% at 550° and is smaller at lower temp. A. A. E.

Equilibrium relations in aluminium-cobalt alloys of high purity. W. L. FINK and H. R. FRECHE (Amer. Inst. Min. Met. Eng. Tech. Pub., 1932, No. 473, 10 pp.).—The Al-Co diagram for 0—8% Co is given. The solid solubility of Co in Al is <0.02% at 655°. The intersection of the (extrapolated) hyper-eutectic liquidus with the eutectic horizontal determines the eutectic composition as 1% Co, a val. which was approx. verified microscopically.

CH. ABS.

Widmannstätten structure. III. Aluminium-rich alloys of aluminium with copper and of aluminium with magnesium and silicon. R. F. MEHL, C. S. BARRETT, and F. N. RHINES (Amer. Inst. Min. Met. Eng., Preprint, 1932, 26 pp.).—The form of the $CuAl_2$ ppt. is described. The ppt. in the

system Al-Mg-Si does not appear to be Mg_2Si , but indications of the presence of Al_3Mg_2 were obtained. The significance of the results in relation to the formation of Widmannstätten figures is discussed and possible relationships to age-hardening theories are examined. CH. ABS.

Use of the polarising microscope in the study of copper alloys. M. VON SCHWARZ (Z. Metallk., 1932, 24, 97—103).—Examination of polished and etched specimens of metals in polarised light affords a ready means of identifying many of the constituents and of characterising the orientation of the crystal grains. In hypereutectic Cu-Cu₂O alloys the excess Cu₂O occurs in dendrites which appear bluish-green under parallel nicols and show a characteristic blood-red colour under crossed nicols. Cu₂S, Cu₂Se, and Cu₂Te in Cu appear greyish-blue under parallel or crossed nicols, whilst SnO₂ in badly oxidised bronze appears as translucent needles which exhibit beautiful polarisation colours under crossed nicols. Similar effects are obtained with Cu₃P in Cu and CuAl₂ in Al. Numerous photomicrographs showing typical polarisation effects are included. A. R. P.

Crystal structures of the compounds formed in the system antimony-cadmium. E. ABEL, J. ADLER, F. HALLA, and O. REDLICH (Z. anorg. Chem., 1932, 205, 398—400; cf. A., 1928, 1190; 1930, 147).—A reply to Chikashige and Yamamoto (A., 1931, 671). There is no ground for supposing that a second modification of CdSb exists nor for denying the existence of the metastable Cd₃Sb₂. M. S. B.

Magnetic susceptibility of some binary alloys. F. L. MEARA (Physics, 1932, 2, 33—41).—For Sb-Cd, Sb-Zn, and Sb-Sn alloys sharp discontinuities in the curves indicate the formation of SbCd, SbZn, and SbSn. In the Sn-Tl series the formation of Sn₂Tl is indicated. The results are correlated with f.-p. data. CH. ABS.

Superconductivity of mercury-cadmium alloys. W. J. DE HAAS and J. DE BOER (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 128—131).—The electrical resistance of alloys of Hg and Cd containing 30, 40, and 50 at.-% Cd, and therefore known from X-ray measurements to crystallise in the same lattice as Hg, have been measured at the temp. of liquid He. They become superconductive at 2.16°, 1.91°, and 1.71° abs., respectively. M. S. B.

The austenite pearlite inversion. (SIR) H. C. H. CARPENTER and J. M. ROBERTSON (Iron and Steel Inst., May, 1932, advance copy).—With ordinary rates of cooling the transformation occurs over a range of temp., but will proceed to completion at any temp. within the range. In presence of other elements the change also occurs over a range, but in this case it does not complete itself if cooling is stopped. In general each austenite grain gives rise to a no. of sets of lamellæ which are not straight and have no apparent relation to the crystallographic planes. In the main the ferrite and cementite form simultaneously and a growing grain of pearlite consists of a group of plates advancing edgewise into the austenite. When alloys of low C content are slowly cooled the pearlite does not assume any particular shape, but

with increasing C content and rate of cooling, it tends to grow radially. Perfect radial growth is obtained when pearlite begins to form in the absence of pro-eutectoid ferrite; with increased rates of cooling the ferrite grains tend to assume elongated shapes. The transformation of pearlite into ferrite commences at the Ac point. The cementite dissolves more slowly than the ferrite and austenite containing globules of cementite is formed. The austenite forms first at points on the ferrite-pearlite boundaries and gives rise to irregularly shaped areas which bear no relation to the form of the original pearlite.

E. H. B.

Equilibrium diagram of iron-manganese-carbon alloys of commercial purity. E. C. BAIN, E. S. DAVENPORT, and W. S. N. WARING (Amer. Inst. Min. Met. Eng. Tech. Pub., 1932, No. 467, 24 pp.).—The alloys contained up to 1.5% C and 15% Mn. The phases austenite, ferrite, and carbide were found. Mn is considered to replace Fe in the carbide phase as the Mn content increases. The ϵ -phase is not stable at any temp. CH. ABS.

Atomic moment, Curie points, and structure of ferro-silicons. M. FALLOT (Compt. rend., 1932, 194, 1801—1803).—The alloys show discontinuities in the magnetic moment and the Curie point at 6.25, 12.5, and 25 at.-% Si; these breaks correspond with changes in the lattice structure. C. A. S.

Utilisation of magnesium alloys: maximal qualities and minimal tolerances. R. DE FLEURY and BENMAKROUHA (Compt. rend., 1932, 194, 1739—1741).—Theoretical. A scheme for indicating the changes in properties of alloys due to repeated refusions etc. is given. C. A. S.

Influence of a third metal on the constitution of brass alloys. IV. Aluminium. II. O. BAUER and M. HANSEN (Z. Metallk., 1932, 24, 73—78, 104—106; cf. this vol., 455).—The system Al-Zn-Cu has been investigated by thermal analysis and micrographic examination in the region 0—10% Al and 50—100% Cu and the results are shown in a series of diagrams for const. Al. for const. Zn, and for const. Cu contents. The structure of the alloys and their solidification are determined by the isomorphism which exists between the corresponding α -, β -, and γ -phases in the Cu-Zn and Cu-Al systems. Addition of Al to Cu-Zn alloys raises the peritectic points, α +liquid \rightleftharpoons β and β +liquid \rightleftharpoons γ , progressively from 905 and 833°, respectively, towards the corresponding points in the Cu-Al system (1031° and 1017°). The α , β , γ , α + β , and β + γ fields of the Cu-Zn system merge into the corresponding fields of the Cu-Al system; in addition the ternary system contains an α + γ field and a ternary α + β + γ field. The latter extends from the α + γ field below 537° with 16% Zn downwards to embrace alloys with 24—30% Zn at room temp. The changes which occur during cooling in the solid state correspond with those which occur under similar conditions in Cu-Al alloys when the ternary alloys are low in Zn, and with those which occur in Cu-Zn alloys when the ternary alloys are higher in Zn; in intermediate alloys the eutectoidal change is incomplete so that the structure contains the three phases. The α -saturated solid solution of

Zn in Cu contains only 72.5% Cu with 3.5% Al and the β -solution 65.5% Cu with 4.25% Al; in each case further addition of Al results in the separation of brittle γ . With constant Al replacement of Cu by Zn results in progressive hardening of the alloys.

A. R. P.

System silver-copper-zinc. M. KEINERT (Z. physikal. Chem., 1932, 160, 15—33).—Micrographic analysis has shown that no crystal species occur in the ternary system other than those observed in the binary systems. Several pairs of analogous crystal species exhibit complete miscibility. There is complete miscibility in the molten state in the ternary system. The results are largely in agreement with those of Ueno (A., 1930, 284).

R. C.

Molecular association of aromatic hydrocarbons with thionyl chloride, sulphuryl chloride, and sulphur dioxide. G. H. LOCKET (J.C.S., 1932, 1501—1512).—Measurements have been made of the viscosities, d , and heats of mixing for the mixtures: SOCl_2 with C_6H_6 , PhMe, xylene, mesitylene, cyclohexane, Et_2O , EtOAc ; SO_2Cl_2 with C_6H_6 , PhMe, xylene, mesitylene, and of the viscosities for SOCl_2 - SnCl_4 , SO_2Cl_2 - SnCl_4 , SO_2 -mesitylene, and SO_2 - EtOAc . The aromatic hydrocarbons associate with these S compounds, in sharp contrast to cyclohexane, and behave like polar (donor) liquids. Methylation of the nucleus increases the association. The S compounds studied appear to be acceptors only; the hydrocarbons may be electron donors, but it appears more probable that they can acquire an induced dipole moment from the inorg. mol., thus giving a dipole association. The mechanism of the Friedel-Crafts reaction is discussed from this viewpoint.

E. S. H.

Physical properties of ternary system acetone-*n*-butyl alcohol-water. R. C. ERNST, E. E. LITKENHOUS, and J. W. SPANYER, jun. (J. Physical Chem., 1932, 36, 842—854).—The viscosity, b , p , surface tension, n , and d of binary and ternary mixtures at 25° were determined.

R. H. F. (c)

Distillation of ternary heterogeneous mixtures. III. System methyl alcohol-benzene-water. J. BARBAUDY (Ann. Office Nat. Combust. Liq., 1931, 6, 229—242; Chem. Zentr., 1932, i, 1061).—Separation, n , and d were studied at 25°. Instability is greater than when EtOH or other homologue replaces MeOH. With little MeOH the aq., with much the C_6H_6 , layer is the heavier. H_2O cannot be removed from the MeOH by distillation at 760°; the azeotropic mixture MeOH- C_6H_6 has the lowest b , p .

A. A. E.

Apparatus for measuring partial vapour pressures of binary liquid systems. O. A. NELSON (J. Amer. Chem. Soc., 1932, 54, 1390—1393).—The liquid is distilled in an apparatus such that liquid flows from the receiver to the still at the same rate as other liquid distils over. Distillation is continued until the temp. becomes const., and the partial v. p. are then calc. from the composition of the distillate. $\text{C}_2\text{H}_4\text{Cl}_2$ - CCl_4 mixtures have been examined.

P. T. N. (c)

Solubility of hydrogen in water under pressure. V. V. IPATIEV, jun., S. I. DRUSHINA-ARTEMOVITSCH, and V. I. TYCHOMIROV (Ber., 1932, 65, [B], 568—571). At 25°, the solubility of H_2 in H_2O is proportional to the pressure between 20 and 140 atm. Under 100 atm. the solubility diminishes markedly between 0.5° and 25°; above 25° the temp. coeff. is very small. Between 65° and 75° the solubility appears to increase.

H. W.

Solubility of sodium carbonate in aqueous solutions of ammonia. G. A. YAKOVKIN (Trans. State Inst. Appl. Chem., Russia, 1930, No. 14, 3—10).—At 25—45° the val. decreases with increasing NH_3 concn.; temp. has little effect at low concns. and no effect at higher concns. NH_3 is superior to MeOH or EtOH for the dehydration of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

CH. ABS.

Solubility of carbamide in water. L. SHNIDMAN and A. A. SUNIER (J. Physical Chem., 1932, 36, 1232—1240).—The solubility may be represented by $\log_{10} N = -609.8(1/T) + 1.468$, where N is the mol. fraction of $\text{CO}(\text{NH}_2)_2$.

E. J. R. (c)

Solvent properties of soap solutions. I. E. L. SMITH (J. Physical Chem., 1932, 36, 1401—1418).—In general, org. liquids having a solubility in H_2O of <2% dissolve to the extent of <10% in a 0.4M aq. solution of Na oleate, lowering its viscosity, and forming unstable emulsions, whilst the reverse is true of liquids which are more sol. in H_2O . These effects are independent of the chemical nature of the liquids. The solubility of some liquids which are almost insol. in H_2O , e.g., C_6H_6 , varies with the method of prep. of the soap solution. Soap colloiddally dispersed in the aq. phase tends to stabilise oil-in- H_2O emulsions, but when salted out has the reverse effect.

O. T. Q. (c)

Hydrotropy. G. LINDAU (Naturwiss., 1932, 20, 396—401).—Hydrotropic phenomena are considered in relation to the phase rule, particular attention being directed to the influence of hydrotropic substances on the crit. solution temp. of the immiscible components of the hydrotropic system.

A. C.

Theories of adsorption of gases. M. POLANYI (Trans. Faraday Soc., 1932, 28, 316—333).—A general survey, chiefly of the potential theory of adsorption.

J. G. A. G.

Theories of adsorption of gases. Quantum mechanics of the reversible electrolytic cell and of electrolysis. R. H. FOWLER (Trans. Faraday Soc., 1932, 28, 368—378).—An exposition (cf. this vol., 25).

J. G. A. G.

Electrical theory of gaseous adsorption. A. MAGNUS (Trans. Faraday Soc., 1932, 28, 386—394).—The theory (A., 1929, 1139) is discussed in relation to the results of the author and co-workers.

J. G. A. G.

Kinetics of adsorption processes. II. Occlusion of hydrogen by palladium. I. Discussion. A. R. UBBELOHDE. II. Dynamic isothermals. A. R. UBBELOHDE and A. EGERTON. III. Influence of nuclear spin on sorption of hydrogen on charcoal. A. R. UBBELOHDE (Trans. Faraday Soc., 1932, 28, 275—283, 284—291, 291—299).—I. Existing data

favour the view that H enters the Pd lattice in the at. state, and equations for the velocity of occlusion are given. The reaction $H_2 \rightarrow 2H$ is catalysed by the surface and is slow compared with $2H \rightarrow H_2$; thus desorption equilibria are much more rapidly established than sorption equilibria.

II. Removal isotherms (cf. this vol., 118) were determined at 306°, 218°, 156°, and 100°. The fraction of impinging mols. sorbed at each temp. is related to the energy of activation and the (small) fraction of surface which is active. Only at 100° is part of the H_2 removed at approx. const. pressure. By varying the activity of the Pd or curtailing the time of exposure to H_2 this region of the isotherm can be eliminated. The data are consistent with the view that this region is associated with the removal of H_2 at a rate small compared with that at which atoms diffuse from the interior to the surface, thus affording a const. pressure of H_2 .

III. H_2 , freshly evaporated from active charcoal at -183° , contains more ortho- H_2 than the equilibrium mixture, probably owing to the ortho- being more strongly adsorbed than para- H_2 . Continuous removal of H_2 at -183° in the range 7–25 cm. shows no definite change (within 1%) in the relative adsorption.

J. G. A. G.

Theory of heat evolved in capillary condensation. E. HUCKEL (Trans. Faraday Soc., 1932, 28, 382–386).—A thermodynamic treatment for adsorbents with capillaries of sufficiently large diameter.

J. G. A. G.

Derivations from "ideal" translational motion of adsorbed molecules. M. G. EVANS (Trans. Faraday Soc., 1932, 28, 364–368; cf. A., 1931, 903).—Mathematical. Effects of "active points" in retarding the mobility of a two-dimensional gas film are considered. The equation developed is consistent with existing data for sorption sufficiently removed from saturation.

J. G. A. G.

Migration of adsorbed molecules on surfaces of solids. M. VOLMER (Trans. Faraday Soc., 1932, 28, 359–363).—A survey.

J. G. A. G.

Processes of adsorption and diffusion on solid surfaces. J. E. LENNARD-JONES (Trans. Faraday Soc., 1932, 28, 333–359).—Theoretical. From a quantum-mechanical treatment of the van der Waals forces between a metal surface and adsorbed gases, the following heats of adsorption on Cu are calc.: A, 6000; N_2 , 2500; and H_2 , 1300 g.-cal. per mol., which are of the same order as those observed experimentally at low temp. Adsorption at crystal surfaces is examined in greater detail (cf. A., 1928, 8). The case in which the cohesion between a metal and the individual atoms of an adsorbed gas mol. is greater than the dissociation energy of the mol. may be identified with "activated" adsorption (A., 1930, 990; 1931, 902). Consideration of the behaviour of an atom on a metallic surface which is traversed by cracks and of which the potential field varies from point to point affords an activated diffusion mechanism for slow adsorption consistent with the results of Ward (A., 1931, 1365).

J. G. A. G.

Nature of activated adsorption. G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1932, 54, 1693–1694).

—Taylor and Sickman's results (this vol., 458) indicate that activated adsorption is limited to particular surface atoms, the adsorbed mols. not having two degrees of freedom. The structure of surfaces may be studied by measuring heats of adsorption for varying amounts at low and high temp.

C. J. W. (c)

Suggested existence of activated adsorption. A. F. H. WARD (Trans. Faraday Soc., 1932, 28, 399–405; cf. A., 1931, 1365).—Dissolution of the gas in the adsorbent accounts for the phenomena attributed to "activated adsorption" (this vol., 331) and objections to the dissolution theory are met. True adsorption must have a finite, although small, energy of activation, and it is considered unlikely that the same process could take place in either of two ways with two different energies of activation.

J. G. A. G.

Mechanism of the adsorption process at the surface of heteropolar crystals. B. TEZAK (Kolloid-Z., 1932, 59, 158–162).—A scheme representing adsorption of electrolytes at a heteropolar crystal surface is devised, in which similarity between the ions of the electrolyte and the crystal plays a leading role. The adsorbability of an ion increases with its similarity to an ion composing the space lattice; e.g., with $BaSO_4$ as adsorbent the following order is observed: $Ba^{++} > Hg^{++} > Pb^{++} > Cd^{++} > Mn^{++} > Zn^{++} > Cu^{++} > Ni^{++} > Mg^{++} > Al^{+++}$. When the solution contains an ion which is also in the crystal space lattice, the adsorption of the oppositely-charged ion is greater the more insol. is the compound which it forms with the common ion. $BaSO_4$ as adsorbent in a solution containing excess of Ba^{++} takes up anions in the following order: $Fe(CN)_6^{4-} > Fe(CN)_6^{3-}$; $NO_3^- > Cl^- > Br^- > I^-$.

E. S. H.

Errors in thermal measurements. W. E. GARNER (Nature, 1932, 129, 832).—A discussion of the precautions necessary in measurements of heats of adsorption and of the use of thermocouple calorimeters (cf. this vol., 592).

L. S. T.

Activated adsorption of hydrogen. H. HOLLINGS and R. H. GRIFFITH (Nature, 1932, 129, 834).—The adsorption of H_2 , C_6H_{14} , cyclohexane, and C_6H_6 on metallic oxides has been measured at temp. up to 450°. Extensive "activated" adsorption of H_2 occurs with the oxides of Mo, V, Cr, and W, and with metallic Sn and Cd. Adsorption of hydrocarbons takes place with every metal or oxide (Cr, Ti, Fe, Cu, Mo, Zn, Cd, Ca, Zr, Mg, Sn, Co, Al, Mn, and W) examined. The velocity and extent of adsorption are considerably influenced by impurities.

L. S. T.

Gaseous adsorption. III. Thermal activation effect in the adsorption of hydrogen on platinum and nickel. E. B. MAXTED and N. HASSID (J.C.S., 1932, 1532–1539).—Thermal activation has been studied quantitatively by exposing Pt and Ni to H_2 at temp. other than that at which the adsorption is measured. When exposure is made at higher temp. there is an increased adsorption on subsequent cooling, which is often greater than the normal adsorption for any point within the temp. range. This effect decreases as the adsorption temp. is raised. Thermal activation does not influence the

reversible adsorption (that part which can be recovered by degassing at the adsorption temp.). The effect may be attributed to adsorption at an energetically heterogeneous surface. E. S. H.

Adsorption of mercury vapour by active carbon. A. M. AGÜES (Anal. Fis. Quím., 1932, 30, 260—266).—Two specimens of active C adsorbed about 0.4 mg. per g. of Hg vapour from air saturated at room temp. The activity of the adsorbent could be restored repeatedly and almost completely by heating the C in a current of dry air at 160° or in superheated steam. H. F. G.

Sorption of gases by copper. A. F. BENTON and T. A. WHITE (J. Amer. Chem. Soc., 1932, 54, 1373—1390).—The sorption by reduced Cu was measured at pressures up to 1 atm. down to -195°. With N₂ there is only rapid physical adsorption, with a small heat effect. With H₂ at low temp. only physical adsorption occurs, at 78-5° activated adsorption predominates, and at 0° both activated adsorption and dissolution occur. With CO there is both physical and activated adsorption, together with either dissolution or a second type of activated adsorption. S. L. (c)

Action of mixed catalysts in the decomposition of nitrous oxide. II. Determination of surface of catalysts by adsorption of dyes. G. M. SCHWAB and H. SCHULTES (Angew. Chem., 1932, 45, 341—347; cf. A., 1930, 1257).—The adsorption of methylene-blue and β -naphthol-orange from H₂O and of anthracene-blue from cyclohexanone by CuO, granulated ZnO and MgO and their mixtures, and Ni powder reaches a temporary equilibrium, but further adsorption occurs. The equilibrium amounts converge to a saturation val. with increasing concn. of the dye. The adsorbent surface can be calc. from the data. Surfaces which are changed by H₂O can be measured by using non-aq. solvents, and by a proper choice of dyes the partial surface of a mixed adsorbent can be determined. The mixed catalysts for the decomp. of N₂O formerly described have an enhanced catalytic activity without showing a marked increase of surface. Measurements of the surface of Ni by the adsorption method agree satisfactorily with those obtained from the velocity of dissolution. E. S. H.

Comparison of adsorption of nitrophenol and iodine by vacuum-sublimed films of barium chloride. J. H. DE BOER [with L. A. H. WOLTERS]. (Z. physikal. Chem., 1932, B, 17, 161—171; cf. this vol., 569).—Since the max. no. (n) of I₂ mols. which the surface can hold is equal to twice the no. of alizarin mols. which react with it, and each alizarin mol. displaces two Cl⁻ ions, n corresponds with a unimol. adsorbed layer, every adsorbing centre being occupied. The max. no. of *o*-nitrophenol mols. adsorbed from the vapour at room temp. is approx. $1.8n$, and to avoid the conclusion that a bimol. layer is formed it must be supposed that the adsorbing centres consist of the surface Cl⁻ ions together with an equal no. of points located between them; when the amount of adsorbed nitrophenol is a max., 90% of these are occupied. *p*-Nitrophenol can occupy

at most only 50% of the centres, perhaps because the dipole moment of the NO₂ group opposes the adsorptive binding of the OH group. R. C.

Discontinuity of isotherms for adsorption of phenol from solution. R. CHAPLIN (J. Physical Chem., 1932, 36, 909—912).—Stepped curves were obtained for the adsorption isotherms of PhOH by an active C from aq. solutions containing 0.1—24.0 g. per litre at 25° and 60°. P. T. N. (c)

Adsorption of electrolytes by crystal surfaces. V. Adsorption of the solvent. (MLLE.) L. DE BROUCKERE (Bull. Acad. roy. Belg., 1932, [v], 18, 361—368).—The quantities of H₂O and KCl adsorbed by BaSO₄ from aq. KCl have been determined. The results suggest that the BaSO₄ becomes completely covered with a unimol. layer, the proportion of H₂O and KCl mols. depending on the concn. and temp. D. R. D.

Effect of adsorbed oxygen on adsorption of electrolytes by activated carbon. O. BRETSCHNEIDER (Z. physikal. Chem., 1932, 159, 436—440).—The adsorption of dissolved succinic acid by activated C containing adsorbed O is slightly increased by removal of adsorbed gas. The adsorption of HCl is reduced, the two isotherms running parallel except at low equilibrium concns.; the probable explanation is the removal by evacuation of a C oxide present on the surface. R. C.

Adsorption of thorium-X by ferric hydroxide at different p_H . I. KURBATOV (J. Physical Chem., 1932, 36, 1241—1247).—The pptn. of Ra with Fe(OH)₃ in alkaline media depends on the formation of a salt-like compound in which Ra acts as a cation and Fe(OH)₃ as an anion. At $p_H > 7$ Th-X is firmly adsorbed by Fe(OH)₃, but at lower p_H there is free exchange with the solution. To obtain highly emanating preps. neither SO₄²⁻ nor HCO₃⁻ is necessary, but the solubility product of the pure Ra salts or isomorphous Ba-Ra salts should not be exceeded in the solution. H. F. J. (c)

Reversal of Traube's adsorption rule. Adsorption of fatty acids by powdered gold in different solvents. E. HEYMANN and E. BOYE (Kolloid-Z., 1932, 53, 153—157).—The adsorption of fatty acids in H₂O, C₆H₆, EtOH, and COMe₂ by powdered Au decreases with increasing mol. wt. of the acid, although the decrease is not regular. E. S. H.

Adsorption of sugars and nitrogenous compounds. V. KNIASEFF (J. Physical Chem., 1932, 36, 1191—1201).—In the adsorption of sugars by norit equilibrium is reached in a few min., but fuller's earth requires more than 1 hr. The earth adsorbs sugars selectively, but norit does not. Reduction of p_H increases the adsorption of lactose by norit and of glucose by the earth, but lessens the adsorption of lactose by the earth. In the adsorption of caffeine by the earth, equilibrium is reached with a few minutes' shaking and is independent of the p_H , and more caffeine is adsorbed from aq. than from EtOH solution. The p_H is shifted by an amount proportional to the wt. of earth, and the disperse phase contains Ca, the amount being small and apparently

independent of both p_H and the wt. of caffeine adsorbed. The adsorption of piperidine and $\text{CO}(\text{NH}_2)_2$ by the earth has been examined. F. E. B. (c)

Absorption of silver oxide by oxides and their compounds at high temperatures. I. WESTERMANN (Z. anorg. Chem., 1932, 206, 97—112).— SiO_2 , Al_2O_3 , or kaolin, after being heated with Ag powder in presence of air, contain varying quantities of Ag chemically combined. In all cases the max. absorption occurs at about 1050° , and amounts to 0.16, 0.45, and 0.40%, respectively. The amount of combined Ag can be increased by increasing the partial pressure of O_2 . In the case of kaolin an equilibrium is reached, depending on the proportion of Ag in the mixture. The rate of absorption can be expressed as a bimol. reaction. F. L. U.

Sorption of water vapour by cellulose and its derivatives. III. Heat of adsorption of water vapour by cellulose acetates. P. T. NEWSOME and S. E. SHEPPARD (J. Physical Chem., 1932, 36, 930—938).—The adsorption isotherms for cellulose acetate sheet have been determined at 30° , 40° , and 50° , the H_2O adsorption decreasing with rise in temp. at all humidities. The calc. heats of adsorption for 30 – 40° and 40 – 50° decrease with increasing H_2O content of the acetate. The heat of adsorption at 25° determined calorimetrically is considerably less than the vals. calc. from the 20° and 30° isotherms. The heat of adsorption of H_2O vapour for cellulose triacetate with 44.8% Ac is less than for acetate with 38% Ac. P. T. N. (c)

Sorption of gases by silica gel. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1932, 7, 133—135; cf. A., 1931, 1120).—The sorption velocities of NH_3 , CO_2 , and C_2H_4 on SiO_2 gel have been measured at 25° and atm. pressure, over an interval of about 60 days. 90% of the extreme sorption observed is reached in 2–10 min. F. L. U.

Base exchange in permutite and surface adsorption by silicic acid gels. E. GRUNER (Chem.-Ztg., 1932, 56, 208). I. R. HAAS (*ibid.*, 353).—Polemical (cf. this vol., 337). E. S. H.

Formation and properties of precipitates. Theory of co-precipitation. I. M. KOLTHOFF (Chem. Weekblad, 1932, 29, 307—310).—A discussion of adsorption of ions by ppts. A ppt. will adsorb ions similar to those which it contains if they exist in excess in the solution; only at a definite ionic activity is the thermodynamic potential zero. The adsorption of Ba salts and K_2SO_4 by BaSO_4 and the potentiometric determination of ionic activities are discussed. H. F. G.

Persorption and unimolecular sieves. J. W. MCBAIN (Trans. Faraday Soc., 1932, 28, 408—409).—The difference between "persorption" and true solution is emphasised (cf. A., 1930, 990), and the relation to mol. sieves is discussed (cf. *ibid.*, 728). J. G. A. G.

Liquid-vapour interface. J. L. SHERESHEFSKY (J. Physical Chem., 1932, 36, 1271—1278).—An equation is derived for the adsorption of a vapour on its own liquid phase. For C_6H_6 from m. p. to

b. p. the heat of adsorption is 1365 g.-cal. per mol., and the thickness of the adsorbed layer is 1.0×10^{-8} cm., which $<$ the mol. diameter. At corresponding temp. the "mol. adsorption" is the same for all vapours. F. E. B. (c)

Thermodynamical study of the variation of surface tension of a surface of contact between two phases with the composition. Conceptions of true and apparent surface concentrations. L. GAY (J. Chim. phys., 1932, 29, 97—107).—Measurements of the variation of surface tension with composition lead to the apparent (not the true) surface concn. Under certain conditions the true surface concn. may be calc. E. S. H.

Surface tension of various aliphatic acids previously studied for bactericidal action on *Mycobacterium leprae*. XX. W. M. STANLEY and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 1548—1557).—The surface tension, γ , of aq. and media solutions of the Na salts of 120 such acids has been determined. Every bactericidal acid markedly depresses γ . The val. of γ is high for the salts of acids of low mol. wt., but, irrespective of structure, decreases with increasing mol. wt. and then begins to increase slightly when the no. of C atoms reaches about 19. With certain α -hydroxy-fatty acids γ increases with the mol. wt. Ring structure increases γ slightly compared with the corresponding straight-chained acids with the CO_2H group within the chain. Introduction of an *iso*-group slightly increases γ , whereas a double linking in the ring or C chain has no appreciable effect. Shift of the CO_2H group to the second C atom causes a very large drop in γ , but as it moves farther down the chain γ increases slightly and then decreases slightly as it reaches the middle C atom. C. J. W. (c)

Behaviour of dyes and silver sols during measurement of surface tension. T. RUEMELE (Z. physikal. Chem., 1932, 160, 8—14).—The surface tensions of aq. solutions of various dyes and the effect of K halides on the surface tension of night-blue solutions have been determined. The surface tension of a Ag sol prepared by development of a nuclear sol increases with diminution in the amount of the latter, but the surface tension of the ultra-filtrate is always equal to that of H_2O . R. C.

Capillary electric phenomena and the wetting of metals by electrolyte solutions. A. FRUMKIN, A. GORODETZKAJA, B. KABANOV, and N. NEKRASSOV (Physikal. Z. Soviet Union, 1932, 1, 255—284).—The relation between the p.d. solution/Hg and the contact angle of the three-phase lines solution-Hg-gas and solution-Hg-oil is discussed. The applicability of Neumann's equation to the former system is vitiated by the presence of an adsorbed film of H_2O containing electrolyte between the Hg and a gas bubble. The readiness of wetting of surfaces of Ag and of PbS by solutions is increased by cathodic polarisation. J. W. S.

Determination of adhesion tension of liquids against solids. Microscopic method for measurement of interfacial contact angles. F. E. BARTELL and E. J. MERRILL (J. Physical Chem., 1932, 36, 1178—1190).—The validity of the assumptions

underlying the determination of contact angles by measuring the pressure set up by H_2O displacing an org. liquid from a powder has been tested. Liquid-air-solid and H_2O -org. liquid-solid contact angles have been determined from measurements of enlarged images obtained by optical projection of photomicrographs of the interfaces in capillary tubes. The former angles usually decrease in the order $SiO_2 > \text{pyrex glass} > \text{Pb glass} > \text{soda-lime glass}$. In the liquid-liquid-solid experiments it was observed that droplets of H_2O appeared between the org. liquid and the wall, the former ultimately being completely enveloped by an H_2O film, at which point the contact angle became 0° . Vals. for adhesion tensions calc. from the above contact angle data agree sufficiently closely with those obtained by the method of fine pores to justify the latter method. F. E. B. (c)

Surface tension of flour suspensions. T. RUE-MELE (Kolloid-Z., 1932, 59, 151-152).—The surface tension of suspensions of flour in aq. lactic acid, $AcOH$, and $H_2C_2O_4$ ($2N-0.001N$) increases as the concn. of acid decreases and is lower for good than for poor kinds of flour. E. S. H.

Energies of immersion of silica in liquids. F. E. BARTELL and E. G. ALMY (J. Physical Chem., 1932, 36, 985-999).—The relation between free and total energy of wetting, measured by the adhesion tension and the heat of wetting, respectively, has been obtained. The relative total energy of wetting for various liquids is independent of the source of the SiO_2 gel for the methods of pptn. used. Vals. of heat of wetting calc. with an assumed area for the gel agree with the observed vals. R. H. L. (c)

Gum surfaces. I. F. V. VON HAHN (Kolloid-Z., 1932, 59, 130-135).—When a drop of aq. dye solution containing a surface-active substance is placed on the surface of a gummy material, it spreads to an extent which decreases with increasing age of the surface, but is independent of the nature of the gum. The figures produced by the spreading are sp. for each gum. E. S. H.

Capillary systems. XIV. Dynamics of osmotic cells. E. MANEGOLD and K. SOLF (Kolloid-Z., 1932, 59, 179-195).—Theoretical. E. S. H.

Blocking phenomena in ultrafilters. F. ERBE (Kolloid-Z., 1932, 59, 195-206; cf. this vol., 461).—The permeability of a membrane for different liquids depends on the thickness of the layer of mols. of liquid lining the capillaries. The phenomenon is related to the varying sedimentation vols. of suspensions. E. S. H.

Osmosis in systems consisting of water and tartaric acid. I. F. A. H. SCHREINEMAKERS and J. P. WERRE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 42-50).—The theory developed previously (cf. A., 1931, 422, 1007) is applied to the system H_2O -tartaric acid. J. W. S.

Osmosis in systems consisting of water and tartaric acid. II. F. A. H. SCHREINEMAKERS and J. P. WERRE (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 162-170).—The behaviour of an osmotic system consisting of two solutions of tartaric acid of different concn., but one invariant, separated by a

membrane of pig's bladder, is discussed with reference to experimental data. M. S. B.

Selective permeability and polarisation of membranes. (MLLE.) CHOUCRON (Compt. rend., 1932, 194, 1661-1663; cf. A., 1928, 953).—Previous results obtained with gelatin are equally obtained with non-amphoteric membranes, e.g., agar, Cr chloride, Al_2O_3 (calcined), or graphite. The statement that a porous membrane which separates solutions of different concns. of the same electrolyte is polarised only when the charge on the walls of the pores is of the same sign as that of the more mobile ion holds generally. C. A. S.

Adsorption of gelatin by collodion membranes. A. H. PALMER (J. Gen. Physiol., 1932, 15, 551-559).—At 37° , with membranes of high permeability, max. adsorption of the gelatin occurs at much higher concn. of gelatin than with membranes of low permeability. With the former, the max. is independent of p_H from 3.8 to 4.8, but with the latter, adsorption is lower on both sides of the isoelectric point. The addition of $NaCl$ neutralises the effect of p_H on the adsorption. The results are explained by previous work on the effect of p_H and $NaCl$ on the size of gelatin particles in solution. A. L.

Influence of electrolytes on specific heat of water. F. URBAN (J. Physical Chem., 1932, 36, 1108-1122).—Sp. heats of $0.1-2M$ - $BaCl_2$, $-KCl$, $-K$ tartrates, $-KOAc$, and $-KCNS$ and of $2M$ - NH_4Cl and $-KBr$ have been determined at $10-40^\circ$. The partial sp. heats of H_2O in $1M$ solutions of several electrolytes and in KCl solutions of several concns. have been calc. The order in which the ions decrease the heat capacity of the solvent H_2O is practically the same as the order in which they appear in the Hofmeister series. The diminution is explained by restriction of the motion of the H_2O mols. by the ionic charges, and perhaps depolymerisation of the H_2O .

Lowering of eutectic points. E. CORNEC and H. MULLER (Compt. rend., 1932, 194, 1735-1736).—The lowering of the eutectic point for ice and KNO_3 on the addition of various substances has been determined. The mol. lowering is not const., but the val. obtained by extrapolating to zero concn. is $16.4-17.6$ for non-electrolytes and n times as great for electrolytes, when n is the no. of foreign ions in the mol. of the added electrolyte. C. A. S.

Colloid-chemical nomenclature. A. LOTTER-MOSER (Kolloid-Z., 1932, 59, 226-228).—The term "micelle" was originally intended for the colloid particle. The electrochemical confusion is avoided by using the term "ultrafiltrate" in place of "intermicellar liquid," and "colloid ion" in place of "micellar ion." "Electrophoresis" is preferable to "cataphoresis" and "anaphoresis." E. S. H.

Absorption spectra of colloidal solutions of gold and silver. A. T. WILLIAMS (J. Chim. phys., 1932, 29, 117-123).—The absorption max. in the visible spectrum vary in position according to the colour of the sol. In all the sols an absorption band was observed in the ultra-violet region, which appears

to be independent of the nature of the colloid and its method of prep. Colloidal Ag, which has been used as a catalyst for decomposing H_2O_2 , loses the absorption band in the visible region, but the band commencing at 3200 Å. remains, although somewhat displaced towards higher frequencies. The max. of the ultra-violet bands have not been determined.

E. S. H.

Solubility and light adsorption of colloidal vanadium pentoxide. B. LANGE (Kolloid-Z., 1932, 59, 162—170).—The mol.-dissolved portion of V_2O_5 sols has very small light-absorptive power and this property may be used for determining the "true" solubility and velocity of dissolution of the colloid. The process of dissolution involves not only the production of mols. from colloid particles, but also a chemical change in the mol.-dispersed part, and there is no simple solution equilibrium. The addition of As_2O_5 , which reduces the velocity of ageing of V_2O_5 sols, does not alter the velocity of dissolution, but increases the proportion in mol. dispersion. An important example of the solid-phase rule has been observed, in that the proportion in mol. solution depends on the concn. of the colloid phase.

E. S. H.

Application of measurements of dielectric loss to the examination of colloid systems. R. KOHLER (Kolloid-Z., 1932, 59, 143—150).—A qual. method for detecting changes of state of polar org. mols. is afforded by the dielectric charge factor, of which the theory and method of measurement are described. With rising temp. the vals. pass through a max. Two max. were observed in the system PhNO_2 -colophony. The method has been applied to a solution of $\text{NH}_2\text{Ph}-\text{CH}_2\text{O}$ condensation products in xylene; with increasing thermal treatment the max val. of the dielectric charge factor decreases and is displaced in the direction of higher viscosity.

E. S. H.

Role of dielectric constant, polarisation, and dipole moment in colloidal systems. X. Dielectric polarisation of cellulose acetate in solution. W. HALLER and H. ORTLOFF (Kolloid-Z., 1932, 59, 137—143; cf. this vol., 462).—A method for measuring the dielectric const. is described. The polarisation of cellulose acetate in simple and mixed solvents has been determined; in general, the val. increases with increasing concn. and varies with the solution activity of the solvent, approaching a limiting val. 0.66 in weakly active liquids. The val. in mixtures is equal to that in the liquid of greater activity, suggesting that the solution-active liquid is preferentially adsorbed. The dielectric const. of pure, dispersed cellulose acetate is 17.25 (obtained by extrapolation), which is considerably higher than the val. for the material in mass. The following dielectric consts. have been determined: Me glycol acetate 8.81, Me glycol 17.18, diacetone alcohol 18.19, Et acetylglycollate 7.96. A method is worked out for deriving the adsorption solution from the polarisation data; 1 g. of cellulose acetate binds dielectrically 0—0.4388 g. of liquid, depending on the solvent. The high viscosity of cellulose acetate solutions is due only in part to solvation and mainly to the formation of aggregates, the production of which is

favoured by dispersion media having little solution activity. E. S. H.

Particle size of colloidal hydrated beryllium oxide sols. W. H. MADSON (J. Physical Chem., 1932, 36, 855—859).—The particle size remained const. for 12—168 hr. at 80°. The largeness of the particles (cube edge = 153.5 m μ) is attributed to hydration. R. H. L. (c)

Determination of emulsion type. R. M. WOODMAN (Chem. News, 1932, 144, 225—230).—The methods available for determining the type of an emulsion are discussed and several examples of misleading results are given. The surest drop tests are those carried out in H_2O and in oil. These can be applied only to stable emulsions and should be supplemented by other observations. In some cases emulsifiers appear to combine or become mechanically admixed with the H_2O phase, giving a jelly-like insol. substance; drop tests in H_2O carried out immediately after the formation of these emulsions may be misleading. E. S. H.

Triangular co-ordinates in colloid chemistry. II. Fehling's solution. A. V. DUMANSKI and A. A. DIKANOVA (J. Gen. Chem., Russia, 1931, 1, 163—167).—The relation between the composition of aq. mixtures of CuSO_4 , Na K tartrate, and NaOH. the amount of ppt., opalescence, colour intensity, and electrophoresis were studied at room temp., 65°, and 70°. Fehling's solution is a colloidal solution; positive or negative sols can be obtained by varying the composition. CH. ABS.

Numerical fixation of the lyotropic series. E. M. BRUINS (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 107—115; cf. A., 1931, 1125).—The behaviour of mixtures of Na salts in the salting-out of agar and gelatin sols is discussed theoretically. J. W. S.

Effect of agitation and supersonic waves on the velocity of coagulation of unstable colloids. A. BOUTARIC and J. BOUCHARD (Bull. Soc. chim., 1932, [iv], 51, 543—549).—Pptn. of hydrophobic colloids rendered unstable by addition of the crit. concn. of an electrolyte is accelerated by mechanical agitation, but is unaffected by supersonic waves when conditions are such that only stationary waves are produced in the colloid. Under conditions in which such waves produce actual agitation in the colloid, pptn. is, however, accelerated by the mechanical action of the convection currents set up. J. W. B.

Ageing and flocculation of solutions of stannic and titanous chlorides. L. MEUNIER, P. SISLEY, and F. GENIN (Chim. et Ind., 1932, 27, 1017—1022).—Hydrolysis of SnCl_4 solutions (0.6—1.3%) leads to the pptn. of hydroxide which contains a little Cl. A state of equilibrium is reached when the unhydrolysed chloride amounts to 2.6—1%. At higher concns. (3%) a ppt. is not formed, but a similar ageing or polymerisation occurs and is revealed by an increasing rate of coagulation with Na_2SO_4 . It is suggested that the $\text{Sn}(\text{OH})_4$ first formed polymerises and that this diminishes its effective surface and thus allows the hydrolysis to proceed. With TiCl_4

the proportion which remains in solution passes through a min. at a concn. of 6%. The addition of TiCl_4 to SnCl_4 protects the latter from coagulation, and this is ascribed to the formation of sol. and non-polymerisable titanate stannates or chlorostannates. A. G.

Colloidal system aged hydrous alumina-basic aluminium chloride. H. V. TARTAR and V. R. DAMERELL (J. Physical Chem., 1932, 36, 1419—1433).—Sols of the composition $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ may be prepared by pptg. $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}(\text{NO}_3)_3$, or AlCl_3 with an excess of aq. NH_3 , washing out the anion in presence of NH_3 , and removing the latter with pure H_2O . Basic AlCl_3 stabilises these sols, $\text{Al}(\text{OH})_2^{++}$ or AlO^+ being absorbed and the acidity of the medium increased, and equilibrium is established in a few days; with HCl as stabiliser months are required. Al_2O_3 more than a few days old does not adsorb Cl^- . The distribution of the ions, which apparently conforms to Gouy's principle, and the diminution in vol. of the solution caused by the colloid both contribute to the increase of acidity. F. E. B. (c)

Dispersion of alumina by acids. H. L. DAVIS (J. Physical Chem., 1932, 36, 949—960).—The peptisation of freshly pptd. Al_2O_3 by AcOH , HCl , and H_2SO_4 has been studied. Na_2SO_4 causes least pptn. when H_2SO_4 is present. Both undissociated AcOH and H^+ peptise. Increasing age favours irreversibility. Heating coagulates. R. H. L. (c)

Complex coacervation. VIII. Autocomplex coacervation of gum arabic sol in presence of desolvating non-electrolytes. H. G. DE JONG and K. C. WINKLER. **IX. Autocomplex coacervation of lecithin sols in pure aqueous medium and in presence of water-soluble desolvating substances.** H. G. DE JONG and R. F. WESTERKAMP (Biochem. Z., 1932, 248, 115—130; 131—162).—VIII. The author's previously suggested subdivision of coacervation (A., 1930, 994) is revised and four types are distinguished.

IX. The pptn. of sols of purified lecithin with hexol salt is an autocomplex process. Various non-electrolytes induce autocomplex coacervation by cations of low valency. P. W. C.

Action of quartz piezoelectric oscillator on sols and suspensions: ultrasonic thixotropy of gels. N. MARINESCO (Compt. rend., 1932, 194, 1824—1827; cf. A., 1928, 141; 1929, 1006).—The effects of compression waves on hydrophilous and thixotropic gels are due to interference of the direct and reflected waves. The violent movements thus produced cause thixotropy, death of small organisms, breaking of filaments, etc. C. A. S.

Effect of gelatin on nuclear silver sols. A. GALECKI and J. MARCHLEWSKA (Kolloid-Z., 1932, 59, 206—208).—Gelatin has a protective effect on the coagulation of olive-yellow nuclear Ag sols to the red (non-nuclear) sols; this effect can be measured by a method similar to the determination of the "Au no." The decolorisation of the nuclear Ag sols by ultra-violet light, through mol. dispersion, is retarded greatly by small amounts of gelatin. E. S. H.

Precipitation of methylene-blue by electrolytes in gelatin. (MLLE.) S. VEIL (Compt. rend., 1932, 194, 1932—1934).—In presence of methylene-blue diffusion of the electrolyte is favoured whereas the electrolyte hinders diffusion of the dye. C. A. S.

Effect of electrolytes on fixation of a colloidal dye on granules of a hydrosol. M. DOLADILHE (Compt. rend., 1932, 194, 1934—1936; cf. A., 1931, 679).—When the charges on the dye and the granules are of the same sign addition of a little electrolyte favours fixation of the dye; with charges of opposite sign such addition hinders fixation. The action in both cases is stronger as the ion of sign opposite that of the granules is of higher valency. C. A. S.

Formation of periodic precipitates in the absence of a foreign gel. N. R. DHAR and R. N. MITTRA (Nature, 1932, 129, 761).—Periodic ppts. have been obtained by the slow coagulation of sols of $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Sn}(\text{OH})_4$ with small amounts of KCl and NaBrO_3 . Adsorption of the sol by its ppt. explains the results. L. S. T.

Structure of cellulose gel. III. Syneresis of viscose. II. K. ATSUKI and H. SOBUE (J. Cellulose Inst. Tokyo, 1932, 8, 70—73).—The nature of the syneresis of viscose is discussed. The amount of liquid separating when the gel coagulates and the degree of swelling of the final gel vary inversely as the concn. of the gel. Syneresis is also affected by the duration and temp. of the reaction. The alkali concn. of the separated liquid increases with the progress of syneresis and continues to do so after the separation of liquid ends. The decomp. of viscose proceeds independently during syneresis, rendering the coagulation process irreversible. V. E. Y.

Extinction coefficients of silicic acid gel-forming mixtures. M. PRASAD, S. M. MEHTA, and J. B. DESAI (J. Physical Chem., 1932, 36, 1324—1336).—The extinction coeff., k , of silicic acid suspensions during gel-formation in presence of NH_4OAc and AcOH rises slowly at first, then more rapidly, but ultimately becomes const. These changes are correlated with increase in the particle size. Constancy of k is a criterion of a set gel. The time of setting determined on this basis decreases with increasing SiO_2 concn., but with increase in $[\text{H}^+]$ it first decreases and then increases. Smoluchowski's coagulation theory holds approx. for gelation within a moderate range of vals. of k . E. J. R. (c)

Viscosity of silicic acid gel-forming mixtures. M. PRASAD, S. M. MEHTA, and J. B. DESAI (J. Physical Chem., 1932, 36, 1384—1390).—When silicic acid gels form in an alkaline medium the rate of increase, v , of the viscosity, η , is initially greater but increases more slowly than when the gels form from the same SiO_2 concns. in acid media. v increases with decrease in concn. of acid, and with increase in alkali concn. The initial increase in η is attributed to the formation of a no. of small colloid particles and the later increase to their increased hydration. F. E. B. (c)

Influence of non-electrolytes on viscosity of silicic acid gel-forming mixtures. M. PRASAD, S. M. MEHTA, and J. B. DESAI (J. Physical Chem., 1932, 36, 1391—1400; cf. A., 1930, 414).—The co-

agulating effect of MeOH, EtOH, and PrOH on 4% and 5% alkaline solutions of SiO_2 has been confirmed. The rate of increase in viscosity increases with the alcohol concn. Small alcohol concns. in feebly acid solutions promote coagulation. In 40 c.c. of a mixture containing 4% SiO_2 and 0.55*N* in respect of AcOH 0.5 c.c. of EtOH has the max. coagulative effect, and with more than 2 c.c. the effect is protective.

F. E. B. (c)

Behaviour of sodium pyrophosphate in the swelling of, and diffusion in, gelatin. F. AX-MACHER (Biochem. Z., 1932, 248, 218—230).— $\text{Na}_4\text{P}_2\text{O}_7$, although alkaline in solution, inhibits the swelling of gelatin. By addition of $\text{Na}_4\text{P}_2\text{O}_7$, more Cl⁻ is taken up from KCl solutions, whilst the absorption of glucose does not keep pace with that of H_2O . In spite of its inhibition of swelling, $\text{Na}_4\text{P}_2\text{O}_7$ accelerates the diffusion of methylene-blue in gelatin gels.

P. W. C.

Freezing of gelatin jellies. T. MORAN (Kolloid-Z., 1932, 59, 217—226).—The forms in which ice crystallises from gelatin jellies on freezing under different conditions are described. A 38% jelly, frozen at -11° , gives spherulites having a concentric periodic structure. Work on the velocity of crystallisation of ice and the activity of H_2O in the jellies is reviewed and a method is developed for calculating the degree of hydration of the gelatin. The addition of sugar reduces the amount of bound H_2O , but not to the same extent as an equiv. concn. of neutral salt.

E. S. H.

Changes in the Röntgen spectrum of gelatin and agar on swelling. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1932, 51, 513—522).—The effect of change in H_2O content on the v. p. and X-ray spectrum of gelatin and agar gels has been investigated. A hysteresis effect is observed. The probable structures and mechanism of swelling are deduced and shown to be different in the two cases.

D. R. D.

Röntgen-spectrographic observations on the gelatinisation of starch sols. J. C. DERKSEN and J. R. KATZ (Rec. trav. chim., 1932, 51, 523—526).—A hot aq. sol of sol. starch is amorphous, but the gel formed on cooling has a β -starch structure. Similar effects are observed with amyloextrin solution, although the latter gives a cryst. ppt. and no gel on cooling. A paste made from wheat starch and 50% H_2C gives an α -starch spectrum, which is also obtained on adding EtOH to the sol.-starch sol.

D. R. D.

Animal and vegetable proteins. Electro-metric analysis. II. J. ERRERA (J. Chim. phys., 1932, 29, 124—130).—The electrometric titration of several proteins and their mixtures has been studied. The compounds formed by proteins with HCl and NaOH are stoichiometric, although in certain cases the results may be masked by hydrolysis. The isoelectric points of protein extracts of certain animal and vegetable substances have been determined.

E. S. H.

Denaturation of proteins. VIII. Effect of denaturation on the viscosity of the solutions of certain proteins. W. J. LOUGHLIN and W. C. M. LEWIS (Biochem. J., 1932, 26, 476—487).—The

viscosity of undenatured or denatured but unflocculated solutions of ovalbumin and oxyhæmoglobin is const. and independent of p_{H} . On denaturation the viscosity increases, the increase being the same at all vals. of p_{H} for any concn. of protein. Dilatometer measurements show no change in the total vol. of the protein solutions where these undergo denaturation. At the isoelectric point denaturation is accompanied by an increase in the size of the protein unit, the vol. of the denatured unit being approx. twice that of the undenatured. Denaturation is therefore accompanied by an increase in the amount of H_2O associated with each individual protein particle, which is probably true at p_{H} vals. other than the isoelectric point.

S. S. Z.

Phase-rule studies on the proteins. VI. Non-aqueous solutions. W. D. BANCROFT and S. L. RIDGWAY (J. Physical Chem., 1932, 36, 1285—1323; cf. A., 1931, 42).—Varying amounts of acid or base were added to a fixed wt. of protein, and the free acid or base was extracted with a fixed vol. of a solvent. A smooth concn. curve for the extract indicates adsorption, a flat portion compound formation. Succinic and uric acids form mono- and disodium salts. Uracil combines with 1 equiv. of NaOH in 95% EtOH, but not with HCl. Alanine combines with 1 equiv. of either NaOH or HCl. Casein, gelatin, and cdestin combine with HCl in EtOH, whereas zein and gliadin merely adsorb HCl, but all five strongly adsorb NaOH from EtOH solution, and possibly also form compounds. Less HCl is taken up from an EtOH solution than from the gas.

C. T. S. (c)

Adsorption of carotenoids. H. VON EULER and U. GARD (Arkiv Kemi, Min., Geol., 1932, 10, B, No. 19, 6 pp.).—Potentiometric and conductometric measurements of β -carotene in H_2O -EtOH or H_2O - COMe_2 solution on addition of HCl or NaOH indicate vals. for K_a and K_b of $<10^{-13}$. β -Carotene is partly adsorbed from its solution in petrol by MgO , MgCO_3 , $\text{Mg}_3(\text{PO}_4)_2$, Al_2O_3 , or acid clay, but not by CaO or Fe_2O_3 . CeO_2 is a good adsorbent, adsorption taking place without oxidation of the carotene, which may be subsequently eluted with CHCl_3 . The adsorption of xanthophyll, lycopene, capsanthin, and dihydro-carotene, -lycopene, and α -crocin was also investigated. The presence of vitamin-A, carotene, esters of lutein, and zeaxanthin in the egg-yolk sac of the dog-fish embryo was established.

F. O. H.

Physico-chemistry of carotenoids. H. VON EULER, H. HELLSTROM, and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1932, 10, B, No. 18, 4 pp.).—The hydrosol of α -carotene (A., 1931, 960) appears redder by transmitted light than that of β -carotene. Both sols show a streaming double refraction, the streaky appearance on stirring indicating a non-spheroidal type of molecular aggregate. Examination of the polarised light due to the Tyndall phenomenon indicates the presence of rod-shaped colloidal particles in both sols.

F. O. H.

Thermodynamics of the transformation of collagen by heat. Collagen and gelatin. E. WOHLISCH (Biochem. Z., 1932, 247, 329—337; cf. Z. Biol., 1927, 85, 406).—The conversion by heat of

collagen (from the tendons of the tails of rats and mice) into gelatin is an endothermic reaction which occurs at temp. above a sharply defined transformation temp. Collagen II is identical with gelatin. The transformation temp. varies with the origin of the material used and its mechanical properties. The heat of transformation is approx. 16.8 g.-cal. per g.

W. M.

Electrokinetic phenomena. VI. Electric mobility, charge, and titration of proteins. H. A. ABRAMSON. VII. Electric mobility, charge, titration curve, and optical rotation of protein. H. A. ABRAMSON and E. B. GROSSMAN (J. Gen. Physiol., 1932, 15, 575—603, 605—610).—VI. In solutions of the same ionic strength, the electric mobilities of the same protein at different p_H vals. should be proportional to the no. of bound H or OH ions and this is confirmed for ovalbumin, serum-albumin, gelatin and deaminised gelatin, and caseinogen. When certain proteins are adsorbed by quartz the apparent dissociation const. of the adsorbed protein is unchanged.

VII. $[\alpha]^{40}$ for ovalbumin, gliadin, and gelatin is discussed in relation to mobility, titration curve, and osmotic pressure, and it appears that change in $[\alpha]$ with p_H of protein solutions is proportional to the change in net charge.

A. L.

Microscopic method of electrophoresis. H. A. ABRAMSON (J. Physical Chem., 1932, 36, 1454).—Criticism of the method (this vol., 464) is refuted.

F. U. (c)

Cataphoresis of colloidal solutions of carbon. H. LACHS and K. GESTEL (Kolloid-Z., 1932, 59, 170—179).—Details are given for the prep. of stable, reproducible colloidal solutions of C free from H_2SO_4 . The electrophoretic migration velocity in presence of KCl, $K_4Fe(CN)_6$, and KOH is discussed in relation to Stern's theory.

E. S. H.

Elastic properties of organic high polymerides and their kinetic significance. K. H. MEYER, G. VON SUSICH, and E. VALKÓ (Kolloid-Z., 1932, 59, 208—216).—Changes in the elastic properties of highly polymerised org. substances (especially caoutchouc) have been followed by means of X-ray interference diagrams and related to the conditions producing them (temp., swelling, stretching, etc.). The reversible extensibility characteristic of caoutchouc is considered to be a very general property exhibited to different extents by all long-chain compounds.

E. S. H.

Adiabatic process of the thermodynamical system in which the entropy cannot be defined. T. IWATSUKI and Y. MINURA (J. Sci. Hiroshima, 1932, 2, 127—138).—Mathematical.

H. F. G.

Hydrogen-chlorine-hydrogen chloride equilibrium at high temperatures. W. F. GIAUQUE and R. OVERSTREET (J. Amer. Chem. Soc., 1932, 54, 1731—1744).—An approx. method is described for calculating the free energy of diat. mols. from spectroscopic data. The values of $(F^\circ - E_0^\circ)/T$ are given from 250° to 3000° abs. for $Cl^{35}Cl^{35}$, $Cl^{35}Cl^{37}$, $Cl^{37}Cl^{37}$, and the equilibrium mixture, and also for HCl^{35} , HCl^{37} , Cl^{35} , Cl^{37} , and their mixtures. Vals. of $\Delta F^\circ/T$

for 250—3000° abs. are given for the reactions $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 = HCl$ and $Cl_2 = 2Cl$. From the e.m.f. of the H-Cl cell and spectroscopic data, —22,028 g.-cal. per mol. is obtained for the change in heat content of the former reaction at 298.1° abs. The entropies of HCl and Cl are given for the various isotopic mols. and their mixtures. The thermodynamic properties of isotopic substances should be based on an average set of energy levels, obtained by weighting the several vals. in proportion to the relative abundance of the different mol. species.

G. M. M. (c)

Free energy of formation of ethyl acetate. Equilibrium in the gaseous state. H. ESSEX and J. D. CLARK (J. Amer. Chem. Soc., 1932, 54, 1290—1306).—The equilibrium const. of the reaction $AcOH + EtOH \rightleftharpoons EtOAc + H_2O$ in the gaseous state is 33.62 at 150°, 26.38 at 165°, and 16.07 at 200°. At 0° the calc. vals. are 14.63 for the liquid and 817.3 for the gaseous state. The free energy change on esterification has been calc. from these data. The standard free energy of formation of liquid $EtOAc$ at 25.1° is —81,610.4 g.-cal.

F. E. B. (c)

Entropy of steam, and water-gas reaction. A. R. GORDON and C. BAENES (J. Physical Chem., 1932, 36, 1143—1151).—From chosen vals. of moments of inertia and "fundamental" frequencies, obtained from spectroscopic data, the entropies and heat capacities of H_2O , H_2 , CO, and CO_2 have been computed from 300° to 1200° abs. The results combined with the heat of the water-gas reaction give vals. of the equilibrium const. in fairly good agreement with the observed vals.

F. D. R. (c)

Keto-enol tautomerism as an example of polymorphism. C. WEYGAND (Z. anorg. Chem., 1932, 205, 414—416).—The behaviour of the system $CH_3AcBz_2-OH \rightleftharpoons CMe_2CBz_2$ suggests that the transition between isomerism and polymorphism should be sought in equilibrium isomerism.

M. S. B.

Determination of ionisation constant of acetic acid at 25° from conductance measurements. D. A. MACINNES and T. SHEDLOVSKY (J. Amer. Chem. Soc., 1932, 54, 1429—1438).—The conductances at 25° of 0.00003—0.2N-AcOH and 0.0001—0.004N-NaOAc have been determined. NaOAc obeys Shedlovsky's equation. Assuming independent migration of ions, the stoichiometric dissociation const., K' , of AcOH varies with the concn. For dil. solutions the variation is entirely attributable to change in the ionic activity coeff., γ , i.e., $K - \gamma^2 K'$ is const. if γ is calc. by the Debye-Hückel theory, the theoretical limiting ratio $\log \gamma/\sqrt{c_i}$ being realised to within 3%. Above 0.01N a strong medium effect of the undissociated acid appears, for K decreases in proportion to c rather than to c_i . AcOH probably reduces the ionic mobilities. Extrapolation of the data for higher dilutions yields $K = 1.753 \times 10^{-5}$, in excellent agreement with e.m.f. data (A., 1931, 308, and following abstract).

L. O. (c)

Dissociation constant of acetic acid from 0° to 35°. H. S. HARNED and R. W. EHLERS (J. Amer. Chem. Soc., 1932, 54, 1350—1357; cf. A., 1931, 308).—E.m.f. measurements at 0—35° are recorded for the cells (a) $H_2|HCl(m) : AgCl|Ag$ and (b) $H_2|AcOH(m_2)$,

NaOAc (m_2), NaCl (m_3) : AgCl|Ag ($m=0.005-0.1M$ and $\mu=m_2+m_3+m_{H^+}=0.00951-0.17994M$). From the cells (b) the dissociation const. of AcOH was calc. at each temp. The result at 25° agrees with that obtained by conductivity methods. G. M. M. (c)

Equilibrium in aqueous solutions of aconitic acid. R. MALACHOWSKI (Bull. Acad. Polonaise, 1931, A, 369—382).—In aq. solutions there are established the equilibria $H^+ + C' \rightleftharpoons HC$, $H^+ + T' \rightleftharpoons HT$, $C' \rightleftharpoons T'$, and $HC \rightleftharpoons HT$, where C' and T' are the anions of the *cis*- and *trans*-acids, respectively. The velocity coeffs. for the last two reactions have been determined conductometrically. Consistent vals. are obtained on assuming that only one H atom of the aconitic acid is ionised. D. R. D.

Acidity of solutions of sodium metaphosphates. Approximate strength of monometaphosphoric acid. VI. S. J. KIEHL and T. M. HILL (J. Amer. Chem. Soc., 1932, 54, 1332—1335).—The $[H^+]$ of a 0.1N solution of NaPO₃ is 2.5×10^{-6} . HPO₃ is slightly weaker than H₂SO₄. B. A. S. (c)

Buffer effect of slightly soluble phosphates. C. ZINZADZÉ (Compt. rend., 1932, 194, 1924—1926).—Although the buffer action of solutions of slightly sol. phosphates is insignificant, the action is greatly increased in presence of the solid salts. C. A. S.

Basicity of rare earths. G. ENDERS (Z. anorg. Chem., 1932, 205, 321—334).—The solubility products of the hydroxides of Y, La, Pr, Nd, Sm, Gd, and Dy have been compared at 25°, 50°, and 100° in buffer solutions of equal p_H obtained by mixing solutions of Cd(NO₃)₂ and NH₄NO₃. On the assumption that the solubility product of the hydroxides is proportional to the basicity, the relative vals. of the latter are 1 : 1300 : 80 : 47 : 8 : 3.4 : 0.5 for the 7 hydroxides in the order given above. There is a close parallelism between ionic radius and basicity. The rare earths may be classified according to basicity and the classification is the same as that obtained by considering such properties as ionic radius, valency, colour, and paramagnetism. All these properties depend on the electronic arrangement in the *N*-level. M. S. B.

Dissociation in organic solvents. E. VELINGER (Compt. rend., 1932, 194, 1820—1822).—Using calomel and Sb electrodes neutralisation curves for H₂SO₄, HCO₂H, AcOH, and propionic, salicylic, oleic, oxalic, malonic, and maleic acids have been determined in a 1 : 3 mixture of EtOH and Et₂O. In general outline these resemble curves for corresponding aq. solutions, but with individual peculiarities, e.g., the two CO₂H groups are scarcely distinguishable in the dibasic acids except in the case of maleic acid. C. A. S.

Constant a in Debye-Hückel limiting equation. C. W. DAVIES (J. Amer. Chem. Soc., 1932, 54, 1698—1699).—Conductivities of mandelic acid at 25° agree, after applying Onsager's correction for the mobility change, with the theoretical val. of a in the above equation. C. J. W. (c)

Heat capacity and related thermodynamic properties of aqueous solutions of lithium chloride, hydrochloric acid, and potassium

hydroxide at 25°. F. T. GUCKER, jun., and K. H. SCHMINKE (J. Amer. Chem. Soc., 1932, 54, 1358—1373).—The heat capacities have been determined with a precision of about 0.1% from 0.01 to 2.5M with an improved form of the apparatus previously described (A., 1928, 592). The linear relation between the apparent mol. heat capacity of the solute and the square root of the molality is confirmed, but the validity of extrapolation to infinite dilution (A., 1927, 208; 1929, 398) is doubtful. Partial mol. heat capacities of solute and solvent have been evaluated. G. M. M. (c)

Activity coefficient of barium hydroxide in aqueous solution at 25°. H. S. HARNED and C. M. MASON (J. Amer. Chem. Soc., 1932, 54, 1439—1442).—The activity coeffs. are calc. from the e.m.f. at 25° of the cells H₂|Ba(OH)₂, M|Ba₂Hg|Ba(OH)₂, 0.12M/H, ($M=0.002-0.23$). For aq. Ba(OH)₂, $\gamma^{25} \pm 0.0001 = 0.9970 + 0.1878M$. G. M. M. (c)

Utilisation of base-exchange reaction for determination of activity coefficients in mixed electrolytes. A. P. VANSELOW (J. Amer. Chem. Soc., 1932, 54, 1307—1311).—Cation-exchange reactions of bentonites may be used for determining relative activity coeffs. in mixed electrolytes. The coeffs. obtained from the Ba-Cd exchange agree with those calc. for BaCl₂ and CdCl₂ solutions. G. M. M. (c)

Theory of concentrated solutions. VIII. Activity coefficient in relation to the freezing curve. J. HIRSHBERG (Bull. Soc. chim. Belg., 1932, 41, 163—195).—The v. p. of mixtures of CS₂ with COMe₃, Et₂O, BuⁿCl, isopentane, cyclohexane, C₆H₆, and CHCl₃ have been measured and partial pressures of the components calc. from the liquid-vapour compositions. The derived activity coeffs. have been compared with the formulæ of Duhem and Margules and of Lewis. The activity coeff. derived from the f.-p. curves for CS₂-C₆H₆ and CS₂-cyclohexane and from the curves for CS₂-CHCl₃ and CS₂-Et₂O are in agreement with the vals. obtained by the v.-p. method. E. S. H.

Constitution of glass in the light of the solvation theory. W. WEYL and W. EITEL (Naturwiss., 1932, 20, 422—425).—Thermal and optical properties of glasses are interpreted in terms of the solvation theory. A. C.

Equilibria between liquid and vapour solutions of paraffin hydrocarbons. M. SOUDERS, jun., C. W. SELHEIMER, and G. G. BROWN (Ind. Eng. Chem., 1932, 24, 517—519).—The equilibrium is considered from the viewpoint of the fugacity of the components. H. I.

Dissociation pressures of hydrated cupric sulphate at 35°. T. S. LOGAN (J. Physical Chem., 1932, 36, 1035—1044).—Dissociation pressures obtained by a statical method are: CuSO₄.5H₂O, 16.4; CuSO₄.3H₂O, 10.8; CuSO₄.H₂O, 0.18 mm. P. T. N. (c)

Decomposition by heat of hydrated ammoniacal metallic complexes. M. AUMÉRAS and A. TAMISIER (Compt. rend., 1932, 194, 1936—1938). The compounds CdSO₄.4NH₃.5H₂O and CuSO₄.4NH₃.10H₂O, prepared by the action at room

temp., of EtOH (d 0.834) on conc. aq. NH_3 solutions of CdSO_4 and CuSO_4 respectively, when subjected to rising temp. give temp.-wt. curves (cf. A., 1925, ii, 559) which indicate the existence of $\text{CdSO}_4 \cdot \text{NH}_3$, $\text{CdSO}_4 \cdot 2\text{NH}_3$, $\text{CuSO}_4 \cdot 2\text{NH}_3$, and $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$.

C. A. S.

Equilibria in reduction, oxidation, and carburization of iron. X. System iron-oxygen; abnormal oxidation; activation of iron without additions. R. SCHENCK, T. DINGMANN, P. H. KIRSCH, and A. KORTENGRABER (Z. anorg. Chem., 1932, 206, 73—96; cf. A., 1930, 43).—Fe, both compact and as powder, takes up 0.05—0.25% O_2 when heated at 800° in a mixture of CO and CO_2 containing 21—47% of the latter. The wt. may remain const. owing to loss of Fe as carbonyl. The abnormally high absorption at 700° (up to 2.5% O_2) previously observed has been confirmed. The phenomenon is attributed to active centres consisting of more electropositive metal. The Fe is deactivated when alloyed with 0.5% of Cu, Ni, or Co. The theory of local activity is discussed in relation to other observations.

F. L. U.

Composition of the compounds of picryl chloride and of *s*-trinitrobenzene with benzene. D. L. HAMMICK, G. M. HILLS, and J. HOWARD (J.C.S., 1932, 1530—1532).—F.-p. curves indicate the existence of $2\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_3$ (m. p. 39°) and $2\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3$ (m. p. 71°).

E. S. H.

Solution equilibria of the three isomeric phenylenediamines with guaiacol. M. DEZELIĆ (Z. physikal. Chem., 1932, 160, 119—122).—Thermal analysis shows the existence of *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot 2\text{G}$, *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot 2\text{G}$, and *m*- $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{G}$ (G = guaiacol).

R. C.

Gas-solid equilibria. IV. Pressure-concentration equilibria between ferric oxide gels and (a) water, (b) ethyl alcohol, (c) benzene, directly determined under isothermal conditions. B. LAMBERT and A. G. FOSTER (Proc. Roy. Soc., 1932, A, 136, 363—377).—The recorded data refer to the systems (a) EtOH- Fe_2O_3 "original" gel, (b) EtOH- Fe_2O_3 "water-treated" gel, (c) C_6H_6 - Fe_2O_3 "water-treated" gel. Comparative pressure-concn. isothermals for all the Fe_2O_3 systems have been drawn. Attempts to determine the pressure-concn. equilibria between Fe_2O_3 gel and H_2O were vitiated by the liberation of small quantities of permanent gas from the gel. On heating the gel in H_2O vapour at 148° , a new kind of gel with a very low retentive power was produced.

L. L. B.

Lead oxides and systems of these with oxygen. M. LE BLANC and E. EBERIUS (Z. physikal. Chem., 1932, 160, 69—100).—There are two forms of PbO, a red form stable below, and a yellow form stable above, 585° . The rate of transformation yellow \rightarrow red at room temp. depends on the mode of prep. and is increased by application of pressure. Between 250° and 390° , both forms take up O, without the appearance of a second solid phase, until the composition reaches about $\text{PbO}_{1.7}$. The original lattice persists up to about $\text{PbO}_{1.13}$, when it is replaced by a lattice which is different from any of those hitherto observed in the system Pb-O and is identified with a dark-coloured modification of Pb_3O_4 . From $\text{PbO}_{1.33}$

onwards the absorption is reversible, and the form of the lattice is unchanged; the pressure curve shows no discontinuity at the composition Pb_2O_3 . When O is removed the pressure falls continuously until the composition $\text{PbO}_{1.33}$ is reached, when PbO appears as a second solid phase and the pressure becomes const. If a solid phase between $\text{PbO}_{1.33}$ and $\text{PbO}_{1.66}$ is heated above 389° , it gives off O_2 and forms ordinary red Pb_3O_4 , which cannot take up an excess of O. The transformation black \rightarrow red Pb_3O_4 is monotropic. When O is removed from PbO_2 by heating at a fixed temp. the PbO_2 lattice persists until the composition is about $\text{PbO}_{1.66}$, when it is replaced by the lattice of black Pb_3O_4 . Since, further, the pressure curve is continuous, there is no reason to believe that a compound Pb_3O_5 exists. The loss of O up to $\text{PbO}_{1.66}$ is irreversible, and PbO_2 cannot take up an excess of O. Oxides from PbO to $\text{PbO}_{1.10}$ dissolve completely in HNO_3 , whilst those between $\text{PbO}_{1.13}$ and $\text{PbO}_{1.66}$ leave a residue of dark-coloured $\text{PbO}_{1.66}$.

R. C.

Phase relations of $\text{K}_2\text{Si}_4\text{O}_9$ under pressure. R. W. GORANSON and F. C. KRACEK (J. Physical Chem., 1932, 36, 913—926).—Temp.-pressure relations, m.-p. and inversion curves, and the equilibria of $\text{K}_2\text{Si}_4\text{O}_9$ in the system $\text{K}_2\text{Si}_4\text{O}_9$ - SiO_2 have been studied at pressures up to 3000 bars. $\text{K}_2\text{Si}_4\text{O}_9$ melts congruently at $765^\circ/1$ atm. The m. p. falls by 60° for 1000 bars increase in pressure, and above 1250 bars the compound cannot exist in equilibrium with liquid.

R. H. F. (c)

System MgO -CO- H_2O at 100° . (MME.) WALTER-LÉVY (Compt. rend., 1932, 194, 1818—1820).—When heated with H_2O at 100° in sealed tubes $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ yields hydromagnesite, H_2O , and CO_2 . The hydromagnesite then passes into MgCO_3 , and this occurs more rapidly when the pressure of CO_2 is increased. Its composition is $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$.

C. A. S.

System potassium carbonate-ammonia water. M. P. APPLEBEY and (MISS) M. A. LEISHMAN (J.C.S., 1932, 1603—1608).—Equilibrium data are recorded for 0° , 18.05° , and 25.06° . Two liquid layers are formed, which, when saturated with solid salt, persist above 155° . The v. p. of the univariant 4-phase system have been measured from 0° to 30° . Application of the "rest" method shows that the stable hydrate is $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$.

E. S. H.

System zinc sulphate-ammonia-water. M. P. APPLEBEY and M. E. D. WINDRIDGE (J.C.S., 1932, 1608—1613).—The system has been investigated at 0° and 18° . Two liquid layers form above a lower crit. solution temp. (approx. 0.5°) and, when saturated with salt, the layers persist above 175° . The solid phases formed at 0° and 18° are $\text{ZnSO}_4 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ and solid solutions of $\text{ZnSO}_4 \cdot 5\text{NH}_3$ and $\text{ZnSO}_4 \cdot 4\text{NH}_3$.

E. S. H.

Polytherms of the systems CuCl_2 -(LiCl) $_2$ - H_2O and NiCl_2 -(LiCl) $_2$ - H_2O . H. BENRATH (Z. anorg. Chem., 1932, 205, 417—424).— LiCl is anhyd. above 98° . Below this temp. the stable form is $\text{LiCl} \cdot \text{H}_2\text{O}$ and at approx. 20° transition to $\text{LiCl} \cdot 2\text{H}_2\text{O}$ occurs. In the first system the only other stable salts are $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the garnet-red double salt

$\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$ which is stable throughout the whole temp. range under suitable conditions. In the second system, in addition to the LiCl hydrates, the following stable salts may be obtained: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, below 29° ; $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, 29 – 64° ; $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, above 64° ; $\text{NiCl}_2 \cdot 4\text{LiCl} \cdot 10\text{H}_2\text{O}$, below 23° (approx.), yellow plates and very hygroscopic; $\text{NiCl}_2 \cdot 2\text{LiCl} \cdot 4\text{H}_2\text{O}$, 23 – 60° (approx.), fine yellowish-green needles; and $\text{NiCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O}$, orange-yellow scales above approx. 60° . The crystals of the double salts in the second system are very small and can be distinguished only under the microscope. The first two double salts are stable only in contact with the mother-liquor.

M. S. B.

System cupric selenate-water-selenic acid at 25° . G. B. MACALPINE and L. A. SAYCE (J.C.S., 1932, 1560–1565).— $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$ exists in equilibrium with free H_2SeO_4 up to 55%, and $\text{CuSeO}_4 \cdot \text{H}_2\text{O}$ at higher concns. of H_2SeO_4 . Anhyd. CuSeO_4 has not been obtained. The v. p. of H_2SeO_4 – H_2O mixtures have been measured and the v. p. of $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$ at 25° found by inference to be 11.0 mm. E. S. H.

System nitrobenzene-sulphuric acid-water. C. W. GIBBY (J.C.S., 1932, 1540–1543).—Miscibility data for 0° , 22° , and 34° are given in tables and shown on a triangular diagram. The position of the tie-lines indicates that the compound $\text{PhNO}_2 \cdot \text{H}_2\text{SO}_4$ is sol. in aq. H_2SO_4 but not in PhNO_2 . Compositions of solutions in equilibrium with the solid compounds have been measured at 0° .

F. L. U.

Determination of the heat of dissociation of fluorine and of the latent heat of vaporisation of lithium. M. S. DESAI (Proc. Roy. Soc., 1932, A, 136, 76–82).—The heat of dissociation of F, has been determined indirectly by interpretation of the absorption spectra of NaF and KF in the vapour state. Using Born and Franck's equation D_F , is found to be 76 ± 2 kg.-cal. The absorption spectrum of LiF has been investigated and the latent heat of vaporisation of Li calc. to be 29.4 kg.-cal. per g.-atom.

L. L. B.

Heat-capacity data on organic compounds obtained with a radiation calorimeter. M. E. SPAGHT, S. B. THOMAS, and G. S. PARKS (J. Physical Chem., 1932, 36, 882–888; cf. A., 1931, 1003).—The heat capacities in the solid and liquid states, and heats of transition and fusion of C_{10}H_8 , C_6Me_6 , erythritol, mannitol, dibenzoylthane, Et azoxybenzoate, CHPh_3 , Ph_2 , pentacosane, and tritriacontane have been measured. The heat-capacity curve of liquid PhEt is quite regular. The formation of liquid crystals by Et azoxybenzoate was investigated, and the heat of fusion of the liquid crystal determined.

F. D. R. (c)

Heats of formation and $-M/N$ ratios. G. B. HEISIG (J. Physical Chem., 1932, 36, 1000–1005).—The $-M/N$ ratio (no. of mols reacting per ion pair) decreases regularly with increase in the heat of formation.

F. D. R. (c)

Integral heats of dilution and relative partial molal heat contents of aqueous sodium chloride solutions at 25° . A. L. ROBINSON (J. Amer. Chem. Soc., 1932, 54, 1311–1318).—By combining the

intermediate heats of dilution from 0.1 to 0.000385M with existing data for higher concns. the integral heats of dilution and relative partial mol. heat contents of the components were obtained from infinite dilution to saturation.

G. M. M. (c)

Heats of dissolution of gaseous methylamine. W. A. FELSING and P. H. WOHLFORD (J. Amer. Chem. Soc., 1932, 54, 1442–1445; cf. A., 1930, 146).—The total heat of dissolution at 35° in g.-cal per mol. of NH_2Me is $10,627 + 0.24193N$, where N is mols. of H_2O per mol. of NH_2Me .

G. M. M. (c)

Calcium nitrate. III. Heats of hydration and of dissolution of binary system calcium nitrate-water. W. W. EWING, A. N. ROGERS, J. Z. MILLER, and E. MCGOVERN (J. Amer. Chem. Soc., 1932, 54, 1335–1343).—The heats of dissolution of anhyd. $\text{Ca}(\text{NO}_3)_2$, its di-, tri-, and tetra-hydrate, and also of $\text{Sr}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ are –18,350, 12,670, 22,000, 33,170, 18,040, and –51,950 joules per mol., respectively. From these data the integral heats of dissolution and changes in heat content and free energy have been calc.

B. A. S. (c)

Transference number of cobalt sulphate. R. C. CANTELO and E. C. PAYNE (J. Physical Chem., 1932, 36, 1045–1050).—The transference no. of Co^{++} is 0.396 in a 0.233N and 0.149 in a 3.994N solution, the decrease being attributed to complex ions rather than to excessive hydration. The val. calc. from the ion conductance is 0.419.

C. L. W. (c)

Electrolytic transport of water in 0.1N-hydrogen iodide and N-potassium iodide. A. WAGNER (Chem. Listy, 1931, 25, 349–352).—5 mols. H_2O are transported per mol. K^+ , and 2.17 mols. per mol. I^- .

Electrolytic water transport and ionic transport numbers. H. C. HEPBURN (Proc. Physical Soc., 1932, 44, 267–273; cf. A., 1931, 1236).—The electrolytic H_2O transport per faraday of N –1.8N- CuSO_4 , determined by the parchment diaphragm method, is const. up to N , but decreases with further rise in concn. The relation of the vals. to the Hittorf transport no. is discussed.

N. M. B.

Hydration of some ions in 0.1M solutions. J. BABOROVSKÝ, O. VIKTORIN, and A. WAGNER (Czech. Chem. Comm., 1932, 4, 200–212).—From transport no. determinations in absence of electro-osmotic effects the following vals. have been calc. for the no. of mols. of H_2O combined with the respective ions in 0.1M solutions at 20° : K^+ 29.3, Na^+ 44.2, Li^+ 62, H^+ 5, Cl^- 26.6, Br^- 29.6, I^- 31.4. As the vals. for halogen ions, compared with those obtained in 1.0M solutions, seem to tend towards a limiting val. with dilution, it is suggested that hydration of the ions is of a chemical nature in conc. solutions, but electrostatic in dil. solutions.

E. S. H.

Moving boundary method for measuring transference numbers. Pyknometer for determining the volume change occurring at an electrode and its application to a cathode of silver chloride in a solution of potassium chloride. E. R. SMITH (Bur. Stand. J. Res., 1932, 8, 457–461).—Apparatus and procedure are described for measuring

the vol. correction to be applied to transference nos., measured by the moving-boundary method, to allow for the change in vol. which occurs at the electrode on the closed side of the transference cell. In the case of a Ag|AgCl electrode in aq. KCl the vol. correction computed from the d of the electrode materials and of the solution, together with a val. for the transference no., is correct up to 0.2*M* within the precision required. E. S. H.

Equation for electrolytic conductance T. SHEDLOVSKY (J. Amer. Chem. Soc., 1932, 54, 1405—1411).—For strong uni-univalent electrolytes, such as HCl, LiNO₃, and Li, Na, and K halides, in aq. solutions <0.1*N*, $\Lambda = (\Lambda_0 + Bc)(1 - \alpha\sqrt{c}) - \beta\sqrt{c}$, where Λ is the equiv. conductance at concn. c . α and β can be derived theoretically (A., 1926, 906; 1927, 517, 1031), whilst B and Λ_0 are adjustable. If c is in mols. per litre, B is numerically equal to, or at most 15% greater than, $A = \alpha\Lambda_0 + \beta$. KNO₃, chlorates, iodates, and Tl salts do not conform to the equation. These electrolytes are apparently weaker, because for a given val. of Λ_0 the decrease of Λ with increasing c is more rapid than for the above electrolytes. L. O. (c)

Electrolytic conductivity of some uni-univalent electrolytes in water at 25°. T. SHEDLOVSKY (J. Amer. Chem. Soc., 1932, 54, 1411—1428).—Measurements with a new type of cell are described. The use of "dipping electrodes" may cause errors due to parasitic currents through capacity and resistance in series. The conductances of 0.00003—0.1*N*-HCl, -KCl, -NaCl, -LiCl, -KNO₃, and -AgNO₃ have been measured. The first three conform to the author's equation (cf. preceding abstract) over the entire range, and LiCl below 0.07*N*. The nitrates do not conform to the equation. For KNO₃ and AgNO₃ Λ_0 is 144.92 and 133.32, respectively. In every case the limiting tangent on a \sqrt{c} graph has the slope predicted by Onsager's theory. For the chlorides and HCl, the deviations from the limiting tangent are consistently positive, but for the nitrates, the conductance curves initially bend downwards, and run a little below the limiting tangent over part of the range <0.01*N*, suggesting association. L. O. (c)

Unhydrated solute element ions. L. H. FLINT (J. Washington Acad. Sci., 1932, 22, 233—237).—Electrical conductivity data for solutions of HCl, RbCl, CsCl, KBr, and KI suggest the association of hydrated with unhydrated ions. C. W. G.

Properties of nicotine and its derivatives. VI. Electrical conductivities. VII. Electrometric titrations. T. M. LOWRY and W. V. LLOYD (J.C.S., 1932, 1623—1634).—VI. The mol. conductivities of 4 mono- and di-iodides derived from nicotine have been measured. The isomethiodide behaves as a strong binary electrolyte with $\Lambda^\infty = 106$, with a cation mobility of about 29. The hydriodide and methiodide derived therefrom behave as strong ternary electrolytes, the mobility of the doubly-charged cation being approx. 4×30 . The dihydriodide of nicotine loses a mol. of HI and gives conductivities up to 500.

VII. Nicotine, two isomeric monomethylated quaternary bases, and one dimethylated quaternary base

derived from it have been titrated electrometrically. A drift of potential in the direction of increased alkalinity, observed in some of the solutions, can be explained by the formation of a ψ -base, as already postulated to account for the optical properties of aq. solutions of nicotine. The conditions under which the drift is observed are explained by the fact that a ψ -base may be formed by the pyridyl radical, but not by the pyrrolidine radical of nicotine. E. S. H.

Conductivity of electrolytes in ethyl cyanoacetate and in *o*-toluonitrile. J. C. PHILIP and P. RANGARAMANUJAM (J.C.S., 1932, 1512—1518).—The conductivities of AgNO₃, KI, LiBr, NMe₄I, NaI, NEt₄I, NEt₄Br, and NPr₄I in CN·CH₂·CO₂Et, and of the same salts (excluding NMe₄I) in *o*-C₆H₄Me·CN have been determined at 25°. In all cases the equiv. conductivity is a linear function of the square root of the concn. The slope of this curve is only slightly greater than that required by the Onsager equation in the case of the tetra-alkylammonium iodides in CN·CH₂·CO₂Et, but in the remaining systems it is definitely greater than the calc. slope. The deviation from the behaviour postulated by the Onsager equation is exhibited to a greater extent in aromatic than in aliphatic solvents. E. S. H.

Influence of electrodes on conductivity of semi-conducting liquids. J. SAMBUSSY (Compt. rend., 1932, 194, 1724—1725; cf. this vol., 9).—A p.d. (up to 3000 volts) was maintained between electrodes of Pt, Pd, Pb, and Ta separated by 5 cm. of dry PhNO₂. With Pt and Pd the distribution of p.d. is linear, but with Pb and Ta there is a large fall in potential at the anode. The results are attributed to traces of H₂O. C. A. S.

Magnitude of crowding effect in current flow through small tubes and slits. H. L. WHITE, L. C. VAN ATTA, and E. A. VAN ATTA (J. Physical Chem., 1932, 36, 1364—1370).—The absence of an effect with capillaries of 0.008—0.1 mm. bore may be deduced theoretically, and from the observation that the resistance of the capillary filled with *N*-or 0.1*N*-KCl has the val. calc. from microscopic measurements and the equiv. conductivity of the solution. If the capillary is broken in two the sum of the resistances of the pieces is, moreover, equal to the original resistance. F. U. (c)

Surface conductance at glass-salt solution interfaces. H. L. WHITE, F. URBAN, and E. A. VAN ATTA (J. Physical Chem., 1932, 36, 1371—1383).—Streaming potentials and resistances have been determined in pyrex capillaries of 0.0018—0.1 mm. bore filled with salt solutions. The sp. surface conductance for 0.0005*M*-KCl is 2.24×10^{-9} mho, which is 1/45 of the extrapolated McBain val. F. U. (c)

Quantum mechanics of electrochemistry. II. R. W. GURNEY (Proc. Roy. Soc., 1932, A, 136, 378—396).—Quantum mechanics are applied to the consideration of electrode potentials, the meaning of solution pressure, the role of contact potential, and of chemical energy. L. L. B.

Quinhydrone electrode. IV. O. M. LAMMERT and J. L. R. MORGAN (J. Amer. Chem. Soc., 1932, 54, 910—918; cf. A., 1931, 914).—Quinhydrone elec-

trodes prepared with pure Pt, Au, and graphite are as reproducible in dil. solutions of all common mineral acids as in 0.1M-HCl, particularly if Pt foil is used and solution resistances are not too high. The p.d. between two like electrodes in acetate (p_H 4.6—5.0) and phosphato (p_H 6.1—6.5) solutions are ten times the corresponding average vals. in 0.1M-HCl. Erratic variations, often > Sorensen's "salt error," occur in quinhydrone electrodes, especially of Au and graphite, in unbuffered salt solutions in the neutral range. There seems to be no relation between reproducibility of the electrode and darkening of the quinhydrone solutions. Before using the quinhydrone half cell as a secondary standard in a given system its reproducibility in that system must be investigated.

F. W. M. (c)

Determination of potential difference between 0.1M and saturated calomel electrodes at 5—50°. H. RIEHM (Z. physikal. Chem., 1932, 160, 1—7).—Between 0° and 35° the p.d., E , in mv., is given by $E = 88.9 + (t - 20)0.58$ and between 35° and 50° by $E = 97.5 + (t - 35)0.52$.

R. C.

Theory of concentrated solutions. IV. E. WILKE and W. MARTIN (Z. physikal. Chem., 1932, 160, 39—44).—Earlier measurements with Br electrodes (A., 1927, 415) have been verified, and similar measurements made with I electrodes. The results confirm the theory of quantised changes in the radii of the ions of the H halides with variation in concn.

R. C.

Equilibrium $Ni + Co^{++} \rightleftharpoons Ni^{++} + Co$ and normal electrode potential of cobalt. T. HEYMANN and K. JELLINEK (Z. physikal. Chem., 1932, 160, 34—38).—The equilibrium has been investigated in aqu. nitrate solutions at 25°. At equilibrium $[Co^{++}]/[Ni^{++}] = 8 \pm 5\%$, which, combined with the normal electrode potential of Ni^{++} , gives -0.268 volt for E_h for Co^{++} at 25°.

R. C.

Liquid junction potentials. I. Reproducible static liquid junctions constant in potential over long periods of time. II. Direct comparison of static and flowing junctions. A. L. FERGUSON, K. VAN LENTE, and R. HITCHENS (J. Amer. Chem. Soc., 1932, 54, 1279—1285, 1285—1290).—I. An improved method for making a "free diffusion" type of static junction is described. Sharply defined static junctions of the type 0.1M-HCl|saturated KCl or 0.01M-HCl|saturated KCl are const. for days to ± 0.04 and reproducible to within 0.1 mv. The potential of the cell $Hg|HgCl, \text{ saturated KCl}|0.01M-HCl|0.10M-HCl|\text{ saturated KCl}, HgCl|Hg^+$ is 38.04 ± 0.04 mv.

II. The potential of concn. cells with 0.10M- and 0.01M-HCl is about the same for both static and flowing junctions. For the junctions 0.10M-HCl|saturated KCl and 0.01M-HCl|saturated KCl the potential depends on the type of junction and rate of flow. For cells with saturated KCl the potentials are nearer the theoretical with static than with flowing junctions.

A. S. S. (c)

Electromotive force of cells containing dilute hydrochloric acid. W. F. K. WYNNE-JONES (J. Amer. Chem. Soc., 1932, 54, 2130—2131).—Car-

mody's results (this vol., 342) when corrected agree satisfactorily with the limiting equation of Debye and Hückel.

C. J. W. (c)

Relation between activity of water and potentials of glass electrode. M. DOLE (J. Amer. Chem. Soc., 1932, 54, 2120—2121).—A discussion.

C. J. W. (c)

Thermodynamic properties of solid solutions of silver chloride and sodium chloride. A. WACHTER (J. Amer. Chem. Soc., 1932, 54, 919—928).—E.m.f. measurements have been made at 150—230° with solid solutions of AgCl and NaCl in which the mol. fraction of AgCl is 0.16—1.0, and from these the activity has been derived. The space distribution of Na⁺ in the AgCl—NaCl lattice is regular.

R. H. L. (c)

Comparison of colorimetric and electrometric methods in determination of p_H values of various gelatin solutions. R. J. HARTMAN and I. F. FLEISCHER (J. Physical Chem., 1932, 36, 1136—1142).— p_H vals. obtained by means of H, glass, and quinhydrone electrodes do not agree amongst themselves, nor with the vals. obtained colorimetrically.

F. U. (c)

Change of equilibrium by adsorption. F. HAHN and R. KLOCKMANN (Naturwiss., 1932, 20, 331).—The p_H of an $N/2000$ -pyridine solution is 7.14; when hydrated Al_2O_3 is suspended in the pyridine solution the p_H rises to 8.8, and with activated charcoal suspended in the pyridine the p_H rises to 9.2.

W. R. A.

Direct measurement of primary, secondary, and total medium effects of acetic acid. B. B. OWEN (J. Amer. Chem. Soc., 1932, 54, 1758—1769; cf. A., 1931, 308).—Primary, secondary, and total medium effects are defined and their calculation from e.m.f. data is described. From e.m.f. data for HCl solutions containing AcOH the total medium effect of AcOH has been calc. Approx. equations connecting the primary medium effects of a particular medium on two similar electrolytes have been obtained.

G. M. M. (c)

ζ -Potential for a double layer of anomalous viscosity. H. REICHARDT (Z. physikal. Chem., 1932, 159, 417—427; cf. A., 1931, 795).—Equations have been derived for the ζ -potential, and the thickness of the double layer and stratum of anomalous viscosity when a certain min. shearing stress, which diminishes continually as the distance from the wall increases, must be applied before any flow occurs in the double layer. Variation of ζ -potential with rate of flow and Kohler's results (this vol., 17) are accounted for.

R. C.

Theory of hydrogen overvoltage. A. FRUMKIN (Z. physikal. Chem., 1932, 160, 116—118).—By treating the electrode charged with H as an acid in Brönsted's sense the relation between current strength and H_2 overvoltage is shown to reduce to an equation of the same form as that relating the affinity const. of a weak acid or base to its catalytic activity.

R. C.

Mechanism of overvoltage and its relation to the combination of hydrogen atoms at metal electrodes. J. A. V. BUTLER (Trans. Faraday Soc., 1932, 28, 379—382; cf. A., 1924, ii, 598; this vol.,

25).—In confirmation of the equation developed, the overvoltage at a Pt cathode varies linearly with c.d. between 10^{-6} and 10^{-7} amp. per sq. cm. The slow decay of H_2 overpotential at Hg in H_2SO_4 persists after drastic treatment for removing traces of alkali metals.

J. G. A. G.

Improved commutator and some sources of error in commutator method for measurement of overvoltage. A. L. FERGUSON and G. M. CHEN (J. Physical Chem., 1932, 36, 1156—1165).—A commutator is described for measuring charge or discharge potentials within 0.0003 sec. of the beginning or end of the charge and discharge intervals for the electrodes either combined or separately.

R. H. C. (c)

Measurement of polarisation by direct and commutator methods. A. L. FERGUSON and G. M. CHEN (J. Physical Chem., 1932, 36, 1166—1177).—Potentials were measured within 0.0005 sec. from end of charge or beginning of discharge. Anode, cathode, and total potentials were measured practically simultaneously during the charge and discharge intervals without stopping the interrupter. For platinised electrodes in $2N-H_2SO_4$ there is no surface resistance of any kind for c.d. of 0.0038—0.150 amp. With smooth Pt electrodes the decrease in discharge potential is so rapid that satisfactory results cannot be obtained with the interrupter-potentiometer system.

R. H. C. (c)

Electrolytic deposition of polonium on metals. M. HAÏSSINSKY (Compt. rend., 1932, 194, 1917—1919; cf. this vol., 236).—The negative crit. potentials in alkaline solution of the Po deposit on cathodes of Pt, Au, Au (beaten), Cu, Ag, Sn, Ni, indicate that the Po is hydrolysed, and, in the form of PoO_3^{2-} , acts as a depolariser. In an acid medium (0.23N- HNO_3) with Ag cathode the crit. potential is +0.36 volt.

C. A. S.

Fortuitous empirical relationships in chemical kinetics. D. T. LEWIS and L. J. HUDLESTON (J.C.S., 1932, 1398—1400).—The simple relation found between E and $\log B$ in the equation of Arrhenius for the variation of the velocity coeff. of a reaction with temp. is a necessary consequence of considering only those reactions for which $\log k$ at the mean temp. of measurement, T , does not vary greatly, and has no theoretical significance. F. L. U.

Kinetics of adsorption in relation to reaction velocity. F. H. CONSTABLE (Trans. Faraday Soc., 1932, 28, 227—228).—See A., 1928, 718.

J. G. A. G.

Measurements of flame velocities. A. BECKER and K. VOGT (Z. Physik, 1932, 75, 804—808).—A precision method, using rotating mirrors, is described.

A. B. D. C.

Kinetics of gas explosions. II. Thermal reaction between ozone and hydrogen bromide. B. LEWIS and W. FEITKNECHT (J. Amer. Chem. Soc., 1932, 54, 1784—1792).—Reaction occurs through reaction chains which start on the wall and proceed rapidly into the gas phase, probably being propagated by the OH radical. The rate of the non-explosive reaction is proportional to the initial concns. of HBr

and O_3 , and the temp. coeff. between -104° and 77° is 1.79, giving 3800 g.-cal. for the heat of activation. He, A, H_2 , and O_2 have a retarding action, which increases in this order, and increase the explosion limit by an amount which increases in the reverse order. Explosion may occur at -104° under 24 mm. total pressure.

C. W. (c)

Kinetics of reaction H_2 (gas) \rightleftharpoons 2H (dissolved in palladium). C. WAGNER (Z. physikal. Chem., 1932, 159, 459—469).—Under such conditions that the changes occurring at the surface are sufficiently slow compared with diffusion within the Pd wire to determine the rate of the process as a whole, the rate of reaction may, depending on the previous thermal treatment of the Pd, be represented by $dc/dt = k'\sqrt{p} - kc = k(c_e - c)$, or $dc/dt = k_1p - k_2c^2 = k_2(c_e^2 - c^2)$, or some combination of these, where c is the concn. of H within the Pd at time t and c_e the equilibrium concn. for the gas pressure p , and k' , k , k_1 , and k_2 are consts. If the slow process were H (adsorbed) \rightleftharpoons H (dissolved) the first equation would result, whilst if it were H_2 (adsorbed) \rightleftharpoons 2H (dissolved in Pd) or H_2 (adsorbed) \rightleftharpoons 2H (adsorbed) the second equation would be valid. The rate of absorption of O_3 by Ag foil (A., 1926, 1089) seems to be determined by reactions at the interface, rather than by diffusion.

R. C.

Explosive combination of hydrogen and oxygen. Function of walls in gaseous reactions. H. W. THOMPSON (Trans. Faraday Soc., 1932, 28, 299—308).—The lower crit. explosion pressures of the gas mixtures were determined at room temp. by the spark method (cf. A., 1931, 174). The crit. partial pressure of H_2 varies greatly, but that of O_2 is approx. const. within a wide range of composition of H_2 - O_2 mixtures. The addition of He, A, N_2 , CO_2 , SO_2 , $CH_3(OEt)_2$, $COMe_2$, N_2O , CCl_4 , and $CHCl_3$ depresses, in order of increasing effect, the partial pressure of H_2 plus O_2 required for explosion. O_2 has the most marked "inert gas" effect. Variation of diameter of the reaction vessel has approx. the effect predicted by the equation (A., 1931, 1014).

J. G. A. G.

Oxidation of phosphorus vapour at low pressures. H. W. MELVILLE (Trans. Faraday Soc., 1932, 28, 308—315).—Theory is developed and correlated with existing data. The equation (A., 1931, 1014) is corrected by replacing \bar{D} by $D^{\frac{1}{2}}$. Whilst PH_3 raises the lower crit. explosion pressure, p , of P_4 - O_2 mixtures, small concns. of O_3 decrease p much more than is required by a normal diffusion effect. P vapour diminishes p for PH_3 - O_2 mixtures. The effects of surfaces are examined.

J. G. A. G.

Energy exchange in unimolecular reactions. I. Decomposition of mixtures of dimethyl and diethyl ether. E. W. R. STEACIE (J. Physical Chem., 1932, 36, 1562—1569).—See this vol., 576.

Influence of hydrogen on the pyrolysis of ethane and ethylene near 600° . I. M. W. TRAVERS and L. E. HOCKIN (Proc. Roy. Soc., 1932, A, 136, 1—27).— C_2H_6 or C_2H_6 - C_2H_4 - H_2 mixtures when heated to 600° in closed tubes give rise to 3 reactions: (1) the reversible C_2H_6 - C_2H_4 - H_2 reaction which is independent of the other two and of the

H₂ concn. except in so far as H₂ is a reactant; (2) the formation of C₆H₆ and CH₄ from C₂H₆ alone; and (3) the formation of C₆H₆ and CH₄ from C₂H₆ and C₂H₄. The formation of C₆H₆ from C₂H₆ is endothermic and of zero order, whilst from C₂H₄ it is exothermic and the rate of formation follows a complex expression.

L. L. B.

Homogeneous first order gas reactions. II. Decomposition of butylidene diacetate and ethylidene dipropionate. C. C. COFFIN (Canad. J. Res., 1932, 6, 417—427).—The thermal decomp. of butylidene diacetate and ethylidene dipropionate, like that of ethylidene diacetate, are homogeneous unimol. reactions, proceeding to completion and each yielding an anhydride and an aldehyde. Measurements were made at 211—265°, and the velocity coeffs. of the three esters in the above order are given by $\log_e k = 24.20 - 32,900/RT$, $\log_e k = 23.96 - 32,900/RT$, and $\log_e k = 23.74 - 32,900/RT$, respectively. The energies of activation are thus equal, but the velocities different. It is suggested that the former is the min. energy that a linking must acquire to enable the mol. to divide, and that this is unaffected by structural changes in other parts of the mol. The velocity, however, depends on the no. of degrees of freedom capable of contributing to this energy and is affected by changes in other parts of the mol., although it is believed that large mols. are divided into sections between which there is no energy exchange.

A. G.

Nitric acid as an oxidising agent. I. Mechanism of oxidation of hydrochloric acid. S. SEITZER (Z. physikal. Chem., 1932, 159, 428—435).—The reaction of HNO₃ with a large excess of HCl in aq. solution at 60° follows the unimol. law, with a temp. coeff. of 2.45, and is represented quantitatively by the equation $3\text{HCl} + \text{HNO}_3 = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$. Ag₂SO₄ has considerable catalytic action, but chlorides seem to have no effect.

R. C.

Neutral salt effect of the ferric-iodide ionic reaction. III. Influence of non-electrolytes on velocity of reaction. A. VON KISS [with P. VASS] (Z. anorg. Chem., 1932, 206, 196—208; cf. A., 1930, 1256; 1931, 802).—The reaction is still unimol. with respect to Fe⁺⁺⁺ and bimol. with respect to I⁻ in presence of MeOH, EtOH, PrⁿOH, glycerol, COMe₂, sucrose, and CO(NH₂)₂. Of these only CO(NH₂)₂ is known to form complexes with Fe⁺⁺⁺. If KI is partly replaced by KCl for const. [Fe⁺⁺⁺], or FeCl₃ by AlCl₃ for const. [I⁻], in presence of CO(NH₂)₂ or EtOH, the Bronsted-Debye-Hückel rule for neutral salt action still holds. Grube and Schmid's rule relating to the action of the medium (A., 1926, 474) is also strictly followed.

M. S. B.

Kinetics of the oxidation of oxalic acid by chlorine. R. O. GRIFFITH and A. MCKEOWN (Trans. Faraday Soc., 1932, 28, 518—522; cf. this vol., 344).—The data obtained at 10°, 15°, and 20° with $M/20 - M/80 - \text{H}_2\text{C}_2\text{O}_4$ in 0.25–0.7N-HCl plus 0–1.9N-KCl and $M/100 - M/150 - \text{Cl}_2$ are consistent with the rate-determining reaction $\text{HOCl} + \text{HC}_2\text{O}_4' \rightarrow \text{H}_2\text{O} + 2\text{CO}_2 + \text{Cl}'$. The temp. coeff. of this reaction and of the initial val. of the unimol. coeff. with respect

to titratable Cl₂ is 2.49 and 4.0, respectively (cf. A., 1930, 175).

J. G. A. G.

Cellulose-cuprammonium solution. IV. Reaction heat and velocity between cellulose and cuprammonium solution. N. ISHII (J. Cellulose Inst. Tokyo, 1932, 8, 44—48).—The lack of data as to the velocity of reaction between cellulose and alkaline Cu solutions is due to the difficulty of determining analytically the amounts of Cu combined with the dispersed cellulose. The heat generated when cellulose dissolves in cuprammonium solution indicates the progress of the reaction. The heat of reaction is independent of any variation in the structural properties of cellulose. The reaction is intramolecular, but is probably not confined to the surface of the micelle.

V. E. Y.

Oxidation of cystine by iodine in aqueous medium. K. SHINOHARA (J. Biol. Chem., 1932, 96, 285—297).—Cystine, oxidised by the iodate method, reacts with more KIO₃ than is required for its oxidation to cysteine in proportion as the concn. of HCl decreases. Measurement of the rate of consumption of I by cystine showed that cysteic acid is the final product; this acid was isolated in theoretical yield according to the reaction $\text{R-S-S-R} + 5\text{I}_2 + 6\text{H}_2\text{O} = 2\text{RSO}_3\text{H} + 10\text{HI}$, and its properties were determined.

[Theory of oxidative processes. Imparity and radical chains in the reaction mechanism of organic and enzymic processes.] J. KENNER (Ber., 1932, 65, [B], 705—710).—A reply to Haber and Willstätter (this vol., 352).

H. W.

Open weighing of hygroscopic substances. J. REHNER, jun. (Z. anal. Chem., 1932, 88, 266—270).—Mathematical expressions are derived for the rate of absorption of H₂O from the air by Ca(NO₃)₂, CaCl₂, Mg(ClO₄)₂, and LiNO₃.

A. R. P.

Rate of dissolution of zinc in acids. C. V. KING and M. M. BRAVERMAN (J. Amer. Chem. Soc., 1932, 54, 1744—1757).—The effects of concn., a common ion, viscosity, rotation speed, and temp. on the rate show it to depend on a diffusion process. Whether ions other than H₃O⁺ are active is undecided. Data are given for the dissolution of Mg, Cd, and CaCO₃ in HCl.

H. A. B. (c)

Mechanism of molecular statistics of the reaction $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$. B. TOPLEY (Proc. Roy. Soc., 1932, A, 136, 413—428).—The intermediate steps in the dehydration of CuSO₄·5H₂O to the monohydrate, and the conditions governing the appearance of the trihydrate instead of the monohydrate as the product of the reaction in vac. are discussed. By means of a model, which takes account of the actual conditions in the reaction zone, a detailed statistical-mechanical interpretation of the relationships between the abs. reaction velocity and its temp. coeff. is attempted.

L. L. B.

Chemical activity and particle size. II. Rate of dissolution with slow stirring of anhydrite and gypsum. P. S. ROLLER (J. Physical Chem., 1932, 36, 1202—1231).—The relative rates of dissolution of powders consisting of particles of uniform diameter, *D*, varying from 1 to 250 μ have been deter-

mined at 20° for a fixed speed of stirring such that dissolution occurs from a settled sediment through which the solvent flows. For all sizes the rate of dissolution, v , is initially high, and falls in 2 min. to a low linear rate, but starting from the dry powder there is a period of induction if $D \leq 17 \mu$. If $D > 8 \mu$, v increases proportionately to the surface exposed, but if $D < 8 \mu$ the increase is more rapid, which is attributed solely to the effect of edges and corners. Entangled air has no effect. The results lend no support to Nernst's theory of heterogeneous reaction.

S. L. (c)

Hydrogenation of adsorbed ethylenic hydrocarbons. C. SCHUSTER (Trans. Faraday Soc., 1932, 28, 406—408; cf. A., 1931, 1374).—The hydrogenation of propylene is of the same order as, but slower than, that of C_2H_4 , the respective energies of activation being 4800 and 3600 g.-cal. on the same surface. With equimol. proportions of H_2 and butylene, the rate is given by $dx/dt = kp^{1.5}$; the activation energies are: Δ^a -butylene 6800, Δ^b -butylene 5600, and *iso*-butylene 6500.

J. G. A. G.

Viscose. XL. Velocity of xanthation. S. IWASAKI and E. SUGINO.—See B., 1932, 498.

Kinetics of acetylation of cellulose fibres. I. SAKURADA.—See B., 1932, 498.

Chemical reactions in concentrated solutions of electrolytes. XIII. Oxidation of hydrogen bromide and chloride by hydrogen peroxide. M. BOBELSKI [with G. RADOVENSKY-CHOLATNIKOV] (Z. anorg. Chem., 1932, 206, 161—170).—In the presence of conc. H_2SO_4 or HCl, and with a const. excess of H_2O_2 , the reaction by which HBr is oxidised to Br is unimol. It is catalytically accelerated by chlorides and the ratio x_1/t_1 is then a const. (x_1 is the amount of Br set free in time t_1). The salt effect is chiefly cationic and increases with the valency of the cation. Zn^{++} and Fe^{+++} are exceptions; the former has practically no effect and the latter has a disproportionately strong accelerating action. In the presence of sulphates the catalytic formula applies for the first half of the reaction and the unimol. for the second half. The rate of Cl evolution in the oxidation of HCl by H_2O_2 obeys the formula $K = x_1/t_1$. For const. HCl the rate is proportional to the H_2O_2 concn. If HCl is partly replaced by conc. H_2SO_4 there is a crit. lower limit above which the rate of Cl evolution is markedly increased. Chlorides have an accelerating effect which is partly due to the anion, but mainly to the cation. Some cations, however, such as Zn^{++} , Cd^{++} , and Cu^{++} , have apparently an inhibiting effect. A method is described for the determination of small quantities of Br' in conc. Cl' solution by H_2O_2 , using a suitable chloride for accelerating the Br evolution.

M. S. B.

Dynamics and catalysis of the thermal decomposition of hydrogen carbonates in aqueous solution. V. Decomposition of calcium hydrogen carbonate in a current of carbon dioxide, hydrogen, or air. R. STUMPER (Z. anorg. Chem., 1932, 206, 217—223; cf. this vol., 234, 477).—The decomp. of boiling aq. $Ca(HCO_3)_2$ is accelerated by a current of H_2 or air and delayed by a current of CO_2 .

The effect is more marked when the gas is passed through the solution than when passed through the gas space only. As the rate of evolution of CO_2 is increased the reaction becomes more nearly bimol., $2HCO_3' \rightleftharpoons CO_3'' + H_2CO_3$. The rate of CO_2 evolution may be reduced by covering the solution with a layer of paraffin and the order of the reaction increases until it approaches 3 in the more conc. solutions.

M. S. B.

Dynamics of thermal decomposition of dissolved alkaline-earth hydrogen carbonates. F. MEUNIER (Z. anorg. Chem., 1932, 206, 44—46).—A claim for priority over Stumper (cf. this vol., 477).

F. L. U.

Dynamics of thermal decomposition of hydrogen carbonates in aqueous solution. R. STUMPER (Z. anorg. Chem., 1932, 206, 47—48).—Reply to Meunier (preceding abstract).

F. L. U.

Atmospheric oxidation of hydrogen sulphide in solution. M. KAPP (Bull. Soc. d'Encour., 1932, 131, 330—334).— H_2S in solution is oxidised by the air in accordance with the equation $H_2S + \frac{1}{2}O_2 = S + H_2O$. The reaction is catalysed by $NiSO_4$.

C. W. G.

Induced oxidations in which sodium sulphite is the inductor. C. VAN DEN POL (Rec. trav. chim., 1932, 51, 490—512).— Na_2SO_3 induces the absorption of O_2 by suitably buffered solutions of Na_3PO_3 , $NaAsO_2$, $NaSbO_2$, bismuthyl K bismuthylotartarate, glycerol, erythritol, mannitol, fructose, sucrose, and pyramidone, but has little or no action with $NaNO_2$, $Bi(OH)_3$, $NaAsO_2$ + quinol or carbamide, $Na_2C_2O_4$, mannitol + $NaAsO_2$, glucose, lactose, and maltose.

D. R. D.

Sulphurous acid and its salts. XI. Catalytic influence of arsenious acid on decomposition of thiosulphate. F. FOERSTER and G. STUMMER (Z. anorg. Chem., 1932, 206, 1—23).—The decomp. of $Na_2S_2O_3$ in acid solution in presence of H_3AsO_3 is shown to depend on the formation of $As(S_2O_3)_3'''$, the hydrolysis of which has been studied. The initial rapid change is expressed by $As(S_2O_3)_3''' + 3H_2O = As(OH)_3 + 3HS_2O_3'$, subsequent reactions being probably (1) $2HS_2O_3' = S_2O_3'' + SO + H_2SO_2$, (2) $SO + 2HS_2O_3' = S_2O_6'' + H_2O$ and (3) $3H_2SO_2 = H_2SO_3 + H_2S_2O_2 + H_2O$. In slightly acid solution the $H_2S_2O_6$ is rapidly degraded to $H_2S_4O_6$ and $H_2S_3O_6$ by the SO_2 , whilst in *N*-HCl a high yield of $H_2S_5O_6$ is obtained, the yield increasing with rise of temp. Addition of H_2SO_3 hinders formation of As_2S_3 by repressing decomp. of the $H_2S_2O_6$ formed in (3), and likewise favours production of polythionic acids.

F. L. U.

Autoxidation. V. Formation of dithionate by the oxidation of aqueous sulphite solutions. H. W. ALBU and H. D. GRAF VON SCHWEINITZ (Ber., 1932, 65, [B], 729—737).—In acid solution (region of stability of SO_2 and HSO_3 ions) reduction of Cu^{++} in presence of alkali sulphite does not occur at room temp.; hence there is no oxidation of SO_3'' , but essentially production of a Cu^{++} - SO_3 complex characterised by greenish-yellow colour. In alkaline solution $CuOH$ is immediately pptd. with simultaneous formation of dithionate and sulphate. The action of

Cu^{++} on SO_3^{--} immediately affords dithionate in the same p_H region in which autoxidation of SO_3^{--} occurs. Under all conditions of acidity employed the action of FeCl_3 on Na_2SO_3 gives a red complex, less stable in acid than in feebly alkaline medium and converted by conc. alkali into $\text{Fe}(\text{OH})_3$ and sulphite. When preserved, the Fe^{+++} is reduced to Fe^{++} with simultaneous oxidation of SO_3^{--} to $\text{S}_4\text{O}_6^{--}$ and SO_4^{--} . Immediate reduction of Fe^{+++} and oxidation of SO_3^{--} never occurs, thus accounting for the absence of acceleration of autoxidation. Persulphate and H_2O_2 , which transitorily accelerate the reaction of alkali sulphite with O_2 , give small amounts of $\text{S}_4\text{O}_6^{--}$ and SO_4^{--} in absence of O_2 . The acceleration of the oxidation of SO_3^{--} in the anodic solution of a galvanic chain with unattackable electrodes occurs under conditions under which, in absence of O_2 , the electrochemical oxidation of SO_3^{--} to $\text{S}_4\text{O}_6^{--}$ is observed. The observations are in accordance with the theories of Franck and Haber (A., 1931, 917). H. W.

Complex catalysis. II. Complex catalysis and its application to the reduction of vanadic acid by concentrated hydrochloric acid. M. BOBTELSKI and S. CZOSNEK (Z. anorg. Chem., 1932, 206, 113—124; cf. A., 1930, 714).—The reaction between V_2O_5 and conc. HCl ($\text{V}^{\text{V}} \rightarrow \text{V}^{\text{IV}}$) proceeds readily at room temp. in presence of CuSO_4 , $\text{Pb}(\text{OAc})_2$, or Ag_2SO_4 , the last being the most active. Salts of other metals had little or no effect. V_2O_5 can be conveniently determined iodometrically by means of the Cl evolved from a mixture containing at least 70 vol.-% of conc. (d 1.19) HCl . F. L. U.

Influence of magnesium and copper on the velocity of decomposition of sodium perborate solutions. S. K. HAGEN and V. A. LARSEN.—See B., 1932, 504.

Mechanism of stabilisation of ether by copper. F. W. NITARDY and E. C. BILLHEIMER.—See B., 1932, 540.

Transference of peroxidic oxygen to hydrogen sulphide by iron. A. WASSERMANN (Ber., 1932, 65, [B], 704—705).—The transference of O_2 from H_2O_2 to H_2S is facilitated by Fe^{III} and hæmin, but not by peroxidase. H. W.

Acceleration of autoxidation of mercaptans by organic catalysts. Explanation of the action of iodoacetic acid on glycolysis in muscle. T. BERSIN (Biochem. Z., 1932, 248, 3—8).— $\text{CH}_3\text{I}\cdot\text{CO}_2\text{Na}$ (0.01 mol.) accelerates the conversion of the SH group of thioglycollanilide into the $\text{S}\cdot\text{S}\cdot$ group almost as strongly as does Cu (this vol., 431). Accelerating action decreases in the following order: $\text{CH}_3\text{I}\cdot\text{CO}_2\text{Na}$, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na}$, $\text{CH}_3\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$. Creatine, creatinine, $\text{CBr}_3\cdot\text{CO}\cdot\text{CO}_2\text{Na}$, and $\text{Na}_2\text{C}_2\text{O}_4$ have a similar but smaller effect, whilst $\text{CBr}_3\cdot\text{CO}_2\text{Na}$, MeCN , CHI_3 , and I have no effect. It is suggested that the observed inhibition of muscle glycolysis by $\text{CH}_3\text{I}\cdot\text{CO}_2\text{Na}$ is due to the destruction of the glutathione system. P. W. C.

Decomposition of benzenediazonium chloride in water solution. C. J. HAGGERTY and B. C. HADLER (J. Amer. Chem. Soc., 1932, 54, 1707—1713).—The retardation at 30° caused by H_2SO_4 is due to

dehydration, not sulphate formation. The acceleration in alkaline media is not due to OH^- as such, but possibly to a heterogeneous reaction on the surface of the ppts. which appear at $p_H > 7$, and after dissolution in acid decompose normally.

H. A. B. (c)

Thermionic emission during catalytic combination of carbon monoxide-oxygen mixtures on a platinum surface. B. W. BRADFORD (J.C.S., 1932, 1544—1560).—The rate of combination of moist CO and O_2 on a heated Pt wire is expressed by the equation $\log(p_t - p_i) = \log \log(p_0 - p_i) - t$, in which p_t , p_0 , p_i are the pressures at time t and the initial and final pressures, respectively. Measurement of the thermionic emission of the Pt heated in CO and/or O_2 indicated that this was invariably higher when the metal was catalytically active than when the surface was fully poisoned. The emissivity underwent complex changes before becoming const. F. L. U.

Catalysts for oxidation of carbon monoxide. I. C. J. ENGELDER and L. E. MILLER. II. C. J. ENGELDER and M. BLUMER (J. Physical Chem., 1932, 36, 1345—1352, 1353—1358).—I. The catalytic oxidation of CO in air at 150° and 300° has been studied. Mixtures of TiO_2 with Fe_2O_3 , NiO , or CuO are more active in respect of a mixture of air with 12% CO at 150° than the constituent oxides singly. Of TiO_2 - CuO mixtures that with 60% TiO_2 is the most active at 50 — 60° . H_2O largely destroys the activity of TiO_2 - CuO catalysts at 50 — 60° , but not at 150° .

II. The catalytic oxidation by metallic oxides and binary mixtures of these has been studied at 0 — 300° . 0.5% CO in air flowing at a rate of 250 litres per hr. over 17 g. of a catalyst consisting of 30% Co_2O_3 and 70% Fe_2O_3 at 0° is practically completely oxidised. Absorption of 2.5% of its wt. of H_2O renders the catalyst inactive. P. H. E. (c)

Mechanism of catalysis of ammonia [decomposition] on tungsten. [Adsorption of hydrogen, nitrogen, and ammonia.] W. FRANKENBURGER and A. HODLER (Trans. Faraday Soc., 1932, 28, 229—242; cf. A., 1931, 1247).—"Active" W of reproducible adsorptive and catalytic properties is obtained by reducing the powder with H_2 and evacuating at 750° . The adsorption of H_2 on "active" W deviates from proportionality to pressure, especially between 0 and 0.5 mm. Between 90° and 150° the H_2 adsorbed at a definite pressure increases with rise of temp. These phenomena are less prominent with less active W . The adsorption of NH_3 at low pressures on "active" W at 20 — 60° increases rapidly with pressure and the adsorption is unaffected by adsorbed H_2 . Small quantities of the decomp. products of NH_3 on W have little effect on H_2 adsorption, but large quantities increase the adsorption of H_2 and NH_3 . At 90 — 250° , NH_3 decomposes at localised patches on "active" W , partly in a bimol. and partly in a unimol. reaction with the formation of W nitride and imide and the liberation of H_2 . The activation energy of the reactions is 12,000 g.-cal. and is independent of the state of the surface. With fresh catalyst, the bimol. reaction predominates, but with decomp. of successive quantities of NH_3 , the % of unimol. decomp. increases until finally decomp. ceases. The net nitride plus

imide formation increases with rise of temp. of the W. J. G. A. G.

Catalysis of reactions between solids. III. Catalytic formation of stannates from strontium oxide and stannic oxide. S. TAMARU and H. SAKURAI (Z. anorg. Chem., 1932, 206, 49—58; cf. A., 1931, 318).—The reaction between SnO_2 and SrO at 900° has been studied in a similar way to that between SnO_2 and CaO , previously described. H_2 or CO is an effective catalyst, but H_2O has much less influence than with CaO . The products were $\text{SnO}_2\cdot\text{SrO}$ or $2\text{SnO}_2\cdot3\text{SrO}$, the determining factor being the ratio of the partial pressures of H_2 and H_2O at equilibrium rather than the proportion of metal oxides.

F. L. U.

Catalytic influence of dried cellulose on hydrolysis of sucrose. M. L. MORSE and W. E. CRAIG (J. Amer. Chem. Soc., 1932, 54, 2121—2122).—The hydrolysis in H_2O at high temp. is greatly accelerated by dried cellulose fibre.

C. J. W. (c)

Catalytic fission of racemates by dextro- and lævo-quartz. G. M. SCHWAB and L. RUDOLPH (Naturwiss., 1932, 20, 363—364).—The dehydration of *r-sec.*- BuOH has been studied. Dextro- and lævo-quartz effect the dehydration by a kind of optical selective catalysis. The quartz alone does not perform the dehydration, but must first be impregnated with a Cu mixture. Increased optical rotation is found. Optically inactive quartz impregnated with Cu has no effect. An explanation is put forward.

W. R. A.

Hydrogenation of phenols. G. L. JUCHINOVSKI and I. I. SOROKIN.—See B., 1932, 493.

Electrolysis of fused sodium metaphosphate. M. CENTNERSZWER and J. SZPER (Bull. Acad. Polonaise, 1931, A, 364—368).—On electrolysing fused NaPO_3 , the following reactions occur: $5\text{Na} + \text{NaPO}_3 = \text{P} + 3\text{Na}_2\text{O}$; $\text{Na}_2\text{O} + \text{NaPO}_3 = \text{Na}_3\text{PO}_4$, at the cathode; $2\text{PO}_3 = \text{P}_2\text{O}_5 + \text{O}$; $\text{P}_2\text{O}_5 + \text{NaPO}_3 = \text{NaP}_3\text{O}_8$; $\text{P}_2\text{O}_5 + 2\text{NaPO}_3 = \text{Na}_2\text{P}_4\text{O}_{11}$, etc., at the anode.

D. R. D.

Electrolysis of fused alkali nitrites. M. CENTNERSZWER and J. SZPER (Bull. Acad. Polonaise, 1931, A, 352—363).—On electrolysing fused NaNO_2 , the following reactions occur: $6\text{Na} + 2\text{NaNO}_2 = 4\text{Na}_2\text{O} + \text{N}_2$ at the cathode; $\text{NaNO}_2 + \text{NO}_2 = \text{NO} + \text{NaNO}_3$ at the anode. At first pure NO is evolved, but the proportion of NO increases as electrolysis is continued. The electrolysis culminates in a violent explosion. KNO_2 behaves similarly.

D. R. D.

Production of zinc by electrolysis. H. HEY.—See B., 1932, 554.

Action of cyanide on gold. G. O. RAMSAY (Chem. Eng. Min. Rev., 1932, 24, 236—237).—The p.d. between a Au electrode and the *N*-calomel electrode in *M*- KCN rises rapidly at first, then more slowly with time of immersion from 0.750 volt to a const. val. of about 0.95 volt. In an atm. of H_2 the initial p.d. is 0.925 volt, and this increases with time to 0.95 volt; passage of O_2 over the electrode produces an immediate fall in p.d. to 0.63 volt. It is suggested that these results support Janin's theory that dissolution of Au in aq. KCN is accompanied by form-

ation of H_2 , oxidation of which is necessary for dissolution to continue.

A. R. P.

Peptisation of cuprous oxide, and electro-deposition from and decolorisation of ammoniacal copper solutions. E. A. VUILLEUMIER (J. Physical Chem., 1932, 36, 1455—1456).—An electrolyte from which an unsatisfactory deposit of Cu is obtained does not peptise Cu_2O , but conc. aq. NH_3 , or $(\text{NH}_4)_2\text{SO}_4$ in the presence of a small amount of aq. NH_3 , does.

F. U. (c)

Relation between dissolution of metals in acids and electrolytic evolution of hydrogen. L. P. HAMMETT and A. E. LORCH (J. Amer. Chem. Soc., 1932, 54, 2128—2129).—A discussion of Bronsted and Kane's work (A., 1931, 1373).

C. J. W. (c)

Alternative electrode reactions. I. Reactions at a platinum cathode in nitric acid solutions. H. J. T. ELLINGHAM (J.C.S., 1932, 1565—1579).—The cathode potential during electrolysis of aq. HNO_3 of various concns. between Pt electrodes has been measured in relation to the applied e.m.f., and during the maintenance of a const. c.d. The results indicate that the discharge of H^+ ions may be followed by the alternative reactions (1) $\text{HNO}_3 + 2\text{H} = \text{HNO}_2 + \text{H}_2\text{O}$ and (2) $2\text{H} = \text{H}_2$ (gas). The relative predominance of these depends on the conditions of electrolysis, (2) occurring only when (1) cannot proceed at a sufficient rate to remove H as fast as it is produced. Reaction (1) is strongly autocatalytic, the c.d. which it can maintain being determined by the concn. of HNO_2 at the cathode. This can account for the catalytic action of HNO_2 on the dissolution of certain metals in HNO_3 .

F. L. U.

Electrolytic reduction of ketones. I. Aromatic ketones. S. SWANN, jun. (Univ. Illinois Eng. Exp. Sta. Bull., 1931, No. 236, 15 pp.).—Optimal reduction of COPh_2 was obtained in H_2O - EtOH - H_2SO_4 at 60° with c.d. 0.02 amp. per sq. cm. and cathodes of Cd , Pb , Hg , or Al ; the principal product was benzpinacolone with some $(\text{CHPh}_2)_2$.

Cu. Abs.

Detection of iodine atoms in the optical dissociation of salt vapours. N. PRILESHAIEVA (Physikal. Z. Soviet Union, 1932, 1, 189—202).—On irradiating the electrically excited vapour of I compounds with ultra-violet light of wave-length below 2500 \AA ., the intensity of the 2062.2 \AA . line of the I atom is increased. With HgI_2 two other band systems at 2114 — 2160 \AA . and 2168 — 2240 \AA ., respectively, which also increase in intensity under these conditions, are attributed to the HgI mol. with vibration frequency 125 cm^{-1} . These effects are brought about by light of the same wave-length as excites the fluorescence of HgI vapour, a phenomenon which has been interpreted as due to dissociation into excited HgI mols. and I atoms. Similar behaviour is observed with NaI and I_2 , which dissociate into an I atom and an excited Na or I atom, respectively.

J. W. S.

Photochemical decomposition of ammonia. E. O. WHIG and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1932, 54, 1806—1820).—The photochemical decomp. has been studied in the radiation of Zn , Al , and Cd sparks. At 25° the quantum yield averages 0.25, and is independent of pressure, intensity, and

time of illumination; at 500° it is 0.5 or more. The products of decomp. are N_2 and H_2 in the vol. ratio of 1:3. W. E. V. (c)

Progress of an isomeric change followed quantitatively by means of Raman effect. H. CONRAD-BILLROTH, K. W. F. KOHLRAUSCH, and A. PONGRATZ (Z. physikal. Chem., 1932, B, 17, 233—240).—The spontaneous transformation of *trans*- $C_2H_2Br_2$ into the *cis-trans* equilibrium mixture has been followed, and the isomerisation consts. of the two forms have been calc. The rate is considerably increased by the light from the Hg-vapour lamp. R. C.

Photochemical chlorination of acetylene. K. PETERS and L. NEUMANN.—See B., 1932, 540.

Primary photochemical processes. I. Decomposition of formaldehyde. R. G. W. NORRISH and F. W. KIRKBRIDE (J.C.S., 1932, 1518—1530).—The quantum efficiency of the photochemical decomp. of CH_2O into CO and H_2 is nearly uniform throughout the whole absorption system and decomp. is not confined to the spectral region of predissociation. The decomp. consists probably in the primary production of H_2 and CO mols., the change being spontaneous in the predissociation region, and due to activation followed by collision in the region of fine structure. F. L. U.

Action of light on some alkyl iodides. G. EMSCHWILLER (Ann. Chim., 1932, [x], 17, 413—517; cf. A., 1930, 1090; this vol., 29).—A *resume* and discussion of previous results. Besides the products previously obtained MeI gives CH_3I_2 , which is slowly affected by further action of light without evolution of gaseous products. Bu^tI gives a little *tert*-BuI. EtI in EtOH gives mainly C_2H_4 and HI. Activity decreases gradually with increase of wave-length and ceases at an indefinite point near the visible spectrum. Alkyl iodides do not fluoresce. A. A. L.

Quantum yield in photochemical decomposition of ethyl diazoacetate. E. WOLF (Z. physikal. Chem., 1932, B, 17, 46—67).—The absorption spectrum of Et diazoacetate both in the pure state and dissolved in various solvents has been determined. The absorption curve is similar to those of compounds containing a CO group not unduly influenced by polar groups or double linkings, and the displacement of the bands with increase in the dipole moment of the solvent occurs in the same way as with ketones. The diazo-group is essentially responsible for both bands. In the photolysis in heptane solution the quantum yield, γ , rises from 0.20 for 4200 to 1.11 for 2600 Å.; the rate of increase is small at first, but becomes greater in the band of shorter wave-length. In EtOH, MeOH, and H_2O there is a similar rise, but compared with heptane the vals. are smaller in the longer ultra-violet and greater in the shorter. For a given wave-length γ either rises or falls in the order heptane, EtOH, MeOH, H_2O . Neither ten-fold increase in concn. nor rise in temp. from 5° to 40° affects γ . Dipole moment measurements have been made in C_6H_6 solution. R. C.

Photodichroism produced by α -particles. A. M. TAYLOR (Nature, 1932, 129, 758).—Dichroism

with a known condition of arrangement of Ag particles can be produced by exposure of a fine-grained photographic plate to α -particles. The results support the view that the selective photo-electric effect plays a direct part in producing the photographic latent image. L. S. T.

Organic photochemistry. I. Spectrochemical and photochemical studies of colour sensitizers. II. Photography with organic compounds. S. SAKURAI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 681—710, 711—728).—I. The relationship between absorption spectrum and chemical constitution has been studied for colour sensitizers of the "lumol" and "illuminol" series. The photographic sensitising maxima and the sensitising limits of these compounds have been determined. II. The prep. and properties of various salts of the tetrazo-compounds of diaminodiphenyl and its derivatives with naphtholdisulphonic acid are described. They are unsuitable for photographic purposes. The diazo-compounds of diaminodiphenylamine, ammodiphenylamine, etc. are very sensitive to light. This fact is utilised in applying the theory of formation of azo-colours to photography. J. W. S.

Photosynthesis in tropical sunlight. V. Reduction of carbonic acid, hydrogen carbonates, and carbonates. N. R. DHAR and A. RAM (Z. anorg. Chem., 1932, 206, 171—173; cf. A., 1931, 1138).—Mg, Zn, or $FeCO_3$ will reduce CO_2 , CO_3^{--} , and HCO_3 to CH_2O in the dark and, with Mg or Zn, to a greater extent in sunlight. ZnO is a photosensitizer. No HCO_2H is obtained. M. S. B.

Preparing cuprous chloride solution for gas analysis. R. E. SUMMERS (Power, 1932, 75, 55).—The ppt. obtained on passing SO_2 into $CuSO_4.5H_2O$ (249.69 g.) and NaCl (87.69 g.) in H_2O (1000 c.c.) is washed quickly with saturated aq. SO_2 and dissolved immediately in 6N-HCl (500 c.c.). CH. ABS.

Fluoroberyllates and their analogy with sulphates. III. Double salts. N. N. RAY (Z. anorg. Chem., 1932, 206, 209—216).—The analogy of fluoroberyllates with sulphates (cf. this vol., 131, 582) is shown by the formation of double salts of the general formula $M^I_2BeF_4.M^{II}BeF_4.6H_2O$ in which, when M^I is NH_4 , M^{II} may be Ni, Co, Mn, Zn, Cd, Cu, or Fe^{II} ; when M^I is K, M^{II} may be Ni or Co, and when M^I is Rb M^{II} is Ni. Sulphatoberyllates have also been obtained in which more than half the BeF_4^{--} in the double salt is replaced by SO_4^{--} : $K_2Ni(SO_4.BeF_4).6H_2O$ and $(NH_4)_2Zn(SO_4.BeF_4).6H_2O$. M. S. B.

[Preparation of] beryllium from the oxide. G. D. FITZPATRICK.—See B., 1932, 553.

Transformation calcium sulphate hemihydrate \rightarrow anhydrite in moist air at atmospheric pressure. R. NACKEN and K. FILL (Tonind.-Ztg., 1931, 55, 1194—1196; Chem. Zentr., 1931, ii, 3651).—The H_2O is expelled from the stable hemihydrate at const. temp. Slow heating is necessary to obtain good heating curves of gypsum, which in a vac. at 20° changes to anhydrite. In dry air at 1 atm., it

gives off its H_2O very slowly. Equilibrium curves for the system $\text{CaSO}_4\text{--H}_2\text{O}$ have been obtained.

L. S. T.

Action of water on dicalcium phosphate. A. SANFOURCHE and J. HENRY (Compt. rend., 1932, 194, 1940—1942).—The discrepancies reported as to the action of cold H_2O on CaHPO_4 (cf. A., 1900, ii, 618; 1907, ii, 261) are due to a false equilibrium analogous to supersaturation, decomp. in the cold occurring only in presence of $\text{Ca}_3(\text{PO}_4)_2$, when $\text{CaH}_2(\text{PO}_4)_2$ passes into solution, the max. decomp. (20% after 240 hr.) occurring in a solution containing 1 g. of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ per litre. At higher temp. and with more conc. solutions decomp. starts at once, the limit at 100° , attained in 1 hr., being 7.02% CaHPO_4 decomposed. At 75° the undecomposed CaHPO_4 is present in both the hydrated (brushite) and anhyd. (monetite) forms, the former disappearing above this temp. C. A. S.

Formation of slightly soluble calcium phosphate from aqueous solution and the relation of this phosphate to the apatite group. G. TROMEL and H. MOLLER (Z. anorg. Chem., 1932, 206, 227—240).—By pptg. aq. $\text{Ca}(\text{NO}_3)_2$ with aq. Na_2HPO_4 in presence of excess of aq. NH_3 , hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is first formed, and not $\text{Ca}_3(\text{PO}_4)_2$. The behaviour of the ppt. on drying depends on the opportunity to adsorb P_2O_5 and on the subsequent calcination at 950° , which causes the adsorbed P_2O_5 to react and become part of the crystal structure. It also prevents adsorption of excess of P_2O_5 . Usually a mixture of $\beta\text{-Ca}_3(\text{PO}_4)_2$ with hydroxyapatite is obtained. The transformation to $\text{Ca}_3(\text{PO}_4)_2$ may also take place by long heating at a lower temp., e.g., 600° . M. S. B.

Hydrothermal synthesis of calcium silicates. S. NAGAI (Z. anorg. Chem., 1932, 206, 177—195).—A collection and discussion of the data, previously obtained by the author, relating to the thermal synthesis of Ca silicates, with and without H_2O vapour, under pressure, and at atm. pressure (cf. A., 1931, 1020, 1380; this vol. 131, 350; B., 1932, 25, 262).

M. S. B.

Hydrothermal synthesis of calcium aluminates and silicates from lime and alumina or kaolin. I. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 182—184b).—The combined H_2O is removed from kaolin by heating at $500\text{--}600^\circ$; only part of the Al_2O_3 content is sol. in 5% HCl after the material has been heated at 900° . $\text{Al}(\text{OH})_3$ loses H_2O at $400\text{--}500^\circ$, and the residue is easily sol. in 5% HCl if it is not heated above 800° . The composition of a wet mixture of CaO and $\text{Al}(\text{OH})_3$ (1 : 2) after heating under normal pressure at temp. between 800° and 1100° is practically the same as that of a dry mixture heated at the same temp. At 10—20 atm., however, wet mixtures of CaO with $\text{Al}(\text{OH})_3$, Al_2O_3 , or kaolin readily yield Ca aluminates and/or silicates. H. F. G.

Preparation, vapour pressures, and densities of boron trifluoride, arsenic pentafluoride, and bromine trifluoride. O. RUFF [with A. BRAIDA, O. BRETSCHNEIDER, W. MENZEL, and H. PLAUT] (Z. anorg. Chem., 1932, 206, 59—64).— SiF_4 , which is always present in BF_3 made in the usual way, cannot be separated by fractional distillation, but may be

greatly reduced in quantity by passage over B_2O_3 at 800° . BF_3 containing <1.7% SiF_4 had m. p. -128° , b. p. $-101^\circ/760$ mm., d (liquid) 2.6999—0.00642(273+ t), d (solid) 1.87 (min. val.). AsF_5 was made by direct combination of the elements; m. p. -79.8° , b. p. -52.8° , v.d. 169.5, d (liquid) 3.505—0.00534(273+ t), d (solid) 3.02 (min. val.). BrF_3 , from Br and F_2 , had m. p. 8.8° , d (liquid) 3.623—0.00277(273+ t), (solid) 3.23 (min. val.). V. p. of BF_3 and AsF_5 are given, and the chemical behaviour of AsF_5 is described. F. L. U.

Selenates of lanthanum and their solubilities in water. J. A. N. FRIEND (J.C.S., 1932, 1597—1602).—Anhyd. $\text{La}_2(\text{SeO}_4)_3$ and its 5-, 6-, 12-, and 22(?)-hydrates have been prepared and analysed, and solubilities of the last two determined between 0° and 95° . The solubility curves closely resemble those of the 12- and 22-hydrates of $\text{Nd}_2(\text{SeO}_4)_3$. F. L. U.

Mesothorium. II. G. GUEBEN (Ann. Soc. Sci. Bruxelles, 1932, [ii], 52, 60—66).— Ms II has been separated from accompanying radioactive elements and its α -radiation measured. E. S. H.

Carbon monoxide from carbonates. S. T. BOWDEN and T. JOHN (Nature, 1932, 129, 833).—Na reacts smoothly with a warm xylene solution of Ph_2CO_3 forming NaOPh and pure CO. The CO is dry enough not to explode with dried O_2 . Alkyl carbonates react in a similar manner. The reaction occurs through the intermediate formation of ketylic derivatives. L. S. T.

Decomposition of lead nitrate in molten potassium nitrate. K. LAYBOURN and W. M. MADGIN (J.C.S., 1932, 1360—1364; cf. this vol., 468).—The primary product of decomp. of $\text{Pb}(\text{NO}_3)_2$ in molten KNO_3 at 357° is $\text{PbO} \cdot 2\text{Pb}(\text{NO}_3)_2$, which is subsequently oxidised to $\text{Pb}_3\text{O}_4 \cdot 3\text{Pb}(\text{NO}_3)_2$. Each of these products is hydrolysed by boiling H_2O to form $\text{Pb}(\text{OH})\text{NO}_3$, whilst the second gives a residue of PbO_2 both when hydrolysed and when treated with dil. acids. F. L. U.

"Mineral caoutchouc" [phosphonitrilic chlorides]. P. RENAUD (Compt. rend., 1932, 194, 2054—2056).—The caoutchouc-like products obtained by heating carefully dried trimeric phosphonitrilic chloride, $\text{P}_3\text{N}_3\text{Cl}_6$ (cf. A., 1924, ii, 752), have been examined. When strongly cooled they become hard and progressively more cryst., returning to the amorphous, soft, gummy condition on warming; the changes were confirmed by X-ray examination. The products swell in C_6H_6 , and partly dissolve, the solution depositing crystals. By heating in vac. at 500° , lighter polymerides, cryst. or liquid, are produced. Mols. of $\text{P}_3\text{N}_3\text{Cl}_6$ probably unite, forming chains including cells, the connexion between which is loosened by heat (cf. A., 1923, ii, 134). C. A. S.

Dehydration of niobic acid. P. SUE (Compt. rend., 1932, 194, 1745—1747).—On drying in vac. over solid KOH niobic acid obtained by the pptn. of an alkaline solution of a niobate by aq. HCl there are doubtful indications of possible hydrates $\text{Nb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ and $\text{Nb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, but these lose H_2O over H_2SO_4 or P_2O_5 . Dehydration at 100° for 4 months, at $195\text{--}260^\circ$ and $400\text{--}540^\circ$, affords products corre-

spending with hydrates containing approx. 1, 0.66, and 0.33H₂O, respectively (cf. A., 1930, 1538).

C. A. S.

Formation of ozone at high temperatures. P. HARTECK (Z. physikal. Chem., 1932, B, 17, 120—126).—The amount of O₃ present in air or O₂ which has been passed over a heated Nernst pencil and then chilled rapidly (A., 1907, ii, 163, 340) is far greater than corresponds with the equilibrium $3\text{O}_2 \rightleftharpoons 2\text{O}_3$ at the high temp. (cf. A., 1911, ii, 1). The O₃ is probably formed by the reaction $\text{O} + \text{O}_2 = \text{O}_3$ during the cooling.

R. C.

Changes of the salts of tervalent metals in solution. C. MONTEMARTINI and E. VERNAZZA (Ind. chim., 1931, 6, 1124—1128; Chem. Zentr., 1931, ii, 3588—3599; cf. this vol., 351).—The change produced by heating and quickly cooling Cr alum solutions prepared from green solutions has been investigated. Two different forms of green Cr₂(SO₄)₃ exist. K and NH₄ Fe alums show no corresponding difference in the CO₂ evolved with Zn oxycarbonate when solutions are heated and cooled.

L. S. T.

Constitution of blue perchromic acid. R. SCHWARZ and H. GIESE (Ber., 1932, 65, [B], 871—876).—Determinations of the mol. wt. of "pyridine perchromate" in freezing C₆H₆, PhNO₂, CHBr₃, or pyridine confirm the unimol. structure. The possibility that perchromic acid is H₂CrO₅ is excluded, since it combines with only 1 mol. of org. bases, e.g., NH₂Pb, pyridine, or quinoline, is decomposed by Ag₂O with formation of Ag₂CrO₄ and O, and immediately evolves O, when brought into contact with alkali hydroxide. Its acidic character is therefore denied and it is considered to be a peroxide $\text{O}:\text{Cr}(\text{O})_2$. In support of this view the following

evidence is adduced. Decomp. of the pyridine salt (actually a mol. compound [C₅H₅N, CrO₅]) with dil. H₂SO₄ yields a Cr⁺⁺⁺ salt and O, $2\text{CrO}_5 = \text{Cr}_2\text{O}_3 + 7\text{O}$. Decomp. of the peroxide in Et₂O by Ag₂O occurs thus: $\text{CrO}_5 = \text{CrO}_3 + 2\text{O}$. Titration with KMnO₄ in neutral solution gives chromate and consumes 4 equivs. of O, showing thus 2·O·O· groups; $\text{CrO}_5 + 2\text{H}_2\text{O} = \text{CrO}_3 + 2\text{H}_2\text{O}_2$ and $2\text{H}_2\text{O}_2 + 2\text{O} = 2\text{H}_2\text{O} + 2\text{O}_2$. The stability of the compound in Et₂O is ascribed to the production of an etherate. The metal is sexavalent in the peroxide.

H. W.

Molybdenum sesquisulphide. GUICHARD (Bull. Soc. chim., 1932, [iv], 51, 563—564).—Failures to prepare Mo₂S₃ (cf. *inter alia*, Picon, A., 1929, 1012) result from heating MoS₂ in a vac., whereas, as originally stated (A., 1901, ii, 659), it is obtained only when MoS₂ is heated under ordinary pressure.

Boro-molybdic blue. P. CRISTOL and J. CAYLA (Compt. rend., 1932, 194, 1942—1944).—On adding Deniges' sulphomolybdic reagent (cf. A., 1920, ii, 770) and SnCl₂ to aq. Na borate in the cold a blue coloration is formed. If hot, Cu or Al may replace SnCl₂. A mixture of Na borate, a mineral acid, an alkali molybdate, and Et₂O exposed to sunlight turns blue. From the aq. solution acidified with H₂SO₄, Et₂O extracts the blue compound, and H₂O removes it from Et₂O solution. When purified by repeated

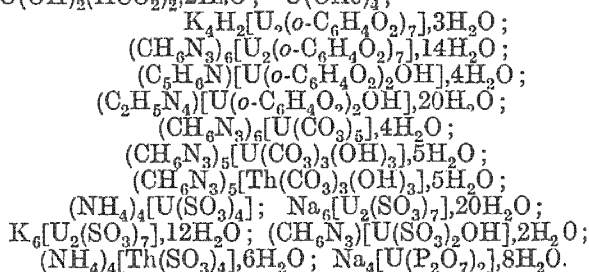
alternate extractions from H₂O and Et₂O it contains B, and is very readily oxidised to a yellow solution, whilst when further reduced it becomes violet-rose. On keeping rhombohedral crystals are deposited. It is stable in presence of Na borate. Si, V, and other elements produce similar compounds.

C. A. S.

Quantitative separation of tungsten monocarbide from hemicarbide and tungsten, and conditions of formation of the carbides. I. IITAKA and Y. AOBI (Bull. Chem. Soc. Japan, 1932, 6, 108—114).—When W and C are heated together the proportion of WC formed increases from 3% at 1600° to 42% at 2500°, and the product always contains W₂C (40—80%). The presence of Fe is not necessary. WC is not noticeably decomposed into W₂C and C even on slow cooling. A method of separation of WC from reaction products is based on the fact that it does not react with Cl₂ below 600°, whereas both W and W₂C are converted into volatile chlorides below 550°.

F. L. U.

Compounds of quadrivalent uranium [and thorium]. A. ROSENHEIM and M. KELMY (Z. anorg. Chem., 1932, 206, 31—43).—The following compounds are described: UCl₄·10H₂O; (C₅H₅N)₄UCl₆·2H₂O; U(OH)₂(HCO₂)₂·2H₂O; U(OAc)₄;



F. L. U.

Esters of fluorosulphonic acid. J. MEYER and G. SCHRÄMM (Z. anorg. Chem., 1932, 205, 24—30).—A nearly quant. yield of FSO₃H is obtained by distilling a mixture of oleum with KHF₂. The dry acid, b. p. 110°/120 mm., 77°/19 mm. *d*₄¹⁵ 1.740, does not attack glass. Many reactions are described. Me₂O and Et₂O give the corresponding esters as colourless liquids immiscible with, but readily hydrolysed by, H₂O. FSO₂·OMe has b. p. 92°, 45°/160 mm., *d*₄¹⁶ 1.427. FSO₂·OEt has b. p. 113°/752 mm., 24°/12 mm., *d* 1.310.

F. L. U.

Rhenium trioxide. W. BILTZ and G. A. LEHRER [with K. MEISEL] (Nachr. Ges. Wiss. Göttingen, 1931, 191—198; Chem. Zentr., 1932, i, 1070).—ReO₃ was prepared by reduction of Re₂O₇ (by oxidation of Re in O₂ at 360—400°) with finely-divided Re (by reduction of NH₄ReO₄) in a sealed tube at 200—250° followed by oxidation with Re₂O₇ at 250°. The m. p. (vac.) of Re₂O₇ is 301.5°; sublimation begins at 220°. ReO₃ is attacked by HNO₃, but not by hot HCl. Disproportionation occurs on thermal decomp. or by dissolution in NaOH. The unit cube has *a* 3.73 Å.; *d*_{obs.} 6.9, *d*_{calc.} 7.4. A. A. E.

Rhenium oxychlorides. A. BRUKL and K. ZIEGLER (Ber., 1932, 65, [B], 916—918).—The interaction of ReCl₄ and Re₂O₇ affords oxychlorides separable from one another with great difficulty.

Re trioxychloride, ReO_3Cl , m. p. $+4.5^\circ$, b. p. 131° (corr.), is prepared by passing O_2 through a tube containing Re in two boats placed so that one can be heated without affecting the other. The front boat is gently warmed, whereby the metal is converted into Re_2O_7 . O_2 is replaced by Cl_2 , and the rear boat is heated, thus giving ReCl_4 , which reacts with Re_2O_7 giving a mixture of oxychlorides condensed at -65° and fractionated. It is readily hydrolysed to perhenic acid and HCl . *Re oxytetrachloride*, ReOCl_4 , m. p. 29.3° , b. p. 223° , is obtained by the action of O_2 on ReCl_4 . When heated in O_2 it passes into ReO_3Cl . H. W.

Ferryll ion, a compound of quadrivalent iron. W. C. BRAY and M. H. GORIN (J. Amer. Chem. Soc., 1932, 54, 2124—2125).—The results of kinetic investigations point to the formation of FeO^{++} as an intermediate compound, and agree with the theory that $2\text{Fe}^{+++} + \text{H}_2\text{O} = \text{Fe}^{++} + \text{FeO}^{++} + 2\text{H}^+$ is a reversible and fairly rapid reaction. C. J. W. (c)

γ -Ferric oxide hydrate. O. BAUDISCH and W. H. ALBRECHT (J. Amer. Chem. Soc., 1932, 54, 943—947).—The γ -hydrate (A., 1929, 869), as well as the α -hydrate, is formed by autoxidation of aq. $\text{Fe}(\text{HCO}_3)_2$. The O-complex theory (A., 1924, i, 1141; 1928, 856) is supported by the formation of the γ -hydrate by atm. oxidation of aq. FeCl_2 and in presence of certain org. N compounds. Magnetic data for the γ -hydrate are given. W. C. F. (c)

Preparation of hexamminetrioldicobaltic chloride and of nuclear polymers. T. DAS-GUPTA and P. B. SARKAR (J. Indian Chem. Soc., 1932, 9, 79—82).—By treating dichloroaquatriaminicobaltic chloride with hexamethylenetetramine instead of with NaOH , the yield of hexamminetrioldicobaltic chloride ($=[\text{A}]\text{Cl}_3$) is increased from 12.5 to 62.5%. Treatment of the latter substance with $\text{Na}_2\text{S}_2\text{O}_3$ gives the *thiosulphate*, $[\text{A}]_2(\text{S}_2\text{O}_3)_3 \cdot 4\text{H}_2\text{O}$, a red powder insol. in H_2O . *Dodecamminehexoltetracobaltic thiosulphate*, $[\text{Co}^{\text{III}}(\text{OH})_2\text{Co}(\text{NH}_3)_4]_3(\text{S}_2\text{O}_3)_3 \cdot 4\text{H}_2\text{O}$, a co-ordination isomeride of the former product, is obtained as black crystals on treating the corresponding nitrate with $\text{Na}_2\text{S}_2\text{O}_3$. F. L. U.

Double and complex salts and circular dichroism. J. P. MATHIEU (Compt. rend., 1932, 194, 1727—1729).—If excess of aq. Na_2 tartrate is added to a Co^{++} solution rosettes of pale rose needles are formed of (dried at 120°) $\text{Na}_2\text{Co}(\text{C}_4\text{H}_4\text{O}_6)_2$, behaving as an ordinary double salt. If to a mixture of equal vols. of $2M$ - $\text{Co}(\text{NO}_3)_2$ and $2M$ - $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ $4M$ - NaOH is added until the ppt. first formed is redissolved, and then slowly, with agitation, more aq. NaOH , a red transparent jelly forms; when kept in a closed vessel this changes to a very easily oxidised solution, and deposits rose-coloured microscopic crystals of (dried at 120°) $\text{Na}_2\text{CoC}_4\text{H}_4\text{O}_6$. This behaves as a complex salt, probably $\text{Na}_2[\text{CoC}_4\text{H}_4\text{O}_6] \cdot n\text{H}_2\text{O}$. Although solutions of both salts show similar absorption bands, their optical activities are different, and only the latter exhibits circular dichroism. C. A. S.

Application of crystallographic measurements to the identification and determination of chemi-

cal products. P. TERPSTRA (Natuurwetensch. Tijds., 1932, 14, 168—170). H. F. G.

Neutral, buffered standard for hydrogen-ion work and accurate titrations, which can be prepared in one minute. R. J. WILLIAMS and C. M. LYMAN (J. Amer. Chem. Soc., 1932, 54, 1911—1912).—The p_H of NH_4OAc solution over a wide range of concn. is almost exactly 7. W. T. H. (c)

Glass electrode in titrimetric work and precipitation reactions. Application of the principle of solubility product to basic precipitates. H. T. S. BRITTON and R. A. ROBINSON (Trans. Faraday Soc., 1932, 28, 531—545).—For accurate work, frequent calibration of the glass electrode is necessary, especially in strongly alkaline solution, and this is effected conveniently by means of the titration of a universal buffer solution (A., 1931, 910). The electrode affords accurate p_H vals. between 2 and 12 in buffered solutions, and errors accompanying the titration of unbuffered solutions are confined to narrow regions in which large variations of p_H val. occur. In general, the results are not affected by ppts. The p_H curves (determined by glass electrode) for the titration of Zn salts with NaOH do not agree with those of others (A., 1931, 565, 1260; cf. A., 1925, ii, 1203). Reasons for the discrepancy are discussed. Whilst the solubility product principle applies to p_H data for the pptn. of AgOH , the use of the p_H val. at a single point in the formation of a basic ppt. does not, in general, lead to an accurate knowledge of the true solubility product. J. G. A. G.

Determination of active hydrogen in small quantities of substances by the method of Tschugaev and Zerevitinov. H. ROTH (Mikrochem., 1932, 11, 140—156).—Errors in the micro-determination of CH_4 produced in a reaction $\text{MeMgI} + \text{ROH} = \text{CH}_4 + \text{ROMgI}$ due to the presence of air or moisture can in practice be eliminated by careful drying of the apparatus and by working in an atm. of dry N_2 . A further error, arising from the production of C_2H_6 when the temp. exceeds 50° , has been traced to the presence of MeI as an impurity, and may be avoided by using MeOPh instead of $(\text{C}_5\text{H}_{11})_2\text{O}$ as a solvent. Details of tests are given. F. L. U.

Determination of ozone in ozonised air. E. H. RIESENFELD; P. KRAIS and H. MARKERT.—See B., 1932, 546.

Determination of water by distillation with liquids lighter than water. H. LUNDIN and M. LUNDIN.—See B., 1932, 531.

Alkalimetric micro-determination of chlorine and bromine in organic substances. M. K. ZACHERL and H. G. KRAINICK (Mikrochem., 1932, 11, 61—73).—4—6 mg. of the substance are mixed with $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Ag}_2\text{Cr}_2\text{O}_7$, and the mixture is heated with conc. H_2SO_4 at 115 — 125° , whilst a stream of O_2 carries the liberated Cl_2 or Br into an absorption vessel containing a measured quantity of $0.01N$ - NaOH to which H_2O_2 has been added. The alkali used ($\text{Cl}_2 + 2\text{NaOH} + \text{H}_2\text{O}_2 = 2\text{NaCl} + \text{O}_2 + \text{H}_2\text{O}$) is then determined by titration. The method is rapid and accurate, but cannot be used for very volatile substances. F. L. U.

Quantitative re-formation of iodine by acidifying an alkaline iodine-potassium iodide solution. M. KOHNE (Z. anal. Chem., 1932, 88, 161—170).—The I in an I-KI solution, which has been transformed into a mixture of IO_3' and I' by the addition of alkali, is not quantitatively re-formed by acidifying. In a 0.1N solution the loss is 0.3—0.5%, in agreement with the results of King and Jette (A., 1930, 441). The error is not sufficient to render the iodometric method useless for the determination of $\text{S}_2\text{O}_8''$. The abnormally large errors observed by other investigators are probably due to impurities in the KI. In 0.01N solution the error is very much larger than in 0.1N-I and varies with alkali of different origin, even when analytically pure. The error is not proportional to the amount of OH' and is probably not due to impurities, but is the result of a slight decomp., with evolution of O_2 , of the KIO formed intermediately, or of a slight volatility of free I in alkaline solution. The error is increased by the presence of large quantities of neutral salt.

M. S. B.

Iodometric determination of total sulphur in polysulphides. P. SZEBERENYI (Z. anal. Chem., 1932, 88, 187—189).—The method depends on the fact that, by direct titration of Na_2S_x with I, NaI and S are formed, but if the solution is made alkaline with NaOH and heated with excess of I solution S is oxidised to SO_4'' and, by acidifying, the unused I is set free from the NaIO and NaI formed in the reaction and can be titrated. A correction must be made for $\text{Na}_2\text{S}_2\text{O}_3$ which is always present and is also oxidised to SO_4'' . The amount of $\text{Na}_2\text{S}_2\text{O}_3$ present can be determined by the titration to $\text{Na}_2\text{S}_4\text{O}_6$ after treating with excess of Zn or Cd acetate and filtering to remove sulphide. The amount of I used by the oxidation of $\text{Na}_2\text{S}_2\text{O}_3$ to Na_2SO_4 is 8 times that required for oxidation to $\text{Na}_2\text{S}_4\text{O}_6$, so this quantity must be subtracted from the total I required for the complete oxidation. The result may be controlled by titration of the H_2SO_4 formed.

M. S. B.

Analysis of hydrogen sulphites. A. PONTE (Boll. Uff. Staz. sperim. Ind. Pelli, 1932, 10, 155—161).—When a solution containing both H sulphite and sulphite is titrated (phenolphthalein), 1 c.c. of N-NaOH=0.064 g. of SO_2 semi-combined as HSO_3 and not, as stated in various text-books, 0.032 g.

T. H. P.

Analysis of hyposulphite by means of azo-dyes. V. I. MINAEV, S. S. FROLOV, and G. M. MATOROV.—See B., 1932, 545.

Volumetric determination of persulphate ion. A. KURTENACKER (Z. anal. Chem., 1932, 88, 171—172).—The error previously observed in the iodometric determination of $\text{S}_2\text{O}_8''$ (A., 1931, 451) was apparently due to the presence, even in the purest commercial KI, of a small quantity of org. impurity with a strong reducing action in alkaline solution. When this is absent the method gives very accurate results.

M. S. B.

Volumetric determination of persulphate. J. H. VAN DER MEULEN (Z. anal. Chem., 1932, 88, 173—179).—The iodometric determination of $\text{S}_2\text{O}_8''$ is not influenced by an excess of pure KI. A 20—40%

excess of NaOH or KOH over that theoretically required is desirable, but a larger excess has no influence. The presence of a few drops of aq. OsO_4 catalyses the IO_3' formation and helps to check the action of any reducing agent present. Boiling the liquid is not necessary. It should be gently warmed on the water-bath until colourless. Very accurate results are obtained. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ cannot be determined by this method and NH_4 salts must not be present. Persulphates, including $(\text{NH}_4)_2\text{S}_2\text{O}_8$, may also be determined by heating with 3—4 times the equiv. of pure neutral H_2O_2 and titrating the H_2SO_4 formed.

M. S. B.

Volumetric micro-determination of ammonia. T. TEORELL (Biochem. Z., 1932, 248, 246—255).—The solution containing 0.0005—0.02 mg. of $\text{NH}_3\text{-N}$ is treated with excess of NaOBr and the excess is titrated with acid solution of naphthyl-red. The p_H of the NH_3 solution must lie between 8.5 and 9.0. Since various substances interfere it is preferable to distil the NH_3 as in the Kjeldahl method, using for this purpose a modification of the apparatus of Parnas and Wagner (*ibid.*, 1926, 173, 224). The error is 1—4%.

W. M.

Determination of nitrate in the sea by means of reduced strychnine. L. H. N. COOPER (J. Marine Biol. Assoc., 1932, 18, 161—166).—The method gives satisfactory results if the H_2SO_4 is heated for 2 hr. at 300° with crystals of $(\text{NH}_4)_2\text{SO}_4$. Org. material in sea-water interferes with the determination; during periods of plankton activity the samples should be centrifuged. The effect of IO_3' at the usual concns. in sea-water is negligible. Discordant results may be obtained in presence of relatively large amounts of NO_2' .

E. S. H.

Nitrate in sea-water and its determination by means of diphenylbenzidine. W. R. G. ATKINS (J. Marine Biol. Assoc., 1932, 18, 167—189).—The diphenylbenzidine method is recommended for sea-water; the intensity of the coloration is increased by the presence of NaCl. Substitution of H_3PO_4 for H_2SO_4 , although allowable in determining NO_3' in H_2O , is not permissible in sea-water. Fe''' causes no error in sea-water, although it gives the reaction; I , AsO_3''' , and AsO_4''' do not interfere; IO_3' , if present, should be removed with dil. aq. NaHSO_3 or NaI. The colour produced in the reaction is stable to light and may be matched in diffused daylight with indigo-tinmonosulphonate.

E. S. H.

Electrometric determination of hypophosphoric acid. L. WOLF, W. JUNG, and L. P. USPENSKAYA (Z. anorg. Chem., 1932, 206, 125—128; cf. this vol., 135).— H_2PO_3 may be determined by potentiometric titration with AgNO_3 , within limits of p_H secured by first neutralising free acid with NaOH and by using Na_2HPO_4 as a buffer. Examples are given.

F. L. U.

Detection of arsenic, phosphoric, and arsenious acids in admixture with one another and with other anions. N. A. TANANAEV and C. N. POTSCHINOK (Z. anal. Chem., 1932, 88, 271—278).— PO_4''' may be detected in the presence of AsO_4''' by the molybdate test if the AsO_4''' is first reduced with

SO_2 . AsO_4''' is pptd. by AgNO_3 from conc. AcOH before pptn. of PO_4''' or AsO_3''' occurs. For the detection of H_3AsO_3 and H_3PO_3 in the presence of H_3AsO_4 and H_3PO_4 the latter two acids are removed by pptn. with aq. NH_3 and MgCl_2 , the filtrate is oxidised with H_2O_2 , and any further ppt. tested for AsO_4''' and PO_4''' . A. R. P.

Determination of carbon dioxide and of alkalinity in hypochlorite. A. VASSILIEV and H. STUTZER.—See B., 1932, 545.

Silicic acid and silicates. III. Determination of silica in soluble silicates. F. W. MEIER and O. FLEISCHMANN.—See B., 1932, 549.

Separation and determination of alkali metals, using perchloric acid. IV. Perchlorato-chloroplatinate method for determination of potassium in presence of sodium. G. F. SMITH and A. C. SHEAD (J. Amer. Chem. Soc., 1932, 54, 1722—1730).—The Na and K are converted into perchlorates by evaporating twice with HClO_4 and heating at 450° , and then weighed. The mixture is dissolved in the min. amount of H_2O , and K_2PtCl_6 pptd. with EtOH and H_2PtCl_6 , washed with 85% EtOH , and weighed. Good results are obtained with 1 g. of alkali chloride containing 1%, but not less, of KCl. W. T. H. (c)

Determination of potassium by the cobaltinitrite method. W. Ü. BEHRENS (Z. Pflanz. Dung., 1932, 24, A, 289—293).—Variations in the composition of the K cobaltinitrite ppt. and in titration vals. induced by varying conditions of pptn. are avoided by the following technique. The NH_3 -free test solution containing ≥ 8 mg. K_2O is acidified with HCl and evaporated dry in a porcelain dish. The residue is dissolved in 2 c.c. of H_2O , 1 c.c. of NaNO_2 solution is added followed by 2 c.c. of cobalt solution, the mixture being stirred rapidly during and for 1 min. after the addition; the whole operation is carried out with cold solutions. After 30 min. the dish is heated on a water-bath for 3 min., cooled, and the liquid filtered on a porcelain filter. The ppt. is washed four times with 2.5% Na_2SO_4 solution. The crucible and contents are immersed in 70 c.c. of H_2O , 1—2 c.c. of 50% H_2SO_4 , and excess of KMnO_4 , previously warmed. After all ppt. is dissolved a portion of the liquid is used to remove any ppt. adhering to the original dish. Excess of KMnO_4 is finally determined by titration with $\text{H}_2\text{C}_2\text{O}_4$. A. G. P.

Micro-chemical determination of potassium. B. V. J. CUVELIER (Natuurwetensch. Tijds., 1932, 14, 107—110).—K (0.005—0.05 mg.) may be determined colorimetrically by centrifugal separation as K_2PtCl_6 , dissolution of the ppt. in H_2O , and addition of NaI solution. A calibration curve for use with the Pulfrich colorimeter is reproduced. The gravimetric K_2PtCl_6 method is accurate to within 0.5% for 1 mg. or more of K, when a micro-filter is employed, but by use of the centrifuge 0.05 mg. may be determined with no greater error. H. F. G.

Determination of potassium and sodium iodides. L. W. WINKLER (Pharm. Zentr., 1932, 73, 324—326).— KBr , CCl_4 , and fuming HNO_3 are added successively and the liquid is titrated with KBrO_3 until the CCl_4 is practically colourless after shaking.

I is at first pptd., but is converted into IBr , which is found entirely in the aq. layer at the end of the titration. The procedure is designed especially for determining the purity of samples of KI or NaI , but may also be used for the determination of I' in the presence of Cl' and Br' . E. S. H.

Solubility of uranyl zinc sodium acetate in alcohol of different concentrations. G. W. B. VAN DER LINGEN (Analyst, 1932, 57, 376—377).—Data are given showing the error introduced into the colorimetric determination of Na by the $\text{NaZn}(\text{UO}_2)_3(\text{OAc})_9$ method by the presence of different proportions of EtOH . Solubility vals. at 25° are also given for the triple salt in EtOH of concns. varying from 50% to abs. M. S. B.

Catalytic detection of extremely dilute silver solutions (also lecture experiment). F. L. HAHN (Ber., 1932, 65, [B], 840—842).—Very minute amounts of dissolved Ag can be detected by the acceleration of the reduction of HgCl_2 to HgCl by NaH_2PO_2 . H. W.

Technical analysis of calcium carbide. H. A. J. PIETERS and H. S. VISSER.—See B., 1932, 463.

Electrochemical methods in the chemistry of radioactive elements. O. ERBACHER (Naturwiss., 1932, 20, 390—393).—Certain radioactive elements can be separated from one another by rotating a freshly annealed and roughened Pt sheet in the solution which is kept in an atm. of H_2 . The H adsorbed on the Pt replaces the elements in solution and causes them to be deposited on the Pt. In this way Ra-E and Po may be separated from Ra-D in 0.1N- H_2SO_4 , and from one another by deposition of Po in 12% HCl after addition of a minute amount of Bi. Th-B and -C are deposited in a similar way from 0.1N-KOH, and Th-C alone is deposited from 0.1N-HCl after addition of 1 mg. of PbCl_2 . Po is deposited free from Ra-E on a Au sheet in N-HCl-0.9M- $\text{CS}(\text{NH}_2)_2$. In all cases a repetition of the procedure is necessary for complete separation. A. R. P.

Potentiometric determination of zinc in coloured alloys. V. F. STEFANOVSKI.—See B., 1932, 553.

Analysis of red lead and lead peroxide. N. BUSVOLD.—See B., 1932, 474.

Determination of lead peroxide. IV. A. V. PAMFILOV and E. G. IVANČEVA.—See B., 1932, 546.

Rhenium. IV. Halogeno-compounds of rhenium. F. KRAUSS and H. DAHLMANN (Ber., 1932, 65, [B], 877—880; cf. A., 1931, 1382).—The brown product of the reduction of K perrhenate with KI and conc. HCl is regarded as $\text{K}_3[\text{Re}^{\text{III}}\text{Cl}_3]$ (cf. Manchot and others, this vol., 133); K_2ReCl_6 is yellow and the "yellowish-green salt" is a hydrolytic product, $\text{K}_2[\text{Re}^{\text{IV}}\text{Cl}_5\cdot\text{OH}]$, which has not been prepared homogeneous. In the reduction of K_2ReCl_6 by Zn and HCl (*loc. cit.*) the green solution is caused by hydrolysis of K_2ReCl_6 as the concn. of the acid gradually falls. The following salts are described: Cs_2ReCl_4 ; $\text{Cs}_2[\text{ReCl}_5\cdot\text{OH}]$; Rb_2ReCl_6 ; $\text{Rb}_2(\text{ReCl}_5\cdot\text{OH})$;

K_2ReCl_6 ; $K_2[ReCl_5 \cdot OH]$; $CsReBr_6$; $Cs_2[ReBr_5 \cdot OH]$; Rb_4ReBr_6 ; K_2ReBr_6 ; Cs_2ReI_6 ; K_2ReI_6 ; Na_2ReI_6 .
H. W.

Determination of iron in solutions containing both bivalent iron and trivalent titanium. W. M. THORNTON, jun., R. ROSEMAN, and S. I. KATZOFF (J. Amer. Chem. Soc., 1932, 54, 2131—2132).— Fe^{++} may be determined in presence of Ti^{+++} by bubbling air through the solution, oxidation of the Ti^{+++} being complete before the Fe^{++} is appreciably oxidised.

C. J. W. (c)

Oxidation reaction with ferricyanides. L. ROSENTHALER (Chem.-Ztg., 1932, 56, 441).—Addition of 0.1% of $K_3Fe(CN)_6$ and 1% $Pb(OAc)_2$ solution to a 1% solution of pyrimidone produces a blue coloration, $Pb_2Fe(CN)_6$ being formed. A similar reaction occurs with the ferricyanides of most of the heavy metals, including Sn (despite its powerful reducing action), but not with those of the alkalis and alkaline earths. Pyrogallol and apomorphine also are oxidised by $K_3Fe(CN)_6$ more rapidly in presence of a heavy metal.

H. F. G.

Micro-electrolytic determination of nickel and cobalt. A. OKAC (Z. anal. Chem., 1932, 88, 189—194).—The quant. separation of Ni and Co, both separately and together from a mixed solution, may be carried out in aq. NH_4 by a micro-electrolytic method similar to that described for Cu (this vol., 590).

M. S. B.

Potassium dithio-oxalate colorimetric method for determination of nickel. J. H. YOE and F. H. WIRSING (J. Amer. Chem. Soc., 1932, 54, 1866—1876).—Addition of Ni^{++} to aq. $K_2C_2O_4S_2$ produces a deep magenta colour. For colorimetric purposes the best results are obtained with a 0.05% solution of reagent when the Ni solution contains 10 mg. of Ni per litre. Many ions, particularly Fe and Co, interfere.

W. T. H. (c)

Characteristic reaction for violet solutions of chromic salts. C. MONTEMARTINI and E. VERNAZZA (Boll. Uff. Staz. sperim. Ind. Pelli, 1932, 10, 29—33, 98—104).—The compositions of the ppts. obtained by adding various proportions of $KHCO_3$ and $ZnSO_4$, $ZnCl_2$, or $Zn(NO_3)_2$ solutions to solutions of Cr alum, $CrCl_3$, and $Cr(NO_3)_3$, respectively, have been examined. Under certain conditions a definite compound, $Cr_2O_3 \cdot 4ZnO \cdot SO_3$, is pptd. from violet solutions of a Cr^{+++} salt.

H. F. G.

Potentiometric determination of chromate in alkaline solution by means of vanadyl sulphate. C. DEL FRESNO and E. MAIRLOT (Anal. Fis. Quím., 1932, 30, 254—259).— CrO_3^{--} may be determined satisfactorily by potentiometric titration in alkaline solution with $VOSO_4$ at 70° provided that the solution contains not less than 15% of NaOH. If insufficient NaOH is present $Cr(OH)_3$ is pptd. and adsorbs $VOSO_4$, and hence high results are obtained.

H. F. G.

Solid cadmium amalgam in volumetric analysis. S. KANEKO and C. NEMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 185B).—Solutions of, e.g., molybdates or Fe^{+++} salts may be reduced in presence of H_2SO_4 by 15% Cd amalgam. The solution should be warmed to melt the amalgam, and after reduction is complete a Pt wire is introduced

into the flask so that when the mixture is cooled the solidified amalgam adheres to the wire and may easily be withdrawn.

H. F. G.

Complete analysis of wolframite. W. STAHL.—See B., 1932, 511.

Analytical applications of sodium hydrosulphite [hyposulphite]. II. Separation of tin from copper, zinc, lead, etc. and from oxalic acid. Determination of tin in steel. B. S. EVANS (Analyst, 1932, 57, 362—368).—Sn can be pptd. as SnS together with metallic Pb, Bi, and Sb, by $Na_2S_2O_4$ in aq. KCN, if $(NH_4)_2S$ is also present, and the method can be used in the determination of Sn in the presence of Cu. Details are given for the determination of Sn in bronze and brass. The separation of Sn from Pb is based on the fact that the pptn. of SnS is inhibited by excess of alkali, whilst that of Pb by $Na_2S_2O_4$ is not. A complete separation of Sn and Sb could not be made. Determinations of Sn in steel are best made by using a known quantity of Sb as co-precipitant. If Clarke's $H_2C_2O_4$ method is used for the separation of Sb from Sn, the latter can be separated subsequently from the $H_2C_2O_4$ solution by $Na_2S_2O_4$ and aq. NH_3 .

M. S. B.

Potassium stannodichlorotetrachloride in volumetric analysis. T. KARANTASSIS and L. CAPATOS (Compt. rend., 1932, 194, 1938—1940).— $K_2[SnCl_4(H_2O)_2]$ is prepared by adding a conc. solution of 15.5 g. of KCl to one of 14.9 g. of $SnCl_4$, with sufficient HCl to prevent any ppt. forming. The mixture is heated on the water-bath, and on cooling slowly (rapid cooling produces the mono-aquo-compound) it crystallises out and can be recryst. from hot aq. HCl. It forms stable, non-hygroscopic, rhombic bipyramids, slowly sol. in H_2O (when it oxidises rapidly if in air), more quickly in hot aq. HCl. For titrations a weighed quantity is dissolved in H_2O to which a little $NaHCO_3$ and HCl have been added, and the $KMnO_4$, I, etc. solution added; the reactions are: $2KMnO_4 + 5K_2[SnCl_4(H_2O)_2] + 16HCl = 5SnCl_4 + 12KCl + 2MnCl_2 + 18H_2O$, and $2I + K_2[SnCl_4(H_2O)_2] + 2HCl = SnCl_4 + 2HI + 2KCl + 2H_2O$.

C. A. S.

Gravimetric separation and determination of titanium. H. T. BEANS and D. R. MOSSMAN (J. Amer. Chem. Soc., 1932, 54, 1905—1911).—The cold solution, containing in 200 c.c. about 0.1 g. of TiO_2 and 27 c.c. of conc. HNO_3 , is pptd. by gradual addition, with stirring, of a slight excess of 10% aq. KIO_3 containing a little HNO_3 . After being stirred occasionally for 1 hr. the $Ti(IO_3)_4$ is filtered off and washed with $N-HNO_3$ containing 2% of KIO_3 , and then SO_2 is passed into the solution in 15 c.c. of conc. HCl until no brown colour of liberated I remains. After dilution to 300 c.c., $Ti(OH)_4$ is pptd. with aq. NH_3 , ignited, and weighed as TiO_2 . If Zr is present, 35 c.c. of "super-oxol" are added to the solution of Zr and Ti in 0.3N- H_2SO_4 to convert Ti into pertitanic acid, so that addition of KIO_3 ppts. only $Zr(IO_3)_4$. After boiling the filtrate with 9 c.c. of H_2SO_4 to decompose the pertitanic acid and H_2O_2 , Ti is determined as above.

W. T. H. (c)

Colorimetric determination of vanadium in titanomagnetites. K. BOLCHAKOV (Tsvet. Met., 1931, 6, 487—493).—The ore (1 g.) is evaporated to

dryness with aqua regia (60 c.c.), the residue being dissolved in HNO_3 (d 1.4, 20–30 c.c.), conc. to small vol., diluted with hot H_2O , and filtered. The residue is washed with dil. HNO_3 , the filtrate evaporated to dryness, heated with HNO_3 (d 1.2, 20 c.c.), and treated with AgNO_3 solution (1–2 c.c.). After boiling, keeping, and filtering, KMnO_4 (8 g. per litre, 10 c.c.) is added to the filtrate, which is boiled until the org. matter is destroyed; MnO_2 is removed with H_2O , the excess being removed by boiling. The solution is diluted to 100 c.c., 10 c.c. of which are treated with HNO_3 (d 1.2, 18 c.c.) and H_3PO_4 (10 c.c.) and diluted to 80 c.c.; then freshly prepared 10% NH_4 molybdate solution (10 c.c.) is added, and the colour compared with that obtained from a standard solution containing 0.2 mg. of V_2O_5 . CH. ABS.

Volumetric assay of gold. W. B. POLLARD.—See B., 1932, 511.

Vacuum calorimeter for high temperatures. L. G. CARPENTER and T. F. HARLE (Proc. Physical Soc., 1932, 44, 383–399).—A form of the Pt thermometer type of calorimeter, in which heat is transferred from the Pt coil to the calorimeter by radiation, is described. Being free from org. insulating materials it is suitable for the determination of true sp. heats at high temp. The general principles of vac. calorimetry are discussed and applied to the design. N. M. B.

Temperature control closet for adiabatic calorimetry. B. C. HENDRICKS and W. H. STEINBACH, jun. (J. Physical Chem., 1932, 36, 1279–1281). H. F. J. (c)

Micro-determination of m. p. and micro-sublimation. L. KOFLER (Arch. Pharm., 1932, 270, 293–303).—A description of the necessary apparatus and technique, and some results achieved.

Simple apparatus for micro-determination of m. p. and micro-sublimation. P. N. SCHURHOFF (Arch. Pharm., 1932, 270, 363–365). R. S. C.

Experiments to lower the temperature limit. W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 136–143).—A temp. of 0.71° abs. has been reached in a vol. of 5 c.c. by drawing off the vapour from liquid He. The lowest pressure obtained was 3.6μ Hg. A vessel for transporting liquid He is described. M. S. B.

Precision thermo-junction needle. R. W. BROWN (J. Sci. Instr., 1932, 9, 198–200).—A thermocouple is held inside a hypodermic needle, in the mounting of which is a small heating coil to prevent loss of heat by conduction. C. W. G.

Temperatures reached with solid carbon dioxide. J. H. AWBERY (J. Sci. Instr., 1932, 9, 200–202).—The temp. of solid CO_2 varies from -78.5° to about -95° , depending on the surface area and the rate at which gaseous CO_2 is removed. C. W. G.

Calibration of the scale of spectral apparatus. G. NEUMANN (Biochem. Z., 1932, 248, 208–217).—A further error is detected in spectrophotometric determinations (cf. Schlesinger, A., 1931, 1026) and the best method of calibration to obviate it is discussed. P. W. C.

"Spekker" photometer for ultra-violet spectrophotometry. F. TWYMAN (Trans. Opt. Soc., 1932, 33, 9–19). N. M. B.

Photo-electric spectro-photometer. F. C. SMITH and E. R. HOLIDAY (Trans. Opt. Soc., 1932, 33, 20–25).—The source of radiation is a H discharge tube. Absorption measurements may be made in the ultra-violet without the use of calibrated wedges or sectors. N. M. B.

Photo-electric cell and its applications. Automatic electrophotometer for light absorption measurements. G. GOLLOW (Chem. Fabr., 1932, 161–163).—The theory of the photo-electric cell is outlined and various commercial cells and suitable electrical circuits are described. Details are given of a new automatic electro-photometer in which the light intensity is measured in terms of the time required for the grid of a thermionic valve to be charged to a given potential by the photo-electric cell on which the light falls; the apparatus may be used for purposes such as determination of turbidity and depth of colour of solutions. H. F. G.

Photo-electric cell in chemical analysis. F. GONZALEZ (Anal. Fis. Quím., 1932, 30, 307–310).—The method of utilising photo-electric cells in colorimetric analysis is outlined. H. F. G.

Projection of the ultra-violet spark spectrum. B. K. JOHNSON (J. Sci. Instr., 1932, 9, 202–203).—An account of a demonstration. C. W. G.

X-Ray micrograph for the examination of metallic specimens. S. ZEIDENFELD (J. Sci. Instr., 1932, 9, 195–198).—The glancing-angle method is used and the X-rays are deviated about 180° . Specimens of any shape can be used. C. W. G.

Determination of refractive indices. A. BIOT (Ann. Soc. Sci. Bruxelles, 1932, [ii], 52, 58–60).—Slight modifications of the method formerly proposed (*ibid.*, 47, 5) permit the determination of n with an accuracy of 0.00001. E. S. H.

Circulating apparatus for experiments with streaming liquids. R. SCHMIDT (Chem. Fabr., 1932, 189–190).—The apparatus is specially suitable for experiments on corrosion. E. S. H.

Continuous laboratory filtration. L. KAUFMANN (Chem. Fabr., 1932, 163–164).—The apparatus described employs an ordinary Buchner funnel, which can readily be replaced when it is desired to change the filter, and is provided with means of sampling the filtrate, returning the filtrate for re-filtration, and washing the residue continuously. H. F. G.

Production of membranes, dialysis sacs, etc. from pure cellulose. G. ETTISCH and E. HELLRIEGEL (Biochem. Z., 1932, 248, 65–66).—The method is described. P. W. C.

Micro-determinations of mol. wt. by the method of molar depression of the m. p. J. PIRSCH (Ber., 1932, 65, [B], 862–865).—The following substances are recommended as solvents for micro-determination of mol. wt. by lowering of the m. p.: camphene, m. p. 49° , E 31.08; pinene hydrochloride, m. p. 124° , E 45.4; pinene dibromide, m. p. 170° ,

E 80.9; borneol, m. p. 204°, *E* 35.8. The substance and solvent are weighed successively into a capillary which is then sealed. Dissolution is effected by heating the capillary about 10° above the expected m.-p., after which it is cooled and then heated at the rate of 0.2° per min. (apparatus described). The temp. at which the crystal threads completely disappear is considered as the m. p. H. W.

Micro-determination of the mol. wt. of liquids. J. PIRSOH (Ber., 1932, 65, [B], 865—868; cf. preceding abstract).—The liquid is weighed in a capillary bulb drawn out to an extremely fine tube. The latter is placed with the open end downwards in the m.-p. tube containing a weighed amount of solvent. The tube is sealed. Dissolution is effected by cautious alternate heating and cooling of the tube. A modification for viscous liquids is described. Good results are obtained with CHCl_3 , AcOEt , C_6H_6 , CS_2 , PhMe , pyridine, and $\text{C}_6\text{H}_4\text{Me}_2$ in camphene. H. W.

Gas analysis apparatus. G. D. HARPER (Chem. Eng. Min. Rev., 1932, 24, 255).—A modified Orsat

apparatus is described in which the absorption pipette is set in an open jar resembling a H_2O jacket, so that, as the reagent is displaced by the gas, it rises in this jacket outside the pipette; the inlet tube of the latter is extended inside almost to the bottom to cause the gas to bubble up through the ball valve, which opens to permit the gas to be withdrawn and joins the inlet tube just below the capillary tap. Modifications of Low's apparatus are also described. A. R. P.

Apparatus for determination of carbon dioxide. J. PRITZKER and R. JUNGKUNZ.—See B., 1932, 546.

Titration apparatus. A. P. SCHULZ (Z. Spiritus-ind., 1932, 55, 128).—The burette can be filled repeatedly through a connecting side-tube from a cylindrical reservoir by merely tilting the apparatus. E. S. H.

Preparation of translucent sections of Waikato coal. W. H. A. PENSELER (New Zealand J. Sci. Tech., 1932, 13, 189—197).—Suitable technique is described. A. G. P.

Geochemistry.

Determination of the density of ozone in the atmosphere. H. MINEUR (J. Phys. Radium, 1932, [vii], 3, 145—149).—A criticism of Rosseland's work. Means of determining the density of O_3 at any altitude are discussed. W. R. A.

Chemical analysis of the Konigsquelle in Boracova (Slatina Radenci). S. S. MIHOLIĆ (Bull. Soc. Chim. Yougoslav., 1932, 3, 43—51).—The Na, K, Li, Ca, Mg, Sr, Ba, Mn, Zn, Pb, Cl, Br, I, SO_4^{--} , HCO_3^- , NO_3^- , SiO_2 , TiO_2 , Al_2O_3 , and Fe_2O_3 contents of the H_2O have been determined. The chief constituent is NaHCO_3 . E. S. H.

Mineral waters of One di Fonte (Treviso). G. BRAGAGNOLO and C. ZAMORANI (Annali Chim. Appl., 1932, 22, 197—204).—The results of the physical and chemical examination of 3 waters are given. O. F. L.

Copper content of sea-water. W. R. G. ATKINS (J. Marine Biol. Assoc., 1932, 18, 193—197).—The Na diethyldithiocarbamate method for determining Cu is preferred to the K Et xanthate method. Cu may be determined by electro-deposition from 1000 c.c. of sea-water at 90—100° for 3 hr. at 2.0 volts, followed by dissolution of the deposit and determination by the above method. The Cu content of sea-water is about 10 mg. per cu. m. E. S. H.

Salinity of the water retained in the muddy foreshore of an estuary. W. B. ALEXANDER, B. A. SOUTHGATE, and R. BASSINDALE (J. Marine Biol. Assoc., 1932, 18, 297—298).—The H_2O retained in the muddy foreshore of an estuary at low tide is more saline than the H_2O of the estuary. E. S. H.

Salinity interchange between salt water in sand and overflowing fresh water at low tide. H. D. M. REID (J. Marine Biol. Assoc., 1932, 18, 299—306).—The displacement of salt H_2O in a sandy beach by an overflowing stream of H_2O increases

with increasing velocity of the stream. The salinity is more quickly increased by the flowing tide than reduced by the stream. E. S. H.

Dissolution and colloidal dispersion of minerals in water. P. G. NUTTING (J. Washington Acad. Sci., 1932, 22, 261—267).—Saturated aq. solutions of many clays and decomposed rocks contain 30—100 p.p.m. When free from suspended particles, they may be conc. to several thousand p.p.m. without pptn. The formation of stable suspensions is favoured near the isoelectric point. Org. matter is commonly associated with SiO_2 as sol. silicates, which may be transported and decomposed elsewhere into SiO_2 and hydrocarbons. A new origin of petroleum is thus suggested. The clay material of a decomposed granite has been converted into a bleaching clay and a commercial bleaching clay into a plastic ball clay by treatment with H_2O alone. E. S. H.

Occurrence of Glauber's salt in the gypsum upper layer of the potash salt beds at Holyn, Kropiwnik, and Siwka. C. KUZNIAR (Bull. Acad. Polonaise, 1931, A, 411—419).—The deposits (99.43% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) have apparently been formed by springs, saturated with Na_2SO_4 and NaCl , cooling as they rose towards the earth's surface. H_2O saturated with these salts at 17.9° deposits pure Na_2SO_4 on cooling. In order to explain the formation of such springs, the action of NaCl solution on salts found lower in the beds has been investigated and a diagram is given for the system $\text{K}_2\text{—Mg—SO}_4$ in saturated NaCl solution at 10°. D. R. D.

Different habits of fluorite crystals. J. DRUGMAN (Min. Mag., 1932, 23, 137—144).—In fluorite the cube is usually the predominating form. Crystals of other habits—octahedral, rhombic-dodecahedral, and triakis-octahedral—are described. The temp.

during the growth of the crystal has perhaps influenced its habit. L. J. S.

Scorodite from Kiura mine, Japan. T. ITO and T. SHIGA (Min. Mag., 1932, 23, 130—136).—The crystals from this locality have been thought to be distinct from scorodite, but analysis (As_2O_5 49.85, Fe_2O_3 34.33, H_2O 15.82%) agrees with the usual formula $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, and goniometric and optical measurements are also in agreement with normal scorodite. L. J. S.

Crystals of brookite tabular to the basal plane. F. C. PHILLIPS (Min. Mag., 1932, 23, 126—129).—Minute crystals in the heavy residues from Jurassic sandstones from Cleveland, Yorkshire, were proved to be brookite, but whilst some crystals are of the usual habit tabular on (100), others are tabular on (001) and on this plane the optic axial dispersion so characteristic of the mineral is not seen. X-Ray measurements gave a 9.20, b 5.44, c 5.14 Å. L. J. S.

Zeolites. II. Thomsonite (including faroe-lite) and gonnardite. M. H. HEY [with F. A. BANNISTER] (Min. Mag., 1932, 23, 51—125).—Analyses are given of 16 specimens of thomsonite from various localities, and d , optical and X-ray data were determined on the same samples. The unit cell (a and b 13.09, c 13.23 Å.; space-group C_{2v}^{20}) contains normally $\text{Na}_4\text{Ca}_3\text{Al}_{20}\text{Si}_{20}\text{O}_{80} \cdot 24\text{H}_2\text{O}$, with isomorphous replacements $\text{CaAl} \rightleftharpoons \text{NaSi}$ and $\text{Ca} \rightleftharpoons \text{Na}_2$. n falls with increasing Si/Al ratio, the mean ranging from 1.535 to 1.517. The v. p. of thomsonite was determined at various temp. and degrees of hydration in a specially designed apparatus. Experiments were made on the absorption of various vapours by dehydrated thomsonite, and on the base-exchange reactions. Thomsonite and faroe-lite form a continuous isomorphous series; gonnardite is probably identical with a high-temp. modification of thomsonite (metathomsonite). L. J. S.

Manner of occurrence and diffusion of phosphoric acid in ancient sedimentary formations. L. CAYEUX (Compt. rend., 1932, 194, 1769—1773).—Samples, shown to be free from recognisable phosphatic minerals or org. remains, of Devonian, Silurian and Cambrian, Precambrian, and Algonkian rocks contained respectively, 0.07—0.37, 0.07—0.245 (cf. A., 1875, 872), 0.116—0.347, and 0.073—0.104% of P_2O_5 . It is considered that this must be due to the presence of unrecognisable org. remains in these rocks. C. A. S.

Hortonolite-gabbro-diabases of the Siberian trap. F. LOEWINSON-LESSING (Compt. rend., 1932, 194, 1751—1753).—The Siberian trap formation, between the Yenisei and the Lena, is an ophitic hortonolite-gabbro-diabase, consisting predominantly of labradorite, an augitic pyroxene of pigeonite type, hortonolite, and titanomagnetite, and is of extraordinarily uniform composition. Analyses of samples from four distantly separated localities show only the following variations: SiO_2 47.78—48.76; TiO_2 1.67—2.02; Al_2O_3 14.26—16.35; Fe_2O_3 1.01—3.10; FeO 10.70—12.61; MnO 0—0.22; MgO 4.70—7.75; CaO 9.68—10.32; Na_2O 2.27—2.60; K_2O 0.62—0.74; H_2O 0—0.70; P_2O_5 0—0.25%; one sample contained

Cr_2O_3 0.02%. The ratio $\text{RO} : \text{SiO}_2$ varied from 2.93 : 4.80 to 4 : 5.49; that of $\text{R}_2\text{O} : \text{RO}$ from 1 : 9.3 to 1 : 12; and the coeff. of acidity from 1.49 to 1.61.

C. A. S.

Actinium-uranium ratio in cleveite. (MLLE.) E. GLEDITSCH and S. KLEMETSSEN (Compt. rend., 1932, 194, 1731—1732; cf. this vol., 590).—The $\text{Ac} : \text{U}$ ratio, determined as previously described, from cleveite of Aust-Agder, Norway, the age of which according to the $\text{Ra-G} : \text{U}$ ratio is 10^9 years, averages 3.2 : 100 with a probable error of 10%.

C. A. S.

Synthetic willemite. A. KARL (Compt. rend., 1932, 194, 1743—1745).—On treating finely-powdered SiO_2 , NaCl , and excess of ZnCl_2 with H_2O at 600° crystals identical with willemite are obtained; even with most carefully purified materials a violet fluorescence is observed. The presence of 0.2—0.1% Ni produces emerald-green phosphorescence, of 0.20—0.05% Cu green to bluish-green, and of 0.1% Ni+0.025% Cu a phosphorescence spectrally similar to that of natural willemite.

C. A. S.

Antimony-rich enargite from Recsk, Hungary. G. VAVRINECZ (Ban. Kohás. Lapok, 1931, 64, 438—439; Chem. Zentr., 1932, i, 931).—The material, d 4.42, contained Cu 44.84, Pb 0.61, Fe 0.99, Zn 0.04, As 7.00, Sb 10.16, S 30.13, H_2O 1.05, rock 0.86, O (diff.) 4.32%.

A. A. E.

Pyroxene-andesites from the Cserhát Mts., Hungary. A. VENDL (Tsch. Min. Petr. Mitt., 1932, 42, 491—550).—Petrographical descriptions with chemical analyses of various types of andesites are given. These rocks indicate a Pacific type of differentiation of the magma.

L. J. S.

Origin of granitic magmas. P. ESKOLA (Tsch. Min. Petr. Mitt., 1932, 42, 455—481).—The more abundant occurrence of granites in the older pre-Cambrian and in the roots of denuded mountain chains appears to be contradictory to the idea of an upper lighter sial and a lower denser sima magma in the earth's crust. By crystallisation-differentiation and squeezing out of the residual magma a granite magma may have originated, whilst basic lavas have been extruded at the surface.

L. J. S.

Chemical constitution of micas. X. Rôle of titanium in phlogopites. J. JAKOB and I. P. PONDAL (Z. Krist., 1932, 82, 271—284; cf. A., 1931, 1266).—Analyses of 12 phlogopites containing from 0 to 2.80% TiO_2 , one containing also 0.54% Ti_2O_3 , are given. The compositions are then expressed by varying nos., always totalling 50, of three of the radicals (SiO_2)₃, $\text{Al}(\text{SiO}_4)$ ₃, $\text{Mg}(\text{SiO}_4)$ ₃, and $\text{Mg}(\text{SiO}_5)$ ₃, where "Al" includes Fe^{III} , Cr^{III} , and Mn^{III} , and "Mg" Fe^{II} and Mn^{II} . Ti never replaces either Al or Si, but, either ter- or quadri-valent, it always replaces 2Mg (or 2Mn^{II} or 2Fe^{II}).

C. A. S.

Dartmoor granites: their genetic relationships. A. BRAMMALL and H. F. HARWOOD (Quart. J. Geol. Soc., 1932, 88, 171—237).—85 detailed chemical analyses are given of granites, inclusions in the granite, the slates at the contact, and of the various constituent minerals. The different types of granite range from aplite (SiO_2 76.32%) to biotite-rich veins

(SiO_2 55.06%). These analyses are considered in a discussion of the origin of the different types of granite. The magma was modified by the assimilation of slate and has undergone differentiation.

L. J. S.

Synthesis of kaolin. W. NOLL (Naturwiss., 1932, 20, 366).—The synthesis of kaolin has been effected from the colloid adsorption compound $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{aq.}$ by heating it in a pressure bomb for 5 days at 250–300°/40–90 atm. H_2O vapour. X-Ray measurements have established the identity of kaolin.

W. R. A.

Phosphatic rocks of the Gaboon coast. R. FURON (Compt. rend., 1932, 194, 1959–1960).—Beds of phosphates, mainly of Ca, occur interstratified with Senonian silicified rocks, between Fernan Vas and Iguela (lat. $1^\circ 50'$ S.) on the Gaboon coast. C. A. S.

Coronadite among manganiferous minerals from Bu Tazult, Imini, Morocco. J. ORCEL (Compt. rend., 1932, 194, 1956–1958).—Coronadite occurs, associated with polianite, in the manganiferous deposits at Bu Tazult; d 5.505, hardness 5, analysis MnO_2 59.60, MnO 8.02, PbO 28.68, BaO 0.23, CaO 0.05, CuO 0.14, Al_2O_3 0.10, Fe_2O_3 0.60, P_2O_5 0.03, As_2O_5 0.04, V_2O_5 0.20, SO_2 0.02, CO_2 0.04, $\text{H}_2\text{O} +$ 1.80, SiO_2 0.26, total 99.81%: $\text{MnO}_2 : \text{RO} = 1.98$. This agrees closely, when SiO_2 is omitted from both, with coronadite from Clifton, Arizona (cf. A., 1905, ii, 96), and corresponds with the formula $2\text{MnO}_2 \cdot \text{PbO}$.

C. A. S.

Water-soluble humus, and its contribution to the formation of lake ores. O. ASCHAN (Arkiv Kemi, Min., Geol., 1932, 10, A, No. 14, 1–143; cf. A., 1908, i, 250).— H_2O -sol. humus plays an important part in many natural processes of biological, hydrographical, and geological character. Its composition corresponds in general with that of the polysaccharides, but it also forms sol. compounds with Fe, Ca, and Mn. As it undergoes partial decomp. at 110° , the earlier analyses, made on material dried at 150° , are untrustworthy. The humus cannot be isolated from its solution by evaporation, but must be pptd. as an Fe compound by the addition of FeCl_3 , and as complete pptn. takes place only within narrow limits, the amount of FeCl_3 to be added must be determined by experiment in each particular case. Analyses of humus from a no. of lakes in Finland showed > 50% C in the case of samples taken from moorland lakes containing brown peaty H_2O , whilst a sample from a lake of clear H_2O showed 45% C. N varied from 2% to 2.5%, and H averaged 4.5%. Five determinations of P gave a val. of 0.22%, whilst S is also present, both P and S being in combination in org. compounds. Humus substance can be divided into two main

groups, mould humus and H_2O -sol. humus, the former group containing six sub-divisions, the latter four; the importance of these substances as geological agents, and their function in the formation of lake Fe ores, are discussed. Analyses of 21 specimens of lake ores and 11 specimens of bog ores from various localities showed that all of them contained residual C and H derived from humus. In a series of synthetic experiments, large carboys were filled with humus-rich H_2O from the river Vanda to which solutions of Fe and Mn salts of various concns. had been added. In order to promote the formation of Fe ores, the solutions were inoculated by the addition of an extremely small amount of finely-divided Fe ore and sludge from the bottom of a lake. The carboys were closed, and set aside for 25 years, when the contents were filtered and analysed. The ratio inorg. residue/loss on ignition was 3.58 for the ppts. formed in the vessels, whilst the corresponding val. for freshly-prepared Fe humates from the same river H_2O was 0.94. Microscopical examination of the deposited particles afforded strong evidence that these had been formed by the agency of an organism, and additional support for this view was given by the carboy containing Mn salt, in which long vertical stripes of Mn oxide had formed on the sides. The theory put forward previously, that lake ores are formed by biological action through the agency of H_2O -sol. humus substances, is thereby corroborated. H. F. H.

Graphical classification of carbonaceous minerals; place of the constituents of common coal. H. BRIGGS (Proc. Roy. Soc. Edin., 1932, 52, 195–199; cf. B., 1931, 659).—Graphical relationships have been developed between the O and C contents of fusain, durain, and vitrain. In the first two the O content decreases linearly with increasing C content, but the vitrain line shows a break at 86.7% C. The curves when produced cut the C axis at points corresponding with $\text{C}_{144}\text{H}_{64}$, $\text{C}_{96}\text{H}_{64}$, and $\text{C}_{32}\text{H}_{64}$, respectively. J. W. S.

Some red and yellow lateritic soils of Brazil. V. AGAFONOFF (Soil Res., 1932, 3, 13–20).—Microscopic-mineralogical examinations of these soils are described and their process of formation is discussed.

A. G. P.

Grootfontein (S.W. Africa) meteoric iron. S. G. GORDON (Proc. Acad. Nat. Sci. Philadelphia, 1931, 83, 251–255).—Analysis of this largest known mass of meteoric Fe, previously described under the name of Hoba (this vol., 359), gave Fe 82.40, Ni 16.76, Co 0.74, S 0.02, P trace = 99.92%, d 7.971; and of the magnetic iron-shale, forming a zone of oxidation around the mass, Fe_2O_3 65.48, FeO 5.60, NiO 8.88, CoO 0.59, H_2O 8.47%, d 4.021. L. J. S.

Organic Chemistry.

Reaction mechanism. IV. Place of severance of C–C linkings in chain molecules. O. SCHMIDT [with O. GROSSKINSKY] (Z. physikal. Chem., 1932, 159, 337–356; cf. A., 1931, 439).—In the pyrolysis of many *n*-acyclic and cyclic paraffins the first step

is the formation of H_2 , usually from the two end groups of the chain. The resulting double linking determines the points at which the C chain subsequently breaks; it strengthens the immediately adjacent single linking and weakens the one beyond,

this alternation probably continuing with diminishing intensity throughout the chain. This double linking effect explains the mode of thermal decomp. of C_2Ph_6 derivatives. To account for the formation of 3-C chains from simple sugars in aq. solution it must be supposed that it is the enolic form which decomposes. In the rupture of the chain of polyhydric alcohols by hydrogenation, the first step is dehydration to give the sugar, which then enolises and decomposes. R. C.

Free ethyl. T. G. PEARSON, P. L. ROBINSON, and E. M. STODDART (*Nature*, 1932, 129, 832).—Confirmation of certain results previously obtained by other workers (this vol., 40). L. S. T.

Influence of hydrogen on the pyrolysis of ethane and ethylene near 600°. I. M. W. TRAVERS and L. E. HOCKIN.—See this vol., 701.

"Bromine-binding number," a simple means of characterising a C:C linking. K. MEINEL (*Naturwiss.*, 1932, 20, 364).—The action of Br in MeOH on the C:C linking results in partial addition of OMe in place of Br. Br' is thereby liberated in the solution. The "Br-binding no." is defined as $100 \times$ amount of added Br as determined argentometrically/amount of Br determined iodometrically. W. R. A.

Colour reactions. I. M. KORENMANN (*Z. anal. Chem.*, 1932, 88, 249—257).—The importance of correct temp. in carrying out certain colour reactions for org. compounds is illustrated with several examples. Max. colour in the reaction between H_2SO_4 , furfuraldehyde, and C_5H_{10} , $C_5H_{11}OH$, or $C_5H_{11}OAc$ is obtained at 100°; at lower temp. the intensity of the colour decreases in the above order, indicating that in the case of the two last-named compounds conversion into C_5H_{10} takes place before development of the colour. Max. colour in the reaction between $NHPhNH_2$, $FeCl_3$, H_2SO_4 , and CH_2O is obtained at 0°, and in the same reaction with hexamethylenetetramine at 20°. A. R. P.

Polymerisation and decomposition of acetylenic hydrocarbons. G. EGLOFF, C. D. LOWRY, jun., and R. E. SCHAAD (*J. Physical Chem.*, 1932, 36, 1457—1520).—A review. H. A. B. (b)

Action of light on some alkyl iodides. G. EMSCHWILLER.—See this vol., 706.

Preparation of bromides from amines with phosphorus trichloride and bromine. J. VON BRAUN and G. IRMISCH (*Ber.*, 1932, 65, [B], 880—882).—When the basic material is plentiful, PBr_3 may economically be replaced by $PCl_3 + Br_2$ in the prep. of bromides the yields of which are more than 50%; small quantities of Cl-derivatives are readily removed. Br (1 mol.) is added slowly to PCl_3 (1 mol.) and the mixture is shaken at 0° until a thin cryst. paste results. After addition of the Bz derivative the mixture is melted over a small flame, allowed to cool, and then distilled under diminished pressure. Examples cited are: *heptadecyl bromide*, m. p. 32°, from *heptadecylamine*; α -dibromobutane from *dibenzoylputrescine*; α -dibromopentane from *1-benzoylpiperidine*; dicyclic *naphthenyl bromide*,

$C_{14}H_{25}Br$ or $C_{15}H_{27}Br$, from the naphthenic acids of Californian petroleum. H. W.

Action of magnesium on polyhalogenated hydrocarbons in ethereal solution. I. Chloroform, bromoform, and carbon tetrachloride. C. L. TSENG (*Nat. Centr. Univ. Sci. Rep.*, 1931, A, 1, No. 2, 1—4).— CBR_4 , but not $CHCl_3$, $CHBr_3$, or CCl_4 , reacts in Et_2O with Mg. CH. ABS.

Carbon tetrabromide as a brominating agent. W. H. HUNTER and D. E. EDGAR (*J. Amer. Chem. Soc.*, 1932, 54, 2025—2028).—Various compounds are brominated by CBR_4 ; $CHBr_3$ is a by-product. The side-chain of the alkylbenzenes undergoes selective bromination. $AcOH$ gives 32.4% of $CH_2Br \cdot CO_2H$; $EtCO_2H$ affords 42.2% of α - and β -Br-derivatives; $(CHBr_2)_2$ gives 10.1% of C_2HBr_5 and 2% of C_2Br_6 ; C_2HBr_5 affords a trace of C_2Br_6 ; C_6H_6 yields 67.6% of $PhBr$; $PhMe$, 76.9% of CH_2PhBr ; $PhEt$ furnishes 66.6% of $CHBrPhMe$ (with 2 mols. of CBR_4 , 70.3% of $CHBrPh \cdot CH_2Br$ results); $PhPr$ gives 46.7% of $CHBrPhEt$; *m*-xylene affords 67.3% of the ω -Br- (with 1 mol. of CBR_4) and 48.4% of the $\omega\omega'$ -Br₂-derivative (with 2 mols. of CBR_4); *durene* gives 33.5% of *bromodurene*, b. p. 110—112°/4 mm., but in CS_2 a 1 : 1 additive compound, m. p. 84—86°, results; $C_{10}H_8$ affords 74.5% of $1-C_{10}H_7Br$; $PhBr$ gives 42.5% of *p*- $C_6H_4Br_2$; CH_2PhBr gives 55.3% $CHPhBr_2$ (74.5% at 210°), whilst with 2 mols. of CBR_4 21.4% of *benzotribromide*, m. p. 56—57° (also obtained in 27.2% from $CHPhBr_2$), results; $PhOH$ gives a bright red compound, possibly *aurin*; NH_2Ph gives (probably) *pararosaniline*. These Br-derivatives are usually prepared more easily by other methods. C. J. W. (b)

Action of aluminium chloride on tri- and dichloroethylene. E. MULLER and C. HONN (*J. pr. Chem.*, 1932, [ii], 133, 289—290).—Passage of HCl into a mixture of $CCl_2 \cdot CHCl$ and $AlCl_3$ at 50° yields pentachlorobutadienes, C_6Cl_6 , $\alpha\alpha\beta\beta$ - and $\alpha\alpha\beta\beta$ -tetrachloroethane (in proportions 1 : 5). Dichloroethylene affords similarly $\alpha\beta$ -trichloroethane and a *penta-chlorobutane*, m. p. 49°, b. p. 230°/760 mm. R. S. C.

Trichloronitrosomethane, dichloroformoxime (phosgene oxime), and certain derivatives. Two new derivatives of carbon dioxide. W. PRANDTL and W. DOLLFUS (*Ber.*, 1932, 65, [B], 754—759; cf. A., 1929, 1037).—Improved directions are given for the prep. of Na trichloromethylsulphinate, CCl_3NO , and dichloroformoxime (I). When preserved at room temp. (I) suffers gradual decomp. into chloropicrin, NH_4Cl , and $NH_2OH \cdot HCl$, whilst $COCl_2$ and $CNCl$ are evolved. (I) in Et_2O is decomposed by 30% $NH_3 \cdot H_2O$ or liquid NH_3 into *chlorocyanamidoformoxime* (II), m. p. 168°, also prepared from (I) and Ag cyanamide, thus establishing the course: $3CCl_3 \cdot N \cdot OH + 3NH_3 = 3NH_4Cl + 3CCl_3 \cdot N \cdot O$; $3CCl_3 \cdot N \cdot O + 2NH_3 = 3ClCN + N_2 + 3H_2O$; $3ClCN + 6NH_3 = 3NH_4CN + 3NH_4Cl$; $3CCl_3 \cdot N \cdot OH + 3NH_3 = 3CN \cdot NH \cdot CCl_3 + 3NH_4Cl$; $6CCl_3 \cdot N \cdot OH + 14NH_3 = 3CN \cdot NH \cdot CCl_3 + 9NH_4Cl + 3H_2O + N_2$. (II) is very stable towards dil. acids, but is transformed by 10% H_2SO_4 at 200° into CO_2 , NH_3 , and NH_2OH . *Bromocyanamido-*

formoxime, from dibromoformoxime and Ag cyanamide, has m. p. 140° (decomp.). In H_2O (I) is reduced by N_2H_4 to HCN, whereas in Et_2O with an ethereal suspension of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ it gives triamino-guanidine hydrochloride. H. W.

Dipole moments and structure of organic compounds. XI. Constitution of tetranitromethane. A. WEISSBERGER and R. SANGEWALD (Ber., 1932, 65, [B], 701—704; cf. A., 1931, 894).—In CCl_4 , $\text{C}(\text{NO}_2)_4$ (I) is free from electric moment. Since measurements of MeNO_2 and amyl nitrite in C_6H_6 show that the moment of $\cdot\text{NO}_2$ is not identical with that of $\cdot\text{O}:\text{N}:\text{O}$, (I) is $\text{C}(\text{NO}_2)_4$ and not $(\text{NO}_2)_3\text{C} \cdot \text{O} \cdot \text{NO}$. H. W.

Nitration of halogenoethylenes. R. B. BULLOWS and L. HUNTER (J.C.S., 1932, 1357—1360).—The action of HNO_3 on di- and tri-chloroethylenes gives respectively chloropirin and dichlorodinitromethane (method recommended for the prep.) and tetrachloro- and tribromo-ethylenes are almost completely decomposed to CO_2 and halogen acid. Di- and tri-chloroethylenes and NO_2 yield $\text{H}_2\text{C}_2\text{O}_4$ and lachrymatory substances of unknown constitution, but tetrachloroethylene gives α -tetrachlorodinitroethane (cf. Biltz, A., 1902, i, 417) and tribromoethylene forms $\alpha\alpha\beta$ -tribromo- $\alpha\beta$ -dinitroethane, m. p. 133 — 134° . F. R. S.

Nitro-chromic acid reaction for the detection of primary and secondary alcohols with special reference to polysaccharides. W. R. FEARON and D. M. MITCHELL (Analyst, 1932, 57, 372—374).—Primary and *sec.* alcohols, all saccharides, CH_2O , and OH-acids such as lactic and tartaric, give a blue colour when 0.1—1.0 c.c. of the solution is added to 5 drops of 5% aq. K_2CrO_4 mixed with 5 c.c. of HNO_3 diluted with H_2O (1:2) and cooled. The test is negative with *tert.* alcohols, aldehydes other than CH_2O , aliphatic ketones, $\text{H}_2\text{C}_2\text{O}_4$, citric acid, acids of AcOH series, NH_3 -acids and NH_2 -compounds such as carbamide, polymeric compounds such as $(\text{CH}_2\text{O})_2$, met-aldehyde, and, under restricted conditions, polysaccharides. Phenols interact with the HNO_3 , but do not give the blue colour. Nitrites, peroxides, and hypohalites give a blue colour which is not the same as the ultramarine-blue of the peroxide test for Cr. In general, the test is sp. for $\cdot\text{CH}_2\cdot\text{OH}$ and $\cdot\text{CH}\cdot\text{OH}$. The delicacy of the test varies with the compound. M. S. B.

Carbohydrates. I. Xanthate reaction with lower alcohols and sugars. T. LIESER and W. NAGEL (Annalen, 1932, 495, 235—249).—Treatment of an alcohol (or sugar) with CS_2 and aq. $\text{Ba}(\text{OH})_2$ at room temp., subsequent decomp. of Na_2CS_3 with CO_2 (whereby BaCO_3 is also pptd.), and treatment of the resulting solution with a metal salt in AcOH give metal alkyl-(or sugar-)xanthates, purified by washing with EtOH (to remove dixanthogen) and Et_2O . The Cu salts of methyl- (*Ag* salt), ethyl-, isopropyl-, allyl-, benzyl-, β -hydroxyethyl-, glyceryl-, methylglucosidyl- (*Ag* salt), glucosyl-, and *l*-glucosanyl-xanthic acids are described. Glycerol $\alpha\gamma$ - Me_2 ether also affords a xanthic acid (*Cu* salt), showing that a *sec.*-OH can react. Only one xanthate group is introduced into

the polyhydric alcohols; attempts to introduce a second into α -methylglucoside failed. H. B.

Griner's divinyl glycol. P. VAN ROMBURGH and W. VAN HASSELT (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 40—42).—Divinyl glycol tetrabromide ($\alpha\beta\epsilon\zeta$ -tetrabromohexane- $\gamma\delta$ -diol) (I), m. p. 174° (Griner, A., 1893, i, 237), is debrominated by Zn dust in EtOH to the glycol (II), b. p. $125^{\circ}/45$ mm., m. p. 10° , which with Br regenerates (I). The tetrabromide (III), m. p. 96° (*loc. cit.*), similarly gives the glycol (IV), b. p. $125^{\circ}/45$ mm., m. p. -40° , converted by Br into (III). (II) and (IV) may be *dl*- and *meso*-forms. H. B.

Reactions of glycerol and mannitol. L. EKKERT (Pharm. Zentr., 1932, 73, 339—340).—The glycerol colour reaction with codeine (A., 1931, 462) is more intense with conc. glycerol. Using resorcinol instead of codeine, a light red (blood-red warm and brownish-red on dilution and addition of aq. NH_3) is obtained. Ca glycerophosphate gives colour reactions with the same reagents: codeine, deep blue, and resorcinol, yellowish-red to deep scarlet which is decolorised with H_2O , but on saturation with NH_3 turns rose-red. In the reactions of mannitol with either resorcinol (yellow, blood-red warm), α -naphthol (light rose, ruby-red warm), β -naphthol (light green, emerald-green warm) or codeine (yellow, garnet-red warm) and $\text{EtOH}-\text{H}_2\text{SO}_4$ (cf. A., 1928, 1114), previous oxidation with Br is unnecessary. E. H. S.

Synthesis of *dl*-mannitol. LESPIEAU and WIE-MANN (Compt. rend., 1932, 194, 1946—1947).—*dl*-Mannitol, m. p. 168° (confirmed by prep. of its tri-benzylidene derivative), is readily obtained by oxidation of *s*-divinyl glycol with AgClO_3 and osmic acid in H_2O , concn. of the filtrate (after removing AgCl and osmic acid) at 60° , and addition of EtOH . J. W. B.

Alteration in properties of chemical compounds by complex formation. VII. Mechanism of ether decomposition by acid chlorides and anhydrides in presence of catalysts. H. MEERWEIN and H. MAIER-HUSER (J. pr. Chem., 1932, [ii], 134, 51—81).—The reaction between Et_2O and BzCl , AcCl , *p*-toluenesulphonyl chloride, Ac_2O , and succinic anhydride, in presence of metallic and non-metallic halides as catalysts, yields differing amounts of esters depending on the time and temp. of heating. The relative stabilities of the complexes formed respectively between the halide and the acid chloride or anhydride, and the halide and ester, determine the final percentage of ester obtained. The following mol. compounds have been isolated: Me amyl ether, BF_3 , b. p. 54.8 — $55^{\circ}/10$ mm.; anisole, BF_3 , m. p. -12 to -13° ; succinic anhydride, BF_3 ; phenetole, BF_3 ; dimethylpyrone, SbCl_5 ; AcCl, BF_3 ; $\text{AcCl}, \text{BCl}_3$; $\text{AcCl}, \text{SbCl}_5$; $\text{BzCl}, \text{SbCl}_5$. Ternary compounds are obtained from dimethylpyrone: $\text{C}_7\text{H}_8\text{O}_2, \text{BzCl}, \text{SbCl}_5$, m. p. 175° ; $\text{C}_7\text{H}_8\text{O}_2, \text{AcCl}, \text{SbCl}_5$; $2\text{C}_7\text{H}_8\text{O}_2, 2\text{BzCl}, \text{SnCl}_4$; $2\text{C}_7\text{H}_8\text{O}_2, 2\text{AcCl}, \text{SnCl}_4$. F. R. S.

Reactivity of atoms and groups in organic compounds. XII. Preparation and properties of mixed aliphatic ethers with special reference to those containing the *tert.*-butyl radical. J. F. NORRIS and G. W. RIGBY (J. Amer. Chem. Soc., 1932,

54, 2088—2100; cf. A., 1931, 197).—The results of the previous study of the relative reactivities of the OH group and the H of this group in alcohols are utilised in devising new and improved methods of prep. of mixed ethers. Those containing *tert.*-Bu and a Me, Et, Pr^α, Pr^β, or Bu group are obtained in yields of 51.5—95% when the two alcohols are heated with 15% aq. H₂SO₄ or NaHSO₄. For the prep. of *n*-alkyl *sec.*-alkyl ethers, 50% (or more conc.) H₂SO₄ must be used; in all cases, three ethers are produced, but the mixed ether predominates. The formation of ethers using H₂SO₄ does not involve the intermediate production of an alkylsulphuric acid; an additive compound of the alcohol and H₂SO₄ is probably the active intermediate. *Pr tert.-Bu ether*, b. p. 97.4° (all b. p. are corr.), *tert.-Bu β-ethoxyethyl ether*, b. p. 147°, *Et sec.-Bu ether*, b. p. 81.2°, and *tert.-Bu benzoate*, b. p. 96°/2 mm., are new. The ethers do not react with AcOH at room temp. or at 100°, or with AcCl (except in presence of ZnCl₂). All the ethers react with BzCl and ZnCl₂ at room temp., but reaction is slower than with AcCl; analogous products (esters and chlorides) are formed. Reaction does not occur with Ac₂O alone at room temp., but does so in presence of ZnCl₂. C. J. W. (b)

Molecular compounds of dioxan. III. Dioxan and organic [iodo-compounds]. H. RHEINBOLDT and A. LUYKEN (J. pr. Chem., 1932, [ii], 133, 284—288; cf. A., 1931, 599).—Mol. compounds of dioxan with the following substances (1:1) were prepared: CHI₃ (I); tetraiodoethylene (II); di-iodoacetylene, m. p. 113—114° after sintering at 110°; tetraiodopyrrole, m. p. 155—158° with decomp. from 150°, αβ-Di-iodo-ethane and -ethylene do not form similar mol. compounds. (I) and, less readily, (II) lose dioxan when kept. R. S. C.

Identification of mercaptans with 1-chloro-2:4-dinitrobenzene. R. W. BOST, J. O. TURNER, and R. D. NORTON (J. Amer. Chem. Soc., 1932, 54, 1985—1987).—1-Chloro-2:4-dinitrobenzene reacts readily with Na mercaptides to form alkyl and aryl 2:4-dinitrophenyl sulphides, oxidised by KMnO₄ in AcOH to the corresponding sulphones. The following 2:4-dinitrophenyl alkyl (aryl) sulphides are prepared: Me, m. p. 128° (all m. p. are corr.); Et, m. p. 115°; Pr, m. p. 81°; Pr^β, m. p. 94.5°; Bu, m. p. 66°; Bu^β, m. p. 76°; amyl, m. p. 80°; isoamyl, m. p. 59°; hexyl, m. p. 74°; heptyl, m. p. 82°; octyl, m. p. 78°; nonyl, m. p. 86°; cetyl, m. p. 91°; Ph, m. p. 121°; p-tolyl, m. p. 103°; benzyl, m. p. 130°; phenylethyl, m. p. 89.5°; thienyl, m. p. 119°; 2-aldehydofuryl, m. p. 130°; diphenyl, m. p. 146°. These are oxidised to 2:4-dinitrophenyl alkyl (aryl) sulphones, viz.: Me, m. p. 189.5°; Et, m. p. 160°; Pr, m. p. 127.5°; Pr^β, m. p. 140.5°; Bu, m. p. 92°; Bu^β, m. p. 105.5°; amyl, m. p. 83°; isoamyl, m. p. 95°; hexyl, m. p. 97°; heptyl, m. p. 101°; octyl, m. p. 98°; nonyl, m. p. 92°; Ph, m. p. 161°; p-tolyl, m. p. 189.5°; benzyl, m. p. 182.5°; phenylethyl, m. p. 133.4°; thienyl, m. p. 143°; diphenyl, m. p. 170°. The reaction can be carried out with 0.001 mol. C. J. W. (b)

Relative mobility of radicals in the alkyl chlorosulphinates. P. CARRÉ (Compt. rend., 1932, 194, 1835—1837).—The temp. of incipient decomp.

of the alkyl chlorosulphinates is determined by heating an equimol. mixture of the alcohol, pyridine, and SOCl₂ until a sudden rise in pressure is observed. The vals. observed are in the order *tert.*>*sec.*>primary alcohols, Me>Et>Pr^α, etc., but with anomalies at C₇—C₁₀; allyl and CH₂Ph>Me. In the case of PhOH and the naphthols decomp. occurs at higher temp. and does not follow a normal course; the presence of ArO·SOCl is, however, inferred by the formation of Ph₂O and NPh:S·O with NH₂Ph. In the case of cyclohexanol some cyclohexene is formed.

H. A. P.

Oxidation of monocarboxylic acids with chromic acid. L. SEMICHON and M. FLANZY (Compt. rend., 1932, 194, 1827—1829).—Aq. CrO₃·H₂SO₄ oxidises HCO₂H quantitatively to CO₂ and H₂O. EtCO₂H is oxidised with some difficulty, and PrCO₂H and higher homologues with greater ease, AcOH being formed quantitatively in every case. Pyruvic, lactic, and α-hydroxybutyric acids also give AcOH, in the last case without intermediate formation of EtCO₂H. Details are given for the determination of lactic acid.

H. A. P.

Anode phenomena in the electrolysis of potassium acetate. III. Formation of methane. S. N. SHUKLA and O. J. WALKER.—See this vol., 580.

Spectroscopic study of the reaction between ferric chloride and ethyl acetate. L. LETELLIER (Bull. Sci. pharmacol., 1931, 38, 145—156; Chem. Zentr., 1932, i, 1078).—The compound obtained when FeCl₃ (1 drop) is added to AcOEt in abs. Et₂O has a wide absorption band, max. λ 4900 Å.; an analogous spectrum is obtained with H₂O, EtOH, etc. In H₂O the increase in colour is not proportional to increase in concn. of either reagent; dilution or rise of temp. decreases the Fe enolate content of the solution. In EtOH the concn. of Fe-enol compound corresponding with a particular absorption could be determined; dilution increases it, whilst rise of temp. decreases it. Traces of H₂O favour the formation of the enol compound in EtOH. Experiments were conducted in PrOH, BuOH, and COMe₂. No relation between the absorption and the mol. wt. of the alcohol could be found.

A. A. E.

Distinction of water-soluble fatty acids by shaking with light petroleum. J. GROSSFELD and A. MIERMEISTER (Z. Unters. Lebensm., 1932, 63, 391—402).—The concn. (c₀) of an aq. solution of a higher H₂O-sol. fatty acid (valeric, isovaleric, hexoic, octoic, also benzoic) is related to the concn. of acid in the aq. (c₁) and solvent (c₂) layers after shaking with light petroleum by $c_1 = -k^2/2 + (c_0k^2 + k^4/4)^{1/2}$, where $k = c_1/\sqrt{c_2}$. Increase in dilution and decrease in order in the homologous series increase the extent of the deviation of the lower fatty acids (up to C₄) from this formula, but in this case if log c₁/c₂ is plotted against log (1000 × normality), two straight lines intersecting at an angle are obtained for each acid. The % decrease of acid in the aq. phase on shaking with an equal vol. of light petroleum may thence be calc. from 100(c₁+c₂)/c₂. Data are tabulated for the various acids and concns., and are compared with those previously obtained

under different experimental conditions for hexoic and butyric acids (B., 1931, 1017). J. G.

Higher fatty acids with branched carbon chain. E. CHARGAFF (Ber., 1932, 65, [B], 745—754).—In connexion with their possible relationship to the lipins of the tubercle bacillus, the following acids have been prepared. *n*-Tetradecanol, m. p. 38.5—39° (corr.), is converted successively into the iodide, b. p. 138—140°/2 mm., *Et ethyltetradecylmalonate*, b. p. 183—186°/2 mm. [acid, m. p. 74—76° (corr.)], *Me α-ethylhexadecate*, b. p. 164—168°/2 mm., and *α-ethyl-n-hexadecate*, m. p. 37.5—38° (corr.) [2:4:6-tribromoanilide, m. p. 118.5° (corr.)]. The acid is not decomposed by alkaline KMnO_4 or molten KOH, which cause an elevation of the m. p. *n*-Docosanol, m. p. 70.5—71.5° (corr.), yields successively the iodide, m. p. 51.5—52.5° (corr.), *Et ethyldocosylmalonate*, m. p. 49—49.5° (corr.) [acid, m. p. 55° (corr.)], and *α-ethyl-n-tetracosate*, m. p. 65.5° (corr.) [2:4:6-tribromoanilide, m. p. 112° (corr.)]. *n*-Eicosanol, m. p. 66.5—67.5° (corr.), gives the iodide, m. p. 42° (corr.), *n-butyl-n-eicosylmalonic acid*, m. p. 92—93° (corr.) [*Et ester*], and *n-butyl-n-docosate*, b. p. 215—218° (corr.)/0.1 mm., m. p. 60—61° (corr.). *Et n-hexylmalonate*, b. p. 144—146°/12 mm., is converted through the non-homogenous *Et n-hexyl-n-octadecylmalonate* and the corresponding acid into *α-n-hexyl-n-eicosate*, m. p. 65° (corr.) [2:4:6-tribromoanilide, m. p. 96° (corr.)]. β -Iodo-octane and *Et malonate* give *Et β-octylmalonate*, b. p. 131—133°/3 mm., which did not yield a homogeneous product with *n*-hexadecyl iodide. *Et tetradecylmalonate*, b. p. 190°/3 mm., appears scarcely affected by decyl iodide and Na, whereas *Et n-decylmalonate*, b. p. 143—147°/2 mm., is transformed by *n*-tetradecyl iodide and Na in *EtOH* into *Et n-decyl-n-tetradecylmalonate* [acid, m. p. 62—63° (corr.)], whence *α-n-decyl-n-hexadecate*, m. p. 54° (corr.) [tribromoanilide, m. p. 88—89° (corr.)]. *Et malonate* and *n*-dodecyl iodide afford *Et di-n-dodecylmalonate* [acid, m. p. 80° (corr.)], whence *α-n-dodecyl-n-tetradecate*, m. p. 70—71° (corr.) [2:4:6-tribromoanilide, m. p. 115° (corr.)]. H. W.

Simple method of assigning optically active hydroxy-acids to the dextro- or lævo-series. I. Monobasic acids. O. LUTZ and B. JIRGENSONS (Ber., 1932, 65, [B], 784—791).—The method used for NH_2 -acids (A., 1931, 943) is not immediately applicable to OH-acids, the activity of which is frequently low and little characteristic. Enhancement of activity can be secured by addition of compounds of Cu, Be, B, Ti, Zr, As, Sb, Mo, W, or U, Na_2MoO_4 being most suitable. Addition of acid or base to the solution decomposes the complex, fission being accompanied by marked and very characteristic change in rotation. The mode of operation is similar to that described (*loc. cit.*). The following arrangements are deduced: *l*-lactic acid, from natural alanine, to the *l*-series; *l*-β-malamic acid $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, obtained by action of NH_3 on the Me_2 ester of natural *l*-malic acid, to the *l*-series; *d*-β-malamic acid, from *l*-chlorosuccinic acid and aq. NH_3 , to the *d*-series; *l*-α-hydroxy-γ-methylvaleric acid, from natural *l*-leucine, to the *l*-series; *l*-α-hydroxy-β-methylvaleric acid, m. p. 47—

49°, from natural isoleucine, to the *l*-series; *l*-α-hydroxy-β-4-aminazolypropionic acid, from natural *l*-histidine, to the *l*-series; *l*-quinic acid to the *l*-series; gluconic acid, from glucose, to the *d*-series; *d*-glucosamic acid, from glucosamine hydrochloride, to the *d*-series. H. W.

Lactic acid. V. Distribution of lactic, glycollic, and α-hydroxybutyric acid as a basis for the analytical determination of these acids. R. DIETZEL and P. SCHMITT (Z. Unters. Lebensm., 1932, 63, 369—391).—Data are tabulated and plotted as graphs relating the partition coeff. at 20° (*f*) and the concn. of non-ionised acid in the aq. phase (*c_w*) for pure and commercial lactic acid (containing, and free from, anhydride) and for glycollic (I) and α-hydroxybutyric acid (II). The ratios of single to double mols. are 1:0.021 and 1:0.126 for lactic acid, and 1:0.0066 and 1:0.070 for (II), in amyl alcohol and Et_2O , respectively, and 1:0.046 for (I) in amyl alcohol. The "true partition coeff." at 20° is given by the concn. of simple mols. of acid in the non-aq. phase/*c_w*, and has the mean vals. of 0.4465 for anhydride-free lactic acid in amyl alcohol + H_2O (0.04469 for 0.5*N*- H_2SO_4), and 0.08896 in Et_2O + H_2O , at 20°. The total concn. of acid (in millimols.) in a given solution may be calc. from $c_a(f + v_a v_w) v_w$, where *c_a* is the final concn. of acid in the amyl alcohol phase, and *v_w* and *v_a* are the final vol. of the aq. and alcoholic phases, respectively. J. G.

Formation of pyruvic acid from methylglyoxal by the catalytic action of hydrocyanic acid. C. V. SMYTHE (Ber., 1932, 65, [B], 819—820).—Dil. solutions of methylglyoxal are shaken with a little HCN at 38° in absence of air until the aldehyde has disappeared and $\text{NHPh}\cdot\text{NH}_2$ is added. Pyruvic acid phenylhydrazone and a non-acidic phenylhydrazone, $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_4$, m. p. 163°, are almost quantitatively obtained. The primary change is a Cannizzaro reaction followed by a benzoin condensation or polymerisation of the reduced product. H. W.

Condensation of pyruvic acid with aldehydes. A. KIRRMANN (Compt. rend., 1932, 194, 1944—1946).—The product obtained by condensation of $\text{COMe}\cdot\text{CO}_2\text{H}$, MeCHO , and Ac_2O is not α-keto-γ-acetoxyvaleric acid (Wohl and Maag, A., 1911, i, 13; 1930, 577), but is α-acetoxyethylpyruvate, $\text{OAc}\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{Ac}$ (*p*-nitrophenylhydrazone, m. p. 195°), since it is readily hydrolysed by H_2O , is not formed when $\text{COMe}\cdot\text{CO}_2\text{Et}$ is used, contains no OH group (Zerevitinov), and does not give a β-acetoxy-alcohol by oxidation with KMnO_4 , which completely disrupts the mol. α-Acetoxypropyl pyruvate, b. p. 108—109°/16 mm. (semicarbazone, m. p. 168°; *p*-nitrophenylhydrazone, m. p. 199°), is similar prepared. The corresponding Bu compound gives a *p*-nitrophenylhydrazone, m. p. 177°. J. W. B.

βλ-Dihydroxypalmitic acid, the non-carbohydrate constituent of rhamnoconvolvulic acid. E. VOTOCEK and V. PRELOG (Chem. Listy, 1931, 25, 489—494).—The acid obtained by Votocek and Valentin (A., 1929, 543) is βλ-dihydroxypalmitic acid, m. p. 83—84° (*Me ester*, m. p. 81—82°; *Et ester*, m. p. 72—73°). On oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ it yields pentadecane-βλ-dione (disemicarbazone, m. p. 132—134°).

AcOH, and *α-ketomyristic acid*, m. p. 69°, the *oxime* (an oil) of which is subjected to the Beckmann change, and the product is hydrolysed, yielding *n*-valeric and sebacic acids, NH_4Bu^+ and ω -aminononoic acid.

R. T.

Corrections. K. VON AUWERS (Ber., 1932, 65, [B], 831—833).—Hydrolysis of dimethylfumaric esters by hot or cold KOH—EtOH gives exclusively dimethylfumaric acid. The observed production of pyrocinchonic anhydride (A., 1929, 1041) is attributed to some undiagnosed cause.

Thionaphthenquinone - 3 - phenylmethylhydrazone was converted by $\text{NPhMe}\cdot\text{NH}_2$ on one occasion into a substance, (?) $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{NPhMe} \\ \text{S} \quad \quad \quad \text{C}\cdot\text{N}\cdot\text{NPhMe} \end{array}$ m. p. 119°, whilst on

other occasions it yielded a compound, m. p. 130—131.5°, with higher S content. The homogeneity of the material m. p. 122—123° (A., 1911, i, 621) is doubtful and it should be deleted from the literature.

1 : 3-Diphenylpyrazoline, m. p. 152—153°, is readily prepared by the action of $\text{NHPH}\cdot\text{NH}_2$ on β -chloropropiophenone; it is obtained slowly and with difficulty by the action of Na on 1 : 3-diphenylpyrazole in EtOH.

H. W.

Ethyl oxalosorbate. W. BORSCHÉ and R. MANTEUFFEL (Ber., 1932, 67, [B], 868—871).—Et sorbate and $\text{Et}_2\text{C}_2\text{O}_4$ in Et_2O in presence of KOEt at 0° afford *Et oxalosorbate* [$\text{Et}_2 \alpha$ -keto- Δ^6 -hexadiene- α -dicarboxylate], m. p. 100° [K derivative (I); 2 : 4-dinitrophenylhydrazones, m. p. 122°], which could not be hydrogenated satisfactorily to Et α -ketosuberate. (I) is transformed by BzCl in Et_2O into *Et₂ α -benzoyloxy- Δ^6 -hexatriene- α -dicarboxylate*, m. p. 77—78°, and by Ac_2O into *Et₂ α -acetoxy- Δ^6 -hexatriene- α -dicarboxylate*, m. p. 50—51°, hydrogenated in presence of Pd to *Et₂ α -acetoxysuberate*, b. p. 180—182°/14 mm. Et_2 oxalocrotonate when hydrogenated affords *Et₂ α -keto-adipate*, b. p. 156—158°/18 mm. (semicarbazone, m. p. 118°; phenylhydrazones, m. p. 77°), and other products. *Et₂ α -benzoyloxymuconate*, m. p. 71—72°, and *Et₂ α -acetoxy-muconate*, b. p. 188—189°/14 mm. (hydrogenated to *Et₂ α -acetoxiadipate*, b. p. 155—160°/12 mm.), are described.

H. W.

Polymorphism phenomena of the stereoisomeric forms of the methyl tartrates. C. WEYGAND, A. WEISSBERGER, and H. BAUMGARTEL (Ber., 1932, 65, [B], 696—701).—Seeding of molten Me *l*-tartrate with Me *d*-tartrate 48° and 50° yields Me *l*-tartrate 48° and a new form, m. p. 50°. They show close resemblance to the seeding forms of the antipodes in mode of solidification, general form, and rate of crystallisation. The two *l*-ester forms are enantiotropic, and the two pairs of forms of the same m. p. correspond completely and are thus analogous pairs of compounds. Me *d*-tartrate 61° does not induce solidification of the molten *l*-ester, although active towards the *d*-melt. Me *dl*-tartrate seeds the molten *d*- or *l*-ester to the forms 48° and the metastable *dl*-ester 84° causes separation of forms 50°; the actions are completely reciprocal. In contrast, the *d*-ester 61° is completely inactive towards the molten *dl*-ester. It appears that seeding action of one antipode is observed towards the other only when an analogous racemate exists and that the racemate is the active

agent. A modification of Me mesotartrate other than the known form, m. p. 111°, could not be obtained. It is completely indifferent to any of its molten stereoisomerides, which, also, do not induce crystallisation in it. The observations of Rumeau (this vol., 22) on the relative stabilities of the forms 50° and 48° are criticised. The transition temp. of the forms lies between 34° and 36° but cannot be determined more accurately by reason of the slowness of the change.

H. W.

ϵ -Keto- α -rhamnohexonic acid. E. VOTOCEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1932, 4, 225—232).— ϵ -Keto- α -rhamnohexonic acid, m. p. 153—154°, $[\alpha]_D^{25} + 6.23^\circ$ in H_2O (marked variation with temp.), is prepared from α -rhamnohexonolactone and HNO_3 . The Ba salt, phenylhydrazones, m. p. 117—118° (Ba salt), *p*-bromophenylhydrazones, m. p. 130—131°, and impure *oxime* are described. It is oxidised by HNO_3 (*d* 1.15) at 100° to mucic acid. E. S. H.

Alginic acid. I. T. MIWA (Sci. Rep. Tokyo Bunrika Daigaku, 1932, 1, 23—27; cf. A., 1930, 892).—Alginic acid from *Undaria pinnatifida* contains a lactone group, and gives on hydrolysis mannuronic acid [cinchonine salt, m. p. 175° (cf. loc. cit.); *brucine* salt (+ $\frac{1}{2}\text{H}_2\text{O}$), m. p. 158—159° (decomp.), (anhyd.) m. p. 175° (decomp.)], oxidised by HNO_3 or Br to mannosaccharic acid. Incomplete hydrolysis of alginic acid gives an acid (*dicinchonine* salt, m. p. 212°), hydrolysed further to mannuronic acid. Alginic acids from various sources give the same products of hydrolysis.

A. A. L.

Reaction of formaldehyde with di-, tri-, and tetra-chloroethylene. H. J. PRINS (Rec. trav. chim., 1932, 51, 469—474).— $(\text{CH}_2\text{O})_x$ condenses with $\text{CHCl}:\text{CCl}_2$ in the presence of conc. H_2SO_4 at 20—25° to give, after pouring into H_2O , the readily polymerised acid $\text{O}(\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CO}_2\text{H})_2$ (I), m. p. 124—126° (1.2—1.4 mols. of HCl being liberated for each mol. of $\text{CHCl}:\text{CCl}_2$ reacting), and a substance, b. p. 135—140°/14 mm., which eliminates HCl in air. Similar condensation of $\text{CCl}_2:\text{CCl}_2$ at 80° affords α -dichloro- β -hydroxypropionic acid, b. p. 145°/4 mm., m. p. 88—89° (40% yield), whilst $\text{CH}_2:\text{CCl}_2$ gives only resinous products.

J. W. B.

Transformation of crystalline trioxymethylene into a polyoxymethylene of higher mol. wt. H. W. KOHLSCHUTTER and L. SPRENGER (Z. physikal. Chem., 1932, B, 16, 284—302; cf. A., 1930, 1408).—Trioxymethylene changes in vac. or in contact with gaseous CH_2O under the ordinary pressure into a substance $(\text{CH}_2\text{O})_x$. Reaction occurs at the solid-gas interface and is possibly due to a change in mol. configuration when solid $(\text{CH}_2\text{O})_3$ vaporises. The resultant forms an oriented deposit on the surface of the reactant, pointing to crystallographic similarity. Neither molten $(\text{CH}_2\text{O})_3$ nor tetraoxymethylene undergoes such a reaction.

R. C.

Ethereal oil from *Eryngium fætídum*, L. Presence of Δ^8 -dodecenaldehyde. D. R. KOOLHAAS (Rec. trav. chim., 1932, 51, 460—468).—The oil (0.02—0.04% yield) obtained by steam-distillation contains 84% of an aldehyde fraction, mainly Δ^8 -dodecenaldehyde (I) [semicarbazone, m. p. 158°, de-

pressing that of Δ^8 -decenaldehyde from *Achasma walang* (B., 1930, 302)], together with a small amount of a semicarbazone, m. p. 254° , of an aldehyde (II) $C_{10}H_{12}O$. The aldehydes could not be regenerated from their semicarbazones. Oxidation of (I) with cold 4% $KMnO_4$ in K_2CO_3 affords *n*-decoic acid [identified as its anilide and by conversion into 2-*n*-nonylbenziminazole, (A., 1931, 600)], together with a small amount of an acid $C_{10}H_{10}O_4$, m. p. $90-94^\circ$, probably derived from (II). Oxidation of (I) with Ag_2O or air gives Δ^8 -dodecenoic acid (III) (amide, m. p. 114° ; 2-*n*-undecenylbenziminazole, m. p. 105° ; *Th* and *Mg* salts), identical, and giving identical derivatives, with a specimen synthesised from *n*-decaldehyde and malonic acid (J.C.S., 1910, 97, 311), but contaminated with an acid $C_{10}H_{12}O_2$, m. p. 164° , derived from (II). Oxidation of (III) with 1% $KMnO_4$ converts it into $\alpha\beta$ -dihydroxy-*n*-dodecoic acid, m. p. 123° (? 183°). The formation of (I) by condensation of decaldehyde and MeCHO in the plant is suggested. J. W. B.

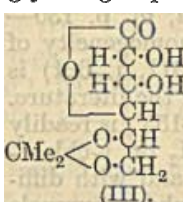
Mechanism of oxidation processes. XXXI. Autoxidation of aldehydes. H. WIELAND and D. RICHTER (Annalen, 1932, 495, 284—291).—MeCHO and AcO_2H do not react in the dry state, but in presence of water the AcO_2H acts as a H-acceptor towards $CHMe(OH)_2$ (cf. A., 1921, i, 889). A dry solution of AcO_2H in MeCHO does not affect dry PhCHO, but dry MeCHO is oxidised by dry BzO_2H (much more slowly than in presence of H_2O), indicating that the following decomp. of an additive compound occurs: $BzO_2H + MeCHO \rightarrow BzO \cdot O \cdot CHMe \cdot OH \rightarrow BzOH + AcOH$. Confirmation that the aldehyde hydrate is responsible for the more rapid oxidation of aldehydes in presence of H_2O is afforded by the observations that $BzCHO$ (which exists solely as the hydrate in aq. solution) is oxidised much more rapidly (by BzO_2H) than is MeCHO in H_2O , and $CCl_3 \cdot CH(OH)_2$ is oxidised faster than chloral in $CHCl_3$. There is little difference in the rate of oxidation of dry and moist PhCHO with BzO_2H . Aq. MeCHO is oxidised more rapidly by BzO_2H at p_H 7.0 (and in presence of NaCl or Na_2SO_4) than in acid solution; a retardation is not effected by I, Pr^iOH , or AcOH. MeCHO is also oxidised slowly by aq. $(NH_4)_2S_2O_8$; the reaction is accelerated by $CuSO_4$. The reactions are carried out in Thunberg tubes in N_2 .

Bz_2O_2 does not react with $CCl_3 \cdot CH(OH)_2$, or $CHBz(OH)_2$ in $CHCl_3$. H. B.

Monosaccharose configurations and inter-relations. J. F. SNELL (Chem. News, 1932, 144, 321—326).—A modification of Rosanoff's chart (J. Amer. Chem. Soc., 1906, 28, 114), an extended terminology, mnemonics, and methods of calculating the no. of isomerides are discussed. D. R. D.

Determination of the ring structure of sugars and sugar derivatives. R. CRIGEE (Annalen, 1932, 495, 211—225).—It is possible to differentiate between furanose and pyranose forms of sugars by oxidation with $Pb(OAc)_4$, since CH_2O can result only when $CH_2 \cdot OH$ is adjacent to a free OH (A., 1931, 461), i.e., from the furanose modification. The danger of rearrangement occurring during the oxid-

ation is remote as an indifferent solvent (AcOH) is used at moderately low temp. The CH_2O produced is collected by steam-distillation under reduced pressure and determined colorimetrically with fuchsin- H_2SO_3 in dil. HCl; a semimicro-method is used. CH_2O is obtained in 81—97% yield from the furanose forms except with α -methylmannofuranoside (I) (10%) and *l*- γ -mannonolactone (II) (7%); no CH_2O (or at most 1—2%) is obtained from the pyranose sugars. The formation of CH_2O from (I) [and (II)] is not a primary reaction (as is usually the case); the initial oxidation is undoubtedly concerned with *cis*- (2:3-)OH groups (the velocity of oxidation of *cis*- is much greater than of *trans*-, whilst the aliphatic glycol group occupies an intermediate position),



whereby an ester of glyoxylic acid and a tetrose results, which can then undergo cyclic acetal formation thus masking the $\cdot CH_2 \cdot OH$ group. In accordance with this view, the yield of CH_2O from (I) is increased to 67% (max.) when oxidation is carried out in presence of HBO_2 ; the yield from (II) is, however, only increased similarly to 12%. In the last case, it is suggested that compound formation occurs (unexpectedly) with the 5:6-OH groups; in agreement with this view, the velocities of oxidation of isopropylidenglucose, *d*- γ -gluconolactone, and β -ethylglucofuranoside are strongly retarded by boric acid. The non-production of CH_2O from isopropylidenemannonolactone (Goodyear and Haworth, A., 1928, 156) indicates structure (III). The method is confined to aldohexoses and their derivatives, of which 18 (and ethylene glycol, glycerol, and mannitol) are examined. H. B.

Preparation of the copper solution for and determination of sugars by Bertrand's method. C. BRUCEAS (Ann. Falsif., 1932, 25, 196—198).—Standardised Fehling's Cu tartrate solution, 0.1*N*- $KMnO_4$, and Bertrand's original $Fe_2(SO_4)_3$ solution only are used. After reduction in a flask the determination is completed in a centrifuge tube. The result may be checked by a determination of un-reduced Cu. T. MoL.

Action of acetic acid on carbohydrates. H. T. CLARKE and H. B. GILLESPIE (J. Amer. Chem. Soc., 1932, 54, 2083—2088).—Reducing carbohydrates, the non-reducing furanoses, sucrose, and inulin are caramelised by boiling AcOH, whilst mannitol and non-reducing glucosides of the pyranose type are completely acetylated. Potato starch yields a continuous series of amorphous acetates, the Ac content of which increases with time of treatment and reaches a limit with the introduction of 3 Ac groups for each glucose residue. The blue colour with I disappears when about 6% Ac is introduced, but the regenerated starch (alkaline hydrolysis) gives the blue coloration. Progressive esterification is accompanied by increasing solubility in non-polar solvents. The products formed from starch and boiling AcOH give (on alkaline hydrolysis) solutions possessing reducing power; the extent of this increases with time, and appears to be mainly due to the degrading action of the H_3PO_4 existing in combination with the 3% of α -amylose present in the

starch, and may be largely suppressed by NaOAc. Apart from its reducing properties, the final product of the action of AcOH on starch resembles the starch triacetates. Completion of the acetylation with Ac_2O gives a non-reducing product. C. J. W. (b)

Action of dilute alkali on *d*-xylose, *d*- and *l*-arabinose, *d*- α -glucoheptose, and *d*-glucoheptulose. W. C. AUSTIN, C. J. SMALLEY, and M. I. SANFORD (J. Amer. Chem. Soc., 1932, 54, 1933—1943).—A 0.5*M* solution of *d*-xylose (I) in saturated $\text{Ca}(\text{OH})_2$ at 30—35° shows $[\alpha]_D^{20-35} +18.2^\circ \rightarrow +10.2^\circ$ (const. after 24 hr.); the p_H of the solution decreases from 10.19 to 6.01 during 1 month. The % of the reducing pentoses decreases from 99.73 to 91.53 and that of the aldopentoses from 97.5 to 88.2 during 1 month. The reaction product (syrup) [freed from unchanged (I)] from (I) and $\text{Ca}(\text{OH})_2$, when redissolved in aq. $\text{Ca}(\text{OH})_2$ shows $[\alpha]_D^{20} -0.26^\circ \rightarrow +2^\circ$ in 144 hr., indicating very little reversibility toward the equilibrium vals. obtained with (I). A 0.5*M* solution of *l*-arabinose in saturated $\text{Ca}(\text{OH})_2$ at 30—35° shows $[\alpha]_D^{20-35} +100^\circ \rightarrow +62^\circ$ (72 hr.), whilst the p_H decreases from 10.8 to 5.28 during 70 days. The % of the reducing pentoses decreases from 94.5 to 86.4 and that of the aldopentoses from 95.0 to 82 during the same time. The syrups obtained from *d*- and *l*-arabinose and alkali (after removal of unchanged material) have not been convertible into cryst. ribose, its *p*-bromophenylhydrazone, or cryst. derivatives of ribonic acid. A syrup obtained from *d*-arabinose and alkali redissolved in $\text{Ca}(\text{OH})_2$, had $[\alpha]_D^{20-35} -7.5^\circ \rightarrow -5^\circ$ (5 days), indicating very little reversibility toward the equilibrium val. (-54.4°) found with *d*-arabinose. In contrast to the very small reversibility in the pentose system, *d*- α -glucoheptose and *d*-glucoheptulose are mutually interconvertible by saturated $\text{Ca}(\text{OH})_2$ to give a common equilibrium val. of $[\alpha]_D^{20-35}$ of approx. $+45^\circ$. C. J. W. (b)

Behaviour of carbohydrates towards thiolacetic acid. B. HOLMBERG and A. OHLSSON (Svensk Pappers-Tidn., 1931, 34, 647—652; Chem. Zentr., 1931, ii, 3458).—Arabinose and xylose react with thiolacetic acid (I) more rapidly than hexoses, for which the reaction velocity diminishes in the order: mannose, galactose, glucose. Filter-paper behaves like cotton wool; maltose and potato starch react with approx. equal velocity only slightly less than that for glucose. Cotton once treated with (I) is less reactive towards that reagent. Treatment of coniferous wood with NaHSO_3 eventually affords cellulose having the same chemical properties as that produced by the action of (I) on cotton. A. A. E.

Fucose. II. Derivatives of *l*-fucose. J. MINSAAS (Rac. trav. chim., 1932, 51, 475—482).—Methylation of *l*-fucose in boiling MeOH containing 0.25% dry HCl for 48—120 hr. (less β -form by long boiling) affords a mixture of α -, m. p. 157.5—158.5°, $[\alpha]_D^{20} -197.45^\circ$ in H_2O , and β -, m. p. 117—119°, $[\alpha]_D^{20} +16.04^\circ$ in H_2O , *l*-methylfucoside, separated by fractional crystallisation from AcOEt (α -form less sol.). From these data by means of Hudson's rule the rotations of α - and β -fucose are calc. to be $[\alpha]_D -153^\circ$ (observed, -158° ; A., 1931, 715) and -44° , respectively. The *d*-methylfucoside (methylrhodose), $[\alpha]_D$

+189.9°, obtained by Votocek and Valentin (A., 1930, 326) probably contains some β -*d*-methylfucoside.

J. W. B.

Carbohydrates. XII. Partial benzoylation with the help of boric acid. P. BRIGL and H. GRÜNER (Annalen, 1932, 495, 60—83).—Anhyd. glucose (1 mol.) and HBO_2 (2 mols.) in boiling COMe_2 give *glucosediboric acid* (I), $\text{C}_6\text{H}_{12}\text{O}_6 \cdot 2\text{HBO}_2$, $[\alpha]_D^{20} +37.1^\circ$ in COMe_2 , which is readily converted into its components by H_2O and EtOH (distillation gives Et borate), and loses $2\text{H}_2\text{O}$ at 100°/vac. over P_2O_5 . (I) and BzCl (5 mols.) in COMe_2 -quinoline give *glucose 2 : 6-dibenzoate* (II), m. p. 182°, $[\alpha]_D^{20} +56.3^\circ$ in EtOH, oxidised by KMnO_4 in COMe_2 to *O*-benzoylglycollic acid, and benzoylated further (Schotten-Baumann) to α -glucopyranose pentabenzoylate. Benzoylation of (II) in presence of HBO_2 (1 mol.) and COMe_2 -quinoline affords *glucose 2 : 3(or 4) : 6-tribenzoate*, m. p. 181°, $[\alpha]_D -51.71^\circ$ in CHCl_3 , also formed in small amount during the prep. of (II). (II), Ac_2O , and NaOAc at 100° give *2 : 6-dibenzoyl-1 : 3 : 4-triacetylglucose*, m. p. 176°, $[\alpha]_D^{20} +64.7^\circ$ in COMe_2 (passes gradually over H_2SO_4 into a labile form, m. p. 125—154°, $[\alpha]_D^{20} +105.9^\circ$ in COMe_2), converted by HBr-AcOH into the amorphous *1-bromo-2 : 6-dibenzoyl-3 : 4-diacetylglucose*, $[\alpha]_D^{20} +176.4^\circ$ in CHCl_3 . This is converted by $\text{Ag}_2\text{CO}_3\text{-MeOH}$ into *2 : 6-dibenzoyl-3 : 4-diacetyl- β -methylglucoside* (III), m. p. 166°, $[\alpha]_D^{20} +54.8^\circ$ in COMe_2 , and by Zn dust and 50% AcOH at room temp. into *6-benzoyl-3 : 4-diacetylglucal* (IV), m. p. 92—93°, $[\alpha]_D^{20} +37.7^\circ$ in CHCl_3 . (II) and 1% MoOH-HCl (or MeI and Ag_2O in MeOH) give *2 : 6-dibenzoyl- β -methylglucoside*, m. p. 171—172°, $[\alpha]_D^{20} -29.25^\circ$ in CHCl_3 , also formed by partial hydrolysis of *2 : 3 : 4-tribenzoyl-6-acetyl- β -methylglucoside* (V) (Bergmann and Koch, A., 1929, 428) by Josephson's method (*ibid.*, 428) (whereby migration of a Bz group must occur), which is acetylated to (III) and benzoylated to tetra-benzoyl- β -methylglucoside. More prolonged hydrolysis of (V) gives *6-benzoylmethylglucoside*, the Ac_3 derivative, m. p. 130—131°, $[\alpha]_D^{20} +16.3^\circ$ in CHCl_3 , of which is identical with the compound from *1-bromo-6-benzoyl-2 : 3 : 4-triacetylglucose* (VI), m. p. 52—53°, $[\alpha]_D^{20} +180.6^\circ$ in CHCl_3 , Ag_2CO_3 , and MeOH. (VI) is prepared from *6-benzoyl-1 : 2 : 3 : 4-tetra-acetylglucose*, m. p. 132°, $[\alpha]_D^{20} +32.9^\circ$ in CHCl_3 (by benzoylation of *1 : 2 : 3 : 4-tetra-acetylglucose*), and HBr-AcOH , and is converted by Zn dust and AcOH into (IV). Glucose diethylmercaptal and BzCl (6 mols.) in presence of HBO_2 (2 mols.), COMe_2 , and quinoline give *6-benzoylglucose diethylmercaptal*, m. p. 111—112°, $[\alpha]_D +45.82^\circ$ in CHCl_3 , converted by successive treatment with HgCl_2 in aq. COMe_2 , Ac_2O in pyridine, HBr-AcOH , and $\text{Ag}_2\text{CO}_3\text{-MeOH}$ into *6-benzoyltri-acetyl- β -methylglucoside*. The α -, m. p. 125—126°, $[\alpha]_D^{20} +141.6^\circ$ in CHCl_3 , and β -, m. p. 132—133°, $[\alpha]_D^{20} +79.3^\circ$ in CHCl_3 , *2 : 3-dibenzoyl-4 : 6-di-acetylmethylglucosides* were prepared (by acetylation of the dibenzoylmethylglucosides) for comparison with (III). *Mannitoldiboric acid*, $\text{C}_6\text{H}_{14}\text{O}_6 \cdot 2\text{HBO}_2$, prepared as (I), and BzCl in COMe_2 -quinoline give mannitol 1 : 6-dibenzoate. H. B.

Colorimetric determination of fructose and sucrose in various mixtures. S. Y. WONG (Ling-

nan J. Sci., 1929, 8, 619—623).—The sample (2 c.c. = 2 mg. of fructose) is treated with 0.3% resorcinol solution in AcOH (5 c.c.) and HCl (1 c.c.). This, together with a standard, is heated at 100°, cooled, and diluted to 25 c.c. with glacial AcOH; the red colours are compared, giving the total fructose. To determine combined fructose a 5 c.c. diluted sample (—10 mg. of sucrose) is heated at 100° with 5 c.c. of 20% NaOH; after 6—10 min. Br-H₂O is added, with shaking, and heating is continued for 1 min. The treatment is repeated if the sample is not colourless. Then BrO' is removed with 5% CO(NH₂)₂ solution (2 c.c.); the cooled solution is neutralised with 20% HCl (phenolphthalein) and diluted to 25 c.c. The total fructose in 2 c.c. is determined. The accuracy obtainable in the determination of sucrose and fructose is 2%.

CH. ABS.

Three new derivatives of *d*-glucoheptulose. W. C. AUSTIN (J. Amer. Chem. Soc., 1932, 54, 1925—1932; cf. A., 1930, 894).—*d*-Glucoheptulose (I) (*hexaacetate*, m. p. 112°, $[\alpha]_D^{25} + 87^\circ$ in CHCl₃) and approx. 1% MeOH-HCl give 63% of *α*-methyl-*d*-glucoheptulose, m. p. 138—140°, $[\alpha]_D^{25} + 108.5^\circ$ in H₂O (*pentaacetate*, m. p. 110°, $[\alpha]_D^{25} + 78.5^\circ$ in CHCl₃). The rotatory powers of the above derivatives indicate that they are *α*-forms and contain a 2:5-ring. The remainder of the paper is devoted to the calculation of rotations, all of which support the view that the known form of (I) contains a 2:5-ring which corresponds with the 1:4-ring in the ethylglucosides of Haworth and Porter (A., 1930, 196). C. J. W. (b)

Structure of *γ*-glucosides. P. A. LEVENE, A. L. RAYMOND, and R. T. DILLON (J. Biol. Chem., 1932, 96, 449—459).—Reduction of *δ*-methylglucoheptonolactone (from 3-methylglucose by the HCN synthesis; A., 1924, i, 944) with 2.5% Na-Hg gives 4-methylglucoheptose (I), sinters 145°, m. p. 158—160°, clears at 185°, $[\alpha]_D^{25} - 26.0^\circ$ to -15.0° in H₂O (*osazone*, m. p. 160°, decomp. 198—200°; $[\alpha]_D^{25} + 10.9^\circ$ to $+20.5^\circ$ in pyridine-EtOH). Comparative determinations (this vol., 500) of free sugar, *γ*- and normal glucosides present, and of optical rotation, during glucoside formation with HCl-MeOH, for (I), and for glucose (II), tetramethyl-glucopyranose, -glucofuranose, 2- (III) and 3-methylglucose (IV), show that, under conditions which lead to the formation of both normal and *γ*-glucosides in the case of (II), (III), and (IV), (I) gives only a normal glucoside. The structure of this as a pyranoside is proved by complete methylation (Purdie) to the *pentamethylmethylheptoside*, hydrolysed by 1.7*N*-HCl at 85° to *α*-pentamethylglucoheptose, m. p. 40°, partial solidification, remelting at 80°, $[\alpha]_D^{25} - 8.0^\circ$ to -44.5° in 48 hr. in H₂O (Haworth and others, this vol., 46, give $[\alpha]_D - 62.5^\circ$ to -42.5° , m. p. 84°, for the *β*-form), oxidised with Ba(IO₃)₂ to 2:3:4:6:7-pentamethyl-*α*-glucoheptonolactone, identical with that obtained by Haworth (*loc. cit.*) and prepared by methylation of *α*-glucoheptonolactone. These results, in conjunction with previous work (A., 1931, 1149), prove the furanose structure of the *γ*-glucosides of unsubstituted sugars. As expected, unmethylated glucoheptose forms both a normal and a *γ*-glucoside.

J. W. B.

Sugar of sarmentocymarin. W. A. JACOBS and N. M. BIGELOW (J. Biol. Chem., 1932, 96, 355).—The *α*-deoxy-sugar *sarmentose*, C₆H₁₁O₃(OMe), m. p. 78—79°, $[\alpha]_D^{25} + 12^\circ$ to $+15.8^\circ$ in H₂O in 24 hr., obtained by hydrolysis of sarmentocymarin (A., 1929, 729) has been obtained cryst.

J. W. B.

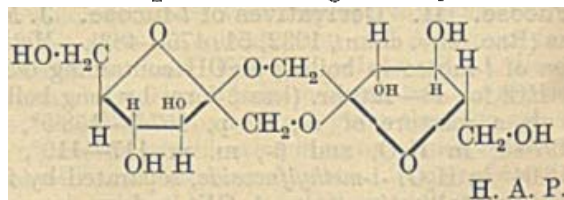
So-called hexosans from starch. E. BERNER and R. PETERSEN (Ber., 1932, 65, [B], 687—693).—“Hexahexosan” prepared according to Pictet has apparent mol. wt. 983 (calc. 972), but contains 2.45% of glycerol and 3.25% of EtOH; after allowance for these impurities, the mean mol. wt. of the degradation product is about 20,000. For various preps. $[\alpha]_D$ varies between $+173^\circ$ and $+186^\circ$. “Trihexosan” has apparent mol. wt. 461 [calc. for (C₆H₁₀O₅)₃ 486], but contains 4.66% of EtOH and 8.80% of glycerol, after allowance for which the residue has mean mol. wt. about 4500. For different preps. $[\alpha]_D$ varies between $+143^\circ$ and $+166^\circ$. Elementary analysis confirms the analytically established proportions of (C₆H₁₀O₅)_n, EtOH, and glycerol. Agitation of a product with EtOH during a week at 40° followed by boiling with frequently-renewed EtOH for 1 week diminished the glycerol content from 12.5% to 5.7%. The “glycerol-monohehexosan” compound of Pictet, $[\alpha]_D + 70^\circ$, apparent mol. wt. 240, contains C₆H₁₀O₅ and glycerol in the ratio 1:1, but H₂O is lost during the prep. The non-homogeneity is established (1) by agitation with COMe₂ or EtOAc, whereby extracts very rich in glycerol are obtained, and (2) by pptn. from EtOH-Et₂O, whereby the glycerol content is greatly diminished. The interpretation given to the thermal degradation of starch by Pictet and co-workers is not valid.

H. W.

Dependence of molecular magnitude in polysaccharides on *p_H*. K. HESS and M. ULMANN (Naturwiss., 1932, 20, 296).—Osmotic measurements show *α*-dextrin to be a tetrasaccharide, its stability depending on the *p_H* of the aq. solution employed. With *p_H* 8—8.5 the osmotic pressure had a val. agreeing with a disaccharide.

W. R. A.

Structure of inulin. Derived difructose anhydrides. W. N. HAWORTH and H. R. L. STREIGHT (Helv. Chim. Acta, 1932, 15, 693—698).—The *Ac₆* derivative of Jackson and Goergen’s “difructose anhydride I” (cf. A., 1931, 72; 1929, 1280), m. p. 137° (sinters 125°), $[\alpha]_D + 0.6^\circ$ in CHCl₃, is converted by Me₂SO₄ and aq. NaOH in COMe₂ into a *Me₆* derivative, $[\alpha]_D^{25} + 24^\circ$ in CHCl₃, which is hydrolysed by 3% aq. HCl at 95° to 3:4:6-trimethylfructofuranose (A., 1928, 510). The formula below is therefore assigned to the original anhydride:



H. A. P.

Acetylation and methylation of inulin. W. N. HAWORTH and H. R. L. STREIGHT (Helv. Chim. Acta, 1932, 15, 609—615).—Inulin triacetate, $[\alpha]_D^{25} - 34^\circ$ in CHCl₃, mol. wt. 6300 (Rast), is obtained in 95% yield

by swelling inulin in pyridine at 80° and then digesting with Ac_2O at room temp. With AcCl in place of Ac_2O a poorer yield of a degraded product is obtained. It is converted by Me_2SO_4 and 30% aq. NaOH in COMe_2 at 55° into trimethylinulin, m. p. 140°, $[\alpha]_D^{20}$ -54° to -55° in CHCl_3 , which on hydrolysis gives 3:4:6-trimethylfructofuranose. Impure trimethylinulin can be purified by deposition from hot EtOH . H. A. P.

Acetylation of inulin. W. E. HAGENBUCH (Helv. Chim. Acta, 1932, 15, 616—618).—Inulin triacetate, $[\alpha]_D^{20}$ -45.5° in AcOH , is rapidly prepared by adding inulin in aq. pyridine to a mixture of pyridine and Ac_2O , and purifying the product by pptn. from MeOH or AcOH . H. A. P.

Cryoscopy and mol. wt. of polymerides of carbohydrates. E. PATERNO (Atti R. Accad. Lincei, 1932, [vi], 15, 260—261).—The worthlessness of cryoscopic determinations of mol. wts. of cellulose derivatives, sol. starch, etc. is emphasised.

T. H. P.

Molecular size of the lower hydrolytic products of cellulose. M. ULMANN and K. HESS (Naturwiss., 1932, 20, 316—317).—Osmotic pressure measurements of "endecamethyltri-ose" (obtained by acetylation of cellulose) in 0.06% aq. solution (p_R 4.5—6) give mol. wt. 457, indicating that the compound is octa-methylcellobiose. W. R. A.

Cellodextrin, amyloid, and pentosans. E. PATERNO (Atti R. Accad. Lincei, 1932, [vi], 15, 263—265).—The statement that parchment-paper is composed of amyloid is criticised. Such paper, prepared from Swedish filter-paper, contained (on dry matter) 6.21% of hemicellulose and 3.7 of β -cellulose, and gave Cu no. 1.26. Amyloid appears to be formed as a transitory product, but it has never been prepared, and so-called cellodextrin is oxycellulose (cf. Caille, A., 1925, i, 371; Samec and Matula, A., 1921, i, 397). Cellulose may be converted into pentosans, with intermediate formation of oxycellulose. T. H. P.

Cellulose in Schweitzer's reagent. E. PATERNO (Atti R. Accad. Lincei, 1932, [vi], 15, 262—263).—Highly viscous and conc. solutions of cellulose in this reagent may be prepared by digesting ground cellulose or cotton in 10% aq. $\text{Cu}(\text{OAc})_2$, rendering alkaline with Na_2CO_3 , filtering after 24 hr., washing, and dissolving in conc. aq. NH_3 . T. H. P.

Analysis and properties of benzylcellulose. L. MEUNIER and M. GONFARD (Compt. rend., 1932, 194, 1839—1842).—Benzylcellulose is heated at the b. p. with Ac_2O and a few drops of conc. H_2SO_4 , the product distilled in superheated steam, the AcOH in the cold distillate neutralised, and the $\text{CH}_2\text{Ph}\cdot\text{OAc}$ determined by hydrolysis with NaOH . Benzylcellulose is much less hygroscopic than cellulose acetate and does not swell appreciably in H_2O ; it swells considerably, however, in 2—3% aq. NH_2Ph or PhOH . It is unaffected by 30% aq. NaOH and 50% aq. H_2SO_4 at 25°. Measurements of η of EtOH -benzene solutions are made by the capillary and ball methods, and the ageing of such solutions is studied. H. A. P.

Mechanism of decomposition of cellulose nitrate. DESMAROUX (Compt. rend., 1932, 194, 1649—1651).—From consideration of observations (cf. B., 1901, 609; 1923, 686A; 1928, 70, 656; 1929, 873; 1930, 412) it is concluded that the first stage in the destruction by heat of cellulose nitrate is the partial combustion, by O of NO_2 , of one of the rings of the glucose residue resulting in breaking the chain, but leaving the other rings intact. C. A. S.

Formation of cellulose xanthate. K. HESS and C. TROGUS (Cellulosechem., 1932, 13, 84—85; cf. following abstract).—When soda-cellulose I is treated with CS_2 the X-ray diagram remains unchanged, and after subsequent drying the material gives a diagram identical with that of soda-cellulose III. When cellulose xanthate and soda-cellulose I are washed with MeOH or EtOH the products from the two at each stage give the same diagrams. It is suggested that treatment with CS_2 affects only the fibre or micelle surfaces, so changing the skin as to destroy the insolubility of the material. Viscose solution consists essentially of dispersed soda-cellulose I. Analysis of cellulose treated with CS_2 does not give the composition of the actual cellulose xanthate, much soda-cellulose being still present. A. G.

Action of alcohols on soda-cellulose. C. TROGUS and K. HESS (Cellulosechem., 1932, 13, 81—83).—X-Ray diagrams show that when soda-cellulose I (fibre period 20.53 Å.), formed by the action on cellulose of 12.5 to 19 wt.-% NaOH , is washed with MeOH or EtOH it is converted successively into soda-cellulose III (fibre period 10.1 Å.), soda-cellulose III', and cellulose hydrate. Soda-cellulose III is also formed by the action of aq.-alcoholic NaOH on cellulose, and the first two steps of the above process are very rapid. When soda-cellulose II (fibre period 15.1 Å.), produced by aq. NaOH of > 21 wt.-%, is similarly washed, products giving diffuse diagrams are obtained, and it is concluded that washing with alcohols is inadvisable in preparing pure soda-celluloses. A. G.

Effect of moderate heat on the chemical compounds of wood. I. SLAVIK (Chem. Listy, 1932, 26, 211—218).—Spruce (*Picea excelsa*) and beech wood lose 10.6 and 13.4% of their wt. after heating at 140—145° for 14 and 9 days, respectively. At the same time the content of H_2O -sol. substances rises (in cold H_2O , spruce, from 2.40 to 3.43%, beech, from 0.89 to 5.68%; in H_2O at 100°, spruce, from 4.0 to 9.67%, beech, from 2.45 to 16.66%); the same applies to substances sol. in 1% NaOH (spruce, from 13.59 to 44.03%, beech, from 18.14 to 55.55%). The content of C_6H_6 - EtOH -sol. substances falls in the case of spruce from 2.45 to 0.92%, and rises in the case of beech from 1.04 to 9.74%. The lignin content of spruce rises from 30.12 to 34.58%, whilst that of beech falls from 22.65 to 22.48%. The cellulose and pentosan contents of spruce fall from 53 to 49.1% and from 11.4 to 7.68%, and of beech from 58.9 to 47.8% and from 25.8 to 17.9%, whilst the OMe group content falls from 5.04 to 4.06% for spruce, and from 5.71 to 4.7% for beech.

Combination of eight biogenic amines with flavianic acid. E. MULLER (Z. Biol., 1932, 92, 513—518).—The following salts of flavianic acid are described (the figures in parentheses are the no. of mols. of acid combined with 1 mol. of base): trimethylamine oxide (1), decomp. 215—219°; NMe₄ (1), decomp. 259—260°; tetramethylenediamine (2), decomp. 268—273°; pentamethylenediamine (2), decomp. 260—267°; betaine (1), decomp. 231—262° after darkening at 220°; isoamylamine (1), m. p. 213—215° after darkening at 180°; methylpyridinium, decomp. 188—190° after sintering at 185°; galegine (A., 1924, i, 502), m. p. 159—160° (decomp.). The solubilities of these salts in H₂O, MeOH, and EtOH and those of previously described flavianates (A., 1929, 916) in MeOH are given.

F. O. H.

Salts of low m. p. V. Alkylated ammonium picrates. P. WALDEN and E. J. BIRR.—See this vol., 685.

Reduction products of certain cyclic methylenamines. II. J. GRAYMORE (J.C.S., 1932, 1353—1357).—Condensation of primary amines with CH₂O gives the corresponding cyclic base (R·N·CH₂)₃, reduced by Zn and HCl to NHMeR. The following have been prepared: *triisobutyltrimethylenetriamine*, b. p. 255° (picrate, m. p. 107°; oxalate, m. p. 165°), reduced to NHMeBu⁸ (picrate, m. p. 103°; hydrobromide, m. p. 203°); 2:4-dinitromethylisobutylaniline, m. p. 92—93°; *tri-n-butyltrimethylenetriamine*, b. p. 285° (picrate, m. p. 75—76°; hydrochloride), reduced to NHMeBu^a (nitrosoamine, b. p. 198°; hydrochloride, m. p. 170°; picrate, m. p. 110—111°); *triisoamyltrimethylenetriamine*, b. p. 290—300° (oxalate, m. p. 115°; picrate, m. p. 75°; hydrochloride; urate), reduced to methylisoamylamine (nitrosoamine, b. p. 204—205°; hydrobromide, m. p. 183°); and *tribenzyltrimethylenetriamine*, b. p. 240° [oxalate, m. p. 135° (decomp.)], reduced to a mixture of the primary and sec. bases (p-toluenesulphonbenzylmethylamide, m. p. 92°; 2:4-dinitromethylbenzylaniline, m. p. 140°).

F. R. S.

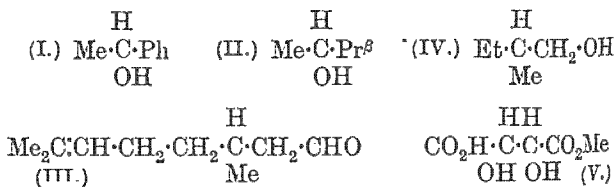
Co-ordination of hexamethylenetetramine. A. PRERET, A. GISLON, and A. KRAWCZYNSKI (Bull. Soc. chim., 1932, [iv], 51, 454—480).—By crystallisation from aq. solutions containing an excess of hexamethylenetetramine (Hex), the following complex salts of Li (1.25, 8.11), Na (1.45, 6.96), K (1.55, 5.28), Mg (0.9, 31.3), Mn (0.98, 26.4), Ca (1.25, 16.23), Sr (1.42, 12.57), Ba (1.56, 10.42), Ni (0.8, 32.7), Zn (0.76, 43.9), and Cu (0.65, 60.02) have been obtained, the vals. in parentheses being, respectively, the ionic radii (r Å.) and charge densities (Δ coulomb × 10⁻²¹/Å.²) (cf. Kapustinski, A., 1929, 1368): LiCl·Hex, 4H₂O; LiI, 3Hex, 7H₂O; LiClO₄·2Hex, 6H₂O; LiCNS, 2Hex, 6H₂O;

NaI, Hex, 4H₂O; MgSO₄·2Hex, 10H₂O, Mg(OAc)₂·2Hex, 10H₂O; CaI₂·4Hex, 12H₂O, Ca(ClO₄)₂·2Hex, 10H₂O; Ca(ClO₄)₂·4Hex, 12H₂O, Ca(NO₃)₂·2Hex, 10H₂O; Sr(ClO₄)₂·2Hex, 10H₂O, Sr(NO₃)₂·2Hex, 10H₂O; Ba(ClO₄)₂·2Hex, 10H₂O, BaI₂·2Hex, 10H₂O; 3ZnCl₂·2Hex, 8H₂O, ZnI₂·2Hex, 8H₂O; ZnSO₄·Hex, 8H₂O; Zn(OAc)₂·Hex; Zn(NO₃)₂·2Hex, 10H₂O; CdCl₂·Hex, 2H₂O;

Cd(NO₃)₂·Hex, 2H₂O; Cd(OAc)₂·2Hex, 2H₂O; HgCl₂·Hex; Hg(CN)₂·Hex, 3H₂O, and Hg(OAc)₂·2Hex. No complexes with Be or K salts could be isolated. Beyond a certain val. of r complex salt formation is prevented, in spite of the increase of surface, by diffusion of the field. For large ionic radii the co-ordination no. is a function mainly of the val. of the electrostatic field in the neighbourhood of the cation, whilst for small vals. of r it depends mainly on the surface area of the ion. Whilst the electrostatic effect of the cation is the major factor, the effect of the anion seems to depend entirely on spatial factors. Halide and SCN⁻ anions with bivalent cations give uniformly complexes of the types MX₂·2Hex, 10H₂O or MX₂·4Hex, 12H₂O, but with univalent cations the types MX·Hex, 4H₂O, MX·2Hex, 5H₂O, and MX·3Hex, 7H₂O are obtained, the co-ordination no. increasing with increasing vol. of the halogen. In the higher hydrates some of the H₂O mols. must be attached by dipolar association, the co-ordination valency of hexamethylenetetramine being 1. The formation of N(CH₂·OH)₃ by hydrolysis of NiCl₂·2Hex, 10H₂O (Duff and Bills, A., 1929, 545) is not confirmed.

J. W. B.

Stereochemistry. Synthesis of derivatives of active amino-acids. XV. Steric series. K. FREUDENBERG (Sitzungsber. Heidel. Akad. Wiss., 1931, No. 9, 3—14; Chem. Zentr., 1932, i, 932—933).—(+)-Phenylmethylcarbinol (I) (–)-methylisopropylcarbinol (II), (+)-citronellal (III) (+)-methyl-ethylcarbinylcarbinol (IV), and (+)-methyl meso-tartrate (V) have the configurations:



Glucosamine and chondrosamine correspond figuratively with glucose and galactose. Hibbert's stereochemical formula for glucose is rejected. Azidopropionylglycine on reduction affords alanyl-glycine, and Ph azidopropionate gives phenyl-alanine (hydrochloride, m. p. 130°).

A. A. E.

New betaine: ε-trimethylammonium α,γ-dimethyloctoate and its derivatives. K. C. CHEN (Lingnan Sci. J., 1929, 8, 637—645).—Hydrolysis of l-menthone isooxime by Wallach's method gave l-ε-amino-βε-dimethyloctoic acid, m. p. 194—195° (decomp.), [α]_D²⁰ –3.12°; treatment with NaOH and MeI gave ε-NHMe₃ βε-dimethyloctoate, m. p. 185° (decomp.), [α]_D²⁰ –16.38° [chloroaurate, m. p. 116—117°; chloroplatinate, m. p. 206°; ferrocyanide, m. p. 225—230 (decomp.); hydrochloride, m. p. 191—192°].

CH. ABS.

Titration constants of αβ-diaminopropionic acid and their relation to the constants of various isomerides. J. P. GREENSTEIN (J. Biol. Chem., 1932, 96, 499—510).—Dissociation consts. of αβ-diaminopropionic acid are determined and compared with those of αδ-diaminovaleric and αε-diaminohexonic acids. The acidity of the mol. decreases with increas-

ing distance between NH_2 groups. The MacInnes equation is applied to a series of NH_2 -acids, diamines, and dicarboxylic acids. The proportionality const. in the equation appears to depend only on the nature of the substituted groups and to be independent of the nature of the ionising group. J. B. B.

Reduction of acetoximino-esters. V. CERCHEZ and (MLLE.) C. COLESIU (Compt. rend., 1932, 194, 1954—1956).—Reduction of the Ac derivatives of oximino-esters, $\text{O}=\text{N}-\text{CR}\cdot\text{CO}_2\text{R}'$, with Al-Hg occurs through the tautomeride $\text{CR}(\text{CO}_2\text{R}')\cdot\text{NOAc}$ to give α -acetamido-esters, $\text{CHR}(\text{NHAc})\cdot\text{CO}_2\text{R}'$. Thus Et α -acetoximino-acetoacetate, -cyanoacetate, b. p. $148^\circ/14$ mm., and -malonate, b. p. $165^\circ/15$ mm., afford, respectively, Et α -acetamido-acetoacetate, m. p. 141° , -cyanoacetate, m. p. 129° , and malonate. J. W. B.

Synthesis of cyanic acid and carbamide by ammoniacal oxidation of carbon compounds. G. LAUDE (Compt. rend., 1932, 194, 2070—2072).—Improved yields of HCNO and $\text{CO}(\text{NH}_2)_2$ have been obtained from the compounds previously examined (A., 1919, i, 152, 313, 459; 1921, i, 165, 321, 500, 652) by diminishing the proportion of substance used.

Action of diethylamine on methyl acetylenedicarboxylate. C. VASSILIADÈS and L. CAPATOS (Compt. rend., 1932, 194, 1830—1832).—Interaction of NHEt_2 with Me , acetylenedicarboxylate in EtOH gives the *bisdiethylamide* (tetrabromide) and the *Me* ester (I), b. p. 171 — $172^\circ/20$ mm. (tetrabromide), of the (mono)diethylamide of acetylenedicarboxylic acid. (I) with MgEtBr (1 equiv.) gives γ -keto- Δ^2 -hexinenodiethylamide, b. p. $131^\circ/22$ mm. [semicarbazone (or $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ additive product?), m. p. 216 — 217°]. H. A. P.

Benzenesulphonylguanidines. H. T. CLARKE and H. B. GILLESPIE (J. Amer. Chem. Soc., 1932, 54, 1964—1968).—The introduction of the PhSO_2 group into guanidine (I) and its derivatives occurs only in presence of alkali hydroxides (not with carbonates). With arginine (II) and carbonate, benzenesulphonylation occurs in the α -position; with excess of alkali hydroxide the guanidino-group is also acylated. Guanidine carbonate, PhSO_2Cl , and aq. K_2CO_3 give the benzenesulphonate, m. p. 209 — 210° (all m. p. are corr.), which can be crystallised from dil. NaOH ; with KOH , the benzenesulphonyl derivative (III) [hydrochloride, m. p. 160 — 163° ; picrate, m. p. 190 — 191° ; Ac derivative, m. p. 197 — 197.5° ; Me derivative, m. p. 180.5 — 181° ; as-Me, derivative, m. p. 164.5 — 165.5° ; piperidino-derivative, m. p. 168.5 — 169° (the last three compounds are prepared by acylation of the corresponding guanidine)] of (I) results. (II), PhSO_2Cl , and aq. K_2CO_3 give the monobenzenesulphonyl derivative (isolated as the picrate, m. p. 161 — 162°); with NaOH , there results the dibenzenesulphonyl derivative, a colourless resin. This with BuOH and AcOEt apparently gives the Bu ester, hydrolysed by aq. $\text{EtOH}\cdot\text{NH}_3$ to the NH_4 salt. (III) is a weak base and shows no tendency to form a Na derivative. C. J. W. (b)

Reactions of aliphatic nitriles. K. ZIEGLER and H. OHLINGER (Annalen, 1932, 495, 84—112).—The

prep. of *tert.*-aliphatic nitriles from *sec.*-nitriles and alkyl halides in presence of metal amides is investigated. $\text{CHEt}_2\cdot\text{CN}$ and NaNH_2 in C_6H_6 at 60 — 70° give (by addition) the compound, $\text{CHEt}_2\cdot\text{C}(\text{NNA})\cdot\text{NH}_2$, hydrolysed to diethylacetamidine, b. p. $110^\circ/9$ mm. (hydrochloride, m. p. 205 — 206°), and converted by allyl bromide into diethylacetylalylamidine, b. p. $116^\circ/13$ mm. (chloroplatinate, m. p. 193 — 195°). LiBu and $\text{CHMe}_2\cdot\text{CN}$ in C_6H_6 give $\text{CHMe}_2\cdot\text{CBu}\cdot\text{NLi}$, hydrolysed by dil. HCl to COPr^nBu . LiNEt_2 (from LiPh and NHEt_2 in Et_2O) and $\text{CHMe}_2\cdot\text{CN}$ give $\text{Li}\cdot\text{CMe}_2\cdot\text{CN}$ (or $\text{CMe}_2\cdot\text{CNLi}$), which with allyl chloride affords α -allyl-isobutyronitrile (I), b. p. 150° ; α -ethyl- α -allylbutyronitrile (II), b. p. 71 — $72^\circ/12$ mm., is similarly prepared from $\text{CHEt}_2\cdot\text{CN}$. (I) and (II) are also obtained by similar reactions using the compounds from MgEtBr and NHEt_2 and dicyclohexylamine, respectively, in place of LiNEt_2 . Successive treatment of a suspension of LiNH_2 (from LiBu and NH_3) in Et_2O with $\text{CHMe}_2\cdot\text{CN}$ and allyl chloride also affords (I). Similar successive treatment of *N*-lithiocyclohexylamine gives (with $\text{CHEt}_2\cdot\text{CN}$) a quant. yield of diethylacetatecyclohexylamidine (III), m. p. 119° (hydrochloride, m. p. 235°), but treatment with a mixture of $\text{CHEt}_2\cdot\text{CN}$ and allyl chloride affords 60% of (II) and 17% of (III). Similarly, NaNH_2 in C_6H_6 suspension heated with $\text{CHEt}_2\cdot\text{CN}$ and allyl chloride affords 53% of (II) and some amidine. $\text{CEt}_2\cdot\text{CN}$ and NaNH_2 give (by addition) $\text{CEt}_2\cdot\text{C}(\text{NNA})\cdot\text{NH}_2$, hydrolysed to triethylacetamidine, b. p. 121 — $124^\circ/10$ mm., m. p. 62 — 63° (hydrochloride, m. p. 186 — 187°), whilst lithio- α -ethylbutyronitrile and NH_3 in Et_2O at -10° afford (primarily) LiNH_2 and $\text{CHEt}_2\cdot\text{CN}$.

The following are prepared by complete or partial alkylation of nitriles using an active suspension of NaNH_2 (details of prep. given) usually in C_6H_6 : triallylacetonitrile, b. p. $95^\circ/12$ mm. (from MeCN); α -diethylbutyronitrile, b. p. 83 — $84^\circ/12$ mm. (from PrCN); α -dibenzylpropionitrile, b. p. $205^\circ/17$ mm., m. p. 101 — 102° (from EtCN); α -diethylhexonitrile, b. p. $86^\circ/11$ mm. (from $\text{CHEt}\cdot\text{CN}$ and BuBr); α -ethyl- α -isopropylbutyronitrile, b. p. 71 — $73^\circ/12$ mm.; α -diisopropylbutyronitrile, b. p. $85^\circ/12$ mm. (from $\text{CHEtPr}^n\cdot\text{CN}$); α -di-*n*-octylhexonitrile, b. p. 191 — $193^\circ/0.03$ mm. (from hexonitrile and octyl bromide); γ -methoxy- α -dimethylbutyronitrile, b. p. $67^\circ/14$ mm. (from $\text{CHMe}_2\cdot\text{CN}$ and $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$); γ -*p*-tolylthiol- α -dimethylbutyronitrile, b. p. 186 — $188^\circ/14$ mm. (from $\text{CHMe}_2\cdot\text{CN}$ and *p*- $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$); γ -diethylamino- α -diethylbutyronitrile, b. p. 129 — $130^\circ/17$ mm. (from $\text{CHEt}_2\cdot\text{CN}$ and $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$); hexonitrile (from MeCN and BuBr); $\text{CHEt}_2\cdot\text{CN}$ (from PrCN or MeCN and EtBr); α -*n*- and α -iso-propylbutyronitriles; γ -phenoxy- α -ethylbutyronitrile, b. p. 169 — $171^\circ/14$ mm. (from PrCN and $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$); α -butylbutyronitrile, b. p. 69 — $70^\circ/12$ mm. (from PrCN and BuCl); $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CN}$ and $\text{CH}(\text{CH}_2\text{Ph})_2\cdot\text{CN}$ (from MeCN and CH_2PhCl). H. B.

Catalytic hydrogenation of amino-nitriles. E. STRACK and H. SCHWANEGER (Ber., 1932, 65, [B], 710—713).—Hydrogenation of α -aminoisobutyronitrile (in 99% MeOH or 96% EtOH), alaninenitrile (in abs. EtOH), dimethylglyoxime, and phenylacetoneitrile (in 80% EtOH) is best effected in presence of large

amounts of Pd to ensure quick action and in acid medium. The following compounds are described: $\alpha\beta$ -diaminopropane (yield 32%, but 5% of reduction is very rapidly effected by Na and EtOH), isolated as picrate, m. p. 236° (decomp.), and *di-m-nitrobenzoyl* derivative, m. p. 222—223°; $\alpha\beta$ -diamino- β -methylpropane [hydrochloride, m. p. 295° (decomp.); *picrate*, m. p. 238° (decomp.) after darkening at 230°; *picrolonate*, m. p. 256—257° (decomp.); *compound* $C_4H_{12}N_2Cl_4Hg_2$, m. p. 151—152°; *chloroplatinate*, (+2H₂O) and anhyd., m. p. 265° (decomp.); *chloroaurate*, m. p. 230° (decomp.) also +2.5H₂O, m. p. about 135° in closed capillary, converted by crystallisation from hot H₂O into the *salt* $C_4H_{12}N_2Cl_6Au_2 \cdot H_2O$, m. p. 225° (decomp.)]; $\beta\gamma$ -diaminobutane (45% yield); β -amino- α -phenylethane.

H. W.

Supposed sodium ferroisocyanide. A. FERRET and A. GISLON (Bull. Soc. chim., 1932, [iv], 51, 480—486).—Identity of all chemical properties and of the X-ray diagrams shows that the compound obtained by the action of CH₂O on Na₂[Fe(CN)₅NO] and stated to possess a carbylamine structure (Brunner, A., 1930, 1009) is ordinary Na₄Fe(CN)₆ + 9H₂O instead of +10H₂O.

J. W. B.

Compounds of arsonium bases. L. CAPATOS (Compt. rend., 1932, 194, 1658—1659).—In MeOH, AsMe₄I treated with Cl gives the corresponding *dichloriodide*, m. p. 121—122°, and with Br the *dibromiodide*, m. p. 126—127°. AsMe₂Et₂I forms mol. compounds with HgI₂ (m. p. 253—254°) and with CdI₂.

E. W. W.

Co-ordination compounds of boron trifluoride and organic esters. G. T. MORGAN and R. TAYLOR (J.C.S., 1932, 1497; cf. A., 1931, 1404).—*BzOMe*, BF₃, m. p. 40—55° (decomp.), and *compounds*, C₈H₈O₃.BF₂, m. p. 128°, and C₃H₆O₃.BF₃, b. p. 60°/3 mm., from BF₃ and Me salicylate and glycolate, respectively, are described.

F. R. S.

Reactions with boron fluoride. I. Preparation of esters. H. D. HINTON and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1932, 54, 2017—2018).—(AcOH)₂.BF₃ is a catalyst (concn. 1—2%) for the prep. of AcOEt (yield 47—50%). AcOPr is similarly obtained in 53.5% yield using PrOH, AcOH, and BF₃. Alkyl propionates are prepared from EtCO₂H, BF₃ and EtOH, PrOH, BuOH, and amyl alcohol.

C. J. W. (b)

Preparation of organolithium compounds. H. GILMAN, E. A. ZOELLNER, and W. M. SELBY (J. Amer. Chem. Soc., 1932, 54, 1957—1962).—Details are given for the prep. of Li aryls and LiBu from Li and the corresponding halides. Excellent yields are readily obtainable under conditions essentially those used for the related Grignard reagents. Simplifications in procedure make possible the prep. and manipulation of organoalkali compounds in readily available apparatus without using sealed glass containers. The following are prepared in yields of 66—95%: LiBu; LiPh; Li *o*-, *m*-, and *p*-tolyls; Li *o*- and *p*-anisyls; Li α - and β -naphthyls.

C. J. W. (b).

Condensation by sodium instead of by the Grignard reaction. IV. Probable existence of

a new intermediate, "metal halyl," in the reaction. A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1932, 54, 1919—1924; cf. this vol., 157).—PhCl, PhBr, and BuCl act as carriers of Na to CPh₃Cl, thus resembling CPh₂ and (CPh₂)₂. NaCl is formed to a greater extent than NaBr from Na, CPh₃Cl, and PhBr. The results indicate the formation of a complex between Na and PhBr, which is designated a "metal halyl." The position of the "metal halyl" as an intermediate (first) step in the formation of a free hydrocarbon radical and metal alkyls or aryls is discussed.

C. J. W. (b)

Factors influencing the yield of Grignard reagents and the ratio of MgR₂ to MgRX. G. O. JOHNSON and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1943—1947).—The yields of Grignard reagent (and the proportion of Mg dialkyl contained therein) as influenced by the presence of Cu, HgCl₂, etc. have been determined for 16 alkyl halides. The proportion in which the Wurtz and Grignard reactions occur varies with the particular alkyl group and the halogen involved, and is modified by the presence of small quantities of Cu and Zn and of Hg and other metal halides. The effect of Cu, *e.g.*, on the proportion of the two competitive reactions, varies both in amount and in direction of change; thus, the Grignard reaction is decreased from 72 to 6% for allyl bromide, but increased with *tert*-BuCl from 28 to 43%. The proportion of the active Grignard reagent existing as MgR₂ varies with the alkyl halide used (the variation is from 6% for EtI to 84% for BuCl), and is modified (also in amount and direction) by the presence of Cu, HgCl₂, etc. Reagents which, for a given alkyl halide, decrease the yield of Grignard reagent also in general decrease the proportion of the reagent existing as MgR₂ and *vice versa*. Alkyl halides, except allyl bromide, are inactive towards the Grignard reagent made from them (and also toward the MgR₂ component) under the conditions of formation of the reagent. It is improbable, therefore, that the formation of hydrocarbons (Wurtz reaction) during the reaction of Mg with RX is dependent on the reaction of the Grignard reagent with the alkyl halide.

C. J. W. (b)

Diisopropyl ether as a solvent in the Grignard reaction. F. H. RATHMANN and J. A. LEIGHTY (Trans. Illinois State Acad., 1931, 24, 312—315).—MeI and Mg did not react in Pr²O in presence of I; the yield of MgEtI was 22.5% (86% in Et₂O). The yields of MgEtBr in Et₂O, Pr²O, and Bu₂O were 75—88, 67.5, and 74—75%, respectively. Mg with *iso*amyl iodide in Pr²O acquired a protective film. The yield of MgPhBr in Pr²O with I was 34%. Yields of CMe₂Et-OH and CH₂EtPh-OH in Pr²O were less than half of those in Et₂O.

CH. ABS.

Action of mercury on organic iodides. I. Formation of mercury methyl and benzyl iodides. J. L. MAYNARD (J. Amer. Chem. Soc., 1932, 54, 2108—2112).—HgMeI is not formed from MeI and Hg on exposure to light until after the appearance of HgI in the reaction mixture. Finely-divided Hg produced by the photochemical decomp. of HgI reacts readily with MeI to form HgMeI. CH₂Ph.HgI,

m. p. 117°, is formed in 94.5% yield from finely-divided Hg and CH_2PhI . C. J. W. (b)

Decomposition of hydroaromatic hydrocarbons. MAILHE, MARTY, and GAUDRY (Compt. rend., 1932, 194, 1947—1949).—Pyrogenic decomp. of cyclohexane with a SiO_2 gel catalyst begins at 600°. At 650° the gaseous products contain olefines (mainly $\text{CH}_2=\text{CH}_2$ and $\text{CHMe}=\text{CH}_2$) 41%, H_2 14%, and paraffins (mainly CH_4) 32%, whilst the liquid products contain higher olefines and much C_6H_6 . The amount of H_2 increases at 700°, and at 750° the liquid products are mainly aromatic hydrocarbons (C_6H_6 , PhMe, C_{10}H_8 , and anthracene) arising from pyrolysis of the olefines. Similar results are obtained with cyclohexene. J. W. B.

tert.-Butylcymenes and nitration products. H. BARBIER (Helv. Chim. Acta, 1932, 15, 592—596).—Interaction of *m*-cymene, AlCl_3 , and *tert*-BuCl gives *tert*-butyl-*m*-cymene, b. p. 227°/737 mm. [$(\text{NO}_2)_2$ -derivative, m. p. 115°]; *p*-cymene is largely decomposed under the same conditions, but readily gives *tert*-butyl-*p*-cymene, b. p. 228°/730 mm., and a small amount of an isomeride, b. p. 236—237°/737 mm., with *tert*-BuOH and conc. H_2SO_4 at -10° to 0°. Dinitro-*tert*-butyl-*p*-cymene, m. p. 132—133°, has a strong odour of musk, and is accompanied by isomerides, m. p. 126° and 145°, respectively. H. A. P.

Conjugated systems. XI. Oxidation of cis-phenylbutadiene by perbenzoic acid. I. E. MUSKAT and M. HERRMAN (J. Amer. Chem. Soc., 1932, 54, 2001—2009; cf. A., 1931, 1148).—*cis*- α -Phenylbutadiene and BzO_2H in CHCl_3 at 0° give (probably) the γ -benzoate (I), m. p. 81—82° (ozonolysis products, PhCHO and BzOH) (dibromide, m. p. 154—155°), of $\gamma\delta$ -dihydroxy- α -phenyl- Δ^2 -butene, m. p. 74° (dibromide, m. p. 94°), converted by PBr_3 into $\gamma\delta$ -dibromo- α -phenyl- Δ^2 -butene, m. p. 94°. (I) heated with 30% H_2SO_4 at 100° (bath) gives dimeric α -phenylbutadiene-oxide, m. p. 192° (tetrabromide, m. p. 220°). (I) and a little dil. HCl in MeOH at 120—130° give α -phenylbutadiene $\gamma\delta$ -oxide, b. p. 88°/1 mm., convertible by hot 30% H_2SO_4 into the above dimeride. Oxidation of *cis*- α -phenylbutadiene with BzO_2H at 25° gives a dioxide, b. p. 97°/1 mm., and $\alpha\beta\gamma\delta$ -tetrahydroxy- α -phenylbutyl $\alpha\gamma$ -dibenzoate, m. p. 186°. The work indicates that BzO_2H is $\text{CPh}(\text{O})\cdot\text{O}\cdot\text{OH}$. C. J. W. (b)

Aryl chlorosulphonates. M. BATTEGAY and L. DENIVELLE (Compt. rend., 1932, 194, 1505—1507).— SO_2Cl_2 (1.25 mol.) in C_6H_6 at 0—5° affords with NaOPh (1 mol.), Ph chlorosulphonate, b. p. 98°/12 mm. Anisyl chlorosulphonate has b. p. 98°/1 mm. These chlorides are stable to boiling Ac_2O and conc. HNO_3 . HCl, cold NaOH, and NH_3 are nearly without action. Boiling NaOH hydrolyses them. J. L. D'S.

Orienting influences of free and bound ionic charges on attached simple or conjugated unsaturated systems. VI. Nitration of phenylalkylsulphones. W. A. BALDWIN and R. ROBINSON (J.C.S., 1932, 1445—1451).—The percentage amount of *m*-nitration of phenylalkylsulphones, PhSO_2R , with cold HNO_3 ($\text{R}=\text{Et}$, 96.0; Pr^n , 93.1; Bu^n , 85.7; Pr^i , 80.0) shows the anticipated effect

due to increase of size of the alkyl group, of which the electron repulsive effect ($-F$) modifies the field of the S atom ($+F$), and is exerted across a strong dipole. The sulphones have been prepared by the action of the corresponding alkyl halide on Na benzenesulphinate, and the *m*- NO_2 -derivatives from the *m*-nitrobenzenesulphinate. The *o*- and *p*- NO_2 -derivatives have been obtained by the oxidation of the sulphides with H_2O_2 : phenyl-*n*-butyl-, b. p. 165—170°/1 mm.; *m*-nitrophenyl-isopropyl-, m. p. 113°, -*n*-propyl-, m. p. 80°, -*n*-butyl-, b. p. 215°/3 mm.; *o*-nitrophenyl-ethyl-, m. p. 45.5°, -*n*-propyl-, m. p. 60.5° (lit. 50°), -isopropyl-, m. p. 59.5°, and -*n*-butylsulphone, b. p. 216—218°/3 mm. The determination of the proportion of the isomerides has been carried out by a modified method of reduction and bromination of the mixed NO_2 -derivatives. F. R. S.

Synthesis of diphenyl. I. R. SHEERWOOD and W. F. SHORT (J.C.S., 1932, 1641).—1-Phenyl-cyclohexanol or Δ^1 -cyclohexene heated with S at 200—240° gives Ph_2 in 70% yield. F. R. S.

Aromatic compounds of fluorine. X. Fluoroderivatives of diphenyl. IV. More highly fluorinated diphenyl compounds. G. SCHIEHMANN and W. ROSELIUS (Ber., 1932, 65, [B], 737—745; cf. A., 1931, 1355).—Contrary to Ullmann and Frenzel (A., 1905, i, 308), the action of CuCl on diazotised *o*-nitroaniline gives mainly *o*-chloronitrobenzene, converted by Cu powder at 240—245° into 2:2'-dinitrodiphenyl, m. p. 123.5—124°, whence 2:2'-diaminodiphenyl, m. p. 77—78°, the corresponding bisdiazonium fluoborate, decomp. 133—134°, and 2:2'-difluorodiphenyl, m. p. 117—117.5°, d_4^{25} 1.379. 3:3'-Diphenylenebisdiazonium fluoborate, decomp. 105.5—106°, and 3:3'-difluorodiphenyl, b. p. 130°/14 mm., m. p. 7—8°, d_4^{25} 1.192, are described. In the *s*-difluorodiphenyls the position 3 does not occupy an isolated place with respect to steric relationships. 2:4:4'-Trifluorodiphenyl is converted by HNO_3 (d 1.50) at 60—100° into 2:4:4'-trifluoro-2':5-dinitrodiphenyl (I), m. p. 110°, whereas in AcOH an isomeric $(\text{NO}_2)_2$ -product, m. p. 118.5°, is produced. (I) with KOH-MeOH affords 4'-fluoro-2':5-dinitro-2:4-dimethoxy-, m. p. 190—191°, and is reduced by Sn and HCl in EtOH to 2:4:4'-trifluoro-2':5-diamino-diphenyl, m. p. 94—95°, which did not yield a fluoborate. 4:4'-Difluoro-6-amino-3:3'-ditolyl, b. p. 175—177°/44 mm. (hydrochloride, m. p. 210° after softening at 208°), is converted through the fluoborate, decomp. 93—94°, into 4:4':6-trifluoro-3:3'-ditolyl (II), b. p. 274—276°/761 mm., 140—141°/12 mm. (II) and HNO_3 yield 4:4'-difluoro-6:6'-dinitro-3:3'-ditolyl, m. p. 143—143.5° (reduced by Na-Hg and MeOH to 4:4'-difluorotolazone, m. p. 228°), and an isomeric $(\text{NO}_2)_2$ -compound, m. p. 154—154.5°. The oxidation of 4:4'-difluoro-3:3'-ditolyl to 4-fluoro-*m*-toluic acid, m. p. 165°, is recorded. H. W.

Dimorphism of tetranitrodiphenyl derivatives. III. J. VAN ALPHEN (Rec. trav. chim., 1932, 51, 453—459).—2:2'-Dichlorodiphenyl with HNO_3 - H_2SO_4 at 100° gives 2:2'-dichloro-4:4':6:6'-tetranitrodiphenyl (I), m. p. 308° and m. p. 316° (block), the structure of which follows from its failure to react

with boiling NaOEt or NHMe₂ in EtOH; (I) could not be synthesised from 1:2-dichloro-4:6-dinitrobenzene with Cu bronze in PhNO₂, whereas similar treatment of 2-chloro-3:5-dinitroanisole (Borsche, A., 1918, i, 11) affords 4:4':6:6'-tetranitro-2:2'-dimethoxydiphenyl, m. p. 168° and m. p. 189°. 2:2':4:4'-Tetranitrodiphenyl is now also found to exist in dimorphous forms, m. p. 166° (by seeding AcOH solution), and m. p. 155° (by seeding COMe₂-EtOH solution). No dimorphism was observed with 2:2'-dibenzoyloxydiphenyl, m. p. 101°, 5:5'-dinitro-2:2'-dimethoxydiphenyl, or 2:2':4:4'-tetranitrodiphenyl ether. Substances containing the group C₆H₃(NO₂)₂X (1:3:4) tend to crystallise in two dimorphous forms with m. p. difference of 7—20°. J. W. B.

Preparation of diphenylene sulphide. C. COURTOT, M. CHAIX, and L. NICOLAS (Compt. rend., 1932, 194, 1660—1661).—Schonberg's method of prep. (A., 1924, i, 39) is improved by the use of C₆H₆; secondary products are described. E. W. W.

Mechanism of action of sodamide on diphenyl sulphoxide. C. COURTOT, M. CHAIX, and J. KELLNER (Compt. rend., 1932, 194, 1837—1839; cf. preceding abstract).—NaH rapidly reduces Ph₂SO to Ph₂S at the temp. used, and occurs to the extent of 3% in the NaNH₂ employed. Ph₂S does not give NH₂Ph with NaNH₂. By carrying out the original reaction in H₂, and adding EtBr to the C₆H₆ solution before hydrolysis, PhSO₂Et is formed, accompanied by PhSEt and Ph₂S, whence it is concluded that PhSONa is first formed and passes by disproportionation into PhSO₂Na and PhSH, the last of which is the source of the Ph₂S₂. H. A. P.

Mechanism of some additive reactions of nitroethylenes. B. FLURSCHEIM and E. L. HOLMES (J.C.S., 1932, 1458—1468).—A pronounced tendency to add EtOH (now measured quantitatively; cf. A., 1902, i, 671) is shown by only three nitroethylenes, *p*-NO₂·C₆H₄·CH·CBrNO₂, CHPh·CBrNO₂, and *p*-NO₂·C₆H₄·CH·C(NO₂)·C₆H₄·NO₂(*p*) (I), out of fourteen, including those containing *tert.* or *sec.* NO₂-groups, and *cis*- and *trans*-forms. It is suggested that the mechanism consists of slow 1:4-addition to give an *isonitro*-compound, followed by two competing rapid reactions, either a reversal of this, or a rearrangement to a "true" nitroethylene derivative. The electropolar factor is more important than the steric and quant. factors, an acidic substituent near the NO₂ facilitating addition. The rapid addition to (I) may be due to 1:8-addition. Other similar reactions are discussed. *β*-Nitro-*α*-phenyl-*β*-m., m. p. 179—180°, *β*-nitro-*α*-*p*-nitrophenyl-*β*-m., m. p. 236—237°, and *β*-nitro-*αβ*-di-*p*-nitrophenylethylene, m. p. 210.5—211°, are described. The known form of *β*-nitro-*β*-phenyl-*α*-*p*-methoxyphenylethylene (II), m. p. 151.5—152°, is converted by evaporation of its solution in EtOH into a stereoisomeric form, m. p. 112—113°, and (II) gives an additive compound *β*-nitro-*α*-ethoxy-*β*-phenyl-*α*-*p*-methoxyphenylethylene, m. p. 107.5—108°, with EtOH-KOH. The *cis-trans* rearrangements of (II) and its isomeride and of *β*-nitro-*αβ*-diphenylethylenes are given. F. R. S.

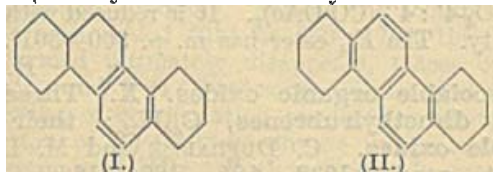
Acetylene derivatives. VIII. *oo'*-Disulphonic acids of stilbene and tolane series. II. P. RUGGLI and M. WELGE (Helv. Chim. Acta, 1932, 15, 576—590).—*K*₂ and *Ba* 4:4'-dinitrostilbene-2:2'-disulphonates are described. Addition of Br (2—4.4 equivs.) to *K*₂ 4:4'-dinitrotolane-2:2'-disulphonate in H₂O at 0° gives the corresponding *dibromide* (*A*₂ salt), which is decomposed by H₂O at 70—80° into the *K* salt of the lactone of *α*-bromo-4:4'-dinitro-*α'*-hydroxystilbene-2:2'-disulphonic acid; this is the main product with Br (2 equivs.) at room temp. The corresponding chloro-lactone (*K* salt) is similarly prepared. Fission of the dilactone of 4:4'-dinitro-*αα'*-dihydroxydibenzyl-2:2'-disulphonic acid with NH₃ gives, not an NH₂-derivative as expected, but the NH₄ salt of the (OH)₂-acid (*Ba* salt), and, under milder conditions, the corresponding monolactone (*NH*₄ and *Ba* salts). Addition of Br (2.2 equivs.) to *K*₂ stilbene-2:2'-disulphonate [*K*₂ salt (+5H₂O); *chloride*, m. p. 161° (decomp.); *Me*₂ ester, m. p. 168—170° (decomp.); *dianilide* m. p. 253°)] at room temp. gives the bromo-lactone (I; R=·CBr·C<) (*K* salt), which with H₂O at 100° gives the corresponding *dilactone*, m. p. 243—245° (decomp.) (+pyridine). The *K* salt of (I; R=CHBr·CH) is similarly prepared from tolane-2:2'-disulphonic acid (*K*₂ and *Ba* salts). Na stilbene- and tolane-2:2'-disulphonates readily give Na dibenzyl-2:2'-disulphonate with Ni and H₂ in H₂O, but the 4:4'-(NH₂)₂-derivative of the second is unaffected under the same conditions. H. A. P.

Formation of *αδ*-diphenyl-*Δ*^{αα}-hexadiene in the reaction between cinnamyl chloride and magnesium. H. GILMAN and S. A. HARRIS (J. Amer. Chem. Soc., 1932, 54, 2072—2075).—The liquid hydrocarbon formed from cinnamyl chloride and Mg in Et₂O is *αδ*-diphenyl-*Δ*^{αα}-hexadiene (I), b. p. 157—160°/2 mm., and not *αδ*-diphenyl-*Δ*^{αα}-hexene as reported by Rupe and Bürgin (A., 1910, i, 161). Catalytic reduction (Adams) of (I) gives *αδ*-diphenylhexane (II), b. p. 147—148°/3 mm., whilst ozonolysis affords CH₃O and PhCHO. Ph[CH₂]₃·MgCl and COPhEt give 64% of *αδ*-diphenylhexan-8-ol, b. p. 177—179°, reduced by HI and red P to (II). The chief product from cinnamyl bromide and Mg is *αζ*-diphenyl-*Δ*^{αα}-hexadiene. C. J. W. (b)

Conversion of naphthalene into tetrahydronaphthalene. M. K. DIAKOVA (J. Appl. Chem., Russia, 1931, 4, 819—830).—C₁₀H₈ is best purified with Na after pre-treatment with 5% KOH. Conversion into tetrahydronaphthalene (together with C₆H₆ and homologues) is accomplished at 435—445° with an initial H₂ pressure of 100 atm. and a final pressure of 235 atm. with Mo compounds (preferably oxide) as catalysts. Hydrogenation proceeds in presence of Ni catalysts at 20 atm. and 180—200°. CH. Abs.

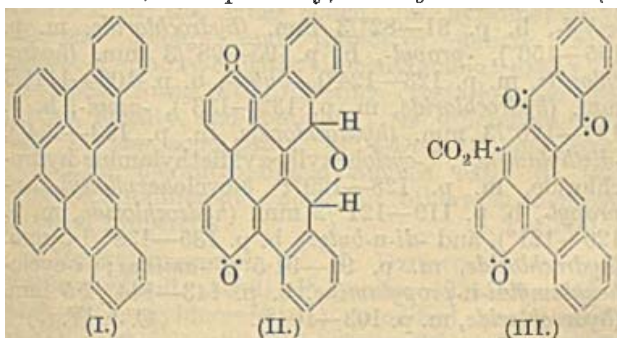
Hydrogenation of chrysene. J. VON BRAUN and G. IRMISCH (Ber., 1932, 65, [B], 883—887).—The first isolable product of the hydrogenation of chrysene in presence of Ni is *dodecahydrochrysene* (I), m. p. 55—57°, which does not yield a picrate and is oxidised by 30% HNO₃ to benzene-1:2:3:4-tetracarboxylic acid. Probably *octahydrochrysene* (II), b. p. 180

181°/0.2 mm., m. p. 138—140°, is intermediately formed (also by reduction of chrysene with Na and



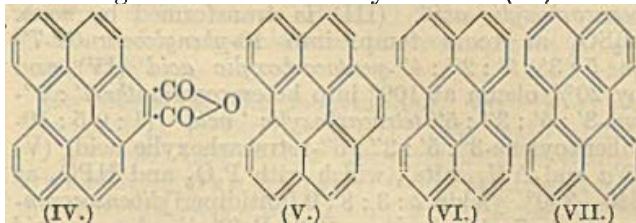
EtOH or amyl alcohol); it is best prepared by dehydrogenation of (I) with S at 200° or Se at 320°. The *picrate* has m. p. 136—139°. It yields benzene-1:2:3:4-tetracarboxylic acid when oxidised. Further hydrogenation of (I) yields *hexadecahydrochrysene*, b. p. 168°/0.5 mm., stable towards KMnO_4 at 0° and decolorising Br in CS_2 very slowly. Perhydrochrysene could not be obtained. Contrary to Liebermann and Spiegel, treatment of chrysene with P and HI gives a solid, m. p. (indef.) 114°, probably a mixture of (II) and tetrahydrochrysene, and a liquid mixture of hydrogenated chrysenes of the mean composition $\text{C}_{18}\text{H}_{24}$. H. W.

Polynuclear, aromatic hydrocarbons and their derivatives. XIV. Constitution of perylene; syntheses of 2:3-10:11-dibenzo- and 1:12-benzo-perylene; constitution of benzanthrone and phenanthrene. E. CLAR [in part with W. HEMPEL] (Ber., 1932, 65, [B], 846—859; cf. this vol., 608).—2:3-10:11-Dibenzoperylene (I), m. p. 343° (*picrate*, decomp. 240°), is prepared by the action of AlCl_3 in C_6H_6 on phenanthrene (preferably in presence of SnCl_4), 9-bromophenanthrene, or phenanthrene 9:10-dibromide (obtained by action of Br on phenanthrene in C_6H_6). It is oxidised by CrO_3 in AcOH to 1:12-furano-2:3-10:11-dibenzoperylene-3:9-quinone or, more probably, its dihydro-derivative (II),



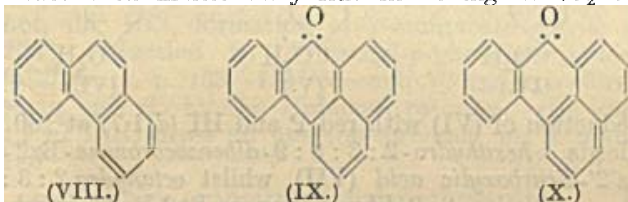
m. p. 360—365° (decomp.), converted by further oxidation into the *acid* (III), m. p. 295° (decomp.) after softening at 270°, which with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gives an *azine*, $\text{C}_{26}\text{H}_{12}\text{O}_3\text{N}_2$. When treated with maleic anhydride, molten or in boiling $\text{C}_6\text{H}_4\text{Me}_2$, perylene appears to form an additive compound from which the hydrocarbon separates unchanged on cooling. In boiling PhNO_2 , 1:12-benzoperylene-Bz1: Bz2-dicarboxylic anhydride (IV), m. p. 465—470° (decomp.) after softening at 415°, is obtained, the non-additive nature of which follows from analysis, stability towards heat, conversion by Br in PhNO_2 into Br- and Br_2 -derivatives, and absorption spectrum; the *K* salt is described. (I) and maleic anhydride in boiling PhNO_2 similarly afford 1:12-2:3-10:11-tribenzoperylenedi-

carboxylic anhydride, m. p. 380—390° (decomp.) after softening at 360°. Decarboxylation of (IV) or the



corresponding acid by CaO-NaOH in N_2 at 450° yields 1:12-dibenzoperylene (V), m. p. 273° (*picrate*, m. p. 267°), which does not react with maleic anhydride in boiling PhNO_2 . Comparison of the absorption spectra of perylene, (I), and (V) and the failure of perylene to react more than once with maleic anhydride exclude the possibility that perylene is composed of two symmetrical naphthalene systems. The structure (VI) is advocated, but the possibility of an equilibrium with the anthraquinonoid form (VII) is not excluded.

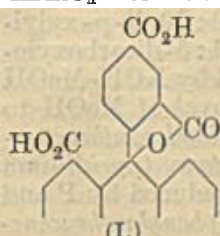
The failure of phenanthrene and benzanthrone to react with maleic anhydride in boiling PhNO_2 is



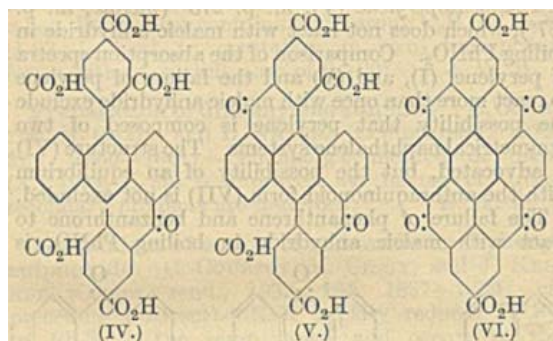
evidence in favour of the structures (VIII) and (IX) or (X), respectively. According to (IX) or (X), benzanthrone is an unsaturated ketone. In harmony with this conception, it is converted by MgPhBr in Et_2O into Bz-3-phenylbenzanthrone, m. p. 186°, oxidised to anthraquinone-1-carboxylic acid and converted by KOH-EtOH into a green dye resembling violanthrone. Bz-3- α -Naphthylbenzanthrone has m. p. 222°. With $\text{CH}_3\text{Ph-MgCl}$, 2(?)-benzylbenzanthrone, m. p. 136°, appears to be formed, converted by passage over Pt-C at 300° CO_2 into 10-keto-4:5:8:9-dibenzo-3-hydropyrene, m. p. 170° (*picrate*, m. p. 180—181°) (cf. Dzięwoński and Moszew, A., 1931, 1294).

H. W.

Synthesis of antidiaperidibenzocoronene and its degradation to coronene [hexabenzobenzene]. R. SCHOLL and K. MEYER [with H. VON HOESSEL and S. BRISSINDJI] (Ber., 1932, 65, [B], 902—915).—9:10-Dihydroxy-9:10-di-*m*-xylyldihydroanthracene-1:5-dicarboxylodilactone is hydrolysed with KOH-MeOH and, after removal of MeOH , oxidised by KMnO_4 to 9:10-dihydroxy-9:10-diphenyldihydroanthracene-1:5:2':4':2'':4''-hexacarboxy-9:2'-10:2''-dilactone [pyridinium salt; Et_4 ester, m. p. 302—303.5° (slight decomp.)], hydrolysed to the very readily lactonised 9:10-dihydroxy-9:10-diphenyldihydroanthracene-1:5:2':4':2'':4''-hexacarboxylic acid (II). (I) is reduced by red P and boiling AcOH to 9:10-diphenylanthracene-4:4':2'':4''-hexacarboxylic acid (III) (Et_6 , m. p. 206—207°). (I) or (II) is reduced in



30% KOH by a large excess of Zn dust to 9:10-diphenyl-9:10-dihydroanthracene-1:5:2':4':2'':4'':hexacarboxylic acid. (III) is transformed by conc. H_2SO_4 at room temp. into 10-phenylcoeranthr-7'-one-5:3':5':2'':4'':pentacarboxylic acid (IV) and by 20% oleum at 100° into heterocoerdianthr-7':7'':one-3:5':3'':5'':tetracarboxylic acid (1:9:5:10-dibenzoylene-3':5':3'':5'':tetracarboxylic acid) (V) (Na and NH_4 salts), which with P_2O_5 and HPO_3 at 340—350° yields 2:3:8:9-[antidiperi]dibenzocoronene-1:4:7:10-diquinone-Bz2:Bz'2'-dicarboxylic acid (VI) (Na_2 salt).



Reduction of (VI) with red P and HI (d 1.7) at 180° affords hexahydro-2:3:8:9-dibenzocoronene-Bz2-Bz'2'-dicarboxylic acid (VII), whilst octahydro-2:3:8:9-dibenzocoronene-Bz2-Bz'2'-dicarboxylic acid (VIII) is derived similarly from (V) at 220°. When heated with NaOH, CaO, and Cu powder in H_2 at 500°/2 mm. it gives 2:3:8:9-(antidiperi)dibenzocoronene (IX), the solutions of which are sensitive to light and in boiling $C_6H_5Me_2$ to air; the corresponding (?)dibromide, dihydrodipyridinium bromide, and dihydrodipyridinium perchlorate are described. Treatment of (IX) with conc. H_2SO_4 at 110—120° followed by reduction with

$Na_2S_2O_4$ and oxidation with air leads to 2:3:8:9-dibenzocoronenequinone, oxidised by dil. HNO_3 at 220° to non-homogeneous coronene-2:3:8:9-tetracarboxylic acid, decarboxylated to coronene (X), m. p. 429—430° (corr.), also obtained from dibenzocoronene bromide or hexahydrodibenzocoronenedicarboxylic acid. The constitution of coronene and dibenzocoronene is discussed in detail.

9:10-Dihydroxy-9:10-di-*p*-xylyldihydroanthracene-1:5-dicarboxylactone is hydrolysed by KOH-MeOH and oxidised by $KMnO_4$ after removal of MeOH to 9:10-dihydroxy-9:10-diphenyldihydroanthracene-1:5:2:5':2'':5'':hexacarboxydilactone (pyridinium salt; Et_1 ester, m. p. 234.5—236°), reduced by P and HI in boiling AcOH to 9:10-diphenylanthracene-1:5:2':5':2'':5'':hexacarboxylic acid (Me_6 ester, m. p. 207—209°; Et_6 ester, m. p. 190—191°). 9:10-Dihydroxy-9:10-diphenyldihydroanthracene-1:5:4':4'':tetracarboxylic acid, prepared similarly from 9:10-

dihydroxy-9:10-di-*p*-tolylidihydroanthracene-1:5-dicarboxylactone, yields a dilactone and the compound $C_{28}H_{14}O_4 \cdot 4':4'':(CO \cdot OAc)_2$. It is reduced with great difficulty. The Et_1 ester has m. p. 300—301°.

H. W.

Dissociable organic oxides. X. Three isomeric dimethylrubrenes, $C_{44}H_{32}$; their dissociable oxides. C. DUFRAISSE and M. LOURY (Compt. rend., 1932, 194, 1664—1666).—From $CPh \cdot C \cdot CPhCl \cdot C_6H_4Me$ three dimethylrubrenes, m. p. 205°, 273°, and 321°, respectively, are obtained, the third being identical with that previously described (A., 1928, 996). Absorption curves are given. Each compound forms a dissociable oxide, $C_{44}H_{30}O_{11}$, + $\frac{1}{2}Et_2O$ or C_6H_6 . E. W. W.

Dissociable organic oxides. Isomerism of the dimethylrubrenes and constitution of the rubrenes. C. DUFRAISSE and M. LOURY (Compt. rend., 1932, 194, 1832—1834).—The formation of a single dimethylrubrene (I) from $CPh_2Cl \cdot C \cdot C \cdot C_6H_4Me$, and of three, one of which is identical with (I), from $CPh \cdot C \cdot CPhCl \cdot C_6H_4Me$ is in accordance with the formula $[C_6H_4 \langle \overset{CPh}{\underset{CPh}{C}} \rangle C]$ for rubrene. H. A. P.

Preparation of ω -cyclohexylalkyl[dialkyl]amines and their bactericidal action to *Mycobacterium leprae*. XXII. G. H. COLEMAN and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 1982—1985; cf. this vol., 690).— ω -cyclohexylamines, $C_6H_{11} \cdot [CH_2]_x \cdot NR_2$, show marked action towards *B. leprae* provided they contain 15 to 18 C atoms, as with the various acids already tested; the distribution of the C atoms has little effect. The following are prepared from the requisite cyclohexylalkyl bromide and NHR_2 : cyclohexyl-methyl-, b. p. 73—75°/3.5 mm. (hydrochloride, m. p. 168—168.5°), -ethyl-, b. p. 81—82°/3 mm. (hydrochloride, m. p. 155—156°), -propyl-, b. p. 95—98°/3 mm. (hydrochloride, m. p. 123—124°), -butyl-, b. p. 109—111°/3 mm. (hydrochloride, m. p. 132—133°), -amyl-, b. p. 124—126°/3 mm. (hydrochloride, m. p. 133—134°), -diethylamines; ζ -cyclohexylhexyldiethylamine hydrochloride, m. p. 128—129°; δ -cyclohexylbutyl-di-n-propyl-, b. p. 119—121°/2 mm. (hydrochloride, m. p. 120—121°), and -di-n-butyl-, b. p. 135—138°/1.5 mm. (hydrochloride, m. p. 91—91.5°), -amines; ϵ -cyclohexylamyl-di-n-propylamine, b. p. 143—144°/2.5 mm. (hydrochloride, m. p. 103—104°). C. J. W. (b)

Interaction of amides with aniline. C. D. HURD, M. F. DULL, and K. E. MARTIN (J. Amer. Chem. Soc., 1932, 54, 1974—1976).—Amides do not react with NH_2Ph at room temp. or 100°, but small amounts of anilides result when mixtures are boiled for a long time. Amide vapours (NH_2Ac , $Et \cdot CO \cdot NH_2$, NH_2Bz) issuing from hot tubes react with cold NH_2Ph to give fair yields of anilides. The possibility of keten formation from amides is discussed. C. J. W. (b)

Transpositions in the benzene nucleus. I. C. SANDONNINI (Atti R. Accad. Lincei. 1932, [vi], 15, 99—103).—Published work is briefly reviewed. When boiled, *p*-bromoaniline yields mostly NH_2Ph and a blue solid, which decomposes rapidly at about



240° giving much HBr; rectification of the distillate results in further decomp. with formation of renewed condensation products. When the compound is heated in a sealed tube at 160–170°, the NH_2Ph first formed ultimately disappears, traces of 2:4-dibromo- and 2:4:6-tribromo-anilines and a large proportion of condensation products resulting; the formation of 2:4-dibromoaniline is accelerated by the presence of HBr. Both *o*- and *m*-bromoanilines distil unchanged and are not decomposed in sealed tubes at 50° above their b. p. The *o*- may be converted almost entirely into the *p*-compound, with traces only of dibromoaniline, by heating its hydrobromide in a sealed tube at 160° for 16–18 hr. in absence of large excess of acid; the 2:4-dibromoaniline appears to be formed, not from the *p*-compound by simple dismutation, but by secondary reactions among highly complex condensation products (cf. Brown and Cumming, B., 1926, 909). T. H. P.

Differently coloured forms of derivatives of diphenylamine. N. M. CULLINANE, O. E. EMBREY, and D. R. DAVIES (J. Physical Chem., 1932, 36, 1434–1448).—Differences in colour of two forms of (apparently) the same compound may be due to traces of impurities, differences in particle fineness or texture, pleochroism, polymorphism (involving differences other than colour in the solid state, which disappear in the gaseous or liquid state or in solution), or changes in structure such as polymerisation, tautomerism, or stereoisomerism (changes persisting for some time in the liquid state or in solution). 2:4:6-Trinitro-4'-methyl- and 2:4-dinitro-2'-methoxy-5-methyldiphenylamines exist in two modifications with differing colour, cryst. structure, and density; the two forms are isomeric, since each forms a different additive compound with C_6H_6 and solutions of the same concn. (in pyridine) have different colours and refractive indices. 2:4-Dinitro-4'-ethoxy-5-methyldiphenylamine exists in dimorphic forms with differing crystallo-optic properties, density, and solubility; the differences exist only in the solid state. 2:4-Dinitro-2'-methoxy- and 2:4:6-trinitro-diphenylamines exist in two forms with different colour but otherwise identical physical properties. A. P. S. (b)

2-Benzylfluorene. I. K. DZIEWOŃSKI and Z. REICHER (Bull. Acad. Polonaise, 1931, A, 643–652).—2-Benzylfluorene (I) (modified prep.) with H_2SO_4 (100%) at 140° gives 2-benzylfluorene-7-sulphonic acid, m. p. 147.5° [*Na* and NH_2Ph (decomp. 345°) salts; sulphonyl chloride, m. p. 153°; amide, m. p. 145°], oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in hot AcOH to 2-benzoylfluorenone-7-sulphonic acid, an oil (*Na* salt), which when fused with KOH at 150°, yields 2-hydroxy-7-fluorenone (proving the position of the SO_3H group) and 4'-hydroxydiphenyl-2-carboxylic acid, m. p. 172°. (I) with HNO_3 (*d* 1.52) and H_2SO_4 in AcOH at 60° gives 7-nitro-2-benzylfluorene (II), m. p. 162°, reduced by SnCl_2 to 7-amino-2-benzylfluorene, m. p. 115° (*Ac* derivative, m. p. 187.5°), which, when diazotised and coupled with β -naphthol, affords 7-2'-naphthol-1'-azo-2-benzylfluorene, m. p. 187–188°. Oxidation of (II) gives 7-nitro-2-benzoylfluorenone, m. p. 206° (phenylhydrazone, m. p. 235°; oxime,

decomp. 285°), reduced to 7-amino-2-benzoylfluorenone, m. p. 228–229° (*Ac* derivative, m. p. 269°; oxime, decomp. 236°), which affords 1-2'-benzoylfluorenone-7'-azo-2-hydroxynaphthalene-3-carboxylanilide, decomp. 286°.

R. S. C.

Structure of the isocyanides. II. R. G. A. NEW and L. E. SUTTON (J.C.S., 1932, 1415–1422; cf. A., 1930, 1239).—The dipole moment of *p*-diisocyanobenzene (I) is (probably) 0, the small observed moment ($0.6\text{--}0.9 \times 10^{-18}$ e.s.u.) being probably due to *p*-aminophenylcarbylamine (II) present as impurity. The formula $\cdot\text{N}\equiv\text{C}$ for the carbylamine group is, therefore, proved, since the alternative, $\cdot\text{N}\cdot\text{C}$, would, by analogy with the oximes, be non-planar and confer a moment of approx. 2.8 on (I). The dipole moment of EtNC is 3.47, whence it is calc. that the distance between the N and C atoms of the N–C group is 1.13 Å., in agreement with the val. (1.15) for the nitrile group. The prep. of (I) [which with Br gives a compound, $\text{C}_6\text{H}_4\text{N}_2\text{Br}_4$, m. p. 141–142° (lit. 137–138°)], is modified, (II), m. p. about 74°, being isolated as intermediate. The constitution of (II) is proved by hydrolysis to *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ by hot, dil. HCl, formation of *p*-aminobenzonitrile at 235°, reduction to *N*-methyl-*p*-phenylenediamine [oxalate, m. p. 153–154° (decomp.)], and transformation into (I) by the Hofmann reaction. (II) with Br in Et_2O gives an unstable product, m. p. above 280°.

R. S. C.

***p*-Dimethylaminotriphenylmethylamine.** P. PFEIFFER and H. HOYER (Ber., 1932, 65, [B], 919–922).—The action of MgPhBr on *p*-dimethylaminobenzophenone in Et_2O followed by treatment of the product with picric acid in EtOH affords *p*-dimethylaminotriphenylcarbenium picrate (I), m. p. 165° (cf. Diltney and Dinklage, A., 1929, 1067). Successive treatment of (I) with 10% NH_3 and $\text{H}_2\text{C}_2\text{O}_4$ leads to *p*-dimethylaminotriphenylmethylammonium oxalate, from which or from (I) *p*-dimethylaminotriphenylmethylamine (II), m. p. 92–93°, is prepared by action of NH_3 . The base and the oxalate have been described by Baeyer and Villiger (A., 1904, i, 786) as *p*-dimethylaminotriphenylcarbinol and its oxalate. Phenyl-*p*-dimethylaminotriphenylmethylcarbamide has m. p. 218–220°. NH_2Ph and (I) in presence of $\text{Et}_2\text{O-H}_2\text{O}$ afford phenyl-*p*-dimethylaminotriphenylmethylamine, m. p. 174–175°, hydrolysed to *p*-dimethylaminotriphenylcarbinol, m. p. 87–88°, prepared less readily from (II). H. W.

Colouring matters derived from triphenylmethane. Constitution of the green colouring matter obtained from dibenzylidenedihydrazinotriphenylmethane. A. GIACALONE [with G. SCARFINETTI] (Gazzetta, 1932, 62, 189–201).—*pp'*-Dibenzylidenedihydrazinotriphenylmethane (I) dissolved in oleum below 40° gives a nearly colourless pentasulphonic acid (II) (*Ba* salt, $\text{C}_{33}\text{H}_{23}\text{O}_{15}\text{N}_4\text{S}_5\text{Ba}_{2.5}$). The green colouring matter (III) obtained when (I) is dissolved in oleum at 100° is a pentasulphonic acid and gives with BaCO_3 a *Ba* salt, $\text{C}_{33}\text{H}_{22}\text{O}_{15}\text{N}_4\text{S}_5\text{Ba}$, with Ba(OH)_2 a *Ba* salt, $\text{C}_{33}\text{H}_{23}\text{O}_{15}\text{N}_4\text{S}_5\text{Ba}_{2.5}$ (IV), and with KCl a *K* salt, $\text{C}_{33}\text{H}_{24}\text{O}_9\text{N}_4\text{ClS}_3\text{K}_3$ (V). With PCl_5 (V) gives a compound, $\text{C}_{33}\text{H}_{24}\text{O}_6\text{N}_4\text{S}_3\text{Cl}_4$, giving with MeOH a *Me*₃ derivative, $\text{C}_{36}\text{H}_{33}\text{O}_9\text{N}_4\text{S}_3\text{Cl}_3$, and

(IV) gives a compound $C_{33}H_{22}O_{10}N_4S_5Cl_6$. Both sulphonation products have three nuclear SO_3H groups and two attached to N. Sulphonation at the higher temp. is accompanied by oxidation, (III) being dibenzylidenedihydrazinotriphenylcarbinolpentasulphonic acid.
E. E. J. M.

Stereoisomerism of azoxybenzenes. II. E. MÜLLER [with W. KREUTZMANN] (Annalen, 1932, 495, 132—143; cf. this vol., 263).—The isomerism exhibited by azoxybenzene (and its 2-substituted derivatives) is probably a general property of all such azoxy-compounds. The formation of isomerides from $R\cdot NO$ (e.g., $o\text{-}OMe\cdot C_6H_4\cdot NO$) and aq. $EtOH$ -alkali (cf. Reissert, A., 1909, i, 435) occurs by way of $R\cdot NH\cdot OH$ and (probably) $OH\cdot NR\cdot NR\cdot OH$, since the isomerides can also be obtained by condensation of $R\cdot NO$ and $R\cdot NH\cdot OH$. Thus, $o\text{-}C_6H_4Me\cdot NO$ and $o\text{-}C_6H_4Me\cdot NH\cdot OH$ in dioxan alone give "normal" $o\text{-}azoxytoluene$; when a solution of $o\text{-}C_6H_4Me\cdot NO$ in dioxan is treated first with aq. $NaOH$ and then with $o\text{-}C_6H_4Me\cdot NH\cdot OH$ in the cold, $iso\text{-}o\text{-}azoxytoluene$ is also produced in about 20% yield. $iso\text{-}Azoxybenzene$, m. p. 86° (lit. $80\text{--}84^\circ$), $iso\text{-}o\text{-}azoxyanisole$, $iso\text{-}2\text{:}2'\text{-}dichloroazoxybenzene$, $iso\text{-}m\text{-}$, m. p. $88\text{--}89^\circ$, and $iso\text{-}p\text{-}$, m. p. $83\text{--}85^\circ$, $-azoxytoluenes$ are similarly prepared. The $iso\text{-}$ are converted into the " n "-forms by short heating above their m. p. The dipole moments of " n " and $iso\text{-}o\text{-}azoxytoluenes$ are 1.73 and 4.36, respectively, and those of " n " and $iso\text{-}o\text{-}azoxyanisoles$ are 2.40 and 6.16×10^{-18} e.s.u., respectively.

Oxidation of 2-chloro-2'-bromoazobenzene, m. p. $130\text{--}131^\circ$ (from $o\text{-}C_6H_4Cl\cdot NH_2$ and $o\text{-}C_6H_4Br\cdot NO$ in $AcOH$), with 30% H_2O_2 in $AcOH$ gives an azoxy-compound, m. p. 79° , whilst $o\text{-}C_6H_4Br\cdot NO$ and $o\text{-}C_6H_4Cl\cdot NH\cdot OH$ in $EtOH$ afford 2:2'-dichloro- and 2:2'-dibromo-azoxybenzenes. The NO -compounds are prepared by oxidation of the $NH\cdot OH$ (formed from the NO_2 -derivative, Zn dust, 60% $EtOH$, and $CaCl_2$) with $FeCl_3$.
H. B.

Reactions of nitrosophenols. I. Diazo-methane as an agent for detecting nitrosophenolic structure. H. H. HODGSON (J.C.S., 1932, 1395—1398).—Nitrosophenols which exist (partly) in the NO -form give glyoxime Ph_2 ethers with diazomethane in Et_2O . With this reagent p -nitrosophenol gives a little glyoxime $NN'\text{-di-4-hydroxyphenyl ether}$ and much glyoxime $NN'\text{-di-4-methoxyphenyl ether}$ (I), m. p. 204° (decomp.), and benzoquinone-4-oxime Me ether (cf. A., 1898, i, 309). p -Nitrosoanisole gives only (I). 2-Chloro-4-nitrosophenol gives glyoxime $NN'\text{-di-3-chloro-4-methoxyphenyl ether}$, m. p. 223° (decomp.), and a little phenolic substance, but in presence of $MeOH$ gives much 2-chlorobenzoquinone-4-oxime Me ether and a little glyoxime $NN'\text{-di-3-chloro-4-hydroxyphenyl ether}$, m. p. 175° (decomp.). 2-Chloro-4-nitrosoanisole gives glyoxime $NN'\text{-di-3-chloro-4-methoxyphenyl ether}$. 3-Chloro-4-nitrosoanisole gives glyoxime $NN'\text{-di-2-chloro-4-methoxyphenyl ether}$, m. p. 182° (decomp.). 3-Chloro-4-nitrosophenol gives a little 3-chlorobenzoquinone-4-oxime Me ether and a mixture, m. p. 100° , and in $MeOH$ the mixture and a little 3-chlorobenzoquinone-4-oxime. Colours given

by the glyoxime ethers in H_2SO_4 are discussed in the light of electronic theories.
R. S. C.

Behaviour of nitrophenols with p -toluenesulphonyl chloride. II. S. M. SANE, S. N. CHAKRAVARTY, and B. N. PARMANICK. III. S. M. SANE and S. S. JOSHI (J. Indian Chem. Soc., 1932, 9, 55—57, 59—65; cf. A., 1925, i, 134).—II. Et 5-nitro- p -cresotol with p -toluenesulphonyl chloride and NEt_3 or Na_2CO_3 gives Et 5-nitro- p -toluenesulphonyloxytoluate, m. p. 110° , converted by $NaOAc$ and NH_3 into Et 2-nitro-4-methyldiphenylamine-2-carboxylate, m. p. 136° (hydrolysed to the acid, m. p. 174°). 2:6-Dinitrothymol and dinitrocarvacrol similarly give p -toluenesulphonates, m. p. 142° and 125° , respectively.

III. Bromination of 3-nitro-4-hydroxybenzoic acid gives 5-bromo-3-nitro-4-hydroxybenzoic acid, m. p. 229° , the Me ester, m. p. 130° , of which with p -toluenesulphonyl chloride and $NPhEt_3$ gives the p -toluenesulphonate, m. p. 127° , converted by NH_3 into Me 6-bromo-2-nitrodiphenylamine-4-carboxylate, m. p. 128° . Me 3-nitro-4- p -toluenesulphonyloxybenzoate has m. p. 86° , Me 2-nitrodiphenylamine-4-carboxylate, m. p. 127° , Me 5-nitro-4-methylsalicylate, m. p. 78° (p -toluenesulphonate, m. p. 93°), Me 4-nitro-5-methyldiphenylamine-2-carboxylate, m. p. 84° , 3:5-dinitro- p -2-xylenol (p -toluenesulphonate, m. p. 137° ; Ac derivative, m. p. 102° ; Bz derivative, m. p. 124°). The following phenols with p -toluenesulphonyl chloride give p -toluenesulphonates in the presence of Na_2CO_3 and replacement of OH by Cl in the presence of $NPhEt_3$: 2-iodo-4:6-dinitrophenol (Ac derivative, m. p. 113° ; p -toluenesulphonate, m. p. 149° ; 1-chloro-2-iodo-4:6-dinitrobenzene, m. p. 106°); 2:6-dinitrophenol (p -toluenesulphonate, m. p. 135°); 4-bromo- (p -toluenesulphonate, m. p. 136° ; 1-chloro-4-bromo-2:6-dinitrobenzene, m. p. 98°); and 4-iodo-2:6-dinitrophenol (Bz derivative, m. p. 175° ; p -toluenesulphonate, m. p. 138° ; 1-chloro-4-iodo-2:6-dinitrobenzene, m. p. 118°); 3-chloro-2-bromo-4:6-dinitrophenol, m. p. 118° (by bromination of 3-chloro-4:6-dinitrophenol) (p -toluenesulphonate, m. p. 150°); 1:3-dichloro-2-bromo-4:6-dinitrobenzene, m. p. 108°); 3-chloro-2-iodo-4:6-dinitrophenol, m. p. 108° (by action of I and HgO on 3-chloro-4:6-dinitrophenol) (p -toluenesulphonate, m. p. 150° ; 1:3-dichloro-2-iodo-4:6-dinitrobenzene, m. p. 108°); and chloropicric acid. The following are described; Ac , m. p. 118° , and Bz derivatives, m. p. 117° , of 6-chloro-2:4-dinitro- $-cresol$; Bz derivative, m. p. 95° , of 2:4-dinitro- m - $cresol$; and Bz derivative, m. p. 94° , of 2-bromo-4:6-dinitrophenol.
A. A. L.

A new ethylnaphthol. G. LEVY (Compt. rend., 1932, 194, 1749—1751; cf. this vol., 266).— Et sodio- β -phenylethylmalonate with $EtBr$ gives Et β -phenylethylmalonate, b. p. $151^\circ/2$ mm. (yield 85%), hydrolysed to the acid, m. p. 129° , which at 180° gives γ -phenyl- α -ethylbutyric acid, b. p. $180^\circ/16$ mm. (amide, m. p. 104°). The chloride, b. p. $142^\circ/15$ mm., of this acid with $AlCl_3$ gives 1-keto-2-ethyl-1:2:3:4-tetrahydronaphthalene, b. p. $145^\circ/15$ mm. (semicarbazone, m. p. 207.5°), converted by heating with Se at 330° into 2-ethyl- α -naphthol, m. p. $68\text{--}68.5^\circ$ (picrate, m. p. 118.5°), which is not identical

with the ethylnaphthol prepared by Marchetti (A., 1882, 410). A. A. L.

Rearrangement of hydroxy-sulphones. II. L. A. WARREN and S. SMILES (J.C.S., 1932, 1040—1047; cf. this vol., 156).—The chlorothiol from di-4-chlorosulphonyldiphenyl disulphide (improved prep.; cf. A., 1909, i, 643) with β -naphthol gives 4-chlorosulphonylphenyl 2-hydroxy-1-naphthyl sulphide (I), m. p. 160° [anilide (II), m. p. 156°; methylanilide (III), m. p. 115°, oxidised to the sulphone (IV), m. p. 181°], oxidised by H_2O_2 in AcOH to 4-chlorosulphonylphenyl-2-hydroxy-1-naphthylsulphone, m. p. 184° [anilide (V), m. p. 204°, also obtained by oxidation of (II)], which with Zn in AcOH-HCl gives 4'-thiolphenyl-2-hydroxy-1-naphthylsulphone, m. p. 129°. The Zn salt of this with MeI in MeOH gives the 4'-methylthiol compound, m. p. 151°, oxidised to 4'-methanesulphonylphenyl-2-hydroxy-1-naphthylsulphone (VI), m. p. 190° (Me ether, m. p. 176°), also obtained through the Zn salt followed by oxidation of 4-methylthiolphenyl 2-hydroxy-1-naphthyl sulphide, m. p. 101°, which results from reduction of (I) with Zn in AcOH-HCl. The sulphones (IV), (V), and (VI) do not react with 2N-NaOH at 100°. (VI) with 1 mol. of NaOH at 150° (2 hr.) undergoes partial rearrangement with loss of SO_2 , forming 4-methanesulphonylphenyl β -naphthyl ether (VII), m. p. 104°, also obtained from K β -naphthoxide and *p*-bromophenylmethylsulphone with a little Cu at 230°. With 2 or 8 mols. of NaOH (VI) gives 2-(4'-methanesulphonylphenoxy)naphthalene-1-sulphinic acid (VII) (Me ester, m. p. 189°), reduced by HI and SO_2 to the disulphide, m. p. 218°, which with Zn in AcOH-HCl gives 2-(4'-methanesulphonylphenoxy)-1-naphthylthiol, m. p. 146°. The latter with NaOH at 100° ($\frac{1}{2}$ hr.) gives 4-methanesulphonylphenyl 2-hydroxy-1-naphthyl sulphide, m. p. 189°, oxidised by H_2O_2 in AcOH to (VI). The Na salt of (VII) with $KMnO_4$ gives a sulphonic acid, converted by 60% H_2SO_4 into (VII). (III) and (V) also undergo rearrangement in presence of alkali, the change being retarded in the latter but not in the former case by excess of alkali. 4-Methylanilinosulphonylphenyl β -naphthyl ether has m. p. 125°. A. A. L.

Rearrangement of hydroxy-sulphones. III. A. A. LEVI and S. SMILES (J.C.S., 1932, 1488—1492; cf. preceding abstract).—The intramol. nature of the rearrangement of hydroxy-sulphones is confirmed by the production of *o*-nitrophenol, and not a Ph_2 ether, when 2-nitro-4'-hydroxydiphenylsulphone, m. p. 255—256° [prepared by oxidation by H_2O_2 -AcOH of 2-nitro-4'-hydroxydiphenyl sulphide (modified prep.)], is boiled with 2N-NaOH. The rearrangement may, however, also be intermol. $PhSNa$ and 2-bromonitrobenzene (excess) at 100° give a good yield of 2-nitrodiphenyl sulphide, oxidised by H_2O_2 in AcOH at 100° to 2-nitrodiphenylsulphone, m. p. 145°, which with boiling NaOH-EtOH gives *o*-nitrophenol, with Na *p*-tolylxide in boiling aq. EtOH *o*-nitrophenyl *p*-tolyl ether, and with boiling NH_2Ph 2-nitrodiphenylamine, m. p. 76° (lit. 75°). The last reaction suggests that similar rearrangement of amino-sulphones may be possible. *p*-Nitrophenylchlorothiol and *p*-cresol in dry $CHCl_3$ give 4-nitrophenyl 4-hydroxy-*m*-tolyl sulphide, m. p. 100°, oxidised (H_2O_2) to the correspond-

ing sulphone (I), m. p. 158°, which with 2N-NaOH at 90° gives 4-*p*-nitrophenoxytoluene-3-sulphinic acid, m. p. 113—114°. This acid with HI and SO_2 in AcOH gives di-4-*p*-nitrophenoxydi-*m*-tolyl disulphide, m. p. 182°, and, when oxidised to the sulphonic acid by $KMnO_4$ and then warmed with 60% H_2SO_4 yields *p*-nitrophenyl *p*-tolyl ether. Rearrangement occurs less readily with (I) than with the corresponding *o*- NO_2 -compound, whence it is concluded that the formation of a quinonoid nitronic ion is not of primary importance in the mechanism of the change.

R. S. C.

Reactions with boron fluoride. II. Rearrangement of phenyl alkyl ethers. F. J. SOWA, H. D. HINTON, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1932, 54, 2019—2021).—Ph alkyl ethers are rearranged by BF_3 in about 35 min. (max. time); the BF_3 can be recovered quantitatively by heating the mixture. *m*-Tolyl Pr^s ether thus gives 64% of 3-methyl-(?)isopropylphenol, b. p. 230—236°. The rearrangements of Ph and *o*- and *p*-tolyl Pr^s ethers are similarly effected. C. J. W. (b).

Constituents of guaiacum resin. I. Synthesis of pyroguaiacin methyl ether. R. D. HAWORTH and C. B. MAVIN (J.C.S., 1932, 1485—1488).—Clemmensen reduction of β -3:4-dimethoxybenzoylpropionic acid (modified prep.) gives γ -3:4-dimethoxyphenylbutyric acid, m. p. 57—59° (2-Br-derivative, m. p. 135—136°), which with hot 95% H_2SO_4 affords 1-keto-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene, m. p. 98—99° [oxime, m. p. 157—158°; semicarbazone, m. p. 247—249° (decomp.)]. This with $MgMeI$ yields 6:7-dimethoxy-1-methylnaphthalene, m. p. 110—111° (picrate, m. p. 116—117°), and, when reduced (Clemmensen) and subsequently heated with Se at 270—290°, gives 2:3-dimethoxynaphthalene, m. p. 115—117° (picrate, m. p. 131—132°). Veratrole, *cis*- or *trans*- $\alpha\beta$ -dimethylsuccinic anhydride, and $AlCl_3$ in $PhNO_2$ give β -3:4-dimethoxybenzoyl- $\alpha\beta$ -dimethylpropionic acid, m. p. 165—166°, which when reduced by Clemmensen's method and then heated with 90% H_2SO_4 , affords 1-keto-6:7-dimethoxy-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene, m. p. 135—136°. This, when reduced (Clemmensen) and heated with Se at 280—320°, gives pyroguaiacin Me ether [6:7-dimethoxy-2:3-dimethylnaphthalene] (picrate, m. p. 130—131°), thus proving the constitution previously (A., 1919, i, 897) assigned to the latter. R. S. C.

Conversion of hydroaromatic into aromatic compounds. V. Influence of the methyl group in 5-phenyl-2-methyldihydroresorcinol. L. E. HINKEL and J. F. J. DIPPEY (J.C.S., 1932, 1468—1472).—5-Phenyl-2-methyldihydroresorcinol (I) resembles in some respects 2-chloro-5:5-dimethyldihydroresorcinol; this is considered to be due to the substituent in the 2-position. (I) with PCl_3 (0.5 mol.) or $POCl_3$ (1 mol.) in hot $CHCl_3$ gives 5-chloro-1-phenyl-4-methyl- Δ^4 -cyclohexen-3-one, m. p. 36°, b. p. 179—180°/10 mm., with PCl_5 (2.5 mols.) in $CHCl_3$ 3:5-dichloro-4-methyldiphenyl (II), m. p. 62°, b. p. 183—184°/11 mm., and with PCl_5 (1.7 mols.) and $POCl_3$ (1.5 mols.) in $CHCl_3$ 3:5-dichloro-1-phenyl-4-methyl-cyclohexadiene (II), b. p. 163—166°/10 mm., and some (II). With Cl_2 in $CHCl_3$ (III) gives 2:3:5-trichloro-

1-phenyl-4-methyl- $\Delta^{3,5}$ -cyclohexadiene, an oil, which at the b. p. yields HCl and (II). (II) with HNO_3 (d 1.5) in AcOH forms 3:5-dichloro-(?)4'-nitro-4-methyl-1-phenyl-, m. p. 157°, reduced by SnCl₂ in aq.-alcoholic HCl to the corresponding amine, m. p. 131° (Ac derivative, m. p. 252—253°), which is oxidised by CrO_3 in hot AcOH to 3:5-dichloro-4-methylbenzoic acid. (II) is stable to ordinary oxidising agents.

R. S. C.

Derivatives of *d*-nor- ψ -ephedrine. J. M. STRATTON and F. J. WILSON (J.C.S., 1932, 1133—1138).—Benzaldehydesemicarbazone with *d*-nor- ψ -ephedrine (I) (benzenesulphonyl derivative, m. p. 103—104°) in PhMe gives NH_3 and benzaldehyde-*d*-nor- ψ -ephedrinoformylhydrazone, m. p. 118° (yield 83%), converted by dil. HCl into *d*-nor- ψ -ephedrinoformylhydrazide hydrochloride (II), m. p. 156°, $[\alpha]_{\text{D}}^{25} +37.8^\circ$ in EtOH, which gives $\text{N}_2\text{H}_4\cdot\text{HCl}$ and (I) with conc. HCl, $\text{N}_2\text{H}_4\cdot\text{HCl}$, $\text{N}_2\text{H}_4\cdot 2\text{HCl}$, unchanged (II), and 5-phenyl-4-methyl-2-oxazolidone (III), m. p. 123°, when heated at 140°/7 mm. (III) is also obtained by interaction of the sulphate of (I) with (a) carbamide at 170—180°, and (b) with KCNO in H_2O , followed by treatment at a high temp. (III) when heated alone gives (I) and a little NH_4Cl , whilst with syrupy H_3PO_4 it evolves 10% of its C as CO_2 . (I) with acetonesemicarbazone in PhMe gives NH_3 , and a product which with cold conc. HCl gives (II). Similar treatment of the product of interaction of acetophenonesemicarbazone and (I) gives $\text{N}_2\text{H}_4\cdot\text{HCl}$ and (III). A. A. L.

Action of nitrous acid on salts of nor(+)- ψ -ephedrine. A. MCKENZIE, E. M. LUIS, and A. G. MITCHELL (Ber., 1932, 65, [B], 798—807).—The action of HNO_3 on nor(+)- ψ -ephedrine sulphate in dil. H_2SO_4 or AcOH gives a nitrogenous oil, usually initially dextrorotatory in EtOH and becoming laevorotatory when preserved but occasionally laevorotatory initially. Distillation results in the isolation of COPhEt, due to "vinyl deamination" and (+)-hydratropaldehyde (isolable as the semicarbazone, m. p. 128—130°, $[\alpha]_{\text{D}}^{15} +42^\circ$ in EtOAc, $[\alpha]_{\text{D}}^{14} +32.0^\circ$ in EtOH) when reaction is effected as rapidly as possible; decomp. with boiling *N*-HCl involves partial isomerisation to COPhEt and partial racemisation. The active aldehyde undergoes racemisation at various rates under the influence of certain catalysts. Its production is attributed to the migration of a Ph group. There is also isolated a compound $(\text{C}_9\text{H}_{10}\text{ON})_2$, m. p. 78—79°, $[\alpha]_{\text{D}}^{17} -216^\circ$ in EtOH, which does not show mutarotation and is slowly converted by hot dil. HCl into COPhEt and other products.

Nor(+)- ψ -ephedrine is transformed by MeI and NaOMe in boiling MeOH into (+)- ψ -methylephedrine methiodide, m. p. 211—212°, $[\alpha]_{\text{D}}^{20} +42.5^\circ$ in H_2O , converted by Ag_2O into (+)- β -phenylpropylene $\alpha\beta$ -oxide, b. p. 80—81°/19 mm., $\alpha_{\text{D}}^{25} +10.11^\circ$ ($l=0.5$), which is non-mutarotatory. It is transformed by conc. H_2SO_4 at 0° into $\text{CH}_2\text{Ph}\cdot\text{COMe}$ (semicarbazone, m. p. 186—188°) and by 2*N*- H_2SO_4 at room temp. into β -phenylpropane- $\alpha\beta$ -diol, b. p. 115—117°/1.2 mm., $\alpha_{\text{D}}^{15} -4.67^\circ$ ($l=0.2$), $[\alpha]_{\text{D}}^{17} -24.8^\circ$ in EtOH. The possibility of the presence of the (+)-oxide in the products of deamination of nor(+)- ψ -ephedrine is therefore excluded. Alteration in the

sp. rotation of the (+)-oxide is not caused by distillation at atm. pressure, but prolonged heating at the b. p. causes marked enhancement, which is probably not due to isomerisation to (+)-hydratropaldehyde. When heated with a little anhyd. ZnCl_2 , the (+)-oxide affords $\text{CH}_2\text{Ph}\cdot\text{COMe}$. With KOH-EtOH it affords a glycol Et ether, $\text{C}_{14}\text{H}_{16}\text{O}_2$, b. p. 111—117°/14 mm., $[\alpha]_{\text{D}}^{25} +28.6^\circ$ in EtOH. H. W.

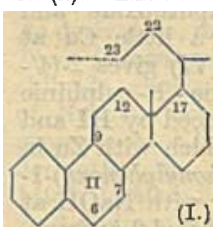
Diarylarylacetylenylcarbinols. Phenyl-*p*-tolyl-, $\text{C}_{22}\text{H}_{18}\text{O}$, and phenyl-*p*-bromophenyl-, $\text{C}_{21}\text{H}_{15}\text{OBr}$, - β -phenylacetylenylcarbinols. M. LOUBY (Compt. rend., 1932, 194, 1747—1749).—Phenyl-*p*-tolyl-, m. p. 55—56° (A., 1928, 522), and phenyl-*p*-bromophenyl-, m. p. 110—111°, - β -phenylacetylenylcarbinols, have been obtained crystalline.

A. A. L.

Metacholesterol. IV. I. LIFSCHÜTZ (Arch. Pharm., 1932, 270, 253—256; cf. A., 1922, i, 541).—Metacholesterol (modified prep.) is not reduced to cholesterol by KOH-EtOH (cf. de Fazi, A., 1931, 1412).

R. S. C.

Ring system of sterols and bile acids. O. ROSENHEIM and H. KING (Chem. and Ind., 1932, 464—466).—It is suggested that the ring system of the sterols and bile acids is that of chrysene as shown in (I). The formation of the (presumably) saturated



apocholic acid from cholic acid is assumed to be due to loss of H_2O whereby ring formation between C_{12} and C_{23} occurs. (I) explains the production (during dehydrogenation with Se) of chrysene from cholic acid and of the hydrocarbons $\text{C}_{18}\text{H}_{16}$ and $\text{C}_{25}\text{H}_{24}$ ($\text{C}_{26}\text{H}_{24}$?) from cholesterol and ergosterol (see A., 1930, 470). The six-membered ring II allows a simple formulation of the degradation of the acid, $\text{C}_{24}\text{H}_{40}\text{O}_6$, to the pyro-acid, $\text{C}_{22}\text{H}_{38}\text{O}_3$ (Windaus *et al.*, A., 1923, i, 1204), whilst a bridge linking allows the migration of the C_6 - C_7 double linking of cholesterol (and its derivatives) to a position connected with C_9 , and explains the abnormal Br absorption of cholestenone and cholesterylene. The one double linking of dihydroxycholenic acid is probably between C_{22} and ; an identical linking occurs in ergosterol, thus making it probable that the resemblance of α -ergosterol to apocholic acid in its behaviour to oxidising (dehydrogenating) agents (Wieland and Deulofeu, A., 1931, 957) is also due to ring closure. Such a ring closure explains the non-production of α -methylisovaleraldehyde by ozonisation of α -ergosterol (this vol., 267), and accounts for (a) the origin of the green coloration produced in the Tortelli-Jaffé reaction (hitherto considered sp. for ergosterol and α -ergosterol, but also given by dihydroxycholenic, apocholic, and apocholanic acids), and (b) the specificity of the oxidative production of toluenetetracarboxylic acid from ergosterol (this vol., 612).

H. B.

Carbon skeleton of the sterols. J. D. BERNAL (Chem. and Ind., 1932, 466).—Rosenheim and King's formula (preceding abstract) for the ergosterol ring system accords with the crystallographic cell dimensions determined by X-ray examination of crystals of sterols, whereas the earlier formulæ do not. H. B.

Preparation of cholesteryl ethers. W. STOLL (Z. physiol. Chem., 1932, 207, 147—151).—Cholesteryl toluenesulphonate when heated with alcohols yields the corresponding cholesteryl ethers; with KOAc in MeOH an isomeric *Me ether*, m. p. 79°, $[\alpha]_D^{25} +55^\circ$, is obtained. Sitosteryl and stigmasteryl toluenesulphonate likewise afford with MeOH *sitosteryl Me ether*, m. p. 100°, $[\alpha]_D^{25} -40.7^\circ$, and *stigmasteryl Me ether*, m. p. 122°. α -Ergostenyl, m. p. 162—163° (decomp.), ergostanyl, m. p. 150—151° (decomp.), cholestanyl, m. p. 134—135°, and sitostanyl, m. p. 154—155° (decomp.), *p*-toluenesulphonates do not produce ethers when boiled with MeOH. J. H. B.

Relation between ergosterol and carotene. H. VON EULER and B. JANSSON (Arkiv Kemi, Min., Geol., 1932, 10, B, No. 17, 1—6).—Solutions of carotene alone and in presence of ergosterol in C_6H_6 experience no change in their absorption spectra on exposure to daylight or ultra-violet light, whilst such solutions in $CHCl_3$ undergo an increase in brightness, especially in absence of the sterol, when the absorption spectrum is significantly displaced. Hence the sensitising action by carotene is not very evident, but the influence of ergosterol on the photochemical oxidation of carotene is well marked. Ergosteryl phosphate behaves similarly. Ultra-violet irradiation of carotene and ergosterol in aq. suspension in presence of Witte's peptone, casein, or Na nucleinate results in partial destruction of the colour, whilst the colloidal state of the components is unaltered. Vals. of n for $CHCl_3$ solutions of α - and β -carotene and xanthophyll are given. F. O. H.

Additive compounds and mixed crystals in the sterol series. H. LETTRE (Annalen, 1932, 495, 41—60).—Additive (1 : 1) compounds of various pairs of sterols are shown to exist by Rheinboldt's method (A., 1926, 25). Of the saturated isomeric sterols cholestanol (I) (+ +), epicoprosterol (II) (— —), epicholestanol (III) (+ —), and coprosterol (IV) (— +) (the signs in parentheses are given arbitrarily to C_1 and C_4 , respectively), only (I) and (II), and (III) and (IV), furnish additive compounds, indicating that additive compound formation occurs only when both asymmetric centres (for a given pair) are of opposite sign. The presence of OH is essential; the corresponding esters or hydrocarbons do not form additive compounds. Ergostanol and (II) also give an additive compound suggesting stereochemical similarity between the former and (I). Dihydroergosterol and epidihydroergosterol (V) form an additive compound (cf. A., 1930, 910) (their acetates do not), the existence of which is probably related to the opposite configurations of C_4 . Ergosterol and (V) also form an unstable additive compound. All the above additive compounds are considered to be "partial racemates," similar to the additive compound from *d*-chloro- and *l*-bromo-succinic acids (Timmermans, A., 1929, 1165). Additive compounds of vitamin- D_2 and lumisterol, pyrocalfiferol and isopyrovitamin (formed with pyrocalfiferol when vitamin- D_2 is heated), lumisterol and isopyrovitamin, dihydrolumisterol and epidihydrolumisterol, and vitamin- D_2 and epidihydrolumisterol exist. The non-existence of additive compounds of lumisterol and pyrocalfiferol, vitamin- D_2

and isopyrovitamin, or vitamin- D_2 and dihydrolumisterol, in conjunction with the above results, suggests that lumisterol and pyrocalfiferol contain a like asymmetric centre as do vitamin- D_2 and isopyrovitamin (of opposite sign). Ergosteryl and dihydroergosteryl acetates furnish a continuous series of mixed crystals as do ergosterol and dihydroergosterol. The f.-p. diagrams of cholesterol-cholestanol, cholesteryl acetate-cholestanyl acetate, and cholestane-cholestene show mixed crystal and eutectic formation. H. B.

Pinacol-pinacolin rearrangement. Rearrangement of unsymmetrical aromatic pinacols. W. E. BACHMANN (J. Amer. Chem. Soc., 1932, 54, 2112—2118).—The relative migration aptitudes of the groups in *as*-pinacols, $OH \cdot CR_2 \cdot CR_2' \cdot OH$, are: Ph 1, *m*-tolyl 1, *p*-tolyl 0.93, anisyl 0.39; the series differs from that with the *s*-compounds (this vol., 515). *as*-Diphenyldi-*p*-tolylethylene glycol, m. p. 167—168° (decomp.); *as*-diphenyldi-*m*-tolylethylene glycol, m. p. 156—158° (decomp.); *as*-diphenyldianisylethylene glycol (I), m. p. 166—168°; *o*-toluoyldiphenylcarbinol, m. p. 116—117° (converted by 25% MeOH-KOH into *o*- $C_6H_4Me \cdot CO_2H$ and benzhydrol), and α -naphthoyldiphenylcarbinol, m. p. 156—157°, are prepared. The product from MgEtI and (I) in Et_2O - C_6H_6 absorbs I slowly at room temp., giving $COPh_2$ and its 4 : 4'-(OMe)₂ derivative. The above pinacols rearrange to pinacolins, using the procedure previously described (*loc. cit.*), with migration of the groups in the following ratios: *p*-tolyl 49, Ph 51; *m*-tolyl 50, Ph 50; anisyl 28, Ph 72. The work of Bergmann and Schuchardt (A., 1931, 1059) is discussed. C. J. W. (b).

Electrochemical researches with cyclohexanecarboxylic acid. F. FICHTER and W. SIEGRIST (Helv. Chim. Acta, 1932, 15, 698—708).—Electrolysis of K cyclohexanecarboxylate in slightly alkaline solution gives cyclohexene, cyclohexanone, cyclohexyl cyclohexylcarboxylate, b. p. 132—132.5°/10 mm., cyclohexanol, dicyclohexyl ether, b. p. 124—126°/20 mm. (prepared for comparison by interaction of cyclohexyl chloride with Na cyclohexyloxide in cyclohexanone), and adipic, succinic, and formic acids. There is no marked variation in the relative proportions of the neutral products over the range 0.206—0.63 amp. per sq. cm. In acid solution electrolysis gives CO_2 and dicyclohexyl. H. A. P.

Dihydroresorcinols. I. Alkylation of substituted dihydroresorcinols. R. D. DESAI (J.C.S., 1932, 1079—1088).—Alkylation of 1-substituted cyclohexane-3 : 5-diones gives greater or smaller amounts of *O* or *O* derivatives according to the nature of the alkyl derivative. The following series indicates the order of preference for the formation of *O* derivatives: $CH_3Ph > allyl > Me > Et > Pr^i > Pr^s > Bu$. Condensation of Et cinnamate and Et sodiocyanoacetate gives *Et* α -cyano- β -phenylglutarate, b. p. 208—210°/18 mm., hydrolysed to β -phenylglutaric acid. The chloride of the Et H ester of this with ZnEtI gives δ -keto- β -phenylhexoic acid (I), m. p. 87—88° [semicarbazone, m. p. 185° (decomp.)]; *Et* ester, b. p. 197°/23 mm.]. The following acids are similarly obtained from appropriate derivatives of glutaric acid: δ -keto- $\beta\beta$ -dimethyl-

heptoic (II), b. p. 177°/35 mm. [semicarbazone, m. p. 138°; *Et* ester (III), b. p. 135°/30 mm. (semicarbazone, m. p. 88°)]; δ -keto- $\beta\beta\epsilon$ -trimethylheptoic (IV), b. p. 160°/15 mm. [semicarbazone, m. p. 155° (decomp.); *Et* ester, b. p. 124°/15 mm. (semicarbazone, m. p. 98°)]; δ -keto- $\beta\beta$ -dimethylheptoic, b. p. 176°/23 mm. [semicarbazone, m. p. 137°; *Et* ester (V), b. p. 139°/22 mm. (semicarbazone, m. p. 68°)]; 1-propionylmethylcyclopentane-, b. p. 215°/50 mm. [semicarbazone, m. p. 157° (decomp.); *Et* ester (VI), b. p. 165°/30 mm. (semicarbazone, m. p. 89°)]; isobutyrylcyclopentane- (VII), b. p. 194—195°/20 mm. [semicarbazone, m. p. 195° (decomp.); *Et* ester, b. p. 153°/15 mm.]; 1-propionylmethylcyclohexane-, m. p. 190°/20 mm. [semicarbazone, m. p. 167° (decomp.); *Et* ester (VIII), b. p. 151°/12 mm. (semicarbazone, m. p. 79°); when heated alone it gives an unsaturated lactone, b. p. 153°/15 mm.]; and 1-isobutyrylcyclohexane-1-acetic acid (IX), b. p. 191°/18 mm. [semicarbazone, m. p. 186° (decomp.)]. The following compounds are obtained from the action of alkyl iodides on 1-substituted derivatives of sodium dihydroresorcinol (yields in parentheses): 4-*Me*, m. p. 163° (50%) [also obtained from (III) by action of NaOEt, and oxidised by NaOBr to $\beta\beta$ -dimethylglutaric acid]; 4:4-*Me*₂, m. p. 95° (25%), hydrolysed by NaOH in aq. MeOH to (IV); O-*Me*, b. p. 135°/17 mm.; 4-*Et*, m. p. 153° (20%); O-*Et*, m. p. 60° (J.C.S., 1899, 75, 771); 4-*CH*₂*Ph*, m. p. 154—155° (36%); 4:4-(*CH*₂*Ph*)₂, m. p. 135° (60%) (hydrolysed to δ -keto- $\epsilon\epsilon$ -dibenzyl- $\beta\beta$ -dimethylhexoic acid, m. p. 61°); 4-*Pr*^a, m. p. 162° (15—20%); O-*Pr*^a, m. p. 65°, b. p. 150°/18 mm.; 4-*Pr* ^{β} , m. p. 156° (10—15%); O-*Pr* ^{β} , m. p. 55°, b. p. 139°/17 mm.; 4-*Bu*, m. p. 155° (20%); O-*Bu*, m. p. 69—70°, b. p. 163°/17 mm.; 4-*allyl*, m. p. 143° (35%); 4:4-*diallyl*, m. p. 75° (35%); and O-*allyl*, b. p. 155°/20 mm., derivatives of 1:1-dimethyldihydroresorcinol; 4-*Me* (A., 1931, 92) (50%), hydrolysed to (I); 4:4-*Me*₂ (A., 1908, 288) (25%), hydrolysed to δ -keto- β -phenyl- ϵ -methylhexoic acid, m. p. 106—107°; 4-*Et*, m. p. 198° (20%); O-*Et*, b. p. 220°/16 mm.; 4-*CH*₂*Ph*, m. p. 170° (45%); 4:4-(*CH*₂*Ph*)₂, m. p. 128—129° (55%) (cf. A., 1897, i, 275) (hydrolysed to δ -keto- β -phenyl- $\epsilon\epsilon$ -dibenzylhexoic acid, m. p. 145°); 4-*Pr*^a, m. p. 184°; O-*Pr*^a, b. p. 230°/16 mm.; 4-*Pr* ^{β} , m. p. 190°; O-*Pr* ^{β} , b. p. 222°/20 mm.; 4-*Bu*, m. p. 188°; and O-*Bu*, b. p. 245°/20 mm., derivatives of 1-phenyldihydroresorcinol; 4-*Me* (45%) (J.C.S., 1922, 121, 1303), methylated to 1:4:4-trimethyl-1-ethylcyclohexane-3:5-dione, m. p. 68°, which is hydrolysed to δ -keto- $\beta\epsilon$ -dimethyl- β -ethylheptoic acid (X), b. p. 170°/15 mm. [semicarbazone, m. p. 157° (decomp.)]; and O-*Me*, b. p. 147°/25 mm., derivatives of 1-methyl-1-ethylcyclohexane-3:5-dione (A., 1929, 1273) (methylene derivative, m. p. 89°); 4-*Me* (A., 1929, 560), also obtained from (VI) with NaOEt; and 4:4-*Me*₂, m. p. 78° [hydrolysed to (VII)], derivatives of cyclopentanespirocyclohexane-3:5-dione; and 4-*Me* (A., 1928, 887), also obtained from (VIII) with NaOEt; and 4:4-*Me*₂, m. p. 95° [hydrolysed to (IX)], derivatives of cyclohexanespirocyclohexane-3:5-dione. By treatment with AcCl lactones of the enol forms are obtained from (II), b. p. 105°/20 mm., (IV), b. p. 99°/20 mm., (VII) (+ $\frac{1}{2}$ H₂O), m. p. 90°, (IX), b. p. 163°/16 mm., and (X), b. p. 110°/18 mm.

A. A. L.

Orienting influences in the benzene ring. Sulphonation of benzoic acid. J. S. REESE IV. (J. Amer. Chem. Soc., 1932, 54, 2009—2017).—A reaction scheme for the sulphonation of BzOH is proposed and supported by a study of the isomerisation of *o*-sulphobenzoic acid (I) and the actual sulphonation reaction. (I) heated with excess of conc. H₂SO₄ at 200° is converted solely into the *m*-isomeride (max. of about 85% in 12 hr.); the rate of conversion is increased more than two-fold (up to 4 hr.) by addition of HgSO₄. Both these reactions appear to be unimol. The amount of *o*-substitution occurring during the sulphonation of BzOH at 200° is 14.3% after 20 min., 5.8% after 1 hr., and 6.3% after 3 hr.; in presence of HgSO₄ the corresponding % are 7.3, 3.8, and 2.3. The curve of log. concn. of unreacted BzOH against time indicates condensation of an additive compound to benzoysulphuric acid during 20 min., and then isomerisation of this to (I). A new relationship between *o*-, *m*-, and *p*-substitution is proposed, and evidence from the sulphonation of BzOH added to that already known (lit.).

C. J. W. (b)

Behaviour of phenylacetonitrile and α -phenylbutyronitrile with sodium ethoxide. M. M. RISING and K. T. SWARTZ (J. Amer. Chem. Soc., 1932, 54, 2021—2025).—NaOEt is not a satisfactory reagent for obtaining the Na derivative of CH₂Ph-CN (in Et₂O); a considerable quantity is undoubtedly formed, but this reacts with the nitrile to form β -imino- $\alpha\gamma$ -diphenylpropionitrile (I), b. p. 222—223°/2.75 mm. (25% yield). NH₂OH and (I) give β -oximino- $\alpha\gamma$ -diphenylpropionitrile. Hydrolysis of (I) with conc. HCl at 150° gives CO₂, CH₂Ph-CO₂H, and CO(CH₂Ph)₂; with MeOH-HCl 76% of CH₂Ph CO-CHPh-CO-NH₂ results. α -Phenylbutyryl chloride, b. p. 122—125°/20 mm., and α -phenylbutyramide, m. p. 83°, are described. α -Phenylbutyronitrile does not undergo self-condensation with NaOEt in Et₂O.

C. J. W. (b)

Metastable modifications of *cis*-cinnamic acid. C. WEYGAND and H. BAUMGÄRTEL (Ber., 1932, 65, [B], 693—696).—Catalytic reduction of phenylpropionic acid according to Paal yields only *cis*-cinnamic acid, m. p. 58°; if crystallised from light petroleum, it does not pass spontaneously into form 42°, which is produced by seeding with *trans*-cinnamic acid formed from solution or the solidified *trans* melt. If purified through the NH₂Ph salt, it yields form 42° when cooled to 0° or seeded with the *trans*-acid. An extremely unstable form 32° is produced by seeding molten *cis*-acid with form 42° or *trans*-acid and cooling to 0° or below 0°, whilst the growth of form 42° proceeds. The seeding relationship, *trans*-cinnamic acid = *cis*-cinnamic acid 42°, probably depends on the intermediate production of the so-called "double acid" and is not due to a simple, further growth of *trans*-crystals in the *cis* melt such as is observed between isomorphous modifications of closely related compounds; de Jong's supposed establishment of the polymorphism of the *cis*-cinnamic acids is adversely criticised. It is proposed to distinguish modifications of isomerides of which the unidirectional or mutual seeding action cannot be

attributed to isomorphism by the term "analogous forms" in contradistinction to "corresponding forms."

H. W.

Course of hydrogenation with amalgam. R. KUHN and A. DEUTSCH (Ber., 1932, 65, [B], 817—818).—Reduction of α -vinylcinnamic acid by Na-Hg affords α -benzylcrotonic acid, m. p. 99° (corr.), in 80% yield. Contrary to the predictions of Burton and Ingold (A., 1929, 1270), addition occurs in the $\alpha\delta$ -position. The possibility that β -phenyl- α -vinylpropionic acid is present in the oily product of the action and suffers isomerisation during distillation is excluded, since the oil and crystals yield AcOH when oxidised by 10*N*-H₂CrO₄ and H₂SO₄ before or after ozonolysis and CH₂O is not formed during the latter process.

H. W.

Synthesis of *cis*- and *trans*-dl-1 : 1-dimethyl-2- γ -ketobutylcyclopropane-3-carboxylic acids. J. OWEN and J. L. SIMONSEN (J.C.S., 1932, 1424—1429).—Methylheptenone, Et diazoacetate, and Cu-bronze at 45—50° give cyclobutane-1 : 2 : 3 : 4-tetra-carboxylic acid, decomp. 287° (Ag₄ salt; Me₄ ester, m. p. 103°), and a mixture of esters, which after hydrolysis yields semicarbazones (I) and (II), m. p. 223—224° and 193—194°, respectively. (I) affords dl-(?)*trans*-1 : 1-dimethyl-2- γ -ketobutylcyclopropane-3-carboxylic acid, m. p. 78—79° (oxime, m. p. 114°), whilst (II) gives the (?) *cis*-isomeride, an oil (oxime, m. p. 102°). These acids with NaOBr form respectively dl-*trans*- and -*cis*-3-carboxy-1 : 1-dimethylcyclopropane-2-propionic acid, m. p. 131—132° and 107—108° (after sintering at 105°), converted by HBr or HCl into homoterpenylic acid. The keto-acids with 20% H₂SO₄ yield dl-homoterpenyl Me ketone (semicarbazone, new m. p. 206—207°), identical with that prepared from dl-pinonic acid.

R. S. C.

Keto-enol determination. G. A. MICHALEK and H. W. POST (J. Amer. Chem. Soc., 1932, 54, 1963—1964; cf. A., 1931, 88).—Redeterminations of the enol content of CHAcPh·CO₂Et at 22°, both by Br titration and by refractive indices, give vals. essentially those obtained previously (*loc. cit.*) and not in accordance with that of von Auwers (A., 1931, 726).

C. J. W. (b)

Hydrogen chloride additive products of tyrosine-*N*-phenylacetic acid and of the corresponding methyl and ethyl esters. D. A. HAHN and A. L. WHITE (J. Amer. Chem. Soc., 1932, 54, 2052—2056).—Tyrosine-*N*- α -phenylacetic acid (I) [Me₂, m. p. 180—180.5°, and Et., m. p. 160—162° (decomp.), ester *hydrochlorides*] [improved method of separation and purification given (cf. A., 1930, 1047)] and boiling 18% HCl give the *hydrochloride* (+H₂O), m. p. 136—137°, converted by conc. HCl in 18% HCl into the *dihydrochloride* (+3H₂O), m. p. 88—92°, also formed directly from (I) and conc. HCl, which slowly loses HCl at room temp.

C. J. W. (b)

Electrolytic reduction of alkylphthalimides. II, III. Phthalic anhydride. B. SAKURAI (Bull. Chem. Soc. Japan, 1932, 7, 127—129, 130—132; cf. A., 1930, 1183).—II. Phthalic anhydride dissolved in aq. solutions of NH₃, (NH₄)₂CO₃, or NH₄OAc was reduced at a Pb cathode to phthalide. No other product was detected.

III. The yield of phthalide increases with rise of temp., being negligibly small below 60° and nearly quant. at 80°. For the largest yield the *p_n* of the electrolyte should lie between 10.5 and 12.

F. L. U.

Rotenone. XX. Structure of tubaica acid. H. L. HALLER and F. B. LAForge. XXI. Structure of *isorotenone*, β -*dihydorotenone*, and *dehydrototenol*. H. L. HALLER (J. Amer. Chem. Soc., 1932, 54, 1988—1994, 2126—2128).—XX. Mainly a more detailed account of work previously reviewed (this vol., 165) (Part XVIII). The following is new. The Ac₂ derivative, m. p. 143°, of tetrahydrotubaica acid (2 : 4-dihydroxy-3-*isoamyl*benzoic acid) (I) is hydrolysed by EtOH-KOAc to the Ac derivative, m. p. 156°. (I) and Me₃SO₄ in 5% KOH give 2-hydroxy-4-methoxy-3-*isoamyl*benzoic acid, m. p. 156°. Tetrahydrotubanol (2-*isoamylresorcinol*), m. p. 85°, formed when (I) is heated to 215—225°, is converted by boiling with saturated NaHCO₃ into (I). Ozonolysis of acetyltubaica acid gives a compound, C₁₃H₁₂O₆, m. p. 145°, probably a Me ketone. The hydrogenation of tubaica acid is analogous to that of deoxycodine-*C*. An explanation of the mechanism of oxidation of rotenone derivatives by H₂O₂ is given.

XXI. A criticism of the rotenone formula of Takei *et al.* (this vol., 400). Structures are assigned to *isorotenone*, β -*dihydorotenone*, and *dehydrototenol*.

C. J. W. (b)

Substituted phenylacetonitriles and derivatives. 1-Cyano-1-phenylcyclopropane, γ -hydroxy- α -phenylbutyronitrile, γ -chloro- α -phenylbutyronitrile, and α -phenylcrotononitrile. E. C. KNOWLES and J. B. CLOKE (J. Amer. Chem. Soc., 1932, 54, 2028—2037).—1-Cyano-1-phenylcyclopropane (I), b. p. 98—100°/1 mm., 250—253°/761 mm., results in 40—45% yield when CH₂Ph·CN is treated first with NaNH₂ and then with CH₂Cl·CH₂Br or *s*-C₂H₄Br₂ (special apparatus described). γ -Hydroxy- α -phenylbutyronitrile, b. p. 146—149°/1.5–2 mm., formed in 40% yield from OH·CH₂·CH₂Cl and the Na compound (II) of CH₂Ph·CN, with SOCl₂ gives γ -chloro- α -phenylbutyronitrile, b. p. 127—129°/3–4 mm., converted by NaNH₂ into (I). Propylene dibromide and (II) give 1-cyano-1-phenyl-2-methylcyclopropane, b. p. 257—260°/761 mm. Hydrolysis of (I) with H₃PO₄ (or alkaline H₂O₂) gives 1-phenylcyclopropane-1-carboxylamide, m. p. 100—101° (corr.) (also formed when the hydrochloride of Et imino-1-phenylcyclopropanecarboxylate is heated to 110°), and (mainly) α -phenylcrotonic acid. Cyanocyclopropane is similarly hydrolysed to cyclopropanecarboxylic acid. CH₂Ph·CN, MeCHO, and NaOEt in EtOH give 36% of α -phenylcrotononitrile, b. p. 244—246°/751 mm., converted by alkaline H₂O₂ into α -phenylacetoacetamide, m. p. 177—178°, hydrolysed by conc. HCl to CH₂Ph·COMe. α -Phenylcrotonic acid is prepared by hydrolysis of the nitrile with H₃PO₄, and by the isomerisation of α -phenyl- Δ^2 -butenoic acid with 10% NaOH.

C. J. W. (b)

Stereochemistry of diphenyl. XXI. Resolution of 2 : 4 : 6 : 2' : 4' : 6'-hexachlorodiphenyl-3 : 3'-dicarboxylic acid. J. WHITE and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 2104—2108).—

2:4:6-Trichloro-3-iodotoluene, m. p. 95—97° (from the trichlorotoluidine), and Cu bronze at 235—250° give 2:4:6:2':4':6'-hexachloro-3:3'-dimethyldiphenyl, m. p. 119—120°, oxidised by KMnO_4 and HNO_3 (d 1.15—1.2) to 2:4:6:2':4':6'-hexachlorodiphenyl-3:3'-dicarboxylic acid (I), m. p. 318—320°. (I) is resolved by brucine into *d*-, m. p. 293—294°, $[\alpha]_D^{25} +1.8^\circ$ in EtOH (brucine salt, m. p. 209°), and *l*-forms, m. p. 292—293°, $[\alpha]_D^{25} -1.7^\circ$ in EtOH (brucine salt, m. p. 206—210°), which are not ordinarily racemised. 2:4:6:2':4':6'-Hexachloro-3:3'-dinitrodiphenyl, m. p. 230—231°, from hexachlorodiphenyl and HNO_3 (d 1.5), is reduced to the 3:3'-diamino-derivative, m. p. 167.5—168.5° [*di*(chloroacetyl) derivative, m. p. 125—126°], which could not be condensed with oxymethylenecamphor or *d*-camphorsulphonic acid. C. J. W. (b)

Isomerisation of tetraphenylsuccinonitrile. G. WITTIG and W. HOPF (Ber., 1932, 65, [B], 760—766).—Tetraphenylsuccinonitrile (I) becomes coloured in solution in boiling anisole or C_{10}H_8 or molten camphor owing to dissociation into cyanodiphenylmethyl. The colourless solutions in NH_3Ph , NPhMe_2 , $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NMe}_2$, or $\text{C}_6\text{H}_4\text{Me}_2$ containing NH_4Et , or 2:6-dimethylpyrone become coloured when heated, but the colour suddenly disappears and does not return on protracted boiling owing to isomerisation of (I) to *p*-cyanobenzyltriphenylacetone (II), $\text{CN}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{CN}$, m. p. 161—161.5°. Treatment of (II) in dioxan under N_2 with Na-K involves combination with 4 atoms of K; the product with EtOH gives a non-uniform material oxidised by CrO_3 in AcOH to terephthalophenone, $\text{C}_6\text{H}_4\text{Bz}_2$, m. p. 160—162°. Oxidation of (II) with KMnO_4 in COMe , gives *p*-benzoyltriphenylacetone (III), m. p. 122—123°, which yields β -acetyl-*p*-nitrophenylhydrazine when heated with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ in AcOH. Terephthalophenone and MgPhBr yield a mixed product or *p*-bisdiphenylhydroxymethylbenzene if an excess of the reagent is used. BzCl and $\text{CPh}_3\cdot\text{CN}$ do not react in presence of AlCl_3 and CS_2 or PhNO_2 . *p*-Benzoylbenzotrichloride, C_6H_6 , and AlCl_3 afford *p*-benzoyltriphenylmethyl chloride, readily hydrolysed to *p*-benzoyltriphenylcarbinol, m. p. 131—132°, and converted by $\text{Hg}(\text{CN})_2$ into (III). The mechanism of the isomerisation is fully discussed. H. W.

Alkylcyclopentanones. II. Effect of the methylcyclopentane ring on the carbon tetrahedral angle. R. D. DESAI (J.C.S., 1932, 1065—1079; cf. A., 1931, 843).—The effect of the methylcyclopentane ring is similar to that of the unsubstituted ring. *Et H* 3-methylcyclopentane-1:1-diacetate (from the anhydride, *loc. cit.*) after esterification of the product of bromination of the acid chloride gives *Et* α -bromo-3-methylcyclopentane-1:1-diacetate (I), b. p. 163°/7 mm. [and a little of the *Et H* bromodiacetate (II)], converted by distillation into the lactone, b. p. 188°/20 mm., of *Et H* α -hydroxy-3-methylcyclopentane-1:1-diacetate, and *EtBr*. (I) with 64% KOH gives the corresponding lactic acid, *A*, m. p. 87° (NH_2Ph salt, m. p. 95°) [also obtained from (I) with Na_2CO_3 ; similar treatment of (II)

gives an isomeride, *B*, m. p. 75°], and *trans*-, *A*, m. p. 230° (dianilide, m. p. 295°), *trans*-, *B*, m. p. 215° (dianilide, m. p. 275°), and *cis*-3-methylcyclopentanespirocyclopropane-2':3'-dicarboxylic acid, m. p. 175°, separated by means of the anhydride, m. p. 75° (anilic acid, m. p. 190°), and also obtained by heating the *trans*-acids, which are hydrolysed by HCl at a high temp. 3-Methylcyclopentane-1:1-diacetic acid (*loc. cit.*) [$(\text{Me}_2\text{ ester (III), b. p. 137°/15 mm.}]$, after esterification of the product of bromination of the acid chloride, gives (II), *Et H* (IV) and *Et*, α' -dibromo-3-methylcyclopentane-1:1-diacetate (V) [acids, *A*, m. p. 195° (decomp.), and *B*, m. p. 163°, obtained from the chloride with anhyd. HCO_2H], which, on distillation, gives a bromolactonic ester, b. p. 195—196°/15 mm. (V) with 64% KOH gives 5% of 3-methylcyclopentylidenecetic acid (VI), m. p. 112°, 45% of α -keto-3-methylcyclopentane-1:1-diacetic acid (VII), m. p. 121° [quinoxaline derivative, m. p. 226—227°; 2:4-dinitrophenylhydrazine, m. p. 185° (decomp.); *Me* ester, b. p. 169°/19 mm. (phenylto hydrazine, m. p. 163°)] [oxidised by H_2O_2 in Na_2CO_3 1-carboxy-3-methylcyclopentane-1-acetic acid (VIII), corrected m. p. 120° (*loc. cit.*)], and a little of the *trans*-lactone, m. p. 146° (*Ac* derivative, m. p. 151°), of α' -dihydroxy-3-methylcyclopentane-1:1-diacetic acid, also obtained from the esterified product of interaction of Na_2CO_3 on (IV), together with the *cis*-lactone, m. p. 125°, and a little (VII). The hydrogen sulphite compound of 3-methylcyclopentanone gives a cyanohydrin, b. p. 128—130°/25 mm. (slight decomp.), which with *Et* sodiocyanoacetate gives a dicyano-ester, hydrolysed to (VIII). 3-Methylcyclopentanone with Zn and *Et* bromoacetate gives unchanged ketone, 4-methyl-2-(3'-methylcyclopentylidene)cyclopentanone, b. p. 132—133°/12 mm. (semicarbazone, m. p. 142—143°) (oxidised by KMnO_4 to 3-methylcyclopentanone and β -methylglutaric acid), and *Et* 3-methylcyclopentane-1-ol-1-acetate, b. p. 121°/20 mm., the acid, m. p. 56°, from which, with Ac_2O , gives (VI) and a little acid, m. p. 81°. (V) with KOH in MeOH gives α -hydroxy- α -methoxy-3-methylcyclopentane-1:1-diacetic acid, m. p. 145°, its lactone, m. p. 150° (previous sintering), *trans*-, *A*, m. p. 190°, *trans*-, *B*, m. p. 178°, *cis*-, *A*, m. p. 175°, and *cis*-3-methylcyclopentanespiro-2-methoxycyclopropane-2':3'-dicarboxylic acid, *B*, m. p. 162° (the two latter separated through the anhydrides, *A*, m. p. 87°, and *B*, m. p. 60°, also obtained by distillation of the *trans*-acids). The above acids with fuming HBr give (VII) and a little (VIII). (III) with *Me* oxalate and NaOMe gives a little methylcyclopentanediacyetic acid, and *Me* 3-methylcyclopentanespiro-3':4'-diketocyclopentane-2':5'-dicarboxylate, m. p. 125° [semicarbazone, m. p. 182° (decomp.)], converted by 20% H_2SO_4 into 3-methylcyclopentanespirocyclopentane-3':4'-dione, m. p. 108° [disemicarbazone, m. p. 245° (decomp.)]. The chloride from the acid ester of (VIII) with ZnMeI gives *Et* 1-acetyl-3-methylcyclopentane-1-acetate, b. p. 135°/11 mm. (semicarbazone, m. p. 105°), isolated as the semicarbazone, m. p. 200° (decomp.) (with a little of an isomeric semicarbazone, m. p. 177°), of the acid, m. p. 83°, which is oxidised to (VII). The above ester with NaOEt gives 3-methylcyclopentanespiro-

cyclopentane-2':4'-dione, m. p. 101° (20% yield), (Br-compound, m. p. 185°). A. A. L.

Formation and stability of spiro-compounds.
XIV. Effect of the methylcyclohexane ring on the carbon tetrahedral angle. R. D. DESAI (J.C.S., 1932, 1047—1065).—The properties of the spirocyclopropane derivatives obtained from 3- and 4-methylcyclohexane-1:1-diacetic acid indicate a strainless structure for 3- and 4-methylcyclohexane, whereas cyclohexane is strained. There may be some factor in the methylcyclohexane ring which invalidates the methods used to demonstrate strain in other rings. The ω -imide of 4-methylcyclohexane-1:1-dicyanoacetic acid (J.C.S., 1913, 103, 1593) gives in cold H_2SO_4 the ω -imide, m. p. 260° (decomp.), of 4-methylcyclohexane-1:1-dicarbamylacetic acid, or in hot H_2SO_4 4-methylcyclohexane-1:1-diacetic acid (I) (*Et* ester, b. p. 178°/24 mm.), the anhydride (two anilic acids, *A*, m. p. 184°, and *B*, m. p. 148°, both giving the same anil, m. p. 140°) of which gives *Et H* 4-methylcyclohexane-1:1-diacetate. The acid chloride of this with Br and subsequent esterification gives a little *Et H* α -bromo-4-methylcyclohexane-1:1-diacetate, and the Et_2 ester, which, when distilled, gives *EtBr* and a lactonic ester, b. p. 205°/20 mm., whilst hydrolysis with 64% KOH at 150° gives trans-, m. p. 212°, and cis-methylcyclohexanespirocyclopropane-2':3'-dicarboxylic acid, m. p. 165° (separated by conversion of the latter with AcCl into the anhydride, m. p. 72°), and a little lactonic acid, m. p. 145° (*Et* ester, b. p. 199—203°/18 mm.). Similar treatment of the acid chloride of (I) gives mono- and dibromo-acid esters, and *Et* α' -dibromo-4-methylcyclohexane-1:1-diacetate (II), which gives a bromolactonic ester, b. p. 235°/21 mm., on being distilled, and with anhyd. formic acid gives a little of the acid, m. p. 185° (decomp.), from (II), and the lactone, m. p. 206°, of α -bromo- α' -hydroxy-4-methylcyclohexane-1:1-diacetic acid. (II) with 64% KOH at 150° gives a little 4-methylcyclohexenylacetic acid (*A*, 1907, i, 616), and two isomeric α -keto-4-methylcyclohexane-1:1-diacetic acids (III), m. p. 147° [quinoxaline derivative, m. p. 226°; 2:4-dinitrophenylhydrazone, m. p. 220° (decomp.); *Me* ester, b. p. 192°/25 mm. (phenylhydrazone, m. p. 163°)], and (IV), m. p. 128—129° [quinoxaline derivative, m. p. 245°; 2:4-dinitrophenylhydrazone, m. p. 205°; phenylhydrazone, m. p. 204° (decomp.); *Me* ester, b. p. 187°/20 mm. (phenylhydrazone, m. p. 227°)]. (III) and (IV) are oxidised respectively by H_2O_2 in Na_2CO_3 to isomerides of 1-carboxy-4-methylcyclohexane-1-acetic acid (V), m. p. 136° (previous sintering), and (VI), m. p. 173° (efferv.) (anhydride, m. p. 104°; anilic acid, m. p. 184°) (cf. *A*, 1931, 1055). (II) with KOH in MeOH gives a mixture of trans- (VII), m. p. 190° (previous sintering), and two cis-4-methylcyclohexanespiro-2'-methoxycyclopropane-2':3'-dicarboxylic acids (VIII), m. p. 182° (efferv.), and (IX), m. p. 162° (efferv.), the cis-acids being separated by means of their anhydrides, *A*, m. p. 148° (anilic acids, m. p. 183° and 160°; anil, m. p. 134°), and m. p. 90° [anilic acids, m. p. 193° (efferv.) and 157°; anil, m. p. 96°], the latter being also obtained by distillation of (VII). (VIII) and (IX) with

fuming HBr give (IV) and (VI), and (III) and (V), respectively. The following derivatives of 3-methylcyclohexane are similarly obtained: ω -imide, m. p. 272° (decomp.), of 3-methylcyclohexane-1:1-diacetic acid (*Et*₂ ester, b. p. 174°/22 mm.; anilic acids, m. p. 172° and 141°; anil, m. p. 137°); *Et*₂ and *Et H* α -bromo-3-methylcyclohexane-1:1-diacetate (lactone ester, b. p. 196°/16 mm.); trans- (*A*), m. p. 270° (dianilide, m. p. 280°), trans- (*B*), m. p. 245° (dianilide, m. p. 260°), and cis-3-methylcyclohexanespirocyclopropane-2':3'-dicarboxylic acid, m. p. 205°; *Et H*, m. p. 162°, and *Et*₂ α' -dibromo-3-methylcyclohexane-1:1-diacetate (bromolactonic ester, b. p. 234°/21 mm., m. p. 130°; bromolactonic acids, m. p. 225° and 201°); cyclohexenylacetic acid (*A*, 1906, i, 563); α -keto-3-methylcyclohexane-1:1-diacetic acids, *A*, m. p. 139—140° [quinoxaline derivative, m. p. 217°; 2:4-dinitrophenylhydrazone, m. p. 198° (decomp.)], and *B* (*X*), m. p. 126—127° [quinoxaline derivative, m. p. 239°; 2:4-dinitrophenylhydrazone, m. p. 194° (decomp.)]; *Me* ester, b. p. 185°/23 mm. (phenylhydrazone, m. p. 220° (decomp.)), oxidised to 1-carboxy-3-methylcyclohexane-1-acetic acid (XI), m. p. 163° (efferv.) [anhydride, m. p. 41°, b. p. 166°/22 mm.; anilic acid, m. p. 170° (efferv.); anil, m. p. 139°]; trans-, m. p. 201° (previous sintering), and cis-3-methylcyclohexanespiro-2'-methoxycyclopropane-2':3'-dicarboxylic acid, *A* (XII), m. p. 194° [anhydride, m. p. 140—141°; anilic acids, m. p. 195° (efferv.) and 135°; anil, m. p. 112°], *B*, m. p. 195° (efferv.) [anhydride, m. p. 116°; anilic acid, m. p. 215° (efferv.)], *C*, m. p. 197° (efferv.) (anhydride, m. p. 101°; anilic acid, m. p. 212°), and *D*, m. p. 196° (efferv.) [anhydride, m. p. 85°; anilic acid, m. p. 192° (efferv.); anil, m. p. 118°]. The m. p. of the acids in the above group are taken in a bath preheated to 140—150°. (XII) with fuming HBr gives (X) and (XI), isolated through the corresponding esters. A. A. L.

Condensation of succindialdehyde, methylamine, and malonic acid. C. MANNICH and H. BUDDE (Arch. Pharm., 1932, 270, 283—290).—Succindialdehyde (prepared in 70% yield from succindialdoxime and *Et* nitrite in cold dioxan) (condensation product with dimethyldihydroresorcinol, m. p. 218°), malonic acid, and cold aq. NH_2Me give CO_2 and 3-methylamino-2:2-dicarboxycyclopentane-1-acetic acid (I), m. p. 186—187° (decomp.) (hydrochloride, decomp. 153°; Ag_2 salt; N-p-nitrobenzoyl derivative, m. p. 168°; Me_3 ester, an oil, which with MeI gives the methiodide, m. p. 168°, of the NMe_3 -compound), which in hot H_2O yields 3-methylamino-2-carboxycyclopentane-1-acetic acid (II), m. p. 202° (decomp.) [N-p-nitrobenzoyl derivative, + H_2O , m. p. 126°; Me_2 ester, b. p. 129—131°/1.5 mm.; NO-derivative, an oil; methiodide (III), m. p. 134°, of the NMe_2 -compound]. (III) with hot 15% NaOH yields NMe_3 and 2-carboxy- Δ^2 -cyclopentene-1-acetic acid (IV), m. p. 156° (*Pb*, *Ag*, and *Cu* salts, amorphous), reduced (*Pd-C*) to 2-carboxycyclopentane-1-acetic acid (V), m. p. 60—61°. When heated at 200°, (I) affords NH_2Me , CO_2 , H_2O , (IV), (II), and the cis- and trans-forms, m. p. 178° and 201—202°, of the lactam of (II). Succindialdehyde, malonic acid, and aq. NH_4Et at room temp. give CO_2 ; (V) is obtained by

evaporating the solution and heating the residue at 200°.

R. S. C.

Lichen acids. II. Constitution of evernic acid and synthesis of methyl evernate. A. ROBERTSON and R. J. STEPHENSON (J.C.S., 1932, 1388—1395; cf. A., 1930, 472).—Everninaldehyde (I) (modified prep.) with hot Ac_2O and NaOAc gives the *Ac* derivative, m. p. 84°, oxidised by KMnO_4 and MgSO_4 in aq. COMe_2 at 50° to *O-acetylevernic acid* (II), m. p. 117°, hydrolysed by *N*- NaOH in 10 mm. at room temp. to evernic acid, which is best acetylated by Ac_2O and pyridine at 37°. *O*-Diacetylevernic acid (modified prep.), m. p. 159° (lit. 144°), gives no colour with FeCl_3 . (I) with EtI and Ag_2O in hot COMe_2 gives *O-ethyleverninaldehyde*, m. p. 64°, oxidised (KMnO_4) to *O-ethyleverninic acid* (III), m. p. 87°. *p*-Carbomethoxyorsellinic acid is similarly ethylated to the *Et* ester, m. p. 89°. Evernic acid (IV), MeI , and Ag_2O in hot COMe_2 give *Me O*-dimethylevernate, and using EtI (or diazoethane) *Et O*-diethylevernate, m. p. 123°, which by hydrolysis with 2.5% KOH - EtOH at 40—50° affords (III) and *Et* 1-*O*-ethylorsellinate. (III) with PCl_5 in CHCl_3 gives the *acid chloride* (V), m. p. 68° [whence the anilide, m. p. 178° (lit. 175°), was prepared], which does not react with orsellinic acid in alkaline aq. COMe_2 at -15° and in C_6H_6 , $(\text{CHCl}_3)_2$, pyridine, or NPhMe , gives oily products resolved into the original acids by H_2O . Dicarbomethoxyorsellinic acid, MeI , and Ag_2O in hot COMe_2 afford *Me* orsellinate, which with (V) in pyridine slowly gives *Me O*-acetylevernate, m. p. 119°, rapidly hydrolysed by *N*- NaOH at room temp. to *Me evernate* (VI), m. p. 148°, identical with that obtained from natural evernic acid and CH_2N_2 in Et_2O . *Et evernate* (prepared by diazoethane) has m. p. 152°. Hydrolysis of (VI) under different conditions gives either *Me* evernate and a mixture of acids, m. p. 160° (decomp.), or *Me* orsellinate, orsellinic and evernic acids. The constitution of evernic acid (A., 1914, i, 417) is thus confirmed.

R. S. C.

Bile acids. XXXIV. M. SCHENCK (Z. physiol. Chem., 1932, 207, 267—274; cf. this vol., 383).—The aminoamide, $\text{C}_{22}\text{H}_{38}\text{O}_{11}\text{N}_2$, by the Van Slyke method loses the NH_2 group with AcOH and 75—82% of the amide group with HCl in 6½ hr. The "oxidation product" (I), $\text{C}_{22}\text{H}_{38(36)}\text{O}_9\text{N}_2$, was prepared from the crude oximino-acid (II) hydrochloride. On boiling with HCl (I) loses NH_3 probably from an acid amide group. HCl does not eliminate NH_3 from the "inversion product" of (II), which is probably a mixture of $\frac{2}{3}$ lactamamino-acid and $\frac{1}{3}$ diaminopentacarboxylic acid.

J. H. B.

Decomposition by water of the bromides of Schiff's bases. J. TURCAN (Bull. Soc. chim., 1932, [iv], 51, 486—500).—Dibromides of Schiff's bases of the type $\text{CHR}\cdot\text{NR}'$ in which tautomerism is not possible are decomposed by H_2O normally: $\text{CHRBr}\cdot\text{NR}'\text{Br} \longrightarrow \text{HBr} + \text{R}\cdot\text{CHO} + \text{NHR}'\text{Br}$ (with subsequent migration of Br to the nucleus if $\text{R}=\text{Ar}$), but with bases of the type $\text{CH}_2\text{R}\cdot\text{CH}\cdot\text{NR}'$, Br addition may occur to the enamic form resulting in the abnormal decomp. observed by Berg (A., 1925, i, 817): $\text{CHRBr}\cdot\text{CHBr}\cdot\text{NHR}' \longrightarrow \text{R}\cdot\text{CHBr}\cdot\text{CHO} + \text{HBr} +$

$\text{NH}_2\text{R}'$, irrespective of whether $\text{R}=\text{aryl}$ or alkyl group. In addition to cases already recorded, abnormal decomp. is observed with the *dibromide* of amylideneamylamine and isobutylidene-*p*-bromoaniline. The *dibromides* of benzylidene- α -naphthylamine and -*p*-bromoaniline decompose to give PhCHO and 4-bromo- α -naphthylamine or 2 : 4-dibromoaniline, respectively. Mechanisms for these reactions and the polymerisation of Schiff's bases are discussed.

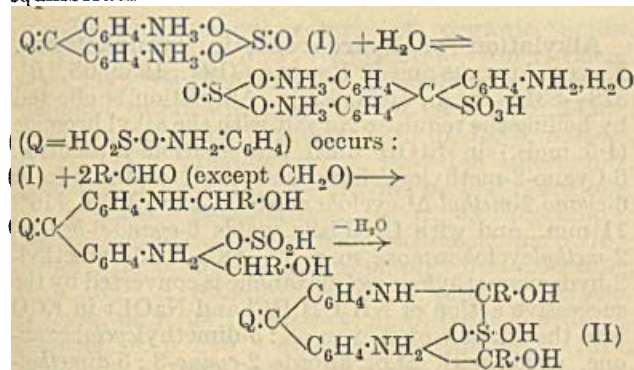
J. W. B.

Iodides of aromatic Schiff's bases. J. TURCAN (Bull. Soc. chim., 1932, [iv], 51, 500—502).—In the hydrolysis of di-iodides of Schiff's bases of the type $\text{CHArI}\cdot\text{NAr}'\text{I}$, migration of the I in the $\text{NHAr}'\text{I}$ formed occurs only if the *p*-position is free. Thus the *di-iodide* of $\text{CHPh}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7(\alpha)$ gives PhCHO and idonaphthylamine, but that of $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br}$ (*p*) gives only PhCHO , *p*- $\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{NH}_2$, and I .

J. W. B.

Schiff's reaction for aldehydes. P. RUMPF (Bull. Soc. chim., 1932, [iv], 51, 503—528).—The recoloration of Schiff's reagent by aldehydes is not due to oxidation, since it occurs in complete absence of O_2 , is unaffected by the presence of the antioxygen quinol, and is a sp. reaction of the $\cdot\text{CH}\cdot\text{O}$ group (ethylene oxide reacts only because of its ready isomerisation to MeCHO , and both $\text{CCl}_3\cdot\text{CHO}$ and salicylaldehyde give the reaction under suitable conditions). The main results of a detailed spectroscopic examination with different aldehydes in varying concns. and with varying concn. of SO_2 are as follows, pure pararosaniline (same spectrum as fuschin) being used throughout. The spectrum of the solution after recoloration by an aldehyde (max. absorption, 5600—5700 Å.) is markedly different from those of fuschin itself, its unstable additive products with aldehydes, or the Schiff's bases (azomethines), and is due to a single chemical individual. With MeCHO , EtCHO , Bu^nCHO , and Bu^sCHO the intensity of the colour rapidly increases to a max. and then slowly fades (accelerated by excess of SO_2), whilst with CH_2O and $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ it increases slowly to a stable max. The curve obtained for a mixture of CH_2O and MeCHO is intermediate, only the colour due to the former persisting after 24 hr. (analytical distinction). With a deficiency of SO_2 , the spectrum changes progressively (without fading) to that of fuschin in acid solution (max. 5560 Å.), whilst with excess of aldehyde decolorisation occurs with formation of a violet ppt., the spectrum of which in HCl proves it to be the Schiff's base. Under identical conditions all aldehydes (except CH_2O) give closely similar but not identical spectra. Ketoses do not give the reaction, whilst the colour obtained only with large concn. of aldoses is that of fuschin in acid solution. Determination of the intensities of the max. with increasing quantities of an aldehyde after 35 min. give a four-branch curve (which is discussed) from which vals. converging on 2 are obtained for the no. of mols. of aldehyde reacting with each mol. of fuschin. The reaction does not occur unless at least 2 of the N atoms have an H atom attached. On the basis of these results the following mechanism is deduced (cf. Wieland and Scheuing, A., 1922, i, 58). In Schiff's reagent (with

excess of SO_2 , intermediate stages discussed) the equilibrium



completely displacing the equilibrium in favour of (I). With CH_3O , which contains 2 reducing H atoms, a similar complex $\text{Q}:\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{O}\cdot\text{S}\cdot\text{OH})$ is obtained, and in this case reaction does occur with a pentamethylated dye. With deficiency of SO_2 and without excess of $\text{R}\cdot\text{CHO}$, slow and complex hydrolysis (mechanism given) to fuschin and $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{SO}_3\text{H}$ occurs (cf. above), whilst with excess of $\text{R}\cdot\text{CHO}$ the liberated fuschin forms the insoluble azomethine. The mechanism of colour fading is also discussed, and the analytical applications of a spectroscopic study of Schiff's reaction permitting the characterisation of an aldehyde, and determination of the effective concn. of free $\cdot\text{CH}\cdot\text{O}$ group in a solution, are outlined.

J. W. B.

Transformation of dithiocarboxylic acids into aldoximes. H. WUYTS and H. KORECK (Bull. Soc. chim. Belg., 1932, 41, 196—201).—Mg *p*-chlorophenyl bromide and CS_2 in Et_2O yield *p*-chlorodithiobenzoic acid, m. p. approx. 30° , which with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in pyridine at 70° gives *p*-chlorobenzaldoxime, m. p. 110.5° . The appropriate dithiocarboxylic acids yield similarly benz-, *o*- and *p*-tolu-, and α -naphth-aldoxime; β -naphthaldoxime, similarly prepared, has m. p. 156° .

R. S. C.

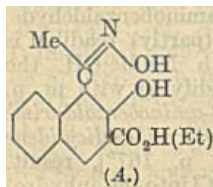
Evidence for the Hantzsch-Werner theory and for the configuration of oximes. J. MEISENHEIMER, W. THEILACKER, and O. BEISSWENGER (Annalen, 1932, 495, 249—283).—The 3- NO_2 -derivative of 2:6-dichlorobenzaldehyde [α -oxime, m. p. 149 — 150° (*Ac* derivative, m. p. 51°)] with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in aq. $\text{MeOH}\text{--}\text{Na}_2\text{CO}_3$ gives α -2:6-dichloro-3-nitrobenzaldoxime (I), m. p. 156 — 157° (*Ac* derivative, m. p. 119°), converted by PCl_5 in Et_2O into 2:6-dichloro-3-nitrobenzonitrile, m. p. 106 — 107° , and by boiling $\text{EtOH}\text{--}2\text{N}\text{--}\text{Na}_2\text{CO}_3$ into 6-chloro-3(or 5)-nitro-2-hydroxybenzonitrile (II), m. p. 129 — 130° (also formed in small amount during the oximation). (I) is equilibrated by HCl in EtOH —conc. HCl to a mixture of 25% of (I) and 75% of β -2:6-dichloro-3-nitrobenzaldoxime (III), m. p. 154 — 155° [readily convertible by cold $0.5\text{N}\text{--}\text{NaOH}$ into (II)]. Reduction of (I) with $\text{Fe}(\text{OH})_2$ gives α -2:6-dichloro-3-aminobenzaldoxime, m. p. 158 — 159° , which is not resolved by α -bromo-*d*-camphor- α - or - π -sulphonic acids. Similar reduction (below 10°) of the mixture of (I) and (III) affords a little 2:6-dichloro-3-amino-

benzonitrile, m. p. 169 — 170° , and β -2:6-dichloro-3-aminobenzaldoxime (obtained pure by fractional crystallisation from C_6H_6), m. p. 174° , which is converted into the α -form by boiling with charcoal and C_6H_6 or by dil. HCl at 0° ; the β -oxime could not be resolved. 2:6-Dichloro-3-aminobenzaldehyde, m. p. 122° , which polymerises (partly) readily, is oximated to the α -oxime; with $\text{NHMe}\cdot\text{OH}$, the labile α -, m. p. 171 — 172° , resolidifying with m. p. 207° , and stable β -2:6-dichloro-3-aminobenzaldoxime *N*-*Me* ethers, m. p. 207° [*d*-glucosidosalicylidene derivative ($+2\text{H}_2\text{O}$, 3EtOH), m. p. 167°], result. Both ethers are converted by dil. HCl into the anhydro-derivative, m. p. above 325° , of the original NH_2 -aldehyde.

Et 2-acetoxy-3-naphthoate and AlCl_3 in PhNO_2 give the *Et* ester (IV), m. p. 116 — 117° , of 2-hydroxy-1-aceto-3-naphthoic acid (V), m. p. 194° [*Me* ester, m. p. 144° (α -oxime, m. p. 191 — 192°); *Me* ether, m. p. 191.5° (*Me* ester, m. p. 42.5°)]. (V) is converted by Br in AcOH into 1-bromo-2-hydroxy-3-naphthoic acid and by boiling 25% HCl into 2:3-hydroxy-naphthoic acid, whilst (IV) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in dil. KOH afford 2-hydroxy-1-aceto-3-naphthohydroxamic acid, m. p. 192 — 193° (decomp.). (IV) and $\text{NHMe}\cdot\text{OH}\cdot\text{HCl}$ in $\text{EtOH}\text{--}\text{NaOAc}$ give (α)-2-hydroxy-3-carbethoxy-1-naphthyl *Me* ketoxime *N*-*Me* ether ($+ \text{CCl}_4$), m. p. 158° , which does not give a Cu complex, is hydrolysed by conc. HCl to 2:3-hydroxynaphthoic acid, and by $\text{EtOH}\text{--}\text{HCl}$ at 140° to (IV). Hydrolysis with 30% $\text{MeOH}\text{--}\text{KOH}$ gives (α)-2-hydroxy-3-carboxy-1-naphthyl *Me* ketoxime *N*-*Me* ether ($+ \text{AcOH}$), m. p. 265° , which affords a cinchonine salt, m. p. 165 — 175° , [α] $^{25}_D$ $+119^\circ$ in EtOH , [α] $^{25}_D$ $+69^\circ \rightarrow +49^\circ$ in pyridine, decomposed by $2\text{N}\text{--}\text{HCl}$ in MeOH at 0° to an active *N*-*Me* ether, [α] $^{25}_D$ $+124^\circ$ in $0.1\text{N}\text{--}\text{NaOH}$ (time of half change at 70° is 74 min.). (IV) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in $\text{MeOH}\text{--}\text{NaOAc}$ give a mixture of α - (VI), m. p. 198° , and β - (VII), m. p. 185.5° , -2-hydroxy-3-carbethoxy-1-naphthyl *Me* ketoximes, both of which are converted by boiling C_6H_6 into an equilibrium mixture of 90% α and 10% β . (VI) and PCl_5 in Et_2O —dioxan afford *Et* 1-acetamido-2-hydroxy-3-naphthoate (VIII), m. p. 214° , also prepared by acetylation of the *NH}_2*-ester, m. p. 108.5° , formed by reduction of *Et* 1-nitro-2-hydroxy-3-naphthoate, m. p. 155° (lit. 160°). Beckmann rearrangement of (VII) gives *Et* 2-hydroxy-1-*N*-methylcarbonyl-3-naphthoate, m. p. 190.5° , hydrolysed by $\text{AcOH}\text{--}\text{HCl}$ and conc. HCl at 180 — 190° to NH_2Me and 2:3-hydroxynaphthoic acid. (VI) is converted by boiling HCO_2H into (VIII) [the free acid passes when heated into (probably) 2-methyl-2':1'-naphthoxazole-9-carboxylic acid (IX), m. p. 295 — 297°], a compound, $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}$, m. p. 163° [hydrolysis and subsequent heating also gives (IX)], and a substance, $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}$, m. p. 69 — 70° [probably the *Et* ester of (IX)]. Hydrolysis of (VI) with 30% $\text{MeOH}\text{--}\text{KOH}$ gives α -2-hydroxy-3-carboxy-1-naphthyl *Me* ketoxime, m. p. 288 — 297° (darkens about 220°) according to rate of heating [cinchonine, m. p. 170 — 173° (decomp.), and cinchine salts], which could not be resolved. β -2-Hydroxy-3-carboxy-1-naphthyl *Me* ketoxime ($+ \text{MeOH}$) affords cinchine, m. p. 179 — 180° (decomp.), cinchonine, m. p. 175 — 176° (decomp.), and strychnine

salts, all of which exhibit mutarotation in pyridine; in no case could the optically active acid be isolated owing to the extreme ease of racemisation.

The non-resolution of the α -oximes (which are the only ones to give complex Cu salts) and the resolution of the above ketoxime prove the correctness of the Hantzsch-Werner theory. The above β -ketoxime [and (VII)] is correctly represented as (A); the angle between C:N and N:O cannot deviate much from 120° . The Beckmann rearrangement gives unequivocal results.



A brief reply is made to Swientoslawski (this vol., 51).

H. B.

Substituted aromatic aldehydes in Hantzsch's pyridine condensation. III. Nitromethoxy- and nitrohydroxy-benzaldehydes. L. E. HINKEL, E. E. AYLING, and W. H. MORGAN (J.C.S., 1932, 1112—1118; cf. A., 1931, 1072).—Improved preps. are given for 2-nitro-3-methoxy-, 2:6-dinitro-3-methoxy-, and 3-nitro-4-methoxy-benzaldehyde. 6-Nitro-3-methoxybenzaldehyde has m. p. 84° . The following compounds are obtained from the appropriate aldehydes by the method previously described (A., 1931, 1072) (% yields in parentheses): *Et* 4-(5'-nitro-2'-methoxyphenyl)-, m. p. 221° (77.2 and 77.7); *Et* 4-(2'-nitro-3'-methoxyphenyl)-, m. p. 137° (50.5 and 52.0); *Et* 4-(4'-nitro-3'-methoxyphenyl)-, m. p. 134° (69.3); *Et* 4-(6'-nitro-3'-methoxyphenyl)-, (I), m. p. 170° (62.4 and 62.9); oxidised with HNO_3 to *Et* 4-(6'-nitro-5'-methoxyphenyl)-2:6-dimethylpyridine-3:5-dicarboxylate, m. p. 99° ; *Et* 4-(3'-nitro-4'-methoxyphenyl)-, m. p. 113° (76.7 and 77.2); *Et* 4-(5'-nitro-2'-hydroxyphenyl)-, m. p. 184° (12.8 and 15.9); *Et* 4-(4'-nitro-3'-hydroxyphenyl)-, m. p. 145° (56.4 and 58.5); *Et* 4-(3'-nitro-4'-hydroxyphenyl)-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate, m. p. 161° (61.5 and 61.0). The product from similar treatment of 6-nitro-3-hydroxybenzaldehyde consists of *Et* 4-(6'-nitro-3'-hydroxyphenyl)-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate, m. p. 214° , methylated to (I), and an isomeric compound, m. p. 205° (*Me* derivative, m. p. 118° , oxidised to a compound, m. p. 91.5°). With 2:6-dinitro-3-methoxybenzaldehyde, condensation does not take place. The influence of substituents in the aldehyde on the yield of dihydropyridine derivative is discussed.

A. A. L.

Reactions catalysed by aluminium chloride.

III. Experiments in the cyclopentane series. C. D. NENITZESCU and I. P. CANTUNIARI (Ber., 1932, 65, [B], 807—812; cf. this vol., 49).—Gradual addition of SnCl_4 to a mixture of cyclopentane and AlCl_3 at 0° affords cyclopentyl *Me* ketone, b. p. $159.5\text{--}160.5^\circ/760\text{ mm.}$ (semicarbazone, m. p. $142\text{--}143^\circ$), oxidised to cyclopentylcarboxylic acid (amide, m. p. 178°), and glassy products. Methylcyclopentane similarly affords 2-acetyl-1-methylcyclopentane (semicarbazone, m. p. 166°) and the semicarbazone, m. p. 220° , of a ketone $\text{C}_8\text{H}_{14}\text{O}$, probably 2-acetyl-1-methyl- Δ^1 -cyclopentene; in addition, the hydrocarbon $\text{C}_{12}\text{H}_{22}$, m. p. 46° , is obtained identical with that derived from cyclohexane

(loc. cit.). The mechanism of the Friedel-Crafts reaction is discussed.

H. W.

Alkylation of hydroaromatic cyanoketones. K. VON AUWERS and F. ENBERGS (Ber., 1932, 65, [B], 828—831; cf. A., 1928, 426).—Alkylation is effected by boiling the requisite Na salt with the alkyl bromide (1.5 mols.) in EtOH until the solution is neutral. 6-Cyano-2-methylcyclohexanone with EtBr affords 6-cyano-2-methyl- Δ^1 -cyclohexenyl *Et* ether, b. p. $116^\circ/11\text{ mm.}$, and with CH_2PhBr yields 6-cyano-6-benzyl-2-methylcyclohexanone, m. p. $87\text{--}88^\circ$. 3:5-Dimethyl-2-hydroxymethylenecyclohexanone is converted by the successive action of NH_2OH , HCl and NaOEt in Et_2O into the Na salt of 2-cyano-3:5-dimethylcyclohexanone, which with EtBr affords 2-cyano-3:5-dimethyl- Δ^1 -cyclohexenyl *Et* ether, b. p. $132^\circ/11\text{ mm.}$ With allyl bromide, 2-cyano-3:5-dimethyl-2-allylcyclohexanone, m. p. 88.5° , is formed. The ethers are hydrolysed unusually slowly and the ketones react very sluggishly with semicarbazide. The course of the change depends on the bromide; steric effects are not observed.

H. W.

Reactions of ω -substituted acetophenone derivatives. II. Mechanism of the interaction of ω -halogenoacetophenones with primary and tertiary bases. J. W. BAKER (J.C.S., 1932, 1148—1157; cf. A., 1931, 1418).—The effect of varying substituents (*p*-OMe, *p*-Me, *m*-NO₂, *p*-NO₂) on the pseudo-unimol. velocity coeffs. of interaction of ω -halogenoacetophenones in EtOH with NH_2Ph and pyridine has been determined, the bases being in large excess. The results are discussed in the light of polarity theories. ω -Bromo-*p*-methylacetophenone with KI in EtOH- H_2O gives ω -iodo-*p*-methylacetophenone, m. p. 44° . The ω -I-derivative, m. p. 61° , is similarly obtained from ω -chloro-*p*-methoxyacetophenone. Propiophenone with Br in AcOH gives ω -Br-, b. p. $137^\circ/15\text{ mm.}$, whilst with HNO_3 in H_2SO_4 it gives *m*-nitro-propiophenone, bromination of which gives *m*-nitrophenyl α -bromoethyl ketone, m. p. 65° . The following bases are obtained by interaction of amines with appropriate ω -halogenoacetophenones: *m*-nitro- ω -anilinoacetophenone, m. p. 175° (decomp.); phenacylpyridinium bromide, m. p. $199\text{--}200^\circ$ (decomp.); *m*-nitrophenacylpyridinium bromide, m. p. 250° ; and *m*-nitrophenacylphenyldiethylammonium bromide, m. p. 140° (decomp.).

A. A. L.

***p*-Halogenophenacyl esters of *n*-fatty acids.** C. G. MOSES and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 2101—2103; cf. A., 1920, i, 480; 1930, 474).—The following are prepared: *p*-chlorophenacyl formate, m. p. 128° , propionate, m. p. 98.2° , butyrate, m. p. 55° , valerate, m. p. 97.8° , hexoate, m. p. $6\text{--}7^\circ$, heptoate, m. p. 65° , octoate, m. p. 63° , nonoate, m. p. 59° , decoate, m. p. 61.6° , undecoate, m. p. 60.2° , tridecoate, m. p. 67° , pentadecoate, m. p. 74° , and margarate, m. p. 78.8° . *p*-Bromophenacyl formate, m. p. 135.2° , heptoate, m. p. 72° , nonoate, m. p. 68.5° , undecoate, m. p. 68.2° , tridecoate, m. p. 75° , and pentadecoate, m. p. 77.2° . *p*-Iodophenacyl formate, m. p. 163° , heptoate, m. p. 78.8° , nonoate, m. p. 77° , undecoate, m. p. 81.8° , laurate, m. p. 85.8° , tridecoate, m. p. 88.0° , myristate, m. p. 89.8° , and pentadecoate, m. p. 90° .

The m. p. of all the esters from C_1 to C_{18} are given; alternation appears in all the series. C. J. W. (b)

p-Phenylphenacyl esters of organic acids. N. L. DRAKE and J. P. SWEENEY (J. Amer. Chem. Soc., 1932, 54, 2059—2061).—The following p-phenylphenacyl esters are prepared (cf. A., 1930, 1436): malonate, m. p. 175°; glutarate, m. p. 152°; adipate, m. p. 148°; pimelate, m. p. 145—148° (decomp.); suberate, m. p. 151°; azelate, m. p. 141°; sebacate, m. p. 140°; phenylacetate, m. p. 63° (decomp.); β -phenylpropionate, m. p. 95°; isohexanoate, m. p. 70°; tartrate, m. p. 203—204° (decomp.); o-nitrobenzoate, m. p. 182°; 3:5-dinitrobenzoate, m. p. 154°; o-bromobenzoate, m. p. 98°; salicylate, m. p. 148°; p-hydroxybenzoate, m. p. 240°; o-methoxybenzoate, m. p. 131°; anisate, m. p. 160°; gallate, m. p. 195—198° (decomp.); phthalate, m. p. 167.5°; 4-nitrophthalate, m. p. 120°; tetrachlorophthalate, m. p. 193°; benzilate, m. p. 122°.

C. J. W. (b)

β -Sulphydryl- β -phenylpropiophenone [phenyl β -thiol- β -phenylethyl ketone]. B. H. NICOLET (J. Amer. Chem. Soc., 1932, 54, 1998—2000; cf. A., 1931, 1156).—The "benzylideneacetophenone hydrosulphide" (I) of Fromm *et al.* (A., 1913, i, 184) is Ph β -thiol- β -phenylethyl ketone. The Bz derivative (Fromm) of (I) is also obtained from BzSH and Ph styryl ketone and is Ph β -benzoylthiol- β -phenylethyl ketone; Ph β -acetylthiol- β -phenylethyl ketone has m. p. 75—77°.

C. J. W. (b)

Action of magnesium p-anisyl bromide on dimethylphenylacetamide. (MME.) BRUZAU (Compt. rend., 1932, 194, 1662—1664).—CPhMe₂·CO·NH₂ and Mg p-anisyl bromide form a product from which HBr liberates p-anisyl α -phenylisopropyl ketimine hydrobromide (A., 1930, 604).

E. W. W.

Abnormal addition of amines to α -bromo- $\alpha\beta$ -ethylenic ketones: influence of a β -alkoxy- or halogen substituent. C. DUFRAISSE and R. NETTER (Bull. Soc. chim., 1932, [iv], 51, 550—562).—A β -alkoxy- or Br-substituent in α -bromo- $\alpha\beta$ -unsaturated ketones of type ArCO·CBr·CAr'·OR causes addition of amines to revert to normal (H on α -position to CO group: cf. A., 1927, 571, 884), the main product losing ROH to give ArCO·CBr·CAr'·NR₂, hydrolysed to ArCO·CHBr·COAr', although a small amount of reverse addition possibly occurs. Thus either stereoisomeride of Ph α -bromo- β -ethoxystyryl ketone (I) with piperidine in Et₂O in a sealed tube gives Ph α -bromo- β -piperidinostyryl ketone (II), m. p. 143—144° (block) (also prepared from CHBz·CPh·OEt, CHBz·Br·CPh·OEt, CHBz·Br·CPh·Br·OEt, CBrBz·CPh·OMe, and from both stereoisomeric forms of CBrBz·CPh·Br), which is stable to alkalis (but Br is eliminated by long boiling with KOH·EtOH) and Br, but is hydrolysed by 10 or 20% H₂SO₄ or H₂C₂O₄ in Et₂O to CHBrBz₂. No stereoisomerides of (II) could be obtained, nor could the red by-product (possibly C₅H₁₀N·CBz·CPh·OEt) be isolated. Similarly Ph α -bromo- β -benzylaminostyryl ketone (III), m. p. 113—114° (block) (probably possessing the ketimine structure CHBrBz·CPh·NCH₂Ph), is obtained from (I), the corresponding OMe-compound, or CHBrBz·CPh·Br·OEt. With bases (III) gives CHBz·CPh·NH·CH₂Ph, similar quant. replacement of

Br by H occurring with KI in AcOH, 1 equiv. of I being liberated. This reaction is also given by CHBrBz₂ and CHBrBz·CPh·OEt, but not by CBrBz·CPh·OEt. (I) with NHEt₂ in a sealed tube at 80° (6 days) gives Ph α -bromo- β -diethylaminostyryl ketone, m. p. 100° (block). No similar cryst. products could be obtained with NH₂Ph, NHPPhEt, or NH₃·EtOH.

J. W. B.

Rearrangement of 9:10-diaryldihydrophenanthrenediols. W. E. BACHMANN (J. Amer. Chem. Soc., 1932, 54, 1969—1974; cf. this vol., 515).—Reduction of 2:2'-dibenzoyldiphenyl by Mg+MgI₂ gives the isomeric 9:10-diphenyldihydrophenanthrenediols, m. p. 179—180° and 202°. Both forms are rearranged by AcCl or I in AcOH to 10:10-diphenyl-9-phenanthrone. 2-Bromo-4'-methylbenzophenone and Cu give 68% of 2:2'-di-p-toluyldiphenyl (I), m. p. 137°, reduced by Mg+MgI₂ or Zn and KOH to 9:10-di-p-tolyldihydrophenanthrenediol, m. p. 213°, and a little of an isomeride, m. p. 136° (also obtained from phenanthraquinone and p-Me·C₆H₄·MgBr); both forms are oxidised by CrO₃·AcOH to (I) and rearranged to di-p-tolylphenanthrone, m. p. 159°. 2:2'-Dianisoyldiphenyl, m. p. 147° and 152—153°, is reduced to 9:10-dianisylldihydrophenanthrenediol, m. p. 188—190° and 154—155° (also synthesised with p-OMe·C₆H₄·MgBr), which is rearranged to dianisylphenanthrone, m. p. 151—152°. In these rearrangements, migration of the Ph, p-Me·C₆H₄·, and p-OMe·C₆H₄· groups occurs practically exclusively.

C. J. W. (b)

Influence of Bz-substituents on some reactions of the anthrones. I. E. DE B. BARNETT and C. L. HEWETT (J.C.S., 1932, 1452—1458).—The effect of substituents in different positions on the reaction of anthrones with (A) hot aq. KOH and CH₂PhCl, (B) pyridine and Ac₂O, (C) Br in CS₂, and (D) pyridine, PhCHO, and a little piperidine, is irregular and incapable of theoretical explanation. The preps. of 1:8- and 4:5-dichloroanthrone are modified. 1:3- and 2:3-dimethylantrone give by (A) 10:10-dibenzyl-1:3- and -2:3-dimethylantrone, m. p. 206° and 199°, respectively. The following 10-nitroanthrones were prepared from the appropriate anthranil acetate, AcOH, and conc. HNO₃, the Ac derivatives (m. p. in brackets) being prepared by (B): 1:3-, m. p. 150° (decomp.) [decomposed by (B)], 1:4-, m. p. 159° (decomp.) [decomposed by (B)], and 2:3-, m. p. 150° (decomp.) [m. p. 242° (decomp.)], -dimethyl-; 1:4-, m. p. 162° (decomp.) [decomposed by (B)], and 2:3-dichloro-, m. p. indef. [m. p. 225—230° (decomp.)]. The following anthranil 9-Me ethers were prepared from the appropriate anthrone, Me p-toluenesulphonate, and aq. KOH: 1:3-, m. p. 58°, 2:3-, m. p. 117°, and 2:4-dimethyl-, m. p. 87°; 4-chloro-, m. p. 120°; 1:4-, m. p. 130°, 1:8-, m. p. 173°, 2:3-, m. p. 147°, and 4:5-dichloro-, m. p. 145°. The 1-chloro- and 1:4-dimethyl ethers are oils, yielding, with maleic anhydride, 1-chloro- and 1:4-dimethyl-9-methoxy-9:10-dihydroanthraquinyl-9:10-endo- $\alpha\beta$ -succinic anhydride, m. p. 266° and 259°, respectively. By (C) the following derivatives were prepared, the other ethers mentioned above losing MeBr to form the bromoanthrones: 10-bromo-2:3-

dimethylanthranyl Me ether, m. p. 151; 1:8- and 2:3-dichloro-10-bromoanthranyl *Me ether*, m. p. 155° and 164°, respectively. 1:4-Dichloro-10-bromoanthrone has m. p. 196°. By (D) were prepared 10-benzylidene-1:3- and -2:3-dimethylanthrone, m. p. 145° and 166°, respectively, whereas 1:4-dichloro-, 1:4- and 2:3-dimethyl-anthrone failed to react. Anthranyl *Me ethers* substituted by Cl or Me in the *peri*-position to the OMe group do not fluoresce, but their acetates and the other isomerides do so. R. S. C.

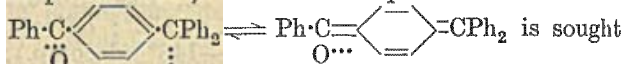
Dibenzylidenecyclopentanones. R. CORNUBERT and M. De DEMO (Compt. rend., 1932, 194, 1587—1589).—Re-investigation (cf. A., 1930, 474) of the distillation of 2:5-dibenzylidenecyclopentanone (I), m. p. 190°, shows the formation of the isomeride (II), m. p. 131° (*loc. cit.* gives 129°) (tetrabromide, m. p. 80—85°), and a trace of another isomeride (?) (III), m. p. 140°. (I) and (II) are reduced catalytically (Ni formate) to a mixture of dibenzylcyclopentanones, m. p. 39—40° and 58°, whilst (III) gives a mixture of 2:5-dibenzylcyclopentanone and two compounds, m. p. 129° and 220—240°; the last-named are also formed as the reduction products of (I) with certain Ni formates. (II) could not be prepared by direct condensation of PhCHO and cyclopentanone. H. B.

Phenyl-*p*-tolylacetophenone [phenyl *p*-methylbenzhydryl ketone]. C. F. KOELSCH (J. Amer. Chem. Soc., 1932, 54, 2049—2052).—Ph *p*-methylbenzylhydryl ketone (I), b. p. 270—275°/29 mm., m. p. 97—98°, could not be prepared from C₆H₅Me·CHPh·COCl and C₆H₅, but is formed in nearly quant. yield from desyl chloride, PhMe, and AlCl₃. Cleavage of (I) with KOH in EtOH gives *p*-methyl-diphenylmethane and BzOH; Na in PhMe gives a Na salt, cleaved by O₂ to NaOBz and Ph *p*-tolyl ketone. MgPhBr and (I) give αβ-triphenyl-β-*p*-tolylethyl alcohol, m. p. 169—170° (the αββ-triphenyl-α-*p*-tolylethyl alcohol has m. p. 185—187°); dehydration of either alcohol gives αββ-triphenyl-β-*p*-tolylethylene, m. p. 150—151°. The work of McKenzie *et al.* (A., 1930, 778) on the dehydration of αβ-diphenyl-α-*p*-tolylethylene glycol is confirmed. C. J. W. (b)

Position of the double linking with respect to the CO group in cholestenone. W. MENSCHICK, I. H. PAGE, and K. BOSSERT (Annalen, 1932, 495, 225—235).—Cholestenone (and its semicarbazone) shows an absorption curve similar to those of the αβ-unsaturated ketones mesityl oxide and pulegone (and their semicarbazones) having max. at 240—250 mμ (strong) and 320 mμ (weak). Cholestenone is, therefore, an αβ-unsaturated ketone. Unsaturated (other than αβ) ketones show no absorption bands between 220 and 260 mμ; their semicarbazones show curves analogous to those of saturated ketonesemicarbazones. Compounds containing C:C·C:C, C:C·C:O, and C:C·C:N groups all show similar max. H. B.

***p*-Benzoyltriphenylmethyl.** Valency tautomerism of unsaturated systems. G. WITTIG, W. KAIRIES, and W. HOFF (Ber., 1932, 65, [B], 767—776).—*p*-Benzoyltriphenylmethyl chloride is converted by Ca powder in C₆H₆ or CHCl₃ in N₂ into *p*-benzoyltriphenylmethyl (I), m. p. 170°, converted by PhICl₂ into C₆H₅Bz·CPh₂Cl; the corresponding peroxide had

m. p. 175—177° (decomp.). (I) is transformed by LiPh into *p*-hydroxydiphenylmethyltriphenylmethyl identified as the peroxide [OH·CPh₂·C₆H₄·CPh₂·O]₂, m. p. 169—171° (similarly, *p*-benzoyltriphenylmethane affords *p*-hydroxydiphenylmethyltriphenylmethane, m. p. 131—134°). Evidence of a possible tautomerism



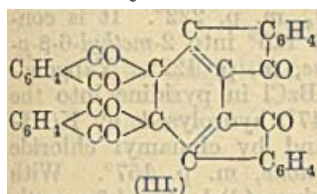
in the spectroscopic absorption. The ultra-violet curves of CPh₂, *p*-benzoyltriphenylmethane, and *p*-benzoyltriphenylmethyl chloride are closely similar and differ markedly from that of (I). The possibility of detecting tautomerism by change in the spectrum caused by rise of temp. or alteration of solvent is discussed. H. W.

Dihydro-1:4-pyrans. III. Synthesis of the 1:2-dibenzoylcyclobutanes. T. Y. KAO and R. C. FUSON (J. Amer. Chem. Soc., 1932, 54, 1120—1124; cf. this vol., 279).—*trans*-cyclobutane-1:2-dicarboxyl chloride (I), C₆H₅, and AlCl₃ give about 79% of α:1:2-dibenzoylcyclobutane (II), m. p. 97° (Br₂-derivative, m. p. 148—149°), and a little of the β-isomeride, m. p. 120—121°. The monoxime, m. p. 147—148°, of (II) and SOCl₂ in CHCl₃ give 2-benzoylcyclobutane-1-carboxylanilide, m. p. 130—131°, whilst the dioxime, m. p. 169—170°, similarly affords α-cyclobutane-1:2-dicarboxylanilide, m. p. 236—236.5°, and a little of the β-dianilide (III), m. p. 219—220°. (III) is also obtained from *trans*-cyclobutane-1:2-dicarboxylic acid and NH₂Ph at 150—160°, and from (I) and NH₂Ph. The dibenzoylcyclobutanes differ from the isomeric dihydro-1:4-pyrans, thus eliminating the possibility that the latter compounds are cyclobutanes (*loc. cit.*), and supporting the pyran structure. C. J. W. (b)

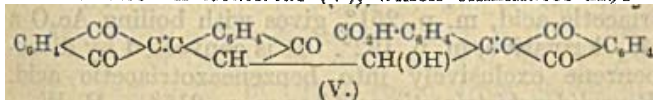
Amino-alcohols derived from mixed benzoin. A. MCKENZIE and E. M. LUIS (Ber., 1932, 65, [B], 794—798).—The action of MgPhBr on *p*-dimethylaminobenzaldehyde cyanohydrin yields benzoyl-*p*-dimethylaminophenylcarbinol (4'-dimethylaminobenzoin), m. p. 157—158° (cf. A., 1930, 224), not identical with Staudinger's *p*-dimethylaminobenzoylphenylcarbinol, m. p. 162—163° (A., 1913, i, 1353), the structure of which is thus established. The last-named compound is converted into its oxime, m. p. 187—188°, reduced by Na-Hg in acid solution to *r*-β-amino-α-phenyl-β-*p*-dimethylaminophenylethan-α-ol, m. p. 149—150°, which gives ill-defined products when deaminated. *r*-β-Amino-α-phenyl-β-anisylethan-α-ol, m. p. 121—122° [hydrochloride, m. p. 230—231° (decomp.)], is converted by HNO₂ in dil. AcOH into α-phenyl-β-anisylethylene glycol, m. p. 111—112°, and oily products which do not appear to contain an aldehyde or a ketone. Benzoyl-*p*-anisylcarbinol, m. p. 100—101°, from anisaldehyde cyanohydrin and MgPhBr, is transformed through the oxime into β-amino-β-phenyl-α-*p*-anisylethan-α-ol, m. p. 103—104°, yielding only small amounts of α-phenyl-β-anisylethylene glycol when deaminated. H. W.

Oxidation of reactive methylene groups. G. WANAG (Latij. Univ. Raksti, 1931, 2, 153—230, and Annalen, 1932, 494, 107—116).—*trans*-Bisindonylene $\left(\text{C}_6\text{H}_4\cdot\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array}\cdot\text{C}:\text{C}\cdot\begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \diagdown \text{CO} \end{array}\right)_2$ (I), violet

(phenylhydrazone, m. p. above 280°), is obtained by oxidation of di-indone by PbO_2 in CHCl_3 . When treated with Br (and in various solvents) it undergoes autoxidation to trans-dioxidobisdi-indonylene, yellow, sublimes above 360° (II) [$>\text{C}=\text{O}-\text{C}=<$ for $>\text{C}:\text{C}<$ in (I)]. (II) undergoes rearrangement to yield an unstable cyclohexadiene derivative (III), which on



treatment with $\text{Pb}(\text{OH})_2$ eliminates Pb phthalate, giving 2-phthaloyl-3:4:5:6-dibenzoylene- $\Delta^{3:5}$ -cyclohexadiene, red, m. p. above 320°. (I) forms compounds with CHCl_3 (1 mol.) and pyridine ($\frac{1}{2}$ mol.), which are readily hydrolysed by dil. NaOH , with the opening of two rings [atoms C in (I)] to yield trans- α -diphthaloyl- β -di-o-carboxyphenyl- $\Delta^{3:5}$ -hexatriene (IV), also obtained by the action of NaOH-EtOH on (I). (I) forms an unstable trihydrate in the presence of H_2SO_4 , which readily loses H_2O to yield a dihydrate, which combines with atm. O_2 to yield (II). (IV) undergoes autoxidation to the corresponding dioxide [O attached as in (II)], which can also be obtained by the alkaline hydrolysis of (III). (IV) yields an unstable dibromide, which readily eliminates Br to yield the green cis-form of (I). This is not autoxidisable, and in solution is rapidly converted into the more stable trans-form; with NaOH it yields the trans-acid (IV), whilst with excess of Br it gives 2 mols. of dibromoisodi-indone, m. p. 250°. (IV) in Et_2O solution is readily converted into an isomeride (V), which eliminates H_2O



to yield the monohydrate of (I), and this again loses a further mol. of H_2O to give (I). All three ethylenic linkings of (I), (II), and (IV) are reduced by Zn and AcOH , and by Na-Hg ; the products from (IV) and from its dioxide are identical when Na-Hg is used, but hydrogenation with Zn and AcOH yields different products, apparently stereoisomerides, from the two acids. The cis-form of (I) is obtained by the interaction of isodi-indone and dibromoisodi-indone with K_2CO_3 in C_6H_6 , and the trans-form in pyridine in small yield; in the latter solvent the chief product of reaction is an unidentified brown condensation product, $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}$, m. p. 290°.

R. T.

Action of dilute acids on phenyliminoquinone diazide. A. KLING and R. SCHMUTZ (Compt. rend., 1932, 194, 1585—1587).—Contrary to Hantzsch's statement (A., 1902, i, 324), *p*-anilinobenzenediazonium sulphate is regenerated when phenyliminoquinone diazide (*loc. cit.*) is treated with dil. H_2SO_4 .

H. B.

Polycyclic aromatic hydrocarbons. X. 1:2:7:8-Dibenzanthracene. J. W. COOK (J.C.S., 1932, 1472—1484; cf. this vol., 374).—1:2:7:8-Dibenzanthracene (I) is synthesised by two methods. Certain naphthoynaphthoic acids undergo intramol. rearrangement under the influence

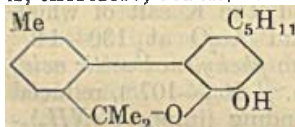
of dehydrating agents. This consists of $\alpha\delta$ -migration, probably by way of a hydroxy-lactone. Alternative explanations of analogous changes (Ann. Repts., 1929, 26, 142) are refuted. 2-Methyl-1:1'-dinaphthyl ketone (not oxidised by alkaline KMnO_4 or by way of the bromomethyl compounds) with SeO_2 and boiling PhNO_2 , or, better, aq. SeO_2 at 230—240°, gives 2-carboxy-1:1'-dinaphthyl ketone (II), m. p. 241—242°, isolated by way of the acetoxy-lactone, m. p. 238—239°. 2-Methyl-1-naphthoic acid and 6-methyl-1:2-benzanthraquinone are not similarly oxidised. (II) with conc. H_2SO_4 at 85—90°, or AlCl_3 and NaCl at 130° gives mixtures of quinones, but with P_2O_5 in PhNO_2 at 150° gives 1:2:5:6-dibenzanthraquinone. Oxidation of 2-methyl-1:2'-dinaphthyl ketone with SeO_2 and subsequent acetylation affords the acetoxy-lactone, m. p. 185—186° after sintering, hydrolysed to 2-carboxy-1:2'-dinaphthyl ketone (III), m. p. 258—259° after sintering, which with P_2O_5 in PhNO_2 at 150° yields a mixture of quinones, reduced by Al powder and H_2SO_4 , followed by Zn dust and *N*- NaOH , to 2':3'-naphtha-2:3-phenanthrene (IV), 1:2:5:6-dibenzanthracene (V), and (I), m. p. 196° (picrate, m. p. 210°). With Zn dust and hot *N*- KOH (III) gives 1:2'-dinaphthylmethane-2-carboxylic acid, m. p. 193—195°, which with ZnCl_2 at 180—185° affords substances reduced by Zn dust and 2*N*- NaOH to (IV) and (V). (II) with Zn dust and *N*- KOH gives an impure product, which with ZnCl_2 at 180—185° and subsequent acetylation gives 1:2:7:8-dibenzanthracenyl 10-acetate, m. p. 255—256° (decomp.), reduced by Zn dust and *N*- NaOH to (I). *m*-Xylylene dicyanide and hot 45% H_2SO_4 give *m*-phenylenediacetic acid, the K salt of which with *o*-nitrobenzaldehyde and Ac_2O at 130—140° yields di- α -*o*-nitrobenzylidene-*m*-phenylenediacetic acid, m. p. 239—240° (Et_2 ester, m. p. 106—107°), reduced by $\text{Fe}(\text{OH})_2$ to the corresponding (impure) $(\text{NH}_2)_2$ -compound (VI), m. p. indef. (dihydrochloride, m. p. 240° after sintering). (VI) gives by the Pschorr reaction α -*o*-hydroxybenzylidene-10-carboxy-2-phenanthrylacetic acid (VII), m. p. 326—327°, and 1:2:7:8-dibenzanthracene-4:5-dicarboxylic acid, m. p. above 365°; the latter, when crude (not if pure), sublimes at 340—350°/3—4 mm., mostly decomposing to yield (I). (I) with $\text{Na}_2\text{Cr}_2\text{O}_7$ and hot AcOH gives 1:2:7:8-dibenzanthraquinone, m. p. 225—226° (impure), sublimes at 200—230°/4 mm. (VII) sublimes at 330—350°/3—4 mm. with simultaneous decomp. to 1':3'-naphtha-3:4-pyren-5-one-10-carboxylic acid (VIII), m. p. variable, 360—380°, the *Me* ester of which, m. p. 253—254°, is formed from the Na salt of (VII) and Me_2SO_4 at 130—140°. (VIII) with $\text{Na}_2\text{Cr}_2\text{O}_7$ and hot AcOH gives 1':3'-naphtha-3:4-pyrene-5:9:10-trione, m. p. above 365°. (VII) at 420° gives 1':3'-naphtha-3:4-pyren-5-one, m. p. 268—269°.

R. S. C.

Cannabis indica resin. III. Constitution of cannabinol. R. S. CAHN (J.C.S., 1932, 1342—1353; cf. A., 1931, 625).—Nitrocannabinolactone is A ($\text{R}=\text{Me}$; $\text{R}'=\text{NO}_2$), since cannabinolactonic acid (A ; $\text{R}=\text{CO}_2\text{H}$; $\text{R}'=\text{H}$) with HNO_3 (*d* 1.2) at 185—195° affords trimellitic acid. The acid, m. p. 228—230° (J.C.S., 1899, 75, 20), is, therefore, 5-nitro-

trimellitic acid; the acid, m. p. 175° (A., 1909, i, 897), previously designated thus, is probably a nitrodimethylbenzoic or nitromethylphthalic acid, since insufficient CrO_3 was used in its prep. Cannabinol (I) [PhSO_2 derivative (prepared in hot pyridine), m. p. 70.5°] is phenolic, because it (i) gives with MeI and K_2CO_3

in COMe_2 a *Me ether*, (II), m. p. 66° [also prepared similarly with Me_2SO_4 , but not diazomethane, from (I) or (with difficulty) from "crude cannabinol" (III)], and (ii) has a "crit. oxidation potential" of 0.995 volt; further, (II) with HNO_3 (d 1.5) in cold AcOH gives a $(\text{NO}_2)_2$ -derivative, m. p. 174—175° (and isomerides), slowly hydrolysed by hot piperidine to *dinitrocannabinol*, m. p. 182—183°, which, when similarly nitrated, gives *trinitrocannabinol*. (I) does not react with 2:4-dinitrophenylhydrazine, whilst (II) is unaffected by Na or acylating agents, and with PCl_5 in Et_2O or chloramine-*T* in AcOH gives, amongst other products, an impure *Cl*-derivative, m. p. 126—127°. The second O atom in (I) is thus probably ethereal. *O*-Derivatives of (I) are stable to cold KMnO_4 solutions, but the *m*-nitrobenzenesulphonyl derivative, m. p. 125—126° after sintering at 123° [also prepared from (III) in 28% yield], with KMnO_4 in hot AcOH gives *K m*-nitrobenzenesulphonate, m. p. above 310°. (I) with mild oxidising agents gives multimol. resins, and with KMnO_4 in cold COMe_2 gives an amorphous substance, further oxidised in hot aq. pyridine to cannabinolactone, cannabinolactonic acid, *n*-hexoic and (?) *n*-valeric acid. (I) is, therefore, considered to have the annexed formula.



The positions of the OH and C_5H_{11} groups, which are uncertain, the nitration of (I) and (II), and the phylogenetic origin of (I) are discussed. (II) is unaffected by NH_2Ph and $\text{NH}_2\text{Ph.HCl}$ at 190—210°, and with Cl_2 in cold AcOH gives an amorphous product. Trinitrocannabinol *Me ether* with hot HNO_3 (d 1.5) gives 6:2(or 5)-*dinitrocannabinolactone*, m. p. 161°. The identity of cannabinolactonic acid with the synthetic substance (modified prep.) is confirmed. Colour reactions for (I), its *Me ether* and *Ac derivative*, are described.

R. S. C.

Constituents of kawa root. XII. Yangonolactone and triacetic acid. W. BORSCHKE and B. K. BLOUNT (Ber., 1932, 65, [B], 820—828; cf. A., 1931, 89).—"Acetylisyangonolactone" (I) (A., 1929, 1453) is obtained with certainty by heating *O*-acetyl-yangonolactone or yangonolactone with Ac_2O and pyridine. The process is identical with the conversion of triacetic into dehydracetic acid; hence (I) is regarded as 3-acetyl-6-*p*-methoxystyryl-2:4-pyrone. (I) and NHPh.NH_2 (1:1) in boiling EtOH afford the *phenylhydrazone*, $\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_2$, m. p. 185—186°, isomerised in boiling AcOH to a yellow compound, m. p. 185°, which is transformed by NHPh.NH_2 in boiling AcOH into the substance $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{CO} \cdot \text{H} \\ \text{NPh} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CR} \cdot \text{N} \cdot \text{NHPh} \end{smallmatrix}$

($\text{R} = \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot$), m. p. 265—266°; all three compounds are sol. in alkali hydroxide, only the

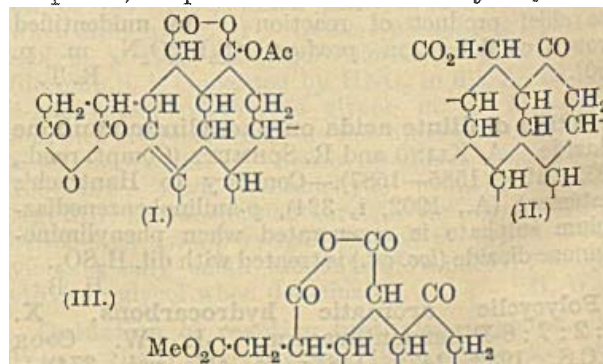
second and third in alkali carbonate. When hydrogenated (I) affords *C*-acetyldihydroyangonolactone, obtained from the *O*-isomeride or from dihydroyangonolactone by Ac_2O in pyridine. With NHPh.NH_2 it gives (i) the normal *phenylhydrazone* $\text{C}_{22}\text{H}_{22}\text{O}_4\text{N}_2$, m. p. 161°, (ii) the isomeric *pyrazolecarboxylic acid*, m. p. 88°, (in) the *phenylhydrazone* of the *pyrazolecarboxylic acid* $\text{C}_{28}\text{H}_{28}\text{O}_3\text{N}_4$, m. p. 222°. It is converted by fuming HCl at 120° into 2-methyl-6-*p*-methoxyphenylethyl-4-pyrone, m. p. 122°. Yangonolactone is converted by BzCl in pyridine into the *O*-*Bz* derivative, m. p. 147°, hydrolysed by KOH - MeOH at room temp. and by cinnamyl chloride into *O*-cinnamylyangonolactone, m. p. 157°. With NHPh.NH_2 in AcOH it gives (?) 1-phenyl-5-*p*-methoxystyrylpyrazole-3-acetphenylhydrazide, m. p. 174°. With diazobenzene chloride in alkaline solution, yangono- and dihydroyangono-lactone yield the azo-derivatives $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_2$, m. p. 233—234°, and $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_2$, m. p. 154°, the former of which is transformed by NHPh.NH_2 in AcOH into the substance $\text{C}_{32}\text{H}_{28}\text{O}_2\text{N}_6$, m. p. 100° (decomp.). Methylenebis-yangonolactone, m. p. 269° (decomp.) (*Ac derivative*, m. p. 252°), methylenebisyangonin, m. p. 253—254°, and methylenebisdihydroyangonolactone, a colourless resin (*Ac derivative*, m. p. 162°), are described.

Triacetic acid is converted by NHPh.NH_2 in boiling AcOH into the *phenylhydrazone*



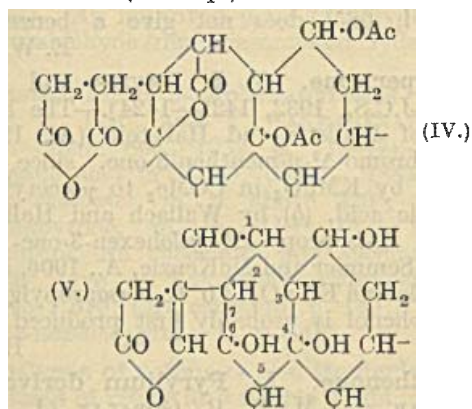
by diazobenzene into benzeneazotriacetic acid, m. p. 188—189° (transformed by NHPh.NH_2 into the substance $\text{C}_{24}\text{H}_{22}\text{ON}_6$, m. p. 183—184°). Methylenebis-triacetic acid, m. p. 251°, gives with boiling Ac_2O a *Ac* derivative, m. p. 192°. It is converted by diazobenzene exclusively into benzeneazotriacetic acid. Benzylidenebistriacetic acid has m. p. 215°. H. W.

Strophanthin. XXV. Allocation of the lactone group of strophanthidin and related aglucoses. W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1932, 96, 357—366).—Hydrolysis of its *Me*₂ ester, $[\alpha]_D + 8^\circ$ (A., 1931, 1297), affords the dibasic lactic acid *deoxy-α-isostrophanthonic acid*, m. p. 260—262° (decomp.), which when heated with Ac_2O - AcCl gives a substance (I) $\text{C}_{25}\text{H}_{30}\text{O}_7$, m. p. 245—247°, reduced catalytically (Adams) in AcOH to a dihydro-compound, m. p. 258—259°. This is hydrolysed by



Ba(OH)_2 in aq. EtOH to a tribasic keto-acid $\text{C}_{27}\text{H}_{32}\text{O}_7$, m. p. 205—215°, resolidifying and then melting at 270—272° (*Me*₂ ester, m. p. 132°), converted by heat-

ing at 210—220°/1 mm. into an *anhydride* $C_{23}H_{30}O_6$ (II), m. p. 273—274°, which with 1% HCl in MeOH gives a *Me* ester, m. p. 236—237°, probably (III), since the CO_2Me group is readily hydrolysed. Ac_2O - $AcCl$ converts either α - or γ -isostrophanthic acid, in small yield, into a *substance* $C_{27}H_{37}O_8$, probably (IV), m. p. 267—268° (decomp.). Oxidation of the Bz



derivative of *Me isostrophanthidate* (A., 1924, i, 1331) with $KMnO_4$ in $COMe_2$ gives the *Bz* derivative, m. p. 261—262° (decomp.), of *Me* α -isostrophanthate, converted by either Ac_2O or Ac_2O - $AcCl$ into a *mixed anhydride*, $C_{33}H_{40}O_{11}$, m. p. 220—221° (decomp.). These results prove that the unsaturated lactone group of strophanthidin (V), digitoxigenin, and related aglucones must be attached in position 7.

J. W. B.

Partial dehydrogenation of oleanolic acid. W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1932, 96, 341—354).—The *Me* ester (I), m. p. 197—198°, $[\alpha]_D^{25} +75^\circ$ in $CHCl_3$, of oleanolic acid, m. p. 312° (corr.), $[\alpha]_D^{25} +79^\circ$ in $CHCl_3$ (prep. from cloves described), gives a *Bz* derivative, m. p. 258—259°, $[\alpha]_D^{25} +86^\circ$ in $CHCl_3$, dehydrogenated by S at 235—245° to the *Bz* derivative (II), m. p. 266—268°, $[\alpha]_D^{25} +32^\circ$ in $CHCl_3$ of *Me dehydrothio-oleanolate*, m. p. 284—285°, which is obtained by hydrolysis with 5% KOH in EtOH. Oxidation of (II) with 6% $KMnO_4$ in AcOH and hydrolysis of the product gives a mixture of an acid, $C_{30}H_{42}O_6$, m. p. 268—269° (no OMe) (*Me* ester, m. p. 288—289°), separated as its *K* salt, and a neutral OMe-free *substance*, $C_{29}H_{42}O_3$, m. p. 287—288°, $[\alpha]_D^{25} +202^\circ$ in pyridine. Oxidation of the *sec*-OH group in (I) with CrO_3 gives the ketonic ester *Me oleanonate*, m. p. 181—182°, $[\alpha]_D^{25} +89^\circ$ in pyridine (Prelog, A., 1930, 1044) [*semicarbazone* (III), m. p. 233—235°]. Stereoisomerisation takes place during reduction of this by Clemmensen's method to give the deoxy-derivative, *Me* β -*oleananate*, $C_{22}H_{52}O_2$, m. p. 170—172°, $[\alpha]_D^{25} -75^\circ$, and a *substance* $C_{30}H_{46}O_2$, m. p. 335—337°, probably the deoxolactone. (I) when heated with HCl-AcOH at 110—120° gives a neutral OMe-free *substance*, $C_{30}H_{46}O_2$, m. p. 246—248° (an anhydrolactone), also obtained, together with (?) the acetyl-lactone of Winterstein and Stein (A., 1931, 1159), by similar treatment of oleanolic acid. Reduction of (III) by Wolff's method occurs with stereochemical change to give *Me* α -*oleananate*, m. p. 159—160°, $[\alpha]_D^{25} +71^\circ$ in pyridine, and γ -*oleananic acid*, p. 266—268° (*Na* salt; *Me* ester, m. p. 168—169°,

$[\alpha]_D^{25} +77^\circ$ in pyridine). Reduction of *Me* hederagonate [A., 1925, i, 948; *semicarbazone* (IV), m. p. 220—222°] by Clemmensen's method gives the *deoxy-deoxomethyl ester*, $C_{32}H_{52}O_2$ (V), m. p. 184—185°, $[\alpha]_D^{25} +78^\circ$ in pyridine, and a *substance*, m. p. 132—135° (possibly a mixture), whilst reduction of (IV) by Wolff's method gives the *acid*, m. p. 246—247° of (V) and, after esterification, the *Me* ester, $C_{32}H_{52}O_3$, m. p. 165—166°, $[\alpha]_D^{25} +84^\circ$ in pyridine (*Bz* derivative, m. p. 182—183°, $[\alpha]_D^{25} +89^\circ$ in pyridine), of the deoxy-hydroxy-acid. J. W. B.

Primary products of the oxidation of lycopene. R. KUHN and C. GRUNDMANN (Ber., 1932, 65, [B], 898—902).—Cautious oxidation of lycopene in C_6H_6 and AcOH with 0.1N- CrO_3 solution (=3O) affords *lycopenal*, $C_{32}H_{42}O$, m. p. 147° (Berl. corr., vac.) [*oxime*, m. p. 198° (Berl. corr., vac.)], and β -methyl- Δ^8 -hepten- ζ -one [*p*-nitrophenylhydrazone, m. p. 103.5—104° (Berl. corr.)]. Spectroscopic comparison of lycopene and its oxime supports the view that the CHO group is in conjugation in conformity with Karrer's formula for lycopene, but the normal structure of the oxime is not placed beyond doubt. Hentriacontane, frequently present in tomatoes and difficultly separable by cryst. from the dye, is readily removed by filtering the solution through Al_2O_3 , which absorbs the dye but not the saturated hydrocarbon. H. W.

Primary products of the oxidation of β -carotene. R. KUHN and H. BROCKMANN (Ber., 1932, 65, [B], 894—898).—Oxidation of β -carotene in C_6H_6 -AcOH with aq. 0.1N- CrO_3 (=1.5O) at room temp. yields β -hydroxycarotene, $C_{40}H_{58}O_3$, m. p. 184° (Berl. high vac.), separated from unchanged carotene by adsorption with Al_2O_3 and elution with light petroleum and from a *dye*, m. p. 233°, by adsorption with $CaCO_3$. It could not be caused to react with diazomethane or NH_4OH . With $MgMeI$ it affords CH_4 . In absorption spectrum it differs sharply from carotene. Towards rats it exhibits marked growth-promoting properties, attributed to the persistence of one β -ionone ring. Oxidation of β -carotene with 4 atoms of O affords β -carotenone, $C_{40}H_{56}O_4$, m. p. 174—175° [*dioxime*, m. p. 198° (corr.)], which does not react with cold $MgMeI$ or with diazomethane; β -hydroxycarotene does not appear to be formed intermediately. β -Carotenone does not show growth-producing action. H. W.

Polyterpenes and polyterpenoids. LXVIII.

Betulin. L. RUZICKA, H. BRUNGER, and E. GUSTUS. LXIX. Acid resins of Manila elemi. L. RUZICKA, E. EICHENBERGER, M. FURTER, M. W. GOLDBERG, and R. L. WAKEMAN (Helv. Chim. Acta, 1932, 15, 634—648, 681—693).—LXVIII. The change of derivatives of betulin into those of *allobetulin* is accompanied by loss of 1 active H (Zerevitinov) and of unsaturation $[C(NO_2)_4]$ in conformity with the formation of an oxide ring by addition of an OH group to an ethylenic linking. Interaction of betulin with HCO_2H gives, in addition to *allobetulin* formate, β -apoallobetulin, m. p. 186—187°, by loss of H_2O ; the former when heated at 320—340° gives γ -apoallobetulin, m. p. 242.5—243°, CO, and H_2O : both β - and γ -allobetulins are unsaturated and free from active H. Dihydrobetulin is dehydrated in presence of

naphthalene-2-sulphonic acid at 220–230° to the diolefinic hydrocarbon, $C_{30}H_{48}$, b. p. 220–225°/15 mm., and oxidised by CrO_3 in AcOH to dihydrobetulonic acid, m. p. 252–253° (semicarbazone, m. p. 285°), hence the presence of a $\cdot CH_2\cdot OH$ (in addition to a $>CH\cdot OH$) group is inferred. Its formate, m. p. 269–270°, merely gives an isomeride, m. p. 254–255°, when heated in H_2 at 300–315°. Oxyallobetulin acetate has no active H, in conformity with the formula $C_{30}H_{48}O_3$ previously assigned; more energetic CrO_3 oxidation of allobetulin gives the saturated, ketonic oxyallobetulonic acid, m. p. 285° [Me ester (CH_3N_2 or Na and MeI), m. p. 255–256°].

LXIX. α -Elemolic acid is accompanied in Manila elemi resin by δ -elemic acid, $C_{30}H_{46}O_3$, m. p. 218–219° [Me ester, m. p. 112–113° (sinters 105°), no active H], from which it is separated by repeated crystallisation from aq. COMe. The m. p. of the Me ester of the δ -acid is unchanged by recrystallisation, but by a combination of fractional distillation and crystallisation the m. p. of the Me and Et esters of α -elemolic acid are raised considerably (to 144–145°, and 132.5–134°, respectively), whilst the empirical formulæ still correspond with that of the original acid. The Ac and Br-derivatives of elemolic acid (A., 1931, 960) are homogeneous, and have the formulæ assigned, but the hydrobromide is a mixture. α -Elemonic acid (A., 1924, i, 1312), m. p. 276°, corresponds with the formula $C_{30}H_{46}O_3$, confirmed by its derivatives [Me ester, m. p. 162° (oxime, m. p. 188–191°)]; reports (lit.) of an acid with the same m. p. but different composition suggest that its m. p. is not a sufficient criterion of purity. The acid of m. p. 295–296°, obtained by oxidation of hydrogenated α -elemolic acid, differs in $[\alpha]_D$ (–93.5° in $CHCl_3$) from the dihydroelemonic acids previously reported (cf. A., 1931, 847; this vol., 397). H. A. P.

Hydrocarbon of the unsaponifiable matter of shea butter. K. H. BAUER and G. UMBACH (Ber., 1932, 65, [B], 859–862).—The portion of the unsaponifiable matter of shea butter insol. in EtOH, after purification from Et_2O and propyl alcohol, affords karitene ($C_{55}H_{90}$, m. p. 64°, possibly identical with illipene. The properties of the substance and its mode of occurrence support the hypothesis that it is a caoutchouc hydrocarbon. When destructively distilled at atm. pressure it yields isoprene and dipentene (additive product with HCl, m. p. 49°; tetrabromide, m. p. 124°). Ozonisation in $CHCl_3$ and decomp. of the ozonide with boiling H_2O yields lævulic acid with small amounts of lævulaldehyde and AcOH. With HNO_3 (d 1.4) at 100°, karitene affords an insol. nitrogenous compound similar to that derived from caoutchouc, $H_2C_2O_4$, and an acid of unknown constitution which yields a yellow, insol. Ag salt. Catalytic hydrogenation is incomplete in presence of Pd– SiO_2 . H. W.

Action of diazonium salts on aliphatic and terpenic hydroxylamineoximes. A. D'AMBROSIO (Gazzetta, 1932, 62, 271–278).—With PhN_2Cl , β -hydroxylamino- β -methylbutan- γ -oneoxime (A., 1911, i, 186) gives a benzeneazo-compound, m. p. 137–138° (Cu^{II} salt, m. p. 142–143°); " α -pinene- o -hydroxylamineoxime" (A., 1910, i, 863) gives a

benzeneazo-compound, m. p. 170–171° (Cu^{II} salt, m. p. 129°). With $(PhN_2)_2SO_4$, " α -terpineolhydroxylamineoxime" gives in AcOH and EtOH a benzeneazo-compound, m. p. 187–188° (Cu^{II} salt, m. p. 142°), isomeric with that obtained in aq.-alcoholic NaOAc (A., 1928, 68); the latter is converted into the former by aq. HCl. " d -Limonene- o -hydroxylamineoxime" (A., 1910, i, 685) does not give a benzeneazo-compound. E. W. W.

Bromopiperitone. G. I. DAVIES and J. L. SIMONSEN (J.C.S., 1932, 1422–1424).—The bromopiperitone of Wallach and Hallstein (A., 1918, i, 442) is 2-bromo- Δ^1 - p -menthen-3-one, since it is oxidised (a) by $KMnO_4$ in COMe, to γ -acetyl- α -isopropylbutyric acid, (b) by Wallach and Hallstein's method to 6-isopropyl- Δ^1 -cyclohexen-3-one-1-carboxylic acid (Semmler and McKenzie, A., 1906, i, 373), and (c) by alkaline $KMnO_4$ at 0° to α -isopropylglutaric acid. Diosphenol is probably first produced in (b) and (c). H. B.

Acenaphthenone. I. Pyrylium derivatives. A. C. SIRCAR and M. D. R. GOPALAN (J. Indian Chem. Soc., 1932, 9, 103–106).—Acenaphthenone and salicylaldehyde with KOH in EtOH give salicylideneacenaphthenone, m. p. 186°, converted by HCl in Et_2O into 2:3-acenaphthbenzopyrylium chloride [decomp. in air; ferrichloride, m. p. 203°; perchlorate, m. p. 255° (decomp.)], which is also obtained from acenaphthenone and salicylaldehyde with HCl in AcOH. 7-Hydroxy-2:3-acenaphthbenzopyrylium chloride, m. p. 131° [decomp. in moist air; ferrichloride, decomp. 236–237°; perchlorate, m. p. 260° (decomp.)], is similarly obtained. A. A. L.

Interaction of flavones and anthocyanins. W. J. C. LAWRENCE (Nature, 1932, 129, 834).—In *Dahlia variabilis* the ivory flavone changes the anthocyanin colour in the direction of blue and apparently acts as a co-pigment for cyanin and pelargonin in *D.* The ivory flavone pigments, independent of $[H^+]$, modify the anthocyanin colour of crude pigment extracts from flowers of widely different plants. The ivory flavone effect may be additional to that of co-pigments and flavones are probably a new and important source of variation of flower colour and intensity. L. S. T.

Synthetical experiments on the nature of betanin and related nitrogenous anthocyanins. I. (Mrs.) A. M. ROBINSON and R. ROBINSON (J.C.S., 1932, 1439–1445).—Aminoflavylum salts are best prepared by condensation of the appropriate o -hydroxyaldehyde and amino-ketone to a Schiff's base, followed by transposition in aq. HCl saturated at 0°, and isolation as the perchlorate. Thus p -aminoacetophenone and the appropriate aldehyde gives 4- o -vanillylideneamino-, m. p. 130°, 4-(2'-hydroxy-4-methoxybenzylideneamino)-, m. p. 159–160°, and 4-(2'-hydroxy-4'-methoxybenzylideneamino)- ω -acetoxy-, m. p. 155°–156° (from 4-amino- ω -acetoxyacetophenone, m. p. 129–130°, by reduction of the 4-nitro-compound with $FeSO_4$ and aq. NH_3), -acetophenone, converted, respectively, into 4'-amino-3-, 4'-amino-7-, and 4'-amino-3-hydroxy-7-methoxyflavylum perchlorate. 4'-Amino-5:7-dimethoxyflavylum perchlorate can be prepared by direct condensation of the components

in conc. HCl and treatment with 20% HClO_4 . These salts are all intensely coloured and give rise to colour bases (treatment with NaOAc) and ψ -bases (Na_2CO_3). Absorption spectra of these salts, in the visible region, are plotted; that of 4'-amino-3:7-dihydroxyflavylium chloride (description reserved) in 1% HCl closely resembles those of betanin and the pigment of *Atriplex hortensis*. An improved prep. of 2-hydroxy-4-methoxybenzaldehyde from β -resorcyaldehyde is described.

J. W. B.

Constitution of β -naphthapyrones. B. B. DEY, B. H. R. RAU, and Y. SANKARANARAYANAN (J. Indian Chem. Soc., 1932, 9, 71—77).— β -Naphthol and malic acid in H_2SO_4 (cf. A., 1884, 1346) give CO, a substance, m. p. above 320° , and 1:2- β -naphthapyrone, m. p. 118° (A., 1883, 1136). β -Naphthol, Na succinate, and succinic anhydride at 180° give 1:2- β -naphthapyrone-3-acetic acid (this vol., 519) (*Me* ester, m. p. 149°), and 3:3-di-1:2- β -naphthapyrone, m. p. 345° .

A. A. L.

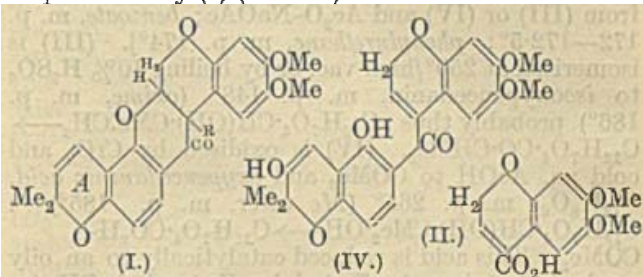
Synthesis of rotenone and its derivatives. II. Synthesis of rissic and derric acids, and the constitution of rotenone, deguelin, and tephrosin. A. ROBERTSON (J.C.S., 1932, 1380—1388).—2-Hydroxy-4:5-dimethoxybenzaldehyde, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and K_2CO_3 in COMe_2 give *Et* 2-aldehyde-4:5-dimethoxyphenoxyacetate (I), m. p. 129° (semicarbazone, m. p. 189°), oxidised by KMnO_4 in aq. COMe_2 to the 2-carboxy-derivative, m. p. 190° , which is hydrolysed to 2-carboxy-4:5-dimethoxyphenoxyacetic (rissic) acid (Takei, A., 1931, 490; La Forge, *ibid.*, 1415), m. p. $257\text{—}258^\circ$ (decomp.) (lit. 256° and $261\text{—}263^\circ$). Hippuric acid, (I), NaOAc , and Ac_2O at 100° (bath) give the corresponding *azlactone*, m. p. 175° , hydrolysed to 2-carboxymethoxy-4:5-dimethoxyphenylpyruvic acid, m. p. 238° (decomp.) (darkens slightly at $220\text{—}225^\circ$), which is oxidised by alkaline H_2O_2 to 2-carboxymethyl-4:5-dimethoxyphenoxyacetic (derric) acid (La Forge and Smith, A., 1930, 782, 1187; La Forge, *loc. cit.*). 2-Carboxy-, 2-carboxy-4-methoxy-, and 3:4-dimethoxy-phenoxyacetic acids are prepared (as above) from $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and *Me* salicylate, *Me* 4-*O*-methyl- β -resorcyate, and 3:4-dimethoxyphenol (improved prep. given; cf. A., 1931, 73), respectively, with subsequent hydrolysis.

A structure is assigned to rotenone; this is identical with that proposed by La Forge and Haller (this vol., 401). The formation of dehydrorotenone (*isoflavone* type) is analogous to the transformation of a flavanone into a flavone, and the hydrolysis of dehydrorotenone to derric acid is analogous to the decomp. of an *isoflavone*. Formulae are proposed for tephrosin and deguelin.

H. B.

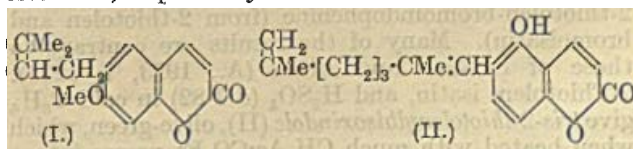
Vegetable, fish, and insect poisons. IV. Constituents of varieties of *Derris* and *Tephrosia*. [Constitution of deguelin, tephrosin, and toxicarol.] A. BUTENANDT and G. HILGETAG. V. Constituents of masterwort (*Imperatoria ostruthium*). A. BUTENANDT and A. MARTEN (Annalen, 1932, 495, 172—186, 187—210).—IV. Deguelin, tephrosin, and a substance, m. p. 231° , are isolated from the leaves of *Tephrosia vogelii*, whilst "rotenone-resin" (the non-cryst. part of the extract of the root of *Derris elliptica*) contains a compound, m. p. 228.5° ,

deguelin, and toxicarol. From work carried out largely by Clark (A., 1931, 1298, and previous abstracts), deguelin is represented as (I) ($\text{R}=\text{H}$), thus differing from rotenone by containing an α -pyran (A) in place of the dihydrofuran ring. Tephrosin is represented by (I) ($\text{R}=\text{OH}$).



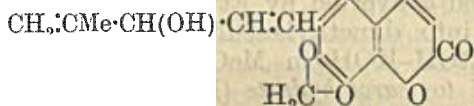
Toxicarol and 30% H_2O_2 in 5% EtOH-KOH give *toxicaric acid* (probably II), m. p. 210° (decomp.), reduced (H_2 , PtO_2 , EtOH) to *netoric acid* (this vol., 619), and converted by *Et* nitrite and conc. HCl in EtOH into dimethylasculetin (?). Toxicarol and 20% EtOH-KOH in MeOH at room temp. give 35% of *toxicarol hydrate* (III), $\text{C}_{23}\text{H}_{21}\text{O}_8$ (?), m. p. 223.5° (*Ac* derivative, m. p. 178°), which is unaffected by hot 20% EtOH-KOH and is converted by EtOH-conc. HCl into dehydratoxicarol, m. p. $233\text{—}234^\circ$ (acetate, m. p. $235\text{—}236^\circ$) (cf. Clark, A., 1931, 1065), also obtained by reduction of iododehydratoxicarol with Zn and AcOH . Reduction (H_2 , Pd-charcoal) of toxicarol in EtOH-KOH gives a compound, $\text{C}_{21}\text{H}_{24}\text{O}_7$ (?), m. p. 217.5° (*Ac* derivative, m. p. 192°), also formed by reduction (H_2 , PtO_2 , AcOH) of (III) and from dihydratoxicarol and 20% EtOH-KOH . Toxicarol, *Et* nitrite, and AcOH-conc. HCl afford toxicarolone, m. p. $283\text{—}284^\circ$. Toxicarol is probably (IV).

V. Osthol, $\text{C}_{15}\text{H}_{16}\text{O}_3$ (Herzog and Krohn, A., 1910, i, 124), contains one *OMe* and a lactone group, has the properties of a coumarin, is reduced (H_2 , Pd-black, EtOAc) to *dihydro-osthol*, m. p. 83° [also formed together with a small amount of an acid, $\text{C}_{15}\text{H}_{20}\text{O}_4$, m. p. 88° , by catalytic reduction (Pd-C) in aq. KOH], and is oxidised by CrO_3 in cold AcOH to COMe_2 and *ostholic acid*, $\text{C}_{12}\text{H}_{10}\text{O}_5$, m. p. 255° (*Me* ester, m. p. 155°). Ostruthin, $\text{C}_{18}\text{H}_{20}\text{O}_3$ (von Gorup-Besanez, A., 1874, 907; 1877, i, 717; Jassoy, A., 1890, i, 1154; Herzog and Krohn, *loc. cit.*), contains one OH and a lactone group and is methylated (diazomethane) to *methylostruthin*, m. p. 55° . This is oxidised by CrO_3 in AcOH at 100° (bath) to an aldehyde, $\text{C}_{11}\text{H}_8\text{O}_4$, m. p. $255\text{—}256^\circ$ [oxime, m. p. 228° (decomp.)], oxidised further to *methylostruthinic acid*, $\text{C}_{11}\text{H}_8\text{O}_5$, m. p. 268° , which when heated at 270° in CO_2 is decarboxylated to a compound, $\text{C}_{10}\text{H}_8\text{O}_3$ (probably 5-methoxycoumarin), m. p. 172° . Constituents (I) and (II) are assigned (provisionally) to osthol and ostruthin, respectively.



Oxypeucedanin (III), most probably $\text{C}_{16}\text{H}_{14}\text{O}_5$ (cf.

Heut, A., 1875, 772; Herzog and Krohn, *loc. cit.*), has m. p. 142°, and contains OH, CH₂O, and lactone groups. (III) boiled with 1% H₂C₂O₄ gives oxy-peucedanin hydrate (IV), m. p. 136° (cf. A., 1910, i, 124) [acetate, m. p. 139°, from (III) and boiling AcOH or from (IV) and Ac₂O-pyridine; diacetate, m. p. 136°, from (III) or (IV) and Ac₂O-NaOAc; benzoate, m. p. 172—172.5°; phenylurethane, m. p. 174°]. (III) is isomerised at 250°/high vac. or by boiling 10% H₂SO₄ to isooxypeucedanin, m. p. 148° (oxime, m. p. 186°), probably thus: C₁₂H₇O₄·CH(OH)·CMe₂·CH₂ → C₁₂H₇O₄·CO·CHMe₂. (IV) is oxidised by CrO₃ and cold aq. AcOH to COMe₂ and oxypeucedanic acid, C₁₂H₈O₆, m. p. 265° (Me ester, m. p. 185°): C₁₂H₇O₄·CH(OH)·CMe₂·OH → C₁₂H₇O₄·CO₂H + COMe₂. This acid is reduced catalytically to an oily product, but is not affected by Zn and AcOH (or alkali) or Na and EtOH; decarboxylation could not be effected. (III) is assigned (provisionally) the constitution

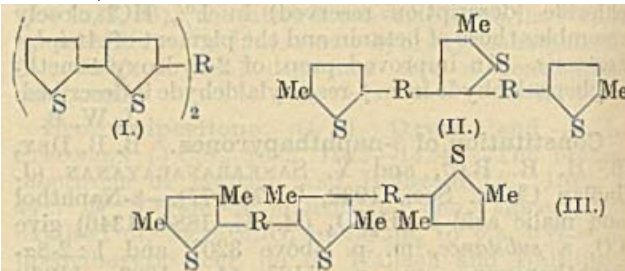


Details of the isolation of (I), (II), and (III) (which are all optically inactive) from the rhizome are given. H. B.

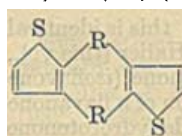
Thiophen series. XXIII. Thioethers of thiophen. W. STEINKOPF and P. LEONHARDT (Annalen, 1932, 495, 166—171).—Et succinate (1 pt.) heated with P₂S₃ (2 pts.) gives small amounts of thiophen, 2-ethoxythiophen [isolated as a *di(chloromercuri)-derivative*], and (mainly) 2-ethylthiolthiophen, b. p. 196—197° [isolated through its 5-chloromercuri-derivative (I), m. p. 140°, and regenerated by distillation of (I) with HCl]. (I) and NaI in COMe₂ afford *Hg di-(5-ethylthiol-2-thienyl)*, m. p. 76°. 2-Methylthiolthiophen, b. p. 181.5—183.5°, is similarly obtained from Me succinate; its 5-chloromercuri-derivative, m. p. 168°, and NaI in COMe₂ give *Hg di-(5-methylthiol-2-thienyl)*, m. p. 149—150°, which with HgBr₂ and HgI₂ in COMe₂ affords 5-bromo-, m. p. 153°, and 5-iodo-, m. p. 105—107°, -mercuri-2-methylthiolthiophen, respectively. H. B.

Thiophen series. XXII. Indophenine. II. W. STEINKOPF and H. HEMPEL (Annalen, 1932, 495, 144—165).—The blue product obtained from dithienyl and isatin under the conditions previously used (A., 1931, 104) is not an indophenine (cf. Heller, *ibid.*, 369), but is probably *bis-α-dithienyloxindole* (I; in this and other formulæ, R = NH—C(=O)—C₆H₄—C(=O)—); (I) is not reducible (vat). The condensation of mono- and di-methyl- and 2-acyl-thiophens with isatin and bromoisatin is investigated; when indophenines are produced, they are designated, e.g., 3:4-thioxen-indophenine (from 3:4-thioxen and isatin), and 2-thiotolen-bromindophenine (from 2-thiotolen and bromoisatin). Many of the results are contrary to those of Schlenk and Blum (A., 1923, i, 1235). 2-Thiotolen, isatin, and H₂SO₄ (d 1.82) in cold C₆H₆ give *tris-2-thiotolenyloxindole* (II), olive-green, which when heated with much CH₂Ac·CO₂Et passes into a yellowish-brown substance of (probably) the same

composition, and probably also formed using ZnCl₂ as the condensing agent. An indophenine (not obtained pure) is produced using hot AcOH—H₂SO₄ for the condensation; 2-thiotolen-bromindophenine is similarly prepared, as are *tris-2:3-thioxenyloxindole*,



type (II), 2:3-thioxen-bromindophenine, bis-2:5-thioxenyl-(3)-oxindole, and *tris-2:4-thioxenyloxindole* (III), from the requisite components. 3:4-Thioxen and bromoisatin in cold H₂SO₄—C₆H₆ give 3:4-thioxen-bromindophenine; with isatin, *tris-3:4-thioxenyloxindole* or 3:4-thioxen-indophenine (neither described) is produced. 2:4- and 2:5-Diphenylthiophens do not condense with isatin; the 3:4-derivative gives a complex, non-reducible product. Thiophen-*N*-methylindophenine is obtained from thiophen, *N*-methylisatin, and H₂SO₄ in cold C₆H₆. Et isatin-*N*-acetate, m. p. 135° (lit. 114°), prepared from sodium isatin and CH₂Br·CO₂Et or from the acid chloride and EtOH, is brominated in AcOH to *Et bromoisatin-N-acetate*, m. p. 141—142°, also obtained from sodium bromoisatin and CH₂Br·CO₂Et. These esters react with thiophen in AcOH—H₂SO₄ forming thiophen-*N*-carbethoxymethylindophenine and thiophen-bromo-*N*-carbethoxymethylindophenine. The last-named has *M* 710, confirming the previous suggestion (*loc. cit.*) that an indophenine results by loss of 2 mols. of H₂O from 2 mols. of isatin and 2 mols. of the thiophen. Indophenine formation occurs with 2- or 3-mono- and 2:3- and 3:4-di-substituted thiophens, but not with 2:4- or 2:5-derivatives. These results disprove Schlenk and Blum's (*loc. cit.*) and Heller's (*loc. cit.*) dithienyl structures for indophenine, which must possess the structure previously proposed (A., 1931, 104) or (IV) (which is assigned to the indophenines from 2-substituted thiophens). The ultra-violet absorption curves of solutions of thiophen-indophenine (V) and 2-thiotolen-bromindophenine (type IV) in conc. H₂SO₄ are very similar and differ somewhat from those of 3:4-thioxen-bromindophenine (slightly) and mesoxophenine. The ease of formation of (V) (improved prep. given) supports the previously proposed formula for (V) (and its analogue from 3-thiotolen).



2-Acetothienone, isatin, and H₂SO₄ (d 1.82) in AcOH at 140—150° give 2-acetothienone-indophenine-sulphonic acid; 2-propiothienone-indophenine-sulphonic acid (containing some disulphonic acid), 2-isovalerothienone-indophenine, and thienone-indophenine-disulphonic acid (*Ba* salt) are similarly prepared. Thienone is best obtained from 2-thienoyl chloride, thiophen, and AlCl₃ in CS₂. Thiophen, alloxan, and SnCl₄ in AcOH give an indophenine, C₁₆H₈O₆N₄S₂, whilst

thiophthen, isatin, and $\text{AcOH-H}_2\text{SO}_4$ afford *tristhiophthenylbisoxindole*. The product, $\text{C}_{24}\text{H}_{16}\text{O}_3\text{N}_2\text{S}_2$, from Mg 2-thienyl bromide and isatin is converted by heating with BzOH , $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, or $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ into (V), a solution of which in AcOH undergoes autoxidation in sunlight to the *disulphoxide dihydrate*.

An apparatus for the analysis of the NH_4 salts produced by reduction of various of the above indophenines by $\text{Na}_2\text{S}_2\text{O}_4$ in aq. NH_3 , is described. Indophenines giving brown vats have one CO reduced, whilst those affording red vats have both CO groups reduced.

H. B.

Indigoid dyes derived from phenanthraquinone. I. Thionaphthenphenanthreneindigotin. P. C. DUTTA (J. Indian Chem. Soc., 1932, 9, 99—101). —3-Oxythionaphthen in AcOH and a little HCl condenses with suitably substituted phenanthraquinones to give the 9'-, m. p. above 290° , and 4'-nitro-, m. p. above 290° , 2':7'-, m. p. above 290° , and 4':5'-dinitro-, m. p. above 290° , 2'-bromo-, m. p. 279° , dibromo-, m. p. above 295° , dibromonitro-, m. p. above 300° , dibromodinitro-, m. p. 281° , 2'-, m. p. above 295° , and 4'-amino-, m. p. above 300° , 2':7'-, m. p. above 300° , and 4':5'-diamino-, m. p. above 295° , 2'-, m. p. 200° , and 4'-hydroxy-, m. p. above 300° , and 2':7'-dihydroxy-, m. p. above 300° , -derivatives of 2-thionaphthen-(?)9'-phenanthreneindigotin (Pummerer and Luther, A., 1931, 738). Dyeing properties of these compounds are described.

A. A. L.

Preparation and dinitration of 1-phenylpiperidine. R. J. W. LE FÈVRE (J.C.S., 1932, 1376—1379). —Dinitration of 1-phenylpiperidine (I) with HNO_3 (d 1.5) at -10° gives the 2':4'-dinitro-derivative (yield about 90%) and proceeds by way of the 4'- NO_2 -compound [the only product isolated by nitration of (I) with HNO_3 (d 1.5) in $\text{AcOH-Ac}_2\text{O}$]. (I) is obtained in 50% yield (by the usual method) from its 2'- NH_2 -derivative but only in small amount from the 4'-isomeride. (I) could not be prepared from piperidine and the Ph esters of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, H_3PO_4 , AcOH , BzOH , $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $o\text{-OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ or KPhSO_4 . Piperidine and o - and p -nitrophenyl p -toluenesulphonates give p -toluenesulphonpiperidide and o - and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, respectively. Piperidine and PhI under pressure and thermal decomp. of benzeneazopiperidide in solvents give unsatisfactory or negative results, whilst successive treatment of piperidine with NaNH_2 (in boiling xylene) and PhI affords a little (I). 1-Chloropiperidine and MgPhBr or MgPhI react violently to give Ph_2 and a little basic oil.

H. B.

Preparation of 1-phenyl-lutidone-3-carboxylic acid. H. KONDO and K. NAKAJIMA (Ber., 1932, 65, [B], 791—792; cf. Limpach, A., 1931, 851). —Et β -anilinoacetonate and Et acetacetate in presence of liquid paraffin and a little SnCl_4 at $180\text{--}190^\circ$ give 4-keto-1-phenyl-2:6-dimethyl-1:4-dihydropyridine-3-carboxylic acid (decomp. $267\text{--}268^\circ$) in more than 20% yield (*Me* ester, m. p. 209°). In absence of SnCl_4 reaction occurs at 220° with production of much resin.

H. W.

Syntheses by means of magnesylpyrroles. XV. True thioindoxyl [3-thiolindole]. B. ODDO and Q. MINGOIA (Gazzetta, 1932, 62, 299—317). —The

name thioindoxyl is considered more suitable for 3-thiolindole than for 3-oxythionaphthen. The reaction product of magnesylindole and S when treated with BzCl gives *S-benzoyl-3-thiolindole* (I), m. p. 157° (*Ag* derivative), di-indolyl sulphide, and *S-benzoyl-2-thiolindole* (II), m. p. 128° (*Ag* and *benzeneazo*-derivatives). Both (I) and (II) on alkali fusion give BzOH and $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. When AcCl is used the products are regarded as 1:S-diacetyl-3-thiolindole, m. p. $129\text{--}130^\circ$, S-acetyl-3-thiolindole, m. p. $208\text{--}210^\circ$ (*Ag* derivative), S-acetyl-2-thiolindole, m. p. 184° (*Ag* and *benzeneazo*-derivatives), and 1-acetyl-3:1'-di-indolyl sulphide, m. p. $95\text{--}96^\circ$. Aq.-alcoholic KOH hydrolyses (I) to 3-thiolindole (true thioindoxyl), m. p. 235° (*Hg*^{II} derivative). This is insol. in cold alkali, and stable towards O_2 in alkaline media, to mild acid oxidising agents, and to hot alkaline oxidising and reducing agents; KMnO_4 in $\text{C}_5\text{H}_5\text{N}$ gives not 3:3'-dithio-indigotin but 2:3-dihydro-3-indolyl sulphoxide, $\text{C}_8\text{H}_7\cdot\text{C}_2\text{SO}\cdot\text{CH}_2\text{-NH}$, m. p. $248\text{--}250^\circ$. $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ gives 3-thio-2-p-nitrobenzylideneindoline, m. p. 170° ; there is no reaction with acenaphthenequinone or with isatin. Hydrolysis of (II) gives 2-thiolindole, m. p. $148\text{--}150^\circ$ (2-thio-3-p-nitrobenzylideneindoline, m. p. 183° ; no reaction with isatin).

Magnesylpyrrole, S, and BzCl give a black infusible insol. product.

E. W. W.

Preparation of 5:7-di-iodoisatin. W. C. SUMPTER and L. AMUNDSEN (J. Amer. Chem. Soc., 1932, 54, 1917—1918). —5:7-Di-iodoisatin is obtained in about 10% yield by the method of Kalb and Berrer (A., 1925, i, 160), and in 60% yield from 5:7:5':7'-tetraiodoindigotin and $\text{CrO}_3\text{-HNO}_3$. C. J. W. (b)

Racemisation of acetyl-L-tryptophan. V. DU VIGNEAUD and R. R. SEALOCK (J. Biol. Chem., 1932, 96, 516—517). —Acetyl-L-tryptophan is racemised by addition of Ac_2O to its solution in $N\text{-NaOH}$ at $35\text{--}40^\circ$ (cf. A., 1929, 431), and hence acetylation of L-tryptophan using excess of Ac_2O by Berg's method (A., 1930, 243) gives *acetyl-dl-tryptophan* (I), m. p. $205\text{--}206^\circ$. If only 2.54 mols. Ac_2O and 5.82 mols. NaOH per mol. of L-tryptophan are used *acetyl-l-tryptophan*, m. p. $189\text{--}190^\circ$, $[\alpha]_D^{25} + 29^\circ$ in aq. NaOH ($d\text{-}\alpha\text{-CHPhMe}\cdot\text{NH}_2$ salt, m. p. $192\text{--}194^\circ$, $[\alpha]_D^{25} + 20.6^\circ$), is obtained. This is confirmed by resolution of the *dl*-compound with $d\text{-CHPhMe}\cdot\text{NH}_2$, the $d\text{-CHPhMe}\cdot\text{NH}_2$ salt, m. p. $194\text{--}196^\circ$, $[\alpha]_D^{25} 19.6^\circ$, of *acetyl-d-tryptophan*, m. p. $189\text{--}190^\circ$, $[\alpha]_D^{25} - 30.2^\circ$, separating. J. W. B.

New dicyclic imine, isogranatanine. G. KOMPFA (Ber., 1932, 65, [B], 792—793). —Hexahydroisophthalic acid is dissolved in aq. NH_3 , the solution is evaporated, and the residue distilled, thereby yielding *hexahydroisophthalimide*, m. p. $185\text{--}186^\circ$, which is electrolytically reduced to *isogranatanine* [3:5-trimethylenepiperidine], m. p. $144\text{--}146^\circ$ [hygroscopic hydrochloride; picrate, m. p. $215\text{--}217^\circ$ (decomp.); chloroplatinate, m. p. 195° (decomp.)]. Owing to the ease of hydrolysis of the imide, the yield of base is only 17%.

H. W.

Quinoline derivatives. XXXVIII. Synthesis of [substituted] 3-hydroxy-2-phenylquinoline-4-

carboxylic acids. H. JOHN (J. pr. Chem., 1932, [ii], 133, 259—272; cf. this vol., 623).—Isatin, phenacyl bromide, and hot 33% aq. KOH give 3-hydroxy-2-phenylquinoline-4-carboxylic acid (I), m. p. 207°. Phenacyl chloride gives poorer yields of (I) and the iodide gives traces. By use of the appropriate substituted isatin and/or acetophenone derivatives the following derivatives of quinoline-4-carboxylic acid were prepared: 6-chloro- (m. p. 211°), 6-bromo- (m. p. 185°), 6-iodo- (m. p. 195°), 6-methyl- (m. p. 193°), 6:8-dibromo- (m. p. 187°), and 6:8-dimethyl- (m. p. 155°); 3-hydroxy-2-phenyl-; 3-hydroxy-2-p-chloro- (m. p. 169°), -p-bromo- (m. p. 152°), and -p-iodo- (m. p. 161°) -phenyl-; 3-hydroxy-2-p-tolyl- (m. p. 180°), -2-(4'-diphenyl)- (m. p. 161°), and -2-mesityl- (m. p. 174°); 6-chloro- (m. p. 191°) and 6-iodo- (m. p. 228°) -3-hydroxy-2-p-chlorophenyl-; 6-bromo- (m. p. 220°) and 6:8-dibromo- (m. p. 208°) -3-hydroxy-2-p-bromophenyl-; 6-iodo-3-hydroxy-2-p-iodo- (m. p. 182°) and -p-bromo- (m. p. 240°) -phenyl-; 6-bromo-3-hydroxy-2-diphenyl-, m. p. 274°; 3-hydroxy-2-p-tolyl-6-methyl-, m. p. 212°; 6:3-hydroxy-2-mesityl-8-dimethyl-, m. p. 202°. Many inorg. salts of the above acids were prepared. The preps. of ω -bromoacetomesitylene, ω -bromo-p-iodo- (m. p. 101°), and -p-phenyl- (m. p. 95°) -acetophenone were modified.

R. S. C.

Acridine. IX. Simple synthesis of acridone and 3-substituted acridones. K. LEHMSTEDT (Ber., 1932, 65, [B], 834—839).—*o*-Nitrobenzaldehyde slowly reacts with C_6H_6 , PhMe, or halogenobenzenes in presence of conc. H_2SO_4 containing a little $NaNO_2$ at room temp. yielding acridones and small amounts of dark, sparingly sol. products; $PhNO_2$, $NPhEt_2$, and $BzOH$ do not react (cf. Bamberger, A., 1909, 1, 510). The following are described: acridone, m. p. 347°; 3-methylacridone, m. p. 312°; 3-fluoroacridone, m. p. 372°; 3-chloroacridone, m. p. above 390° [by-product 4-chloro-2'-nitrobenzophenone, m. p. 151° (corr.)], converted by successive treatment with $NPhMe_2$ and $POCl_3$ into 3-chloro-9-p-dimethylamino-phenylacridine, m. p. 238—239°; 3-bromoacridone.

H. W.

Hetero-ring formation from anilino-derivatives of succinosuccinic ester. G. P. PENDSE and S. DUTT (J. Indian Chem. Soc., 1932, 9, 67—70).—Condensation of Et succinosuccinate with *m*-toluidine (cf. A., 1928, 289) gives Et 2:5-di-*m*-toluidinocyclohexadiene-1:4-dicarboxylate, m. p. 143°. Similarly are obtained Et 2:5-di-*o*-m. p. 122°, and Et 2:5-di-*p*-hydroxyanilino-, m. p. 113°, Et 2:5-di-*p*-acetylanilino-, m. p. 119°, Et 2:5-di-*p*-acetilamino-anilino-, m. p. 179°, and Et 2:5-di-1:3:4-xylydino-cyclohexadiene-1:4-dicarboxylate, m. p. 155°. Action of NaOEt (or in some cases of NaOH) on these and similar compounds gives the 1:17-, m. p. 255° (decomp.), 2:18-, m. p. 253°, and 3:19-dimethyl-, m. p. 212°, 1:17-, m. p. above 260°, and 3:19-dimethoxy-, m. p. above 260°, 1:17-, m. p. above 260°, and 3:19-diethoxy-, m. p. 218°, 1:18:3:19-tetramethoxy-, m. p. above 280°, 1:2:17:18-, m. p. above 260°, and 3:4:19:20-diphenylene-, m. p. above 260°, 1:17-, m. p. 236°, and 3:19-dihydroxy-, m. p. 205°, 3:19-diacetamido-, m. p. 212°, and

3:19-diacetyl-, m. p. 158°, derivatives of 6:9-dihydro-5:22-dihydroxyacriquinoline, m. p. above 280°. Absorption spectra max. are recorded for the latter group of compounds.

A. A. L.

Action of diazo-compounds on butadiene. E. MULLER and O. ROSER (J. pr. Chem., 1932 [ii], 133, 291—304).—Butadiene (I) and aliphatic diazo-compounds give first derivatives of vinylpyrazoline and later of dipyrazoline. When kept with diazomethane in Et_2O for 2 days, (I) yields 5-vinylpyrazoline, b. p. 50°/11 mm., unstable (picrate; chloroplatinate), the constitution of which is proved because (a) the aq. solution gives the pyrazoline reaction with woodshavings, (b) it is transformed by Cl_2 in $CHCl_3$ into 4-chloro-5- α - β -dichloroethylpyrazoline hydrochloride, hygroscopic, m. p. 109°, and (c) prolonged action of diazomethane in Et_2O gives 5:5'-dipyrazoline (II),

$$\begin{array}{c} CH < CH_2 < CH \\ | & | & | \\ N & - & N & - & H \end{array}$$
, m. p. 138°, unstable [hydrochloride, stable, m. p. 176°; picrate, m. p. 174° (decomp.); chloroplatinate], oxidised by alkaline $KMnO_4$ to $\beta\beta'$ -dihydroxyadipic acid. With Cl_2 in $CHCl_3$ (II) gives a mixture of hydrochlorides, m. p. 210° (decomp.), probably $C_6H_7N_4Cl_3$ and $C_6H_6N_4Cl_4$. With diazoethane (I) gives similarly 3-methyl-5-vinylpyrazoline, b. p. 55°/11 mm. (picrate; chloroplatinate), transformed slowly by diazoethane into 3:3'-dimethyl-5:5'-dipyrazoline, m. p. 69° [hydrochloride, m. p. 169° (decomp.); chloroplatinate]. When heated with Et diazoacetate for 4 days at 100°, (I) yields Et 5:5'-dipyrazoline-3:3'-dicarboxylate (III), m. p. 195° (decomp.), and 1:1'-dicyclopropane-2:2'-dicarboxylate, b. p. 60°/12 mm., also formed by prolonged heating of (III) [corresponding acid, an oil (Na salt)]. (III) yields the dihydrazide, m. p. 245° (decomp.) [dibenzylidene compound, m. p. 280° (decomp.); diazide], and on hydrolysis gives the corresponding acid, an oil, which at 150° in vac. gives CO_2 and 5:5'-dipyrazoline.

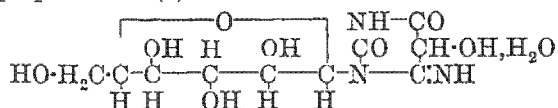
R. S. C.

Preparations of uracil-4-acetic and orotic acids. Orotic acid as the possible intermediate in the synthesis of purines from histidine. G. E. HILBERT (J. Amer. Chem. Soc., 1932, 54, 2076—2083).—Uracil-4-acetic acid (I) is obtained from carbamide, citric acid, and oleum (15% SO_3). It is hydrolysed by aq. $Ba(OH)_2$ to the Ba salt of β -carbamidoglutaconic acid, which with HCl regenerates (I). Oxidation of (I) with alkaline $K_3Fe(CN)_6$ gives K orotate. Catalytic reduction of the Et ester of (I) gives Et 4:5-dihydrouracil-4-acetate, m. p. 155—156°; similarly, 3-methyluracil gives 3-methyl-4:5-dihydrouracil, m. p. 175—176°. The possibility that orotic acid is an intermediate in the synthesis of purines from histidine is discussed. C. J. W. (b)

Stereoisomeric 2:3:5:6-tetramethylpiperazines. III. Reduction products of 2:3:5:6-tetramethylpyrazine methiodide. F. B. KIPPING (J.C.S., 1932, 1336—1342; cf. A., 1931, 851).—Reduction (H_2 , Pt-PtO₂, moist EtOH) of 2:3:5:6-tetramethylpyrazine methiodide gives (mainly) the hydriodide, m. p. 161—162°, of the hygroscopic γ -2:3:4:5:6 (or 1:2:3:5:6)-pentamethylpiperazine (I), b. p. 201—202°, m. p. 4—5° [monohydrate, m. p. 73—74°; dihydrochloride, m. p. about 300°;

dihydriodide, m. p. 240° (decomp.); phenylthiocarbamide, m. p. 154°; 1-NO-derivative, b. p. 155—157°/15 mm., m. p. 24—25° (hydrochloride); *p*-toluenesulphonyl derivative, m. p. 124° (hydrochloride), also formed by methylation (MeI or CH₃O) of 1-*p*-toluenesulphonyl- γ -2:3:5:6-tetramethylpiperazine (A., 1930, 223), and a little of an isomeride (II) (phenylthiocarbamide, m. p. 122—123°), separable through its *p*-toluenesulphonyl derivative, m. p. 99—100°. (II) has not been correlated with any Me₄ base. Methylation (CH₃O) of (I) (as hydrochloride) gives γ -1:2:3:4:5:6-hexamethylpiperazine, b. p. 211—212° [dihydrochloride; methiodide, m. p. 272—274° (decomp.)], whilst (II) similarly affords a hexamethylpiperazine [methiodide, m. p. 275° (decomp.)]. Methylation (MeI or CH₃O) of 1-*p*-toluenesulphonyl- β -2:3:5:6-tetramethylpiperazine [4-NO-derivative, m. p. 153—154°, reduced (Al-Hg, aq. EtOH) to the 4-NH₂-derivative, m. p. 140—141° (hydrochloride)] gives the *p*-toluenesulphonyl derivative, m. p. 100—101°, of *dl*- β -2:3:4:5:6-pentamethylpiperazine (phenylthiocarbamide, m. p. 95°). *dl*- β -1:2:3:4:5:6-hexamethylpiperazine, b. p. 203—204° (from the corresponding Me₄ base and CH₃O), affords a methiodide, m. p. 275° (decomp.), whilst α -1:2:3:4:5:6-hexamethylpiperazine, b. p. 198—200° (ethiodide), from the Me₄ base dihydrochloride and 40% CH₃O at 160—180°, gives a dimethiodide, m. p. 272—273° (decomp.). H. B.

Pyrimidines. CXXVII. Structure of convicine. H. J. FISHER and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 2038—2045).—The presence of convicine (I) in broad beans (*Vicia faba*), reported by Ritthausen (A., 1881, 1158), is confirmed. Hydrolysis of (I) with 6*N*-H₂SO₄ gives alloxantin, NH₂ (1 mol.), and glucose. Oxidation with KClO₃ gives carbamide but no guanidine. (I) does not react with KCNO to form a carbamide. The following structure is proposed for (I):



C. J. W. (b).

Pyrimidines. CXXVIII. Rearrangement of 2-ethylthiol-6-thiocyano-4-methylpyrimidine into its thiocarbimide modification. Y. F. CHU and Y. H. CHEN (J. Amer. Chem. Soc., 1932, 54, 2056—2059).—2-Ethylthiol-6-thiocyano-4-methylpyrimidine, b. p. 155—158°/5 mm., m. p. 69—70°, obtained from the corresponding chloropyrimidine and KSCN, rearranges when heated with EtOH at 100° or (boiling) xylene to 2-ethylthiol-6-thiocarbimido-4-methylpyrimidine (I), b. p. 146—158°/1 mm. (decomp.); prolonged heating gives a polymeric form, m. p. 108—109°. (I) and conc. aq. NH₃ in Et₂O give the 6-thiocarbamido-derivative, m. p. 229—231°; with NH₂Ph, the 6-phenylthiocarbamido-derivative, m. p. 209—210°, results. (I) and MeOH and EtOH give the corresponding thiourethanes, m. p. 84—86° and 97—98°, respectively. C. J. W. (b)

New reaction of certain diazosulphonates derived from β -naphthol-1-sulphonic acid. X. Preparation of phthalazine derivatives from 4-

aminoazobenzene and 4'-nitro-4-aminoazobenzene. F. M. ROWE and F. S. TOMLINSON (J.C.S., 1932, 1118—1125; cf. this vol., 404).—Na β -naphthol-1-sulphonate and azobenzene-4-diazosulphonate give benzeneazobenzene- β -naphthol-1-diazosulphonate, converted by Na₂CO₃ into Na 1-(benzeneazobenzeneazo)- β -naphthaquinone-1-sulphonate, which with NaOH gives Na H 3-(benzeneazobenzene)-1:3-dihydrophthalazine-1-sulphonate-4-acetate (also +2 $\frac{1}{2}$ EtOH) (yield 19.3%) (Ba salt, +7H₂O and anhyd.). This in boiling H₂O with gradual addition of HCl gives 1-hydroxy-3-(benzeneazobenzene)-1:3-dihydrophthalazine-4-acetic acid, m. p. 177° (yield 64.2%) (Me ester, m. p. 153°; Et ester, m. p. 142—143°; Ac derivative, m. p. 229°; anilide, m. p. 250°), isolated through the Na salt, and reduced by SnCl₂ in HCl to 1-hydroxy-3-(4'-aminophenyl)-tetrahydrophthalazine-4-acetic acid (A., 1926, 625) and NH₂Ph. Reduction with Na₂S₂O₄ gives NH₂Ph. With hot H₂SO₄ 4'-amino-3-phenyl-4-methylphthalazone (A., 1931, 835) is obtained. The following are similarly obtained from 4'-nitroazobenzene-4-diazosulphonate: Na H 3-(4'-nitrobenzeneazobenzene)-1:3-dihydrophthalazine-1-sulphonate-4-acetate (also +1 $\frac{1}{2}$ EtOH) (yield 63.4%); 1-hydroxy-3-(4'-nitrobenzeneazobenzene)-1:3-dihydrophthalazine-4-acetic acid, m. p. 222—223° [Ac derivative, m. p. 197° (decomp.)]; anilide, m. p. 281° (decomp.)]; 1-hydroxy-3-(4'-aminophenyl)tetrahydrophthalazine-4-acetic acid (by reduction with Na₂S₂O₄, together with a little *p*-phenylenediamine) (yield 51.9%); and 4'-amino-3-phenyl-4-methylphthalaz-1-one (and *p*-nitroaniline). A. A. L.

Quinazolines. III. Interaction of aniline with 2-chloro-4-alkoxyquinazolines and 2-chloro-4-ketodihydroquinazoline. N. A. LANGE and F. E. SREIBLEY (J. Amer. Chem. Soc., 1932, 54, 1994—1998; cf. A., 1931, 1431).—2-Chloro-4-methoxyquinazoline and EtOH-NH₂Ph give the hydrochloride (I), m. p. 158—161° (decomp.), of 2-anilino-4-methoxyquinazoline, m. p. 113° (chloroplatinate, softens and decomp. 225—230°; picrate, m. p. 210°). Hydrolysis of (I) with dil. HCl in EtOH-NH₂Ph gives 2-anilino-4-ketodihydroquinazoline (II), m. p. 261°, also prepared from the corresponding 2-Cl-compound and EtOH-NH₂Ph, from phenyl- ψ -methylthiocarbamide and anthranilic acid, and when (I) is heated. 2-Anilino-4-ethoxyquinazoline, m. p. 110—111° [picrate, m. p. 183°; hydrochloride, m. p. 168—171° (decomp.)], is also hydrolysed to (II). These results confirm the orientation of the halogen and alkoxy-groups in the chloro-alkoxy-derivatives previously described. All m. p. are corr. C. J. W. (b)

Stereochemistry of dipyridyls. Preparation and resolution of 6:6'-diphenyl-3:3'-dipyridyl-2:4:2':4'-tetracarboxylic acid. XX. E. H. WOODRUFF and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 1977—1982; cf. A., 1931, 1295, 1306).—The Schiff base from *p*-C₆H₄(NH₂)₂ (1 mol.) and PhCHO (2 mols.) with pyruvic acid in boiling EtOH gives 42—50% of 3:8-diphenyl-4:7-phenanthroline-1:10-dicarboxylic acid, m. p. 250.5—251.5° (decomp.) (Ag salt), oxidised by alkaline KMnO₄ at 20—25° to 6:6'-diphenyl-3:3'-dipyridyl-2:4:2':4'-tetracarboxylic acid (I), decomp. without melting at 181°.

(I) is resolved by brucine into active forms, $[\alpha]_D +6.1^\circ$ and -5.9° in EtOH (brucine salts), which are readily racemised by warming with EtOH.

C. J. W. (b)

Substituted piperazines. III. Stereoisomeric bistetramethylenepiperazines [dodecahydrophenazines]. GODCHOT and MOUSSERON (Bull. Soc. chim., 1932, [iv], 51, 528—542).—The following derivatives of the three stereoisomeric bistetramethylenepiperazines (this vol., 625) have been prepared: α -, m. p. 132—133° [dinitroso-, m. p. 161—162°, tetrabromo- and Bz_2 , m. p. 234—235°, derivatives; picrate, decomp. 270°; chloroplatinate $+3H_2O$, decomp. 240°; chloroaurate, decomp. 220°; chloromercurate, $B_2HCl_2 \cdot 2HgCl_2$; chlorostannate $B_2HCl_2 \cdot SnCl_2$; hydrochloride $+6H_2O$, sublimes above 200°; hydrobromide $+6H_2O$; hydriodide $+6H_2O$; sulphate; d-tartrate $+2.5H_2O$, $[\alpha]_D +11.1^\circ$; d-camphor- β -sulphonate, m. p. 290°; urate], gives a dimethiodide, m. p. 300° (decomp.), converted by 3N-NaOH into a monomethiodide, m. p. 260°, and by Ag_2SO_4 into a N-Me₂ derivative, m. p. 108—109°. The β -compound, m. p. 106—107°, gives a dinitroso-derivative, m. p. 182—183° (also obtained from the product of reduction of phenazine with H₂ and Pt); picrate, decomp. 250°; chloroplatinate $+2H_2O$, decomp. 230°; chloroaurate $+3H_2O$, decomp. 230°; chloromercurate; hydrochloride $+6H_2O$, decomp. 200°; tartrate $+4H_2O$ (solubility of urate, 1 in 31 of H₂O at 35°). The γ -compound, m. p. 62—63°, gives a dinitroso-derivative, m. p. 107° (also from the reduced phenazine); picrate, decomp. 230°; dithiocarbamate (not obtained with α - and β -compounds); chloroplatinate $+3H_2O$, decomp. 260°; chloroaurate, decomp. 200°; chloromercurate; hydrochloride $+6H_2O$, decomp. 240°; and tartrate $+4H_2O$ (solubility of urate 1 in 24 of H₂O at 35°). Dehydrogenation of the α -compound with Zn at 350° affords phenazine, but attempts to synthesise these piperazines from NH₃ or NaNH₂ and 1:2-dibromocyclohexane were unsuccessful. J. W. B.

Cyanine dyes. III. Tautomerism of carbo-cyanines. T. OGATA (Proc. Imp. Acad. Tokyo, 1932, 8, 119—122; cf. A., 1927, 1089).—Quinaldine, lepidine, and 6-ethoxyquinaldine ethiodides and trimethylindolenium and α -picoline methiodides when heated with diphenylformamidine give 2-anilinoethenylquinoline, $C_9H_6N(EtI) \cdot CH:CH \cdot NHPh$ (I), m. p. 281°, 4-anilinoethenylquinoline, m. p. 241° (II), and 2-anilinoethenyl-6-ethoxyquinoline, m. p. 295° (III), ethiodides, and 2-anilinoethenyl-3:3-dimethylindolenium (IV), m. p. 241°, and 2-anilinoethenylpyridine (V), m. p. 203°, methiodides, which with Ac₂O and Et orthoformate give Ac derivatives, m. p. 225°, 98°, 126°, 233°, and 177°, respectively. 1:1'-Diethyl-2:4'-(or 2':4)-carboquinocyanine 1-iodide, m. p. 153° (decomp.), is obtained from (I) (or its Ac derivative) and lepidine ethiodide or from (II) (or Ac derivative) and quinaldine ethiodide in presence of Ac₂O and KOAc. Similarly 6-(or 6'-)ethoxy-1:1'-diethyl-2:2'-carboquinocyanine 1-iodide, m. p. 278° (decomp.), is obtained from (I) and 6-ethoxyquinaldine ethiodide or from (III) and quinaldine ethiodide, 1'-ethyl-1:3:3-trimethyl-2:2'-carboquinocyanine 1-(or 1'-)iodide, m. p. 245°, from (IV) and quinaldine ethiodide or (I) and trimethylindolen-

ium methiodide, and 1-ethyl-1'-methyl-2:2'-carboquinopyricyanine 1-(or 1'-)iodide, m. p. 268°, from (I) and α -picoline methiodide or (V) and quinaldine ethiodide. The identity of each pair of dyes is shown by the methods of mixed m. p. and absorption spectra.

E. E. J. M.

γ -Triazines. XXIII. Synthesis of isobutyl- and isoamyl-diamino- γ -triazines. A. OSTROGOVICH and G. GHEORGHIU (Gazzetta, 1932, 62, 317—332; cf. A., 1911, i, 332).—Cyanoguanidine and the hydrochloride of isovaleroamidine (picrate, m. p. 231—232° obtained from Me isovaleroimino-ester) at 175—230° yield NH₃ and 4:6-diamino-2-isobutyl-1:3:5-triazine [picrate, m. p. 245° (decomp); hydrochloride, m. p. 259—260° (decomp.); neutral sulphate, m. p. 267° (decomp.); Ac, m. p. 227—228°, and Ac₂, m. p. 129—130°, derivatives]. The hydrochloride of isohexoamidine (picrate, m. p. 195—196°; from Me isohexoimino-ester) gives similarly 4:6-diamino-2-isoamyl-1:3:5-triazine [picrate, m. p. 247—248° (decomp.); hydrochloride, m. p. 253—255°; neutral sulphate, m. p. 226—228°; Ac, m. p. 233—234°, and Ac₂, m. p. 124—125°, derivatives]. Descriptions of some of the above compounds by Bandrowski (A., 1876, ii, 190) are corrected. No condensation occurs between cyanoguanidine and isovalero- or isohexonitrile.

E. W. W.

NN'-Substituted pyrimidine and purine derivatives. III. Methylated 3-phenyluric acids. B. HEPNER and S. FRENKENBERG (Helv. Chim. Acta, 1932, 15, 533—539).—Interaction of 4:5-diamino-3-phenyluracil with KCNO and HCl gives 4-imino-3-phenyl- ψ -uric acid, decomp. 210—220°, which with Na₂CO₃ at 220° gives ammonia and 3-phenyluric acid ($+1H_2O$), decomp. 227—230°; 4-imino-3-phenyl-1-methyl- ψ -uric acid ($+1H_2O$) is similarly prepared, and decomposes $>230^\circ$ into NH₃ and 3-phenyl-1-methyluric acid, m. p. $>340^\circ$, converted by Me₂SO₄ and NaOH into 3-phenyl-1:7:9-trimethyluric acid, m. p. 229°. Cyanoacetyl-p-phenetylcarbamide, m. p. 228° (decomp.), prepared from p-phenetylcarbamide, CN·CHN₂·CO₂Et, and POCl₃ in AcOH-Ac₂O, gives with 30% NaOH 4-imino-3-p-phenetylbarbituric acid, m. p. 295—300° (decomp.), the 1-Me derivative, m. p. 211°, of which (Me₂SO₄ and NaOH) is converted by NaNO₂ and AcOH into 4-imino-3-p-phenetyl-1-methylvioluric acid, m. p. 235° (decomp.); this is reduced by Na₂S₂O₄ and NH₃ to 4:5-diamino-3-p-phenetyl-1-methyluracil, m. p. 210°. This, finally, is converted in the above manner into 4-imino-3-p-phenetyl-1-methyl- ψ -uric acid, decomp. 210—230°, 3-p-phenetyl-1-methyluric acid, m. p. $>310^\circ$, and 3-p-phenetyl-1:7:9-trimethyluric acid, m. p. 241°.

A P

Chlorophyll. XXII. Phaeoporphyrin a_6 , allomerisation of chlorophyll, and introduction of magnesium into chlorophyll derivatives. H. FISCHER, L. FILSER, and E. PLOTZ (Annalen, 1932, 495, 1—40).—At least three types of allomerisation are distinguished: (a) involving dehydrogenation accompanied by etherification (occurs only with chlorophyllides and benzoquinone in MeOH or EtOH in absence of air); reduction of the allomerised products with HI-AcOH gives phaeoporphyrin a_6 ,

(b) involving fission of the isocyclic ring whereby (possible) nuclear dehydrogenation occurs, under the action of atm. O_2 in MeOH or EtOH; reduction affords phaeoporphyrin a_- ; (c) dehydrogenation (?) unaccompanied by etherification of the OH group which is replaced (at least partly) by H; treatment is with benzoquinone, I, or air in MeOH, EtOH, $COMe_2$, or $CHCl_3$, and reduction gives phaeoporphyrin a_5 . Thus, the product from phaeophorbide a , benzoquinone, and MeOH in N_2 is degraded by HI-AcOH to rhodoporphyrin (I) and phaeoporphyrin a_5 (II) (as Me ester), whilst that from phaeophytin, benzoquinone, and EtOH in N_2 affords a trace of (I) and (II). The product from methylphaeophorbide a (III) and benzoquinone in MeOH is also reduced to (I) and (II) (as Me_2 ester). Contrary to Conant *et al.* (A., 1931, 1075), methyldehydrophaeophorbide a is not produced by oxidation of (III) with $K_3Mo(CN)_8$, since reduction (HI) gives the Me_2 esters of phaeoporphyrins a_5 and a_7 . These esters are also obtained similarly from the allomerised product (*oxime*) from (III), benzoquinone, and EtOH. (III) affords an *oxime*, degraded by 30% MeOH-KOH to verdoporphyrin and by HBr-AcOH at 160° to deoxyphyloerythrin. (III), HI, AcOH, and PH_4I in N_2 in the cold give a *leuco*-compound, oxidised (in 10% HCl solution) to (II) or phyloerythrin, whilst (III), 20% HCl, and a little KI in N_2 give rhodo- and pyrroporphyrins and (mainly) phyloerythrin. Phaeophytin is converted by EtOH-HCl into Me ethylphaeophorbide a (IV), which when decarboxylated and then reduced (HI-AcOH) affords phyloerythrin Et ester. The product from (IV), benzoquinone, and EtOH in N_2 is reduced to Me ethylphaeoporphyrin a_5 . Methylpyrroporphorbide a and 25% MeOH-KOH in O_2 give a purpurin-like compound (reduced to rhodoporphyrin), whilst with pyridine- Na_2CO_3 and subsequent reduction (HI), phyloerythrin results.

Methylchlorophyllide (V) is allomerised by benzoquinone-EtOH in N_2 to an amorphous compound, $C_{38}H_{40}O_6N_4Mg$, reduced (HI-AcOH) to a phaeoporphyrin a_6 ester (VI), m. p. 276° (*oxime*, m. p. 270°). The use of I for benzoquinone leads to the formation of (VI) and (II) (as ester), whilst with MeOH for EtOH, phaeoporphyrin a_6 Me_2 ester Me ether probably results. (V) and benzoquinone-*isoamyl* alcohol give, however, after reduction, (II) (as ester); in this case, etherification does not occur. (II) (as ester) is, of course, obtained from (V) and benzoquinone in an indifferent solvent (e.g., $CHCl_3$); (II) (as Me Et ester) is similarly produced by reduction of the product from ethylchlorophyllide and O_2-COMe_2 . Phaeophytin (VII) is allomerised by EtOH- H_2O_2 in absence of air; the product is reduced to (II) and converted by Me_2SO_4 and KOH into chlorin e and a trace of rhodin g . (II) is also produced from the allomerised products of (VII) and I-EtOH or benzoquinone-EtOH. Quinol has no action on (V), and (V) and (VII) are unaffected by diazomethane. The product from (V) and benzoquinone-EtOH is hydrolysed by 30% MeOH-KOH in pyridine to chlorin e and a rhodin, and by PrOH-KOH in Et_2O -pyridine to a purpurin; treatment with 4% HCl gives allomerised methylphaeophorbide. (VI) is hydrolysed by 10% MeOH-KOH in EtOH-pyridine to a green substance [spectroscopically

identical with that from (II) and PrOH-KOH] and (after esterification) an ester, $C_{36.37}H_{40.42}O_6N_4$, m. p. $230-233^\circ$ (spectroscopically identical with chloroporphyrin e_6 ester, but unlike this, not convertible into phaeoporphyrin a_6 ester), degraded by HCO_2H to rhodoporphyrin. (VI) is hydrolysed by 18% HCl to an isophaeoporphyrin a_7 Me_2 ester, $C_{36}H_{40}O_6N_4$ [Me_3 esters, m. p. 287° (diazomethane) and 248° (MeOH-HCl)], converted by HBr-AcOH at 50° or by fusion with succinic acid into phyloerythrin, by 20% oleum into phaeoporphyrin a_7 Me ester and rhodoporphyrin, by PrOH-KOH into a compound identical (spectrum) with rhodoporphyrin- γ -carboxylic acid anhydride, and by pyridine- Na_2CO_3 into a trace of rhodoporphyrin. Hydrolysis of (VI) with cold HBr-AcOH gives a porphyrin, $C_{37}H_{40}O_6N_4$, m. p. 269° , converted by diazomethane into (VI). Many of these results support the structure previously proposed (A., 1931, 1431) for phaeoporphyrin a_6 .

The ester groups of mesoporphyrin Me_2 ester react with $MgMeI$; removal of Mg from the product with 5% HCl gives a compound, $C_{38}H_{50}O_2N_4$, m. p. 295° . Phaeophytin a and $MgMeI$ afford a green substance (phase test negative). *Phyllins* are obtained from mesoporphyrin Me_2 ester and *ætio*- and pyrroporphyrins by treatment with $MgBr_2$ in pyridine at $150-160^\circ$.

H. B.

Iminazole-hæmatins. W. LANGENBECK (Ber., 1932, 65, [B], 842-845).—Hæmatin and glyoxaline in $CHCl_3$ -MeOH or pyridine give the additive product (I) $C_{34}H_{33}O_5N_4Fe \cdot 2C_3H_4N_2$. 4(5)-Methylglyoxaline and pilocarpine yield the compounds

$C_{34}H_{33}O_5N_4Fe \cdot 2C_4H_6N_2$ and $C_{34}H_{33}O_5N_4Fe \cdot 2C_4H_8O_2N_2$. The changes are time reactions probably of the third order. The compounds are very stable. The spectrum of (I) in alkaline solution has two bands at $589-567 m\mu$ and $552-527 m\mu$ when base is present in excess. A third band appears at $625-608 m\mu$, due to partial dissociation when the concns. of hæmatin and glyoxaline are of the same order of magnitude. A relationship is suggested between the iminazole-hæmatins and methæmoglobin.

H. W.

Action of ephedrine on benzaldehyde. W. DAVIES (J.C.S., 1932, 1580-1581).—"Benzylidene-ephedrine" obtained by condensation of ephedrine with $PhCHO$ has not the constitution assigned by Schmidt (A., 1914, i, 989), but is 2:5-diphenyl-3:4-

dimethyltetrahydro-oxazole, $\begin{array}{c} CHMe \cdot CHPh \\ NMe \cdot CHPh \end{array} > O$ m. p. 73.5° , since it contains no double linking, OH, or NH groups.

J. W. B.

Formation of furo-2:4-diazoles from acyl imidothiocarbonates and acyl pseudothiocarbamides. S. T. YANG and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 2066-2071; cf. A., 1904, i, 948).—Me benzoylimidothiocarbonate and NH_2OH in 95% EtOH at 0° give 3-methoxy-5-phenyl-1:2:4-oxadiazole (I), m. p. $58-59^\circ$; the 3-ethoxy-derivative has m. p. $49-50^\circ$. These compounds do not form salts with mineral acids, are unaffected by warm conc. HCl, do not react with NH_2Ph or $EtOH-NH_3$ (at $200-250^\circ$), but are decomposed by HI at 100° (with

the formation of BzOH). Reduction of (I) with Zn and AcOH gives some $\text{NH}_2\cdot\text{CO}\cdot\text{NHBz}$. $\text{NBz}\cdot\text{C}(\text{SMe})\cdot\text{NHPh}$ and NH_4OH give 3-anilino-5-phenyl-1:2:4-oxadiazole, m. p. 139—140°, which does not react with Ac_2O and is reduced to benzoylphenylguanidine. β -Chloroethyl benzoylthiocarbamate, m. p. 179—180°, results from $\text{CH}_3\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{Bz}\cdot\text{NCS}$.

C. J. W. (b)

Penthiazolines. I. Action of halogens on the dimethylmalonate additive product of allylthiocarbimide. D. E. WORRALE (J. Amer. Chem. Soc., 1932, 54, 2061—2066).—Allylthiocarbimide and $\text{CHNa}(\text{CO}_2\text{Me})_2$ in dry Et_2O give (after acidification) 66% of dicarbomethoxythioacetallylamide (I), $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{CH}(\text{CO}_2\text{Me})_2$, m. p. 42—43°, an alkaline solution of which decomposes when kept at room temp. (I) and N_2H_4 in EtOH give carboxythioacetallylamide (II), m. p. 120—121° (decomp.); with Br in CHCl_3 , Me 5-bromo-2-penthiazolylmalonate (III), m. p. 153—154° (5-Cl-, m. p. 145—146°, and 5-I-, m. p. 156—157°, derivatives). These halogeno-esters do not reduce KMnO_4 , do not react with MeI, and are recovered unchanged by decomp. of the additive compounds with MeMgI ; (III) decomposes in hot H_2O giving CO_2 and HBr. Me α -hydroxy-2-penthiazolylmalonate, m. p. 104—105°, is prepared from (III) and EtOH- AgNO_3 . 5-Chloro-, m. p. 179—180°, -bromo-, m. p. 188—190°, and -iodo-, m. p. 213—214°, -2-penthiazolylacetic acids (all $+2\text{H}_2\text{O}$) are obtained from (II) and the halogens in AcOH. (I), NaOMe, and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ in MeOH give 2-allylimino-3-dicarbomethoxy-4-ketotetrahydrothiophen, m. p. 78—79°. No definite product was isolated from allylthiocarbimide and $\text{CHMe}(\text{CO}_2\text{Me})_2$.

C. J. W. (b)

Synthesis of 2-acetylthiazoles. XI. D. W. MACCORQUODALE and T. B. JOHNSON (Rec. trav. chim., 1932, 51, 483—489).—Condensation of chloroacetylveratrole [from $\text{C}_6\text{H}_4(\text{OMe})_2$ and $\text{CH}_2\text{Cl}\cdot\text{COCl}$; best yield 20%] with α -benzoyloxypropionthioamide (A., 1931, 353) in boiling 95% EtOH affords 2-(α -benzoyloxyethyl) - 4-(3':4'-dimethoxyphenyl)thiazole, m. p. 86° (76% yield), hydrolysed by KOH in EtOH to the corresponding hydroxyethyl compound, m. p. 101—102° [also, in small yield, by methylation and hydrolysis of (I)], oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ and AcOH to 2-acetyl-4-(3':4'-dimethoxyphenyl)thiazole, m. p. 78.5—79.5°. 2- α -Benzoyloxyethyl-4-(3':4'-dihydroxyphenyl)thiazole (I), m. p. 157—159° (decomp.), is similarly obtained from chloroacetylpyrocatechol. Although, like chloroacetal, bromoacetal will not condense with K phthalimide, aminoacetal and phthalic anhydride heated in NPhMe, give phthalimidoacetal, b. p. 203—205°/20 mm., m. p. 75°, converted by heating with anhyd. $\text{H}_2\text{C}_2\text{O}_4$ into phthalimidoacetaldehyde. The Bz derivative, b. p. 170—171°/14 mm., of β -chloro- α -hydroxypropionitrile is obtained by the interaction of $\text{CH}_2\text{Cl}\cdot\text{CHO}$, NaCN, and BzCl. *p*-Acetamidobenzonitrile heated at 100° with a solution of triethanolamine in 95% EtOH saturated with H_2S at 0° gives *p*-acetamidobenzthioamide, m. p. 215° (decomp.), which with CH_2BzCl in EtOH and pyridine at 100° gives the Ac derivative, m. p. 199—200°, of 2-(*p*-amino-phenyl)-4-phenylthiazole, m. p. 146—146.5°, which by the Bart-Schmidt reaction affords *p*-(4-phenylthiazolyl-2-phenylarsinic acid, decomp. 300°.

J. W. B.

Condensation of $\alpha\alpha'$ -dibromo-dicarboxylic esters with thiocarbamides and synthesis of dithiazolidylmethane derivatives. R. G. ATKINSON and R. F. HUNTER (J.C.S., 1932, 1579—1580).—Et $\alpha\alpha'$ -dibromoglutarate (yield improved to 75%) condenses with $\text{CS}(\text{NHPh})_2$ or $\text{NH}_2\cdot\text{CS}\cdot\text{NHPh}$ in the presence of pyridine in EtOH to give, respectively, 2:2'-diphenylimino-, m. p. 210°, and 2:2'-di-imino-, m. p. 276° (decomp.), -4:4'-diketo-3:3'-diphenyl-5:5'-dithiazolidylmethane. Similar condensation could not be effected with Et $\alpha\alpha'$ -dibromocyclopentane-1:1-diacetate.

J. W. B.

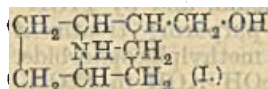
Behaviour of the pyridine group on electrochemical oxidation. III. Nicotine. M. YOKOYAMA (Bull. Chem. Soc. Japan, 1932, 7, 103—108; cf. this vol., 401).—The primary product of the anodic (PbO_2) oxidation of nicotine in dil. H_2SO_4 is oxynicotine, which is further oxidised to nicotinic, malonic, and formic acids. NH_2Me , CO, and CO_2 are also produced.

F. L. U.

Alkaloids of Anabasis aphylla. IV. N-Alkyl derivatives of anabasine and supposed occurrence of methylanabasine in A. aphylla. A. OREKOV and S. NORKINA (Ber., 1932, 65, [B], 724—729).—Anabasine is readily methylated with CH_3O and HCO_2H , but the method is inapplicable to the higher homologues. Exhaustive methylation with MeI is accompanied by addition at the *tert.* N atom; the best results are obtained with MeI in MeOH, but poorer results are yielded by the higher alkyl compounds. The most suitable method consists in converting anabasine by MgMeI into $(\text{C}_{10}\text{H}_{13}\text{N})\cdot\text{N}\cdot\text{MgI}$, which is treated with the requisite alkyl halide. The occurrence of N-methylanabasine in A. aphylla reported by Smith (this vol., 287) could not be confirmed; lupinine and anabasine are the only bases of low b. p. present. The following are described: N-methylanabasine, b. p. 127—128°/12 mm., $[\alpha]_D^{20}$ -85.1° [picrate, m. p. 237—238° (decomp.)]; picrolonate, m. p. 234—236° (decomp.); compound with HgCl_2 , m. p. 129° (decomp.); very hygroscopic hydrochloride; methiodide hydriodide, m. p. 245—247°; N-ethylanabasine, b. p. 123—124°/5 mm., $[\alpha]_D^{20}$ -63.5° [picrate, m. p. 186—187°]; picrolonate, m. p. 218° (decomp.); N-allylanabasine, b. p. 123—124°/6 mm., $[\alpha]_D^{20}$ -71.19 in EtOH (picrate, m. p. 189—190°; picrolonate, m. p. 195—197°); N-benzylanabasine, b. p. 170—171°/7 mm., m. p. 47—48°, $[\alpha]_D^{20}$ -22.5° in EtOH (picrate, m. p. 185°).

H. W.

Transformations of cocaine. II. J. VON BRAUN [with R. MICHAELIS and K. WEISSBACH] (Ber., 1932, 65, [B], 888—893; cf. A., 1918, i, 233).—Cocaine can be distilled in a high vac. (b. p. 187—188°/0.1 mm.) which causes depression of $[\alpha]_D$ from -15.8° to -13° in CHCl_3 without altering the m. p. Cyanococaine, $[\alpha]_D$ -22.7° in CHCl_3 , is converted successively into norecgonidine ester and dihydroecgonidine ester, b. p. 130—132°/12 mm. (chloroaurate, m. p. 133°), which is reduced by Na and abs. EtOH to norhomotropine (I), b. p. 154—156°/12 mm., $[\alpha]_D^{20}$ +18.59 m EtOH (chloroaurate, m. p. 220°; chloroplatinate, de-



comp. 230°; *picrate*, m. p. 180°); since successive treatment of Et 2:6-dimethylene-1:2:5:6-tetrahydropyridine-5-carboxylate with Na-EtOH and Pd-H₂ affords norhomotropine, $[\alpha]_D +18.8^\circ$, both products must be regarded as approx. sterically homogeneous. (I) and Et β -iodopropionate in C₆H₆ at room temp. afford Et β -2-hydroxymethylnortropylpropionate, b. p. 140—145°/0.3 mm. (non-cryst. *picrate* and *chloroplatinate*; *chloroaurate*, m. p. 98—101°); the Bz derivative is almost inactive pharmacologically.

3-Hydroxymethylpiperidine and Et β -iodopropionate yield Et β -3-hydroxymethylpiperidylpropionate, b. p. 146—148°/0.3 mm. (*hydrochloride* of Bz derivative, m. p. 187°); the *p*-nitrobenzoyl, m. p. 164°, is reduced to the non-cryst. *p*-aminobenzoyl derivative (very hygroscopic *dihydrochloride*, m. p. 96°). Both acyl derivatives are only very feeble anaesthetics. 2- β -Hydroxyethylpiperidine is transformed into Et 2- β -hydroxyethylpiperidylpropionate, b. p. 145—147°/0.2 mm. (*hydrochloride* of Bz derivative, m. p. 140°, and of *p*-nitrobenzoyl derivative, m. p. 131°, and *dihydrochloride* of *p*-aminobenzoyl derivative, m. p. 80—82°). Et β -N-methyl-N'- γ -benzoyloxypropylpropionate, from Et β -methylaminopropionate and γ -benzoyloxypropyl bromide, b. p. 215—217°/15 mm. (*hydrochloride*; *methiodide*, m. p. 124°), has no distinct anaesthetising action.

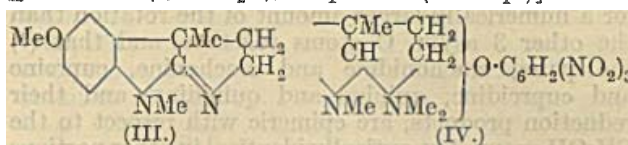
H. W.

A ring homologue of tropacocaine. B. K. BLOUNT and R. ROBINSON (J.C.S., 1932, 1429—1433).—Adipaldehyde, Ca acetonedicarboxylate, and NH₂Me condensed essentially by the method previously described (A., 1924, i, 1335) give about 18% of *N*-methylhomogranatone (duplohomotropinone) (I), an oil [*picrate*, m. p. 206° (decomp.); *methiodide*, m. p. 277° (decomp.); *dipiperonylidene* derivative, m. p. 209—210°], reduced by Na and BuOH to *N*-methylhomogranatoline, an oil [*picrate*, m. p. 236—237° (decomp.)]. The *O*-Bz derivative (as *hydrochloride*) (*picrate*, m. p. 175—177°) of this possesses strong local anaesthetic properties and is termed duplohomotropacocaine.

H. B.

Synthesis of physostigmine (eserine). VI. **Synthesis of *dl*-esermethole methopicate.** F. E. KING and R. ROBINSON (J.C.S., 1932, 1433—1438).—5-Methoxy-1:3-dimethyl-3- β -bromoethyl-2-indolinone (I) (this vol., 287) and MeOH-NH₃ at 150° give *di*-(5-methoxy-1:3-dimethyl-2-indolinone-3- β -ethyl)amine, m. p. 166—168°. 5-Methoxy-1:3-dimethyl-3- β -phthalimidoethyl-2-indolinone, m. p. 108—109°, from (I) and *o*-C₆H₄(CO)₂NK at 170° (bath), is hydrolysed (N₂H₄, H₂O method) to 5-methoxy-1:3-dimethyl-3- β -aminoethyl-2-indolinone (II) [*picrate*, m. p. 161—162°; *picrolonate*, m. p. 250° (decomp.)], converted by MeI into *dl*-dehydroesermetholemethine methiodide (*loc. cit.*). (II) is not reduced electrolytically, but with Na and amyl alcohol, 5-methoxy-1:3-dimethyl-3- β -aminoethylindoline, b. p. 113—116°/1 mm. [*picrate*, m. p. 159°; *picrolonate*, m. p. 220° (decomp.)], results. (II) is dehydrated by P₂O₅ in xylene at 170° (bath) to impure *dehydroesermethole* (III), b. p. about 145—155°/1 mm. [readily hydrolysed by acids to salts of (II)], reduced (H., Pt, EtOAc) to *dl*-*nore*esermethole

(III, -C \cdot N=CH \cdot NH \cdot), b. p. 130—132°/high vac. [*picrolonate* (+0.5H₂O), m. p. 227° (decomp.)]. This



with Me₂SO₄ (or MeI) and subsequent treatment with picric acid gives *dl*-esermethole methopicate (IV), m. p. 183—184°, which closely resembles the natural (active) salt (*loc. cit.*).

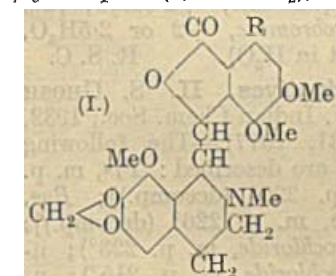
H. B.

Alkaloids of ergot. IV. **Complex group common to ergotoxine and ergotamine.** S. SMITH and G. M. TRIMIS (J.C.S., 1932, 1543—1544).—Ergotamine and ergotamine treated with *N*-KOH in MeOH under the same conditions as those used with ergotoxine and ergotinine (this vol., 526) also give NH₃ and the same base ergine, this half of the mol. having the same constitution in all four compounds.

J. W. B.

β - ψ -Gnoscopine. M. GREENWOOD and R. ROBINSON (J.C.S., 1932, 1370—1376; cf. Proc. C.S., 1910, 26, 228).—Me 6-nitroveratrate and boiling 10% NaOH give 6-nitrosovanillic acid (+2H₂O), yellow, m. p. 181° (decomp.) (shrinks and becomes colourless at 108°) [*Ac* derivative, m. p. 214° (decomp.)], nitrated to 2:6-dinitroisovanillic acid, m. p. 211° (lit. 206°), and converted by boiling with 40% CH₂O and HCl (*d* 1.16) into 6-nitro-3-hydroxy-4-methoxyphthalide, m. p. 221° (*Ac* derivative, m. p. 188°). This is methylated (Ag₂O-MeI in MeOH) to 6-nitro- ψ -meconine [also prepared from ψ -meconine by a modification of Salomon's method (A., 1887, 585)], which with cotarnine in boiling EtOH gives *nitro*- ψ -gnoscopine (I, R=NO₂), m. p. 186° [*hydrochloride*; *picrate*, m. p. 173° (decomp.)]. This decomposes in boiling AcOH into its components and is reduced by Sn and SnCl₂ in AcOH-conc. HCl to a mixture (cf. Hope *et al.*, A., 1931, 499) of *amino*- α - ψ -gnoscopine (I, R=NH₂), m. p. 235° (*Ac* derivative, m. p. 227°), and *amino*- β - ψ -gnoscopine (I, R=NH₂), m. p. 193° (*Ac* derivative, m. p. 163°), separable through their differing solubilities in MeOH. Iodo- β - ψ -gnoscopine (I, R=I), m. p. 222° (decomp.) (*picrate*, m. p. 187°), is reduced by Al-Hg in boiling MeOH to β - ψ -gnoscopine (I, R=H), m. p. 137—138°, m. p. (+MeOH) 80—82°, resolidifying with m. p. 136° (*picrate*, m. p. 216°), oxidised by dil. HNO₃ to cotarnine and ψ -opianic acid.

H. B.



Diastereomerism. VII. **Stereochemistry of the cinchona alkaloids.** H. EMDE [with N. FIDELMAN] (Helv. Chim. Acta, 1932, 15, 557—576; cf. A., 1930, 1456).—By application of the principle of optical superposition to (mostly) the hydrobromides of the cinchona alkaloids it is concluded that (*a*) the asym. C atom (4) carrying the second OH group is responsible for the fact that the alkaloids have

max. rotation when just above 2 equivs. of HCl are present in solution, (b) this C atom is responsible for a numerically larger amount of the rotation than the other 3 asym. C atoms together, and that (c) the pairs, cinchonidine and cinchonine, cupreine and cupreidine, quinine and quinidine, and their reduction products, are epimeric with respect to the CH·OH group, but optically identical in other portions of the mol. Reduction of the vinyl group decreases, and methylation of the phenolic group increases, the numerical val. (positive or negative) of the rotation, both changes being due to effects on C atom (4).

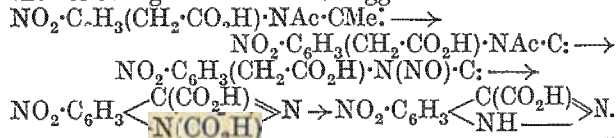
The following vals. are recorded, the purification of the bases being improved: cinchonidine, $[\alpha]_D^{25}$ -110° in 97% EtOH (dihydrobromide, $+2H_2O$, $[\alpha]_D^{25}$ -112.5° in H_2O); dihydrocinchonidine, m. p. 237° , $[\alpha]_D^{25}$ -95.8° in 99% EtOH, $[\alpha]_D^{25}$ -136.6° in H_2O + 3 mols. of HCl (vals. also given for varying concns. and amounts of HCl) (dihydrobromide, $+2H_2O$, $[\alpha]_D^{25}$ (anhyd. salt) -91.9° in H_2O); dihydrocinchonine, m. p. 112° , $[\alpha]_D^{25}$ $+42.9^\circ$ in 99% EtOH and $+38.7^\circ$ in H_2O + 3 mols. of HCl [hydrochloride, m. p. 230° (decomp.), $[\alpha]_D^{25}$ $+42.8^\circ$]; cinchonine, $[\alpha]_D^{25}$ $+229^\circ$ in 97% EtOH (dihydrobromide, $[\alpha]_D^{25}$ $+163.2^\circ$ in H_2O); dihydrocinchonine, m. p. 266° (decomp.) (Berl block), $[\alpha]_D^{25}$ $+150.5^\circ$ in abs. EtOH and $+220.1^\circ$ in H_2O + 3 mols. of HCl [hydrochloride, $+1.5H_2O$, $[\alpha]_D^{25}$ $+154.7^\circ$ (anhyd.) in H_2O ; dihydrobromide, $[\alpha]_D^{25}$ $+142^\circ$ in H_2O]; quinine, $[\alpha]_D^{25}$ -169° in EtOH [dihydrobromide, $+2H_2O$, $[\alpha]_D^{25}$ (anhyd. salt) -181.04° in H_2O]; dihydroquinine, hydrobromide, $+2H_2O$, $[\alpha]_D^{25}$ (anhyd.) -105.6° in H_2O , and dihydrobromide, $+2H_2O$, $[\alpha]_D^{25}$ -152.7° (anhyd. salt) in H_2O ; quinidine, $[\alpha]_D^{25}$ $+265^\circ$ in EtOH [dihydrobromide, $+2H_2O$, $[\alpha]_D^{25}$ $+209.5^\circ$ and $+210.7^\circ$ (anhyd. salt) in H_2O]; dihydroquinidine, $+2.5H_2O$, $[\alpha]_D^{25}$ $+265^\circ$ in EtOH (dihydrobromide, $+2$ or $2.5H_2O$, $[\alpha]_D^{25}$ $+196^\circ$ for anhyd. salt in H_2O). R. S. C.

Hydrocupreidine derivatives. II. S. GHOSH and N. R. CHATTERJEE (J. Indian Chem. Soc., 1932, 9, 83—85; cf. A., 1931, 1077).—The following ethers of hydrocupreidine are described: *Pr*^a, m. p. 182° [hydrochloride, m. p. 222° (decomp.)]; *Bu*^a, m. p. 176° [hydrochloride, m. p. 226° (decomp.)]; *n*-amyl, m. p. 164° (hydrochloride, m. p. 223°); *n*-heptyl, m. p. 158° (hydrochloride, m. p. 215°); *n*-octyl, m. p. 151° (hydrochloride, m. p. 210°); and *Bu*^b, m. p. 175° . A. A. L.

Yohimbe and quebrachine. Existence of isoyohimbine and identity of yohimbine and quebrachine. G. HAHN and F. JUST (Ber., 1932, 65, [B], 714—717; cf. Warnat, A., 1931, 243).—Re-examination of technical residue of the yohimbe alkaloids shows that isoyohimbine is not identical with yohimbine or α -yohimbine and that it is a subsidiary alkaloid of yohimbine. β -Yohimbine is a mixture of yohimbine and a further alkaloid which has not been isolated. *iso*-Yohimbine has $[\alpha]_D^{25}$ $+57.1^\circ$ in EtOH, $+108.8^\circ$ in pyridine. H. W.

Yohimbe alkaloids. VII. Oxidative degradation of diacetylyohimbine with nitric acid. G. HAHN and F. JUST (Ber., 1932, 65, [B], 717—724).—Oxidation of diacetylyohimbine with HNO_3 (1:1)

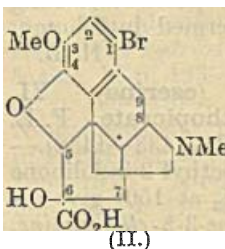
at 100° affords succinic acid (NH_4 H salt, m. p. $158-159^\circ$) and 6-nitroindazole-3-carboxylic acid ($+AcOH$), decomp. $277-282^\circ$ (*Et* ester, decomp. $264-266^\circ$), which loses CO_2 at $280-285^\circ$ with formation of 6-nitroindazole, decomp. 178° . 6-Nitro-1-methylindazole, m. p. 159° , and *Et* 6-nitro-1-methylindazole-3-carboxylate, m. p. 178° , are described. The indazole compounds are prepared also from *o*-toluidine or 5-nitro-*o*-toluidine and HNO_2 . The presence of the indazole complex in the yohimbine mol. is regarded as unlikely and the formation of nitroindazolecarboxylic acid is attributed to the action of HNO_2 on an *o*-aminophenylacetic acid group produced by degradation; if the oxidation is conducted in the presence of a large excess of carbamide, the formation of an indazolecarboxylic acid is not observed. Since in absence of carbamide yohimbine and yohimboic acid do not afford 6-nitroindazole-3-carboxylic acid, the following mechanism is suggested:



The N atom in indazolecarboxylic acid is the "latent" N of yohimbine which suffers abnormal acetylation. The constitution of yohimbine is discussed. H. W.

Thebainone. L. F. SMALL and D. E. MORRIS (J. Amer. Chem. Soc., 1932, 54, 2122—2123).—Pschorr's S-free ketone, obtained by hydrolysis of β -ethylthiocodide, is identical with the true thebainone of Schopf and Hirsch (A., 1931, 1313). C. J. W. (b)

Sinomenine. XXXI. 1-Bromosinomenilic acid and 1-bromosinomenilone. K. GOTO, H. SHISHIDO, and K. TAKUBO (Annalen, 1932, 495, 122—132).—The amorphous product from 1-bromosinomeninone (I) and Br (1 mol.) in AcOH at 16° is converted by warm 5% NaOH into 1-bromosinomenilic acid (II), m. p. 285° (decomp.) (sinters from 260°) [*Ba* salt; *Et* ester, m. p. 62° ; *Ac*, m. p. 265° (decomp.) and *Bz*, m. p. 267° , derivatives; methiodide, decomp. slowly from 180°], also formed (by a benzylic acid rearrangement) from 1-bromosinomenineketone and alkali, and in 30% yield from sinemeninone and Br (1 mol.). (II) gives negative $FeCl_3$ and $CH_2O-H_2SO_4$ reactions and is converted by 20% oleum at



$30-35^\circ$ into 1-bromosinomenilone [II, where $>C(OH) \cdot CO_2H = >CO$], m. p. 179° , $[\alpha]_D^{25}$ $+243.26^\circ$ in EtOH [oxime, m. p. 270° (decomp.)]; methiodide, m. p. 220° (decomp.)], in 30% yield. Sinomeninone and Br (3 mols.) or (I) and Br (2 mols.) in AcOH give 1:5:8-tribromosinomeninone hydrobromide (III), m. p. 235° (decomp.), reduced (Pd-charcoal, dil. AcOH) to (I). (III) is also reduced (Clemmensen) to 1-bromo- d - β -tetrahydrodeoxycodine and converted by aq. MeOH-NaOH into 1:7-dibromosinomenilic acid (IV), m. p. 225° [*Ba* salt, decomp. $213-230^\circ$; *Me* ester hydrochloride, m. p. $209-212^\circ$, decomp. 250° ; *Et* ester, m. p. 80° (hydrochloride, m. p. $234-236^\circ$); *Ac*, m. p. 202° , and *Bz*, m. p. 216° , derivatives;

methiodide, m. p. 213° (decomp.), which loses H_2O at 150°/vac. over P_2O_5 forming the lactide. (IV) is also obtained in 30% yield by the action of aq. NaOH on the product from 1-bromosinomenoneketone and Br (1 mol.), but not by bromination of (II). (IV) is reduced by Na-Hg in dil. NaOH to (II).

H. B.

Oxydimorphine. A. LEULIER and B. DREVON (Bull. Soc. Chim. biol., 1932, 14, 521—555).—The pptn. of oxydimorphine by a mixture of NaOAc and $\text{K}_3\text{Fe}(\text{CN})_6$ cannot be used as a sp. test in presence of morphine owing to oxidation of the latter. If a few drops of Ac_2O are poured on the surface of a H_2SO_4 solution of oxydimorphine, a green ring forms at the junction of the liquids; this colour reaction is sp. The transformation of morphine into oxydimorphine could not be demonstrated *in vivo*. Oxydimorphine is less toxic in guinea-pigs by virtue of the insolubility of its compounds and consequent pptn. at the site of injection.

P. G. M.

Alkaloidal reagents. III. Propadrine, its homologues and derivatives. J. C. MUNCH, F. C. CROSSLEY, and W. H. HARTUNG (J. Amer. Pharm. Assoc., 1932, 21, 463—467).—The behaviour of 17 alkaloidal reagents with adrenaline, ephedrine, and various analogous NH_2 -alcohols is described (cf. this vol., 157).

E. H. S.

Hydrolysis of arylthioarsinites. H. J. BARBER (J.C.S., 1932, 1365—1369; cf. A., 1929, 833).—In part a criticism of Gough and King's view (A., 1930, 796; cf. this vol., 70) that all thioarsinites undergo partial hydrolysis in weakly alkaline and neutral aq. solution. When equimol. mixtures of two arsinic acids (e.g., *p*-aminophenyl- and 3-acetamido-4-hydroxyphenyl-) are treated with thiolacetic acid (= 1 mol. of arsinic acid), the latter distributes itself between the two arsenicals (e.g., 28 and 72%, respectively). The change, $\text{Ar} \cdot \text{As}(\text{SR})_2 + \text{Ar}' \cdot \text{As}(\text{OH})_2 \rightarrow \text{Ar}' \cdot \text{As}(\text{SR})_2$, occurs (in neutral solution) with $\text{Ar} = \text{p-NH}_2 \cdot \text{C}_6\text{H}_4$ (I), $\text{Ar}' = 3$ -acetamido-4-hydroxyphenyl or 8-acetamido-3-hydroxy-1:4-benzisooxazinyl-6- (II), and $\text{R} = \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ [and in NaHCO_3] when $\text{Ar} =$ (I), $\text{Ar}' =$ (II), and $\text{R} = \text{CH}_2 \cdot \text{CO}_2\text{H}$. This is considered to be the most definite (but not conclusive) evidence for the hydrolysis of arylthioarsinites.

4-Chloro-3-nitrophenylarsinic acid and *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SH}$ in boiling EtOH give *di-p-tolyl 4-chloro-3-nitrophenylthioarsinite*, m. p. 88—90°; *di-p-tolyl 3-acetamido-4-hydroxyphenylthioarsinite*, m. p. 173—174°, is similarly prepared. Cacodylic acid and thiolacetamide in H_2O give *carbamyldimethyl dimethylthioarsinite*, m. p. 107°, oxidised by I in aq. NaHCO_3 (probably) thus: $2\text{AsMe}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2 + 3\text{I}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Me}_2\text{AsO}_2\text{H} + (\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2 + 6\text{HI}$. *Di(carboxymethyl) 4-amino-3-hydroxyphenylthioarsinite* (4-Ac derivative, m. p. 156—158°) has m. p. 161—162°.

H. B.

Arsinic acids of the fluorenone series. Derivatives of aminofluorenone-2-arsinic acid. G. T. MORGAN and (Miss) J. STEWART (J.C.S., 1932, 1634—1641).—By condensation of aminofluorenone-2-arsinic acid (I) with the appropriate chloro-acid amide in boiling *N*- NaOH are obtained: *fluorenone-7-glycinemethylamide* ($\text{Na} + 2\text{H}_2\text{O}$ salt), *-7-glycineanilide* ($\text{Na} + \text{H}_2\text{O}$ salt), and *-7-glycine-p-acetophenonylamide* (Na salt),

-2-arsinic acid. Trypanocidal activity decreases in this order, being absent in the last named. Homologues of 7-acetamidofluorenone-2-arsinic acid (A., 1931, 637) (15, 10) are prepared by interaction of (I) with the appropriate acid anhydride, and thus are obtained: *7-form-* ($\text{Na} + 3\text{H}_2\text{O}$ salt; 20, 20), *-propionyl-* ($\text{Na} + \text{H}_2\text{O}$; 5, 5), *-n-butyryl-* ($\text{Na} + 2\text{H}_2\text{O}$ salt), *-benz-* (Na and $\text{Na}_2 + \text{H}_2\text{O}$ salts), and *-oxalyl-* ($\text{Na}_2 + \text{H}_2\text{O}$ salt) *-amidofluorenone-2-arsinic acid*, the figures given in parentheses being, respectively, the min. lethal and curative doses in mg. per 20-g. mouse of those Na salts which exert a curative action (Yorke). The Na salt of (I) heated with $\text{H}_2\text{C}_2\text{O}_4$ at 180—190° gives *7-oxamido-pp'-fluorenone-2-arsinic acid* ($\text{Na}_2 + 4\text{H}_2\text{O}$ salt). Similar condensation with KCNO , MeNCO , PhNCO , and COCl_2 affords *7-carbamido-* ($\text{Na} + 2\text{H}_2\text{O}$ salt; 30, 15), *7-methylcarbamido-* ($\text{Na} + \text{H}_2\text{O}$ salt; 10—20, 20), *7-phenylcarbamido-* ($\text{Na} + 2\text{H}_2\text{O}$, and $\text{Na}_2 + 2\text{H}_2\text{O}$ salts only), and *7-ureidoamino-* (Na_2 salt) *-fluorenone-2-arsinic acid*. By the diazo-reaction (I) gives *7-hydroxyfluorenone-2-arsinic acid* ($\text{Na} + \text{H}_2\text{O}$ salt; 10—20, 5), which with Ac_2O gives the *7-acetoxy-derivative* ($\text{Na} + \text{H}_2\text{O}$ salt; 6, 3).

J. W. B.

Introduction of arsenic into the coumarin nucleus. II. M. GOSWAMI and H. N. DAS-GUPTA (J. Indian Chem. Soc., 1932, 9, 91—94; cf. A., 1931, 1316).—1:2- α -Naphthapyrone gives the (?)6- NO_2 -derivative, m. p. 180°, reduced by SnCl_2 in HCl to the NH_2 -derivative, m. p. 194°. This by the diazo-reaction gives α -*naphthapyrone*-(?)6-*arsinic acid*, m. p. above 360°. The following are similarly obtained from the corresponding NH_2 -compounds: *7-methyl-*, m. p. 290° (decomp.); and *4:7-dimethyl-coumarin-*, m. p. 285° (decomp.), and *4-methyl-1:2- α -naphthapyrone-6-arsinic acid*, m. p. above 360° (shrinks at 340°).

A. A. L.

Pyridine arsenicals. N. P. McCLELAND and R. H. WILSON (J.C.S., 1932, 1497—1500).—3-Chloromercurypyridine boiled with AsCl_3 affords the *hydrochloride* (I), $+ \text{H}_2\text{O}$ and anhyd., m. p. 216—233° with loss of HCl , of 3-pyridyldichloroarsine, which, however, contrary to Binz and others (A., 1929, 83), could not be obtained by the action of *N*- NaOH , 3:3'-dipyridylchloroarsine dihydrochloride being obtained. (I) heated with NaH_2PO_2 and conc. HCl , followed by NH_3 and oxidation of the resulting 3:3'-arsenopyridine with H_2O_2 , gives *3-pyridylarsinic acid*, m. p. 158—159° (*hydrochloride*, m. p. 196—198°), the properties of which differ considerably from those described by Binz (*loc. cit.*); contrary to Rath (A., 1931, 740) it is obtained in 6% yield from 3-aminopyridine by the Bart reaction. (I) heated with 3-pyridylarsenoxide (II) [by NaOH on (I)] gives *di-3-pyridylchloroarsine*, b. p. 207—210°/10 mm., as its *dihydrochloride*, m. p. 283—285°, from which *di-3-pyridylarsinic acid*, m. p. 203—204°, was similarly obtained. Distillation of (II) at 320—360°/10 mm. and oxidation of the product with H_2O_2 gives *tri-3-pyridylarsenoxide*, m. p. 226° (*hydrochloride*, m. p. 221° with loss of HCl).

J. W. B.

Quinquevalent boron. H. E. BENT and M. DORFMAN (J. Amer. Chem. Soc., 1932, 54, 2132—2133).— $\text{B}(\alpha\text{-C}_{10}\text{H}_7)_3$ and 40% Na-Hg in Et_2O in

absence of air and H_2O give the compound, $\text{C}_{30}\text{H}_{21}\text{BNa}_2$ ($+\text{Et}_2\text{O}$, which is lost at 175°), in which B completes its octet by taking two electrons from different atoms to give ionic linkings. C. J. W. (b)

Preparation of mercury dibenzyl. J. L. MAYNARD (J. Amer. Chem. Soc., 1932, 54, 2118—2120).— $\text{CH}_2\text{Ph}\cdot\text{HgI}$ and Na_2SnO_2 in dil. EtOH give 93.2% of $\text{Hg}(\text{CH}_2\text{Ph})_2$, m. p. 111° . C. J. W. (b)

Magnesium triphenylvinyl bromide. C. F. KOELSCH (J. Amer. Chem. Soc., 1932, 54, 2045—2048).—Triphenylvinyl bromide (I) forms a Grignard reagent which reacts normally with I , H_2O , CH_3O , PhCHO , BzCl , Bz_2O_2 , CO_2 , and CS_2 to give triphenylvinyl iodide, m. p. $125\text{--}126^\circ$; $\text{CPh}_2\cdot\text{CHPh}$; $\beta\gamma\gamma$ -triphenylallyl alcohol, m. p. $126\text{--}128^\circ$ (*Me*, m. p. $131\text{--}132.5^\circ$, and *Et*, m. p. $125\text{--}128^\circ$, ethers); crude $\alpha\beta\gamma\gamma$ -tetraphenylallyl alcohol (converted by $\text{AcOH}\text{--}\text{H}_2\text{SO}_4$ into 1 : 2 : 3-triphenylindene); Ph triphenylvinyl ketone; the enol benzoate of Ph benzhydryl ketone; triphenylacrylic acid, and triphenylvinylcarbithionic acid, m. p. 135° , respectively. Air (or O_2) and (I) give a yellow Et_2O -insol. compound, decomposed to a tar; SOCl_2 gives an oil, whilst CH_2PhCl and COPh_2 do not react; CPh_2Cl is reduced to CPh_3 , and COMe_2 is apparently condensed with the formation of mesityl oxide and $\text{CPh}_2\cdot\text{CHPh}$. C. J. W. (b)

Action of halogen on aryl selenocyanates. O. BEHAGHEL and H. SEIBERT (Ber., 1932, 65, [B], 812—816).—Diazotisation of NH_2Ph and treatment of the solution with NaOAc followed by KSeCN affords Ph selenocyanate (I), b. p. $117\text{--}118^\circ/11\text{ mm.}$, and varying amounts of Ph_2Se , b. p. $149\text{--}150^\circ$ (identified as the dibromide, m. p. 144°). (I) and $\text{KOH}\text{--}\text{MeOH}$ or $\text{NH}_3\text{--}\text{EtOH}$ yield Ph_2Se_2 , m. p. 62.5° , HCN , and $\text{H}_2\text{C}_2\text{O}_4$. The action of Br in CHCl_3 or CCl_4 converts (I) into *Se Ph bromide*, b. p. $107\text{--}108^\circ/15\text{ mm.}$, m. p. 62° . Excess of Br as vapour or in CCl_4 or CHCl_3 transforms (I) into *Se Ph tribromide*, m. p. 105° . SePhBr with Zn dust in Et_2O , C_6H_6 , or, preferably, PhMe affords Se_2Ph_2 , also obtained from SePhBr_3 . Phenylseleninic acid is prepared by hydrolysis of SePhBr or SePhBr_3 by H_2O or alkali. H. W.

Metallic derivatives of thiophen. III. Germanium, antimony, tellurium, and boron thienyls. E. KRAUSE and G. RENWANZ (Ber., 1932, 65, [B], 777—784; cf. A., 1929, 1092).—The action of excess of Mg 2-thienyl bromide on GeCl_4 in Et_2O affords *Ge tetra-2-thienyl*, m. p. $149\text{--}150^\circ$ (corr.). *Sb tri-2-thienyl*, m. p. $49\text{--}49.5^\circ$, obtained similarly, is very sensitive to air. In Et_2O in presence of air it slowly gives the pure, inorg. oxide. H_2O_2 causes elimination of at least one thienyl group. I in Et_2O gives SbI_3 and 2-iodothiophen, whereas Cl_2 and Br afford the corresponding dichloride, m. p. 229° (corr., decomp.), and dibromide, m. p. 182.5° , transformed into the oxide, m. p. 217° (corr., decomp.), by KOH but not by Ag_2O . Sb and Bi tri-2-thienyl and Sn and Pb tetra-2-thienyl with AgNO_3 give an organo-silver compound. In C_6H_6 , air or 3% H_2O_2 has little action on Bi tri-2-thienyl. With Cl_2 (Br, I) in CCl_4 an almost completely inorg. ppt. and halogenothiophen are produced. Sn Ph_2 thienyl and HgCl_2 in hot EtOH yield HgPhCl , m. p. 252° , also produced from the Pb

compound, whereas Sn tetra-2-thienyl gives Hg thienyl chloride, m. p. 183° , and Pb tetra-2 thienyl gives an immediate yellow colour followed by pptn. of PbCl_2 . Te di-2-thienyl, m. p. 50.5° , gives ppts. with O_2 in Et_2O or with H_2O_2 and (?) the product $\text{HgCl}_2\cdot 2\text{C}_4\text{H}_5\text{S}$ with HgCl_2 . Te di-2-thienyl methiodide readily decomposed into its components when heated and hence has indef. m. p. $106\text{--}115^\circ$ according to rate of heating. $\text{Te}(\text{C}_4\text{H}_5\text{S})_2\text{I}_2$ is converted by MgMeI into $\text{Te}(\text{C}_4\text{H}_5\text{S})_2$; similar reduction is effected by $\text{Na}_2\text{S}_2\text{O}_3$ in $\text{EtOH}\text{--}\text{H}_2\text{O}$. BF_3 is converted by Mg 2-thienyl bromide and treatment of the product with H_2O into 2-thienylboric acid, $(\text{C}_4\text{H}_5\text{S})\text{B}(\text{OH})_2\cdot\text{H}_2\text{O}$, m. p. 134° (corr.). H. W.

Physical and chemical properties of polypeptides containing glutathione (S·S) and their behaviour towards erepsin, trypsin-kinase, and cathepsin. E. ABDERHALDEN and W. GEIDEL (Fermentforsch., 1932, 13, 160—165).—The following polypeptides and precursors were prepared: glutathione, d- α -bromoisohexoylglutathione from d- α -bromoisohexoyl chloride, $[\alpha]_D^{20} +51.6^\circ$; di-(1-leucyl)glutathione (S·S·) (I), m. p. about 165° (decomp.), $[\alpha]_D^{20} -39.5^\circ$; di(chloroacetyl-1-leucyl)glutathione (S·S·) (II), m. p. about 180° (decomp.), $[\alpha]_D^{20} -52.4^\circ$; di-(d- α -bromoisohexoyl)glycyl-1-leucylglutathione (S·S·) (III), m. p. about 135° (decomp.), $[\alpha]_D^{20} -35.8^\circ$; di(chloroacetyl-1-leucyl)glycyl-1-leucylglutathione (S·S·) (IV), m. p. 175° (decomp.), $[\alpha]_D^{20} -50.6^\circ$. In these polypeptides the glycyl group increases and the l(-)-leucyl group lowers the l-rotation. Erepsin hydrolyses (I)—(IV) (more readily as chain-length increases), trypsin-kinase only (III) and (IV), cathepsin none of the polypeptides. J. H. B.

Casein. I. Its heterogeneity; fractionation by ammonium chloride. E. CHERBULIEZ and M. L. SCHNEIDER (Helv. Chim. Acta, 1932, 15, 597—609).—Casein is dissolved by aq. solutions of neutral salts in the order $\text{NH}_4\text{Cl} > \text{MgSO}_4 > \text{sea salt} > \text{NaCl} > (\text{NH}_4)_2\text{SO}_4$. It is separated by 5% NH_4Cl into α - (insol.) and β - (sol.) ppts. by COMe_2 fractions, apparently without degradation. These occur in the proportions 1 : 5 to 1 : 8 (cows' milk), and have the same equiv. wt. (NaOH titration) and empirical formula except for P and S; they differ in solubility in pyridine, flocculation by $(\text{NH}_4)_2\text{SO}_4$, and coagulation by rennin. H. A. P.

Identification of methionine in the keratin of ox-horn. E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1932, 207, 191—192).—Methionine was isolated from the products of acid hydrolysis of ox-horn. J. H. B.

Detection of oxygen in organic liquids by iodine. H. WUSTNER (Z. anal. Chem., 1932, 88, 194—195).—The method for the detection of O in org. compounds described by the author (this vol., 529) has a more extensive application than that described by Piccard (A., 1922, ii, 389). The method does not apply to substances which also contain S. M. S. B.

Determination of arsenic in organo-arsenic derivatives. I. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1932, 9, 95—97).—Compounds containing As^V liberate an equiv. amount of I from KI in conc. HCl or HCl-AcOH solution. A. A. L.

Determination of methyl alcohol in presence of ethyl alcohol. F. S. MORTIMER (Trans. Illinois State Acad. Sci., 1931, 24, 279—283).—Vals. of n are tabulated for $\text{EtOH-H}_2\text{O}$ and $\text{MeOH-H}_2\text{O}$ mixtures; from the factors derived the % of EtOH and MeOH in a mixture can be calc. CH. ABS.

Ammoniacal fuchsin solution as a reagent for aldehydes. A. B. WANG (Nat. Centr. Univ. Nanking, Sei. Rep., 1931, A, 1, 21—26).—A sensitive reagent (times for colour development tabulated) is prepared from 0.05 g. of rosaniline in 100 c.c. H_2O and 2 c.c. aq. NH_3 , excess of NH_3 being removed by boiling, diluted to 200 c.c. with CO_2 -free H_2O . CH. ABS.

Microchemistry of saccharin. M. WAGENAAR (Mikrochem., 1932, 11, 132—135).—Saccharin is best identified microscopically by means of its compounds with Cu^{II} salts and $\text{C}_5\text{H}_5\text{N}$ (limit 0.02 mg.), with HgCl_2 (0.01 mg.), or with I in aq. KI (0.01 mg.). F. L. U.

Potentiometric determination of papaverine and its synthetic derivatives. B. ISSEKUTZ (Magyar Gyóg. Társas. Ert., 1931, 7, 429—436; Chem.

Zentr., 1931, ii, 3644).—Papaverine, eupaverine, and perparine were determined potentiometrically in 0.01—0.05*N*-HCl using the quinhydrone electrode. The equiv. point changes according to the concn. of the alkaloid between p_H 3.9 and 4.80. L. S. T.

Determination of furfuraldehyde and methylfurfuraldehyde as the 2:4-dinitrophenylhydrazones. E. SIMON (Biochem. Z., 1932, 247, 171—177).—Furfuraldehyde and methylfurfuraldehyde may be determined gravimetrically by pptn. with 2:4-dinitrophenylhydrazine in HCl, the ppt. being dried at 110—115° to const. wt. P. W. C.

Alkaloidal reagents. II. Aromatic monohomocyclic derivatives. J. C. MUNCH, F. S. CROSSLEY, and W. H. HARTUNG (J. Amer. Pharm. Assoc., 1932, 21, 341—348).—The behaviour of 17 alkaloidal reagents with hydroxy-, amino-, amino-hydroxy-, and alkyl-benzenes is given (cf. A., 1931, 1438). E. H. S.

Determination of dissolved volatile solvents in water and other liquids. F. ROTH (Gesundheitsing., 1931, 54, 674; Chem. Zentr., 1932, i, 975).—A finely-divided stream of air is passed through the liquid and then through a bulb tube to an absorption vessel containing active C. After 3—4 hr. the volatile solvent is removed in the usual way from the C and measured. A. A. E.

Biochemistry.

Manometric determination of respiration in intact mammalian lung. H. LASER (Biochem. Z., 1932, 248, 9—15).—The method and apparatus are described. The R.Q., Q_{O_2} , of the lung of young rats is 7.8 and is max. in air, decreasing in 10% O_2 (90% N_2). The respiration in 20% O_2 is not inhibited by the presence of 80% CO . Anaerobic formation and aerobic disappearance of $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ are small. P. W. C.

Diffusion and chemical reaction velocity as joint factors in determining the rate of uptake of oxygen and carbon monoxide by the red blood-corpuscle. F. J. W. ROUGHTON (Proc. Roy. Soc., 1932, B, 111, 1—36).—The rates of uptake and release of O_2 and CO from the red blood-corpuscle are not identical with the corresponding vals. for hæmoglobin solution. This is due to one or more of three factors: diffusion through the corpuscular membrane, diffusion within the corpuscle, and the chemical reaction inside the corpuscle. Formulae are developed for the rate of uptake of O_2 and CO by a layer of hæmoglobin solution of the same concn. and thickness as in the corpuscle. These lead to max. and min. solutions which indicate the true solution with an accuracy of $\pm 10\%$. The rates of uptake of O_2 and CO by corpuscles and by hæmoglobin indicate the following reductions in (a) diffusion through corpuscular membrane and (b) diffusion within the corpuscle for the reactions studied when compared with the corresponding rates for hæmoglobin solution:
 $\text{nb} + \text{O}_2 \longrightarrow \text{HbO}_2$, (a) not known, (b) 75% or more;
 $\text{Hb} + \text{CO} \longrightarrow \text{HbCO}$, (a) <40%, (b) 33%; $\text{HbO}_2 \longrightarrow$

$\text{Hb} + \text{O}_2$, (a) <70%, (b) <50%; $\text{HbCO} + \text{O}_2 \longrightarrow \text{HbO}_2 + \text{CO}$, (a) negligible, (b) negligible. F. O. H.

Cryptohæmin. E. NEGELEIN (Biochem. Z., 1932, 248, 243—245).—Ordinary cryst. (but not recryst.) blood-hæmin contains about 0.2% of a cryst. ketoporphyrin *cryptohæmin* (most probably $\text{C}_{33}\text{H}_{32}\text{O}_5\text{N}_4$). Introduction of Fe into cryptohæmin gives a cryst. hæmin possibly identical with that observed by Anson and Mirsky (A., 1925, i, 1476). Cryptohæmin also occurs in bakers' yeast. It combines with globin to yield a hæmoglobin which reversibly binds CO and O_2 . It is possibly the hæmin of the O_2 -carrying enzyme and of the MacMunn histo-hæmatin of longest wave-length. W. M.

Isoelectric points and dissociation constants of natural and denatured globin. M. LAPORTA (Austral. J. Exp. Biol. Med. Sci., 1932, 9, 69—81).—By electrometric titration of solutions in NaOH and HCl the following vals. have been obtained for (a) natural and (b) denatured ox globin: isoelectric point: p_H (a) 7.33, (b) 8.37; p_{K_a} (a) 6.34, (b) 6.53; p_{K_b} (a) 8.30, (b) 10.27. The isoelectric points of denatured globin from ox, horse, pig, and dog are very similar. The use of urea as solvent for protein in electrometric titration is advantageous and similar vals. are obtained. R. K. C.

Validity of determination of colloid-osmotic pressure of serum. A. H. TURNER (J. Biol. Chem., 1932, 96, 487—498).—Many different types of membrane are used in the Krogh-Nakazawa apparatus. J. B. B.

Colloid-osmotic ("onkotic") pressure. X. Simplified clinical onkometry. XI. Onkotic pressure in different animals. XII. Effect of various substances on the colloid-osmotic pressure in serum. E. KYLIN and H. VON PEIN (*Z. ges. exp. Med.*, 1931, 76, 549—560; *Chem. Zentr.*, 1932, i, 965).

Changes in the blood-serum produced by injection of concentrated serum and by plasmatic bleeding. C. ACHARD, J. LÉVY, and F. GALLAIS (*Compt. rend.*, 1932, 194, 1773—1777).—Serum from a dog when conc. in vac. and intravenously injected into the same animal resulted in a lowered hydration of the serum-colloids as evidenced by the changes in viscosity with rise of temp. The dehydration persisted for several hr. and was accompanied by an increase in total serum-proteins. In dogs removal of whole blood also produced a dehydration, whereas if the corpuscular fraction of the shed blood was returned to the animal by injection the dehydration was not apparent. The bearing of these phenomena on the cedema of Bright's disease is discussed.

F. O. H.

Serum-proteins of the eel and their change with salinity. S. FIRLY and M. FONTAINE (*Compt. rend.*, 1932, 194, 1854—1856).—The serum-proteins of eels from fresh H_2O are considerably lowered on transference to sea-water for some days. The reverse process occurs on transference to fresh H_2O of eels habituated to sea-water, but the proteins increase more slowly.

F. O. H.

Critical temperature of serum. Ultra-violet absorption spectrum of horse serum. P. L. DU NOÛY and M. L. DU NOÛY (*Compt. rend.*, 1932, 194, 1815—1817).—Normal serum exhibits feeble absorption at 300—400 $m\mu$, whilst at 260—290 $m\mu$ strong absorption occurs with a max. at 275 $m\mu$. The absorption diminishes at 250—255 $m\mu$ and increases almost linearly at the region of 220 $m\mu$. Heating at 55° for 10 min. increases the absorption at 275 $m\mu$ and decreases it at 250—255 $m\mu$. Heating at 65° for 10 min. in addition to increasing the absorption at 275 $m\mu$ also increases that at 250—255 $m\mu$.

F. O. H.

Iodine index of blood. I. Absorption of iodine by blood. M. DELAVILLE and L. KOWARSKI. II. Experimental application. L. KOWARSKI (*Bull. Soc. Chim. biol.*, 1932, 14, 660—667, 668—681).—I. The term "I index" is proposed for the mg-equiv. of I fixed by 100 g. of tissue. The kinetics of I combination indicate that for the apparent index to equal the theoretical index the reaction must be total and irreversible. The reaction, however, is reversible but with excess of I the two indices approximate.

II. The application of the theoretical basis to the determination of glutathione and other substances reacting with I is discussed.

F. O. H.

Determination of iron in blood and biological fluids. A. BERNHARD and I. J. DREKTER (*Science*, 1932, 75, 517).—Ethylene glycol Bu ether + Et_2O (equal vols.) satisfactorily replaces $C_5H_{11}OH$ and Et_2O in extracting $Fe(CNS)_3$. The colour is more intense and does not fade during 24 hr. L. S. T.

Blood-calcium in fasting men. R. NICOLAYSEN (*Biochem. Z.*, 1932, 248, 275—277).—During the course of 24 hr. the Ca content of the blood of fasting men may vary irregularly by as much as 2 mg. per 100 c.c. and the max. variation from day to day may reach 3 mg. per 100 c.c. Administration of Ca lactate before the fasting period may result in a rise in the content.

W. M.

Determination of magnesium in blood with 8-hydroxyquinoline. D. M. GREENBERG and M. A. MACKAY (*J. Biol. Chem.*, 1932, 96, 419—429).—Mg in oxalated whole blood and plasma is determined by adding to the protein-free filtrate 1% NH_4Cl , conc. aq. NH_3 , and a 1% $EtOH$ solution of 8-hydroxyquinoline, and warming at 70—80° for 20—30 min. The ppt. is washed with 2% aq. NH_3 and 95% $EtOH$ and more 2% aq. NH_3 , dried, and dissolved in hot HCl . To the HCl solution are added 50% KBr and standard $KBrO_3$ solutions. After shaking for 1 min. 20% KI is added and the excess of I titrated with $Na_2S_2O_3$. Serum-Mg is determined in the same way after removal of Ca.

H. D.

Blood-sugar and -chloride curves. J. PUYAL and J. CASTELLANO (*Anal. Fis. Quím.*, 1932, 30, 224—227).—In accordance with the tendency to preserve osmotic equilibrium it is found that the successive increase and decrease of blood-sugar following oral administration of glucose are accompanied by a decrease and increase, respectively, in blood- Cl' , whilst when $NaCl$ is injected intravenously there is an analogous, but smaller, inverse variation of blood-sugar with blood- Cl' .

R. K. C.

Reducing substances of blood. Glucose and non-fermentable reducing substances. R. J. PICKARD (*Bull. Soc. Chim. biol.*, 1932, 14, 598—613).—With nephritic blood hyperglycemia may occur without increase in the non-fermentable fraction. The part played by glutathione in the non-fermentable reducing fraction was investigated.

F. O. H.

Effect of amino-acids on blood-sugar. I. KANAI (*Biochem. Z.*, 1932, 248, 383—388).—In rabbits intravenous administration of NH_2 -acids (glycine, glycyglycine, alanine, glutamic acid hydrochloride, asparagine) and of mixtures of NH_2 -acids (hydrolysed vegetable protein and hydrolysed caseinogen) leads to increases of up to 40 mg. per 100 c.c. in the blood-sugar, these increases usually being proportional to the amounts of material given. If the administration is peroral the amounts of material must be greatly increased (2—5 times) in order to produce the same results, which are irregular in both cases. Of the acids used hydrolysed vegetable protein had the greatest, glycine and glycyglycine the least, effect on the blood-sugar.

W. M.

Factors influencing the blood-sugar level of dairy cattle. R. E. HODGSON, W. H. RIDDELL, and J. S. HUGHES (*J. Agric. Res.*, 1932, 44, 357—365).—The blood-sugar val. (mg. per 100 c.c.) of calves decreases from about 100 at one week to a mean level of 53 at 2 years, and is subsequently uninfluenced by age. Vals. are temporarily increased by excitement or by administration of glucose, and are higher

in cows and heifers during œstrus. No change accompanies feeding, but fasting causes a depression.

W. G. E.

Changes of blood-sugar in decapods. F. C. STOTT (Biochem. Z., 1932, 248, 55—64).—The blood-sugar of different fasting decapods (*Carcinus maenas*, *Portunus depurator*, *P. puber*, *Hyas araneus*, *Cancer pagurus*) is very small but increases very greatly both on feeding and on moving the animals out of O_2 .

P. W. C.

Plasma-catalase. Y. TAKIZAWA (Tohoku J. Exp. Med., 1931, 18, 223—238).—Ligation of the bile duct increases plasma-catalase; bile constituents appear within 0.5 hr. The red cells become more resistant to hæmolysis and the serum inhibits the hæmolytic action of saponin.

CH. ABS.

Appearance of invertase in blood-serum or urine after parenteral injection of sucrose. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1932, 13, 228—243).—After parenteral injection of sucrose into dogs, the urine contains invertase but not proteolytic defence enzymes. On renewal of the injection the invertase reappears more rapidly than at the first injection.

J. H. B.

Appearance of lactase in blood-plasma or -serum or in urine after parenteral injection of lactose. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1932, 13, 291—297).—After parenteral injection of dogs with lactose a lactase appears in the blood-plasma or -serum and in the urine. Considerably less inversion of sucrose is observed.

J. H. B.

Specificity of defence enzymes using fibrinogen and fibrin or peptones of high mol. wt. prepared from these. Species, age, and sex specificity. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1932, 13, 166—200).—After subcutaneous injection of fibrin or fibrin peptones, proteases are produced in the blood-plasma or -serum or urine, sp. for the fibrin employed. An age- and sex- in addition to species-specificity is observed. Proteases are present in fibrin from whipped blood and are unsp. They are absent from pure plasma unless induced by injection of protein or fibrin, in which case they are sp. The unsp. proteases are inhibited and the sp. are accelerated by serum. The whipped blood proteases arise from cell decomp.; they are inactive after boiling. Boiled fibrin is hydrolysed by serum or urine of pregnancy, but not by that of non-pregnant persons or by animal serum.

J. H. B.

Significance of electrolytes of the axons of nerve fibres. A. B. MACALLUM (Austral. J. Exp. Biol., 1932, 9, 159—172).—A review of micro-chemical methods for demonstrating the occurrence of inorg. ions (K, Cl, PO_4 , Fe, and possibly Na) in the various parts of nerves and a discussion of the significance of results obtained.

W. M.

Brain and nutrition. E. SCHMITZ (Biochem. Z., 1932, 247, 224—245).—Tables summarise the fresh wt., the H_2O and dry substance contents, and the distribution of phosphatide, cholesterol, and cerebroside in the two hemispheres of the same animal (guinea-pigs, rabbits, cats), the lipin fractions in cats being

obtained with normal nutrition and after administration of lecithin.

P. W. C.

Chemistry of the antigen of brain. I. H. RUDY (Biochem. Z., 1932, 248, 426—436).—Antigen from brain (ox) is freed from phosphatides and cerebroside by pptn. with $CdCl_2$ and from cholesterol by extraction with Et_2O . After removal of the phosphatides and cerebroside (and without removal of the sterol) adsorption on $Al(OH)_3$ and elution with $EtOH$ leads to further purification. Chemical examination of the purified material has not revealed any connexion between composition and activity.

W. M.

Determination of cholesterol and cholesteryl esters in muscle. E. BAUER (Z. physiol. Chem., 1932, 208, 1—8).—The pulp is dried by mixing with Na_2SO_4 , extracted with $COMe$, and then with Et_2O , and the free cholesterol determined by digitonin pptn. The ester is hydrolysed by $NaOEt$ and the cholesterol determined by the digitonin micro-method (A., 1923, ii, 344).

J. H. B.

Lecithin. V. A. PERTZOFF and M. AISNER (Urusvati J., 1932, 2, 133—148).—Various arrangements of the fatty acids in egg lecithin give a possibility of 18 different lecithins from this source. A lecithin free from cephalin may be obtained by extracting the $CdCl_2$ derivatives with solvents, $EtOH-CCl_4$ and $-C_6H_6$ mixtures being the most effective. The products are mixtures, since their solubilities depend on the amount of solid phase present. Indications of the presence of lecithins with only one fatty acid were obtained. The Cd in the $CdCl_2$ derivatives may be determined by electrolysis, which may also be used to recover the lecithin.

A. A. L.

Determination of choline in animal tissues. A. BOLAFFI (Annali Chim. Appl., 1932, 22, 205—220).—The procedure consists in adding $HAuCl_4$ soln. before evaporation. This prevents decomp. during subsequent concn. Choline is then pptd. from the alcoholic concentrate by phosphotungstic acid. The ppt. is decomposed with $Ba(OH)_2$, Ba is pptd. by excess of H_2SO_4 , and from the acid solution choline is pptd. as choline periodide by I-KI reagent. The periodide is titrated with 0.01N- $Na_2S_2O_3$ in $CHCl_3$ solution. The errors are $\pm 2\%$ in defect.

O. F. L.

Acetylcholine in warm-blooded animals. IV. C. BISCHOFF, W. GRAB, and J. KAPFHAMMER (Z. physiol. Chem., 1932, 207, 57—77; cf. A., 1931, 1320).—From all the organs and tissues (except the uterus) of cattle examined acetylcholine was isolated as Reinecke salt. It was present in human placenta. The amount present in whole animals (guinea-pig, dog, cat, rabbit) was isolated and determined.

J. H. B.

Glycogen and water storage in the liver. H. L. PUCKETT and F. H. WILEY (J. Biol. Chem., 1932, 96, 367—371).—The livers of albino rats, killed after being fed on varying diets, show const. $H_2O\%$ with varying quantities of glycogen. Hence glycogen retains proportionally as much H_2O as the non-carbohydrate solids of the liver.

H. D.

Glycogen and water storage in the liver. E. M. MACKAY and H. C. BERGMAN (J. Biol. Chem., 1932,

96, 373—380).—The % of H_2O in the livers of rabbits fed on varying diets showing different glycogen contents is relatively const. H. D.

Glycogen and water storage in the liver. E. M. BRIDGE and E. M. BRIDGES (J. Biol. Chem., 1932, 96, 381—386; cf. A., 1931, 1325).—The validity of the deductions of Puckett and Wiley and of MacKay and Bergman (preceding abstracts) is questioned, and the authors reaffirm that from the data available it is unjustifiable to define an exact relationship between glycogen storage and the H_2O content of the liver. II. D.

Pigment of the skin of the gold-fish. A. WEISSBERGER and H. BACH (Naturwiss., 1932, 20, 350).—The pigment from the dried scales and fins of gold-fish (*Carassius auratus*) is completely extracted by light petroleum giving a golden-yellow solution exhibiting the characteristic carotenoid reaction with $SbCl_3$. The residue left on evaporation of the solvent reacts with atm. O_2 to give a colourless product. W. R. A.

Pigmentary system and the Dopa reaction. E. BOYD (Proc. Roy. Soc. Edin., 1932, 52, 218—235).—The colour produced in solutions of 3:4-dihydroxyphenylalanine by oxidation with H_2O_2 increases with concn. of the substrate, is max. in presence of a suitable concn. of H_2O_2 , increases with rise of temp. over the range observed (0—55°), and is increased by NaOH, but decreased by HCl. The deposition of the pigment is max. at p_H 7.4. The Dopa oxidase reaction may be used in the analysis of the genetics of the pigmentation of animal hair. W. O. K.

Staining of fixed cell-structures. G. YAMAHARA (Sci. Rep. Tokyo Bunrika Daigaku, 1932, B1, 1—21).—Staining is not affected by fixatives in low concn. but, in more conc. solution, $HgCl_2$, EtOH, and CH_2O intensify the colour, whilst $CCl_3 \cdot CO_2H$ and HNO_3 diminish it. The p_H of the fixative has an appreciable effect. Fixation with EtOH+AcOH allows good differential nuclear staining. P. G. M.

Union of biocolloids. V. S. J. VON PRZYLECKI and S. KISIEL (Biochem. Z., 1932, 247, 1—7).—Part of the uric acid of tissues is readily removed by washing and part must first be liberated by hydrolysis, the amount of the two fractions being very different for different tissues. A method for determination of these fractions is described and applied to hen's and human muscle and liver. P. W. C.

Composition of gum from silk of *Bombyx mori*. E. ABDERHALDEN and O. ZUMSTEIN (Z. physiol. Chem., 1932, 207, 141—146).—The NH_2 -acids present in silk-gum differ from those of the fibroin. In the former, *l*(—)-tryptophan and *l*(+)-norvaline are present. Oxidation of the gum with HNO_3 gave norisoscacharic and saccharic acids, indicating the presence of chitosamine and probably of glucuronic acid. J. H. B.

State of calcium and of phosphoric acid in cow's milk. C. PORCHER and J. BRIGANDO (Compt. rend., 1932, 194, 1539—1541).—The colloidal residue when milk is filtered through a porcelain candle, and consisting of caseinogen together with Ca and H_3PO_4 , was redispersed (1) in the filtrate and (2) in distilled H_2O . The resulting suspension was coagulated by

rennin in case (1), but not (2) until sol. Ca salts were added. The results of Piettre (cf. this vol., 78) are criticised on the grounds that dialysis against solutions of Na salts may by double decomp. alter the state of the Ca combined with the casein. W. O. K.

Caseinogen complexes and calcium caseinophosphates in milk. M. PIETTRE (Compt. rend., 1932, 194, 1988—1991).—Mainly a reply to Porcher and Brigando (preceding abstract). The deduction that all the colloidal phosphate in milk is not in the same degree of micellar aggregation is confirmed (this vol., 78). J. W. B.

Application to milk of Jolles' reaction for indican. C. HERVIEUX (Compt. rend., 1932, 194, 1603—1604).—Pure thymol in the absence of indoxyl does not give a colour under conditions employed in Jolles' reaction (cf. Porcher and Tapernoux, this vol., 295) but impure thymol may do so. In the presence of pure lactose a reddish tint is developed in the reaction; hence modification is necessary in the application to milk. W. O. K.

Occurrence of uncoupled bile-acids in human bile. R. SCHÖNHHEIMER, E. ANDREWS, and L. HRDINA (Z. physiol. Chem., 1932, 208, 182—184).—In a case of human biliary fistula with biliary cirrhosis of the liver, considerable amounts of uncoupled bile-acids (cholic and deoxycholic acids) were isolated from the bile in cryst. form. J. H. B.

Relation of bile-acid formation to fat and carbohydrate components. L. SCHINDEL (Arch. exp. Path. Pharm., 1932, 166, 36—41).—An unsuccessful attempt was made to influence bile-acid secretion by feeding 3- and 4-C chains (succinic, fumaric, pyruvic acids and dihydroxyacetone). J. B. B.

Participation of the spleen in the formation of bile-pigment. Cause of tolylenediamine icterus jaundice. T. NAEGELI and F. MEYTHALER (Arch. exp. Path. Pharm., 1932, 165, 571—582).—In dogs the concn. of bilirubin in the splenic vein and in the peripheral circulation rises during and after stasis of the blood in the spleen. The spleen thus appears to play a rôle in the genesis of bile-pigments, at least under pathological conditions, but in this function it is closely associated with the liver. Blockage of the circulation of the spleen results in an abnormally low degree of jaundice after tolylenediamine poisoning. The jaundice produced by tolylenediamine is probably of the resorption type and the spleen plays an important rôle in its production. W. O. K.

Hydrolysable phosphorus compounds of saliva and urine. F. AXMACHER (Biochem. Z., 1932, 248, 231—242).—The presence of hydrolysable P in saliva and urine is detected, and from the rate of hydrolysis, the presence of at least two P fractions is suggested, one of which probably arises from the conversion of $H_4P_2O_7$ into H_3PO_4 . Oral administration of $Na_4P_2O_7$ increases readily hydrolysable urinary P. When $Na_4P_2O_7$ is intravenously infused into animals, although the blood-P increases by >100%, only a small part (7.2%) is excreted in the urine and most is therefore either hydrolysed or combined. An enzyme which hydrolyses pyrophosphate at p_H is detected in saliva but not in urine. P. W. C.

Urinary acid-base balance. CHATRON (J. Pharm. Chim., 1932, [viii], 15, 510—527).—The production of NH_3 by the kidney is considered to be an attempt to neutralise abnormal amounts of any acid and not, as postulated by Goiffon, primarily of org. acids.

P. G. M.

Determination of bases, particularly magnesia, in urine. R. NICOLAYSEN (Biochem. Z., 1932, 248, 278—279).—A method for the determination of Na, K, Ca, and Mg in small amounts of urine is described.

W. M.

Occurrence of methylamine in urine. R. KAPPELLER-ADLER and K. TODA (Biochem. Z., 1932, 248, 403—425; cf. A., 1931, 1185).—The NH_2Me in dogs' urine is partly of endogenous and partly of exogenous origin and its amount is doubled as a result of a diet rich in meat. $\text{NH}_2\text{Me}\cdot\text{HCl}$, given perorally, is destroyed in the organism and such administration of arginine does not lead to increase in the NH_2Me content of the urine. Betaine, given by the mouth, is apparently partly demethylated, since it leads to increased excretion of NH_2Me , and such excretion is increased three- to six-fold by giving creatine or creatinine. In man, male urine contains less NH_2Me than does female and the NH_2Me content of the urine is affected by various physiological and pathological conditions, but is independent of the total N excretion. It follows that, in addition to creatinine, NH_2Me is a biological degradation product of creatine. W. M.

Occurrence of pyridine derivatives in normal urine. W. LINNEWER and H. REINWEIN (Z. physiol. Chem., 1932, 207, 48—56).—Trigonelline [with which Kutscher's gynesine (A., 1906, ii, 875) is probably identical] was isolated from various samples of normal urine. The occurrence of methylpyridinium hydroxide was confirmed.

J. H. B.

Determination of "uroselectan" in urine. J. PUYAL and I. TORRES (Anal. Fis. Quím., 1932, 30, 222—223).—Addition of $\text{N}\cdot\text{HCl}$ to the urine ppts. "uroselectan acid" (5-iodo-2-hydroxypyridone- N -acetic acid). This is removed, and the filtrate is titrated with NaOH . The difference between the titre and that before injection indicates the amount of "uroselectan," 0.029 g. corresponding with 1 c.c. 0.1N-HCl.

R. K. C.

Sugar of normal urine. I. The phenyl-osazones. M. R. EVERETT and F. SHEPPARD (J. Biol. Chem., 1932, 96, 431—441).—Phenylsemicarbazide was isolated from normal urine by treatment with $\text{NHPh}\cdot\text{NH}_2$; this substance was probably confused with a pentosazone by other workers. Increased concn. of urine, increased acidity, prolonged heating, and the previous formation of HCNO by hydrolytic procedures all favour phenylsemicarbazide formation.

H. D.

Identification of glucose and lactose in urine by the osazone reaction. E. J. BIGWOOD and J. SNOECK (Bull. Soc. Chim. biol., 1932, 14, 570—597).—For the detection of glucose and lactose by osazone formation in untreated urine the presence of at least 0.2 and 1.0% respectively is necessary. A technique for the formation of the osazones using $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$ in $\text{AcOH}\text{--}\text{NaOAc}$ solution is described. The urine

(5 c.c.) is first pptd. with $\text{Hg}(\text{OAc})_2$ or Lloyd's reagent and preliminary reduction tests before and after fermentation are performed. Urine giving a positive Benedict test may be utilised directly for the osazone test; a glycosuria <0.1—0.2% necessitates preliminary treatment. For the recognition of lactosazone in lactosuria associated with glycosuria a recrystallisation of the osazone derived from non-pptd. urine is essential; in addition consideration must be given to the fermentation test. The crystal habits of osazones from normal and pregnancy urines are described.

F. O. H.

Behaviour of homogentisic acid in normal and alkaptonuric sera. R. HURTHLE (Z. klin. Med., 1931, 119, 14—18; Chem. Zentr., 1932, i, 832).—The degradation of homogentisic acid depends on the but not on the nature, of the solvent; it is unattacked in acid solution.

A. A. E.

Synthetic homogentisic acid. G. KATSON and R. HURTHLE (Z. klin. Med., 1931, 119, 10—13; Chem. Zentr., 1932, i, 835).—Synthetic homogentisic acid is chemically and biologically identical with acid isolated from alkaptonuric urine.

A. A. E.

Beri-beri and neuritis. H. H. WOOLLARD (Austral. J. Exp. Biol., 1932, 9, 173—178).—Although there are significant differences between the results of deprivation of food and those of deprivation of vitamin-B only, there is no satisfactory evidence that, in the second case, toxic factors are involved. Experimental deprivation of the vitamin does not cause characteristic neuritis nor are nervous manifestations an essential feature of such deprivation.

W. M.

Cancer-producing substances. J. E. NYROP (Protoplasma, 1932, 15, 294—300).—In many cases carcinogenic agents are active only when particles of C etc. are also present. Low-boiling tar is not, whilst tar produced at 850° is, carcinogenic. Substances with a low energy of ionisation, e.g., $\text{CH}_2\text{Ph}\cdot\text{OH}$, should be effective therapeutic agents, since they protect the glycolysis-producing centres by adsorption.

P. G. M.

Metabolism of tumours. III. Phosphatases. S. EDLBACHER and W. KUTSCHER (Z. physiol. Chem., 1932, 207, 1—15; cf. A., 1931, 1180).—The activity of the nucleotidase of liver and tumours is increased by COMe_2 extraction of the tissue. The COMe_2 removes an inhibitor of the enzyme. HCN , cysteine, glutathione, and Cu^{++} also inhibit nucleotidase. The natural inhibitor may be glutathione. The nucleotidases of liver and mouse carcinoma behave similarly with regard to inhibition and activation by COMe_2 . The activation of nucleotidase in liver-pulp shown by HCN , cysteine, and glutathione at concns. <M/333 may be due to the high heavy metal content of this organ. The hexosephosphoric acid fission by liver is less strongly inhibited by HCN and practically unaffected by cysteine and glutathione, in contrast to the corresponding enzyme of mouse carcinoma which behaves like the nucleotidase in respect of inhibition.

J. H. B.

Presence of tyrosine and other free amino-acids in a non-pigmented naevocarcinoma. R. MONCEAUX and H. GODARD (Compt. rend., 1932,

194, 1987—1988).—The presence of free tyrosine (and small amounts of other NH_2 -acids) in a non-pigmented naevocarcinoma was proved by isolation after extraction with $\text{H}_2\text{O}-\text{CHCl}_3$. Maceration with glycerol showed the absence of oxidases, thus accounting for the non-conversion of the chromogen into melanin. J. W. B.

Normal tissues as a possible source of inhibitors for tumours. J. B. MURPHY and E. STURM (Science, 1932, 75, 540—541).—Extracts from normal tissues, the placenta, and embryo of the mouse showed an inhibiting effect in carcinoma grafts on the mouse with one type of carcinoma but not with another. L. S. T.

Fat of dermoid cysts. A. DIMTER (Z. physiol. Chem., 1932, 208, 55—61).—The fat of dermoid cysts contained 7.5% of cerebrosides, 20.9% of unsaponifiable matter, and 20% of a hydrocarbon which is probably squalene. J. H. B.

Examination of the fat of dermoid cysts for substances of special biological importance. G. BEHME (Z. physiol. Chem., 1932, 208, 62—66).—The fat of ovarian dermoids contained much steryl ester. Saturated sterols were present; unsaturated, absent. Monoglyceryl esters could not be detected. Ergosterol was indicated by its colour reaction and the biological action of the irradiated fat. Vitamin-A and oestrus hormone were lacking. J. H. B.

Effect of opium on blood-sugar. R. N. CHOPRA, J. P. BOSE, and N. N. DE (Indian Med. Gaz., 1931, 66, 625—627).—Opium ($\frac{1}{8}$ grain doses) may reduce blood-sugar in early and mild diabetes, but increases it in severe cases. In some subjects urinary sugar disappears, whilst blood-sugar increases. Normally, or in nephritis, small or moderate doses have no effect on blood-sugar. CH. ABS.

Eclampsia. I. Relationship between glycogen and the detoxicating function of the placenta. II. Glycogen content of the eclamptic placenta. M. MURAKAMI (Tôhoku J. Exp. Med., 1931, 11, 298—319, 320—326).—I. Detoxication by solutions of liver- or placenta-glycogen increases with the concn. Eclamptic placenta is less effective.

II. In eclampsia the placenta contains less glycogen than normally. CH. ABS.

Increase in blood-posterior pituitary hormone, and symptoms of nephropathy and eclampsia in pregnancy. K. J. ANSELMINO and F. HOFFMANN (Arch. Gynakol., 1931, 147, 621—643; Chem. Zentr., 1932, i, 963).—In normal pregnancy the antidiuretic substance was not detected in the blood. In nephropathy and eclampsia it was present in 19 of 21 cases. A. A. E.

Change in blood-thyroid hormone in nephropathy and eclampsia of pregnancy. F. HOFFMANN and K. J. ANSELMINO (Arch. Gynakol., 1931, 147, 645—651; Chem. Zentr., 1932, i, 963).—In the blood in nephropathy the content of thyroid hormone is smaller than in normal pregnancy; in eclampsia it is greater. A. A. E.

Lipins and proteins of non-purulent effusions. M. MACHEBŒUF and N. FETHKE (Bull. Soc. Chim.

biol., 1932, 14, 507—520).—The difference between exudates and transudates is physical rather than chemical; the dilution, not the proportion, of the components varies. In a case of neoplastic dropsy with a cryst. deposit (cholesterol etc.) in the ascitic fluid, a disturbance of the lipo-protein complexes is postulated. P. G. M.

Chemistry and metabolism in experimental yellow fever in *Macacus rhesus*. V. A. M. WAKEMAN and C. A. MORRELL (Arch. Int. Med., 1932, 49, 826—835).—Serum-albumin decreases steadily from the onset of the disease, whilst the globulin increases in the initial stages and thereafter falls. There is a tendency for reduction of the alkali-reserve, accompanied by increased serum-P and increased excretion in the urine both of phosphates and org. acids. P. G. M.

Occurrence of iodine in relation to endemic goitre in New Zealand; iodine metabolism. C. E. HERCUS, H. A. A. AITKEN, H. M. S. THOMPSON, and G. H. COX (J. Hyg., 1931, 31, 493—522).—Most artificial manures, but particularly superphosphates, increase the I content of crops. Considerable time is required for adjustment of I metabolism. Iodised salt is most effective when associated with a meat diet. Excretion of I decreases much more in fasting than on a low-I diet. The blood-I is subnormal in simple goitre but variable in Graves' disease. About 12% of the body-I of white rats is normally in the thyroid, but the ratio varies with the I intake. CH. ABS.

Sugar elimination in obstructive jaundice. II. Injection of sugars. III. Injection of sugars in conjunction with bile acids. S. OKAMURA (Arch. Med. Okayama, 1931, 2, 471—504, 505—532).—II. The glycogen content of the (dog's) liver indicates that glycogen is synthesised from sugars in the order: fructose, glucose, mannose, galactose. Five days after production of jaundice the synthesis of glycogen shows no proportionality with the urinary sugar.

III. The elimination of glucose injected intravenously into dogs with experimental jaundice is subnormal and that of fructose above normal. The introduction of bile acids stimulates glycogen synthesis from glucose or fructose. Hence the inability of the liver in experimental obstructive jaundice to synthesise glycogen is due to a lowering of the production of bile acids by the liver. CH. ABS.

Proteolytic leucocytic enzyme in leucæmia. J. V. COOKE (Arch. Int. Med., 1932, 49, 836—845).—The non-granular leucocytes have, as a rule, a high protease activity, although the enzyme content decreases in the terminal stages. The seat of the disturbance is the bone marrow. P. G. M.

Growth in height and weight and retention of nitrogen, calcium, and phosphorus during recovery from severe malnutrition. G. STEARNS and D. L. R. MOORE (Amer. J. Dis. Children, 1931, 42, 774).—The N retained per kg. became greater, and the Ca equiv. to that retained by rapidly growing normal infants. CH. ABS.

Porphyrins in clinical and experimental porphyrinuria. H. FISCHER and R. DUESBERG (Arch.

exp. Path. Pharm., 1932, 166, 95—100).—In two cases of porphyrinuria uroporphyrin I was isolated from the urine. In congenital porphyrinuria a small amount of a different porphyrin, probably coproporphyrin III, was obtained from the urine. In experimental Pb poisoning in rabbits the urine appeared to contain coproporphyrin III. In sulphonal poisoning uroporphyrin was formed. The faeces of Pb- or sulphonal-poisoned rabbits contained no coproporphyrin, but an ester, perhaps impure deuterio-III-porphyrin ester, was isolated. J. B. B.

Acid-base equilibrium in psychotic patients. Affective psychoses. K. E. APPEL, C. B. FARR, and P. J. HODES (J. Nerv. Mental Dis., 1932, 75, 22—33).—The blood-Cl and plasma-total base are normal in maniac-depressive psychosis. There is an increased but insignificant "acid-residue" in involutional depressions. Plasma- CO_2 was normal except in complicated cases. CH. ABS.

Causes and origin of "incurable" rickets and the serum-phosphorus of the rachitic animal. A. VAN HARREVELD (Arch. Neerl. Physiol., 1931, 16, 234—243; Chem. Zentr., 1932, i, 3626).—Rats fed with diet deficient in vitamin-B and protein and free from P developed rickets which was incurable by administration of cod-liver oil, although this increased the serum-P. Vitamin-D administered with the diet has a partly prophylactic effect. A. A. E.

Additional factors in the treatment of late rickets and osteomalacia. D. C. WILSON (Lancet, 1932, 222, 1142—1143).—Waste distillery yeast after irradiation in direct sunlight is a source of vitamin-D in the treatment of late rickets. L. S. T.

Mineral metabolism in late rickets. G. STEARNS, M. J. ORLKE, and J. D. BOYD (Amer. J. Dis. Children, 1931, 42, 88—101).—During recovery, children (12—13 yr.) retain ample Ca and P. Excretion of Ca and P is similar to that during recovery from infantile rickets, except that the urinary Ca remains low. Serum-Ca is normal, whilst -inorg. P may remain low. The acid-base relationships and the total fixed base retained are normal. CH. ABS.

Phosphorus balance in the rat on a rachitic diet rich in calcium, strontium, or magnesium. A. ROCHE (Bull. Soc. Chim. biol., 1932, 14, 634—644). In rats fed with a rachitic diet rich in Ca and poor in P the occurrence of bone lesions coincides with a diminution or abolition of P absorption; after several weeks the balance becomes positive and spontaneous healing occurs before the P deficit is recovered. Addition of SrCO_3 to the diet leads to a decrease in wt. of the animal and an increasing negative P balance terminating in death. CaCO_3 and MgCO_3 exhibit the same action but to a smaller degree. The bearing of these findings on PO_4 retention and on ossification is discussed. F. O. H.

Effect of feeding rachitic diets, containing different ratios of calcium to phosphorus, on the calcium and inorganic phosphorus of the blood-serum of chicks. O. N. MASSENGALE (Poultry Sci., 1929, 8, 335—343).—With a rachitic diet low in Ca but high in P, leg weakness appeared earlier than with a rachitic diet low in P but higher in Ca. When

the Ca content was higher than the P content the blood-serum-Ca was higher than -P. The reverse held with diets high in P and low in Ca. Addition of cod-liver oil to rachitic diets increased the serum-Ca regardless of the food Ca : P ratio. Addition of cod-liver oil to rachitic diets in which the P content was approx. 3 times that of the Ca tended to lower the serum-inorg. P; when the Ca was higher than the P the serum-inorg. P was increased. CH. ABS.

Effect of sodium and potassium on experimental scurvy. A. MICHAUX (Bull. Soc. Chim. biol., 1932, 14, 649—659).—The urinary excretion of Na in the normal guinea-pig is far less than that of K. Scurvy is accompanied by a fall in the vol. of urine and in the amounts of Na and K excreted. The Na is retained as NaCl in the muscle and blood, but with K there also occurs a decrease in the muscle and blood levels, indicating that elimination must take place in the faeces. During advanced experimental scurvy there is a marked fall in the K of the whole blood and a slight rise in the serum level. F. O. H.

m-Amino-p-hydroxyphenylarsine oxide as an antisyphilitic agent. A. L. TATUM and G. A. COOPER (Science, 1932, 75, 541—542).—The therapeutic index of m-amino-p-hydroxyphenylarsine oxide in rabbit syphilis is higher than that of any known antisyphilitic agent. Clinical treatment in human beings is promising. L. S. T.

Intermediate metabolism of guinea-pigs infected with trypanosomes. G. SCHEFF (Biochem. Z., 1932, 248, 168—180).—The metabolism of guinea-pigs infected with trypanosomes proceeds in general similarly to that of rats, but is of longer duration. The essential changes are a hypoglycaemia, the lowest vals. being reached shortly before death, a hyperglycaemia following the disappearance of the trypanosomes, a hyperlipaemia in the advanced stages of infection, considerable decrease of glycogen, and increase in neutral fat in the liver, also in the later stages. P. W. C.

Behaviour of liver-lipins in experimental infections. G. SCHEFF and E. HORNER (Biochem. Z., 1932, 248, 181—188).—The changes of liver-fat in guinea-pigs due to trypanosome infection, poisoning with diphtheria toxin, infection with *B. paratyphosus-B*, type Breslau, and poisoning with P are investigated. With diphtheria toxin, no infiltration of fat occurs, liver-fat eventually completely disappearing, although the other fat reserves are retained intact. Paratyphosus infection does not appear to have any sp. influence on the fat-carbohydrate metabolism. In trypanosome and P poisoning considerable increase in liver neutral fat and disappearance of glycogen occur. The liver-phosphatide and -sterol contents remain practically unchanged in all cases. P. W. C.

Urinary acidity in tuberculosis. K. L. McCLUSKEY (Amer. Rev. Tuberculosis, 1931, 24, 182—192).—The p_H is high; in crit. illness the $[\text{H}^+]$ is lower owing to decrease in titratable acidity with increase in NH_3 . Creatine and creatinine decrease. Variations in night and day excretion of H^+ , NH_3 , and org. acids are recorded for various groups of

patients. The mild acidosis is at first met by conservation of blood-alkali, this being later depleted by increase in urinary NH_3 . CH. ABS.

Proportions of water and other inorganic constituents in the heart muscles of tuberculous individuals. L. C. SCOTT (Amer. Rev. Tuberculosis, 1931, 23, 429—434).—The H_2O content is high, but other inorg. constituents are normal. CH. ABS.

Distribution of diffusible and non-diffusible calcium in phthisis. F. B. COOPER (Amer. Rev. Tuberculosis, 1931, 24, 346—350).—The vals. and the total Ca are normal. CH. ABS.

Phosphorus in blood and plasma of people suffering from phthisis. M. W. MARSMAN (Arch. Néerl. Physiol., 1932, 17, 124—131).—In the blood or plasma of 30 tuberculous patients the inorg. P, acid-sol. P, and total P did not differ significantly from corresponding vals. for 10 normal individuals, but the lipid P in both blood and plasma was significantly less in the tuberculous patients. W. O. K.

Calcification following massive doses of viosterol in acute experimental bovine tuberculosis of guinea-pigs. T. T. WALKER and T. D. SPIES (Amer. Rev. Tuberculosis, 1931, 24, 65—71).—Calcification within the caseous lesion is more marked than when viosterol is not used. Ca is deposited also in apparently normal tissue of the heart, liver, and kidneys of tuberculous animals treated with viosterol. CH. ABS.

Effect of viosterol (irradiated ergosterol) on calcification in pulmonary tuberculosis. J. KAMINSKY and D. L. DAVIDSON (Amer. Rev. Tuberculosis, 1931, 24, 483—489).—Small oral doses increased the serum-Ca but did not appreciably affect the degree of calcification in the lung lesions. CH. ABS.

Comparison of the effects of viosterol in acute experimental avian and bovine tuberculosis. T. D. SPIES and T. T. WALKER (Amer. Rev. Tuberculosis, 1931, 24, 723—728).—Administration of repeated large doses to guinea-pigs with acute avian tuberculosis causes little or no increase in the calcification of the lesions or within otherwise normal parenchyma of certain organs. The degree of Ca deposition is much less marked than in acute bovine tuberculosis. CH. ABS.

Vitamin-D in bone tuberculosis in children. H. G. GRAYZEL, M. J. SHEAR, and B. KRAMER (Amer. Rev. Tuberculosis, 1931, 24, 106—112).—Relatively large doses of irradiated ergosterol (equiv. to 0.6—1 litre of cod-liver oil daily) did not increase the serum-Ca or -P and caused no toxic symptoms, pathological calcification, or acceleration of healing of bone tuberculosis in children. CH. ABS.

Lysozyme and tuberculosis. H. J. CORPER (Amer. Rev. Tuberculosis, 1932, 25, 59—66).—Lysozyme, prepared from dog or guinea-pig liver or spleen, has no appreciable inhibitory effect on tubercle bacilli *in vitro* and probably plays no significant part in human susceptibility to tuberculosis. CH. ABS.

Relationship between the water content and oxygen consumption of the organism. W. R. DURYEE (Science, 1932, 75, 520).—Experiments with *Planaria dorotocephala* and *Amblystoma punctatum* are summarised. H_2O changes appear to be both inter- and intra-cellular, but no general conclusions can be reached. L. S. T.

Thermoelectric determination of metabolism in tissue cultures. E. TIEDEMANN and A. FISCHER (Biochem. Z., 1932, 247, 68—84).—A method for the determination of the CO_2 -production of tissue cultures employing the principle of the different thermal conductivities of gases is described. The apparatus detects 0.0004% CO_2 , the accuracy being $\pm 0.02\%$ CO_2 . Inserting a manometer, the O_2 -utilisation is also obtained in the same experiment. The apparatus is readily adapted to self-registration. P. W. C.

Cell metabolism. C. SELLEI, P. WEINSTEIN, and J. JANY (Biochem. Z., 1932, 247, 146—150).—The metabolism of the retina and of the grey matter of the brain can be characterised by the heat quotients in virtue of their marked tendency to glycolysis. For both tissues the inhibition of the Pasteur reaction and the absence of the decreasing action of respiration on glycolysis are also characteristic. P. W. C.

Metabolism of sympathetic nerves and ganglia. H. ROSENBAUM (Biochem. Z., 1932, 247, 189—215).—The mean utilisations of O_2 by ox splenic nerve in blood and Ringer's solution respectively are at room temp. 65.3 and 63.7 cu. mm. and at 37° 541.8 and 547.6 cu. mm. per g. per hr. Young animals give vals. about 27% higher. In nervous tissue a respiratory substance is present which diffuses into inorg. salt solutions; it is also present in serum and blood and is inactivated by heat. Addition of glucose to Ringer's solution at 37° causes considerable increase of O_2 consumption. Trustworthy figures could not be given for the O_2 utilisation of sympathetic ganglia. P. W. C.

Sugar metabolism of stimulated nerve. H. WINTERSTEIN and H. FRANKEL-CONRAT (Biochem. Z., 1932, 247, 178—188).—Reflex stimulation of the isolated frog's spinal cord and of the cord in mammals increases, by several hundred % of the resting vals., the rate of sugar disappearance from the surrounding solution. P. W. C.

Glycogen formation in the livers of rats fed on a pure fat diet. Sugar formation from fat. R. KAPELER-ADLER and M. RUBINSTEIN (Biochem. Z., 1932, 248, 196—207).—On a pure fat diet (lard corresponding with 25—40 g.-cal. per day per 100 g. body-wt.), the mean total carbohydrate content of rat's liver is 2.5% (normal vals.). Small doses of adrenaline (0.05 mg. hydrochloride per day per 100 g. body-wt.) and cocaine (0.2 c.c. of a 4% solution of the hydrochloride per day per 100 g. body-wt.) do not change the carbohydrate vals. With larger doses of adrenaline (0.1 mg. daily for 5 days) the liver-glycogen falls to about $\frac{1}{2}$ and of cocaine (0.4 c.c. daily for 6 days) to about $\frac{1}{3}$. When the small doses of adrenaline and cocaine, which individually are inactive, are given together, the liver-carbohydrate is

decreased to $\frac{1}{2}$. Phloridzin with and without addition of adrenaline causes a decrease of liver-carbohydrate to With insulin, the carbohydrate vals. were subnormal, but were not uniform. The fat contents of the livers were very variable and could not be correlated with the carbohydrate vals. No support was obtained for the view that fat is converted into carbohydrate.

P. W. C.

Bile acids and carbohydrate metabolism.
XVI. Production of glycogen in muscle by bile acids and hormones. K. FUJIZAWA (Biochem. Z., 1932, 248, 264—274; cf. this vol., 644).—Increased production of glycogen resulting from administration of cholic acid to rabbits occurs not only in the liver but also, to a much slighter degree, in the muscles. The cholic acid administration also counteracts the hyperglycemia produced by glucose, but is much less effective in this respect than is insulin. Both in liver and muscle the glycogen-producing power of cholic acid is much greater than that of insulin; there is synergy, which is much more pronounced in liver than in muscle, between the actions of the two substances. Cholic acid and adrenaline act antagonistically with regard to their effect on the production of glycogen, this antagonism being much more pronounced in liver than in muscle, but the decrease in the production of glycogen caused by adrenaline is much greater in muscle than in liver, whereas when phloridzin is the active agent the opposite is the case. As regards production of glycogen in liver and muscle, cholic acid and phloridzin exhibit antagonism equally pronounced in both organs and the latter substance has no effect on experimental hyperglycemia.

W. M.

Gluconeogenesis and the energy material of muscle. J. J. R. MACLEOD (Austral. J. Exp. Biol., 1932, 9, 119—125).—Study of the chemistry of muscle and of the metabolism of diabetic animals shows that, whilst there is no evidence that fatty acid can be directly oxidised by the tissues, some form of carbohydrate intermediate between glycogen and the lactic acid is the immediate fuel of muscular activity. This intermediate form is closely related to muscle-glycogen and may be linked to H_3PO_4 and even also to lecithin compounds.

W. M.

Effect of administration of various amounts of carbohydrate on the blood-sugar and -phosphorus during muscular work. Z. DISCHE and H. GOLDHAMMER (Biochem. Z., 1932, 247, 8—34).—Periods of 1—2 hr. in the treadmill cause, in dogs, decrease of blood-sugar and -P and increase of acid-sol. P. Oral administration of glucose, maltose, dextrin, or fructose does not affect this result, but 1.0—3 g. per kg. of sucrose or the equiv. amount of a mixture of glucose and fructose completely inhibits the fall in blood-sugar and often leads to a smaller drop in inorg. P and to a decrease of acid-sol. P. Administration of sucrose with 0.05 g. NaH_2PO_4 per kg. or with Ca glycerophosphate leads sometimes to an increase and sometimes to a decrease of inorg. and acid-sol. P and to a considerable increase in blood-sugar.

P. W. C.

Contraction of frog's muscle by ammonia. R. MIURA (Biochem. Z., 1932, 248, 189—195).—During

the initial stages of the action of aq. NH_3 on frog's muscle, the amount of $OH \cdot CHMe \cdot CO_2H$ is only slightly increased and the phosphagen and pyrophosphate fractions are unchanged. In the later phase of slow contraction and rigidity in the gastrocnemius and of complete relaxation in the rectus, a stage in which complete loss of electric excitability occurs, a considerable formation of $OH \cdot CHMe \cdot CO_2H$ and decomp. of creatinephosphoric acid and pyrophosphate occurs. These changes are therefore the result of progressive muscle injury and not due to the initial NH_3 contraction.

P. W. C.

Production of ammonia in hearts. III. Adenine nucleotide in surviving frog hearts. J. K. PARNAS and P. OSTERN (Biochem. Z., 1932, 248, 398—402; cf. A., 1931, 869).—The production of NH_3 in surviving frog hearts is accompanied by a decrease in the amount of adenine nucleotide present, but added nucleotide is destroyed by the beating hearts. It is concluded that during the process of recovery the nucleotide which has been destroyed is re-synthesised from its deamination product, but that the eliminated NH_3 does not take part in the re-synthesis.

W. M.

Determination of adenosine derivatives in the surviving frog heart. P. OSTERN and J. K. PARNAS (Biochem. Z., 1932, 248, 389—397).—A biological method, involving the use of surviving frog hearts, for the determination of very small amounts of adenosine derivatives is described and its applications are indicated.

W. M.

Comparative efficiency of various proteins in poultry feeding. C. W. ACKERSON, M. J. BLISH, and F. E. MUSSEHL (Poultry Sci., 1930, 9, 112—132).—Comparison of the oviducts of pullets with those of hens after a 5-week period on a low N intake indicated that 95% of the N is lost from the oviduct by such treatment. A fixed procedure is recommended for the determination of biological vals. of proteins; vals. for proteins of maize, wheat, oats, rye, barley, and soya beans are tabulated.

CH. ABS.

Protein requirements of chickens. J. S. CARVER, J. L. ST. JOHN, T. E. ASPINALL, and I. H. FLOR (Poultry Sci., 1932, 11, 45—57).—During the first 12 weeks a protein level of $\leq 15\%$ is required for max. growth; from the 10th to the 26th week 12—15% of skim-milk protein is more advantageous. The efficiency of utilisation decreases with age.

CH. ABS.

Effect of glutathione on autolysis and on protein metabolism. E. ABDERHALDEN, S. BUADZE, and W. GEIDEL (Fermentforsch., 1932, 13, 147—155).—Glutathione had no effect on protein fission *in vitro* by liver, spleen, and kidney. Parenterally administered to a dog, glutathione sometimes caused an increase in the excretion of all the N- and S-containing products, in other cases no change.

J. H. B.

Behaviour of ω -amino-acids in the animal body. W. KEIL (Z. physiol. Chem., 1932, 207, 248—252).—A fair proportion of δ -aminovaleric acid administered to a dog is recovered unchanged. No degradation products of γ -aminobutyric acid were

isolated from dog's urine after injection of this substance. J. H. B.

Production of wool fleece by merino sheep. H. R. MARSTON (Austral. J. Exp. Biol., 1932, 9, 235—246).—Wool-keratin has a relatively very high content of cystine and almost the whole of the S present occurs in this form. Plant-proteins usually have low cystine contents, whilst the animal organism cannot synthesise the acid. The merino sheep is unique in its high demand for cystine (for the production of wool fleece), and hence the yield of wool clip was increased by more than 35% when protein-deficient pasture was supplemented with blood-meal containing 2.7% of cystine. About 40% of the cystine administered was recovered in the increased fleece. W. M.

Nomogram connecting standard metabolism, weight, and surface area of merino sheep. E. W. LINES (Austral. J. Exp. Biol., 1932, 9, 227—229).

Metabolism during rest and protein consumption in Europeans living in the tropics. W. RADSMÅ and G. M. STREEF (Arch. Neerl. Physiol., 1932, 17, 97—123).—Young male Europeans living in the tropics have basal metabolic rates about 5—10% less than the standard rates in temperate zones. This low rate cannot be attributed to a difference in the protein content of the diet. Increased protein consumption resulted in increases in basal metabolism and pulse rate, and in the residual N and urea of the blood. W. O. K.

Variation with age of the nucleo-cytoplasmic ratio of the white mouse. M. C. DAWBARN (Austral. J. Exp. Biol., 1932, 9, 213—226; cf. A., 1930, 369).—In male white mice the nucleo-cytoplasmic ratio (determined by a modification of the method of Robertson and Dawbarn) falls to 60% of its val. at the age of 35 days by the 150th day and thereafter until the 350th day continues to fall slightly. After the 350th day an increase occurs such that the val. at the 700th day equals that at the 150th. For calculation of the ratio the vals. nucleic acid-N and coagulable N were used. W. M.

Influence of diet on the blood-uric acid and the excretion of uric acid after food rich in nucleins. W. V. MORACZEWSKI, S. GRZYCKI, H. JANKOWSKI, and R. SŁIWINSKI (Arch. exp. Path. Pharm., 1932, 165, 482—493).—The blood-uric acid is higher on a diet rich in proteins than on a carbohydrate diet, whilst diet rich in fat has an intermediate effect. The excretion of uric acid in the urine is influenced by the nature of the diet, being depressed on a diet rich in proteins or fat. Administration of nucleins usually decreases the alkali reserve if the diet is rich in proteins, but increases it if the diet is rich in carbohydrates. W. O. K.

Is unirradiated ergosterol resorbable? R. SCHONHEIMER, H. VON BEHRING, and K. VON GOTTBERG (Z. physiol. Chem., 1932, 208, 77—85).—Mice, rats, and rabbits fed with ergosterol or its acetate contained no more ergosterol than controls. In dogs, the lymph of the thoracic duct was examined after feeding a mixture of cholesterol and ergosterol to the animals; the ergosterol content was not in-

creased above the normal. The possibility of a very slow resorption of ergosterol is not excluded.

J. H. B.

Biochemistry of hibernation. (a) **Constituents of the muscle of hibernating animals.** D. FERDMANN and O. FEINSCHMIDT. (b) **Constituents of the brain of hibernating animals.** (c) **Constituents of the blood of hibernating animals.** O. FEINSCHMIDT and D. FERDMANN (Biochem. Z., 1932, 248, 67—100, 101—106, 107—114). (a). The creatinephosphoric acid, hexosemonophosphoric acid, and pyrophosphate contents of the muscle of *Arctomys bobac* (I) and *Citellus gularis* (II) are considerably smaller during hibernation than in activity. In (II) during hibernation, the creatine- and residual-N contents of the muscle are decreased, the latter to a greater extent than the former. The inorg., acid-sol., and total P of heart-muscle are all considerably decreased. Artificial wakening of (II) increases the heart-muscle inorg. P at the expense of the acid-sol. org. P.

(b). The residual N and the ratio of residual/total N in the grey matter of the brain (and to a smaller extent in the white) and also in the cerebellum of (I) are decreased during hibernation, but the total N remains unchanged. The H_2PO_4 content of the grey and white matter is unchanged, but of the cerebellum is decreased. The acid-sol. and total P are decreased throughout the nervous system. The P insol. in acid of grey and to a smaller extent of white matter is decreased, but of the cerebellum is unchanged.

(c). In (II) and to a smaller extent in (I), the blood-sugar is decreased by about 27% during hibernation. The H_3PO_4 content of the blood is increased in (II) by about 175%, but is unchanged in (I). The acid-sol. P is unchanged in (II) and decreased in (I) (but not at the expense of the pyrophosphate, which is unchanged). The total P and the P insol. in acid are decreased in both types of animal. The K content of the serum of (I) is decreased and the Ca content increased during hibernation. P. W. C.

Influence of diet on acetylation processes. H. REINWEIN (Z. physiol. Chem., 1932, 207, 253—258).—Rabbits injected with *p*-aminobenzoic acid excrete in the urine more of the Ac derivative on a diet of turnips than when fasting. J. H. B.

Calculation of coefficients of digestibility of poultry feed. V. G. HELLER, L. MORRIS, and H. E. SHIRLEY (Poultry Sci., 1930, 10, 3—9).—Bergeim's Fe ratio method is more rapid and accurate than Katayama's method. Vals. are tabulated.

CH. ABS.

Comparisons of the alimentary values of certain pulses with those of certain cereals. V. ZAGAMI and V. FAMIANI (Atti R. Accad. Lincei, 1932, [vi], 15, 229—234).—Retardation in development of young rats fed exclusively on one or other of the following seeds is observed: *Cicer arietum*, *Lathyrus sativus*, *Ervum lens*, *Triticum sativum*, *Zea mais*, *Hordeum vulgare*, *Oryza sativa*. In the case of rats fed on cereals, although there is general retardation of development correct proportions are maintained. This is not the case with rats fed on pulses. The effect

of pulses is ascribed to deficiency mainly in salts and to a smaller extent in vitamins. E. E. J. M.

Digestibility of wood-sugar. F. HONCAMP, H. HILGERT, and W. WOHLBIER (Biochem. Z., 1932, 248, 474—482).—The sugar obtained from wood and similar materials (straw etc.) by saccharification (hydrolysis) consists very largely of carbohydrates, up to 80% of which can serve, after partial purification, as completely satisfactory constituents of the food of sheep and pigs. W. M.

Availability of calcium in calcium salts and minerals for bone formation in the growing chick. R. M. BETHKE, D. C. KENNARD, and C. H. KICK (Poultry Sci., 1929, 9, 45—50).—No difference was found in the availability of Ca as the carbonate, sulphate, or lactate or as limestone, steamed bone meal, rock phosphate, phosphatic limestone, or oyster shells fed on a min. requirement basis. CH. ABS.

Calcium: phosphorus ratio in the nutrition of growing chicks. E. B. HART, H. T. SCOTT, O. L. KLINE, and J. G. HALPIN (Poultry Sci., 1930, 9, 296—306).—In presence of vitamin-D and with rations containing 0.61—1.13% Ca and 0.30% P, the optimum Ca:P ratio for growth and calcification was 1:0.50—0.25. With a min. amount of vitamin-D the optimum Ca:P ratio was 1:0.26—0.30, with Ca 2.49—2.71 and P 0.66—0.83%. CH. ABS.

Calcium-phosphorus metabolism in the chicken. I. Effect of irradiated ergosterol (vitamin-D). II. "Range paralysis." G. E. HALL and E. J. KING (Poultry Sci., 1931, 10, 132—156, 259—268). CH. ABS.

Quantitative requirement of the growing chick for calcium and phosphorus. H. S. WILGUS, jun. (Poultry Sci., 1931, 10, 107—117).—When an optimum supply of the antirachitic factor is provided the Ca requirement of the growing chick approaches a min. level of 0.66%. Under similar conditions the P requirement is >0.5% of the ration. The Ca:P ratio may vary between 1.0 and 2.2:1.0 with normal results, whilst 2.5:1.0 is on the borderline and 3.3:1.0 is detrimental. CH. ABS.

Significance of the retention ratio calcium:phosphorus in infants and in children. G. STEARNS (Amer. J. Dis. Children, 1931, 42, 749—759).—The retention ratio Ca:P for the normal infant is 1.5—2:1 and is somewhat higher in older children. A retention of 40 mg. Ca and 20—25 mg. P per kg. of body-wt. per day is desirable for artificially fed infants, and for older children 10 mg. of each. CH. ABS.

Effect of magnesium carbonate when added to diets of growing chicks. G. D. BUCKNER, J. H. MARTIN, and W. M. INSKO, jun. (Poultry Sci., 1932, 11, 58—62).—The Ca-P balance necessary for normal formation of bones was disturbed by MgCO_3 alone or in presence of $\text{Ca}_3(\text{PO}_4)_2$ or CaCO_3 . The ash of the leg bones contained more MgO and P_2O_5 and less CaO. CH. ABS.

Magnesium deficiency in animals. I. Symptomatology resulting from magnesium deprivation. H. D. KRUSE, E. R. ORENT, and E. V.

McCOLLUM (J. Biol. Chem., 1932, 96, 519—539).—A diet containing 1.8 p.p.m. Mg, but otherwise adequate, was prepared. Butter-fat, "viosterol," and salts were obtainable Mg-free; starch, caseinogen, and yeast were specially extracted. Mg was determined spectrographically. Rats on this diet show a characteristic symptom complex, resembling tetany in many respects, and die in 3—5 days. Mg is essential for certain bodily activities, growth, and life. J. B. B.

Nutrition of sheep. Analysis of paunch contents. J. C. BRÜNNICH and W. R. WINKS (Queensland Agric. J., 1931, 35, 183—188).—More P_2O_5 than that contained in the food is present; the P_2O_5 content of the saliva is high. CH. ABS.

Iron metabolism and the influence of copper. H. W. JOSEPHS (J. Biol. Chem., 1932, 96, 559—571).—Tissue Fe appears to exist in 2 fractions, mobile and fixed; the mobile part in rats is reduced when Cu is administered and the fixed part unaffected. Extra Fe in a milk diet is divided between hæmoglobin and tissues; with a Cu supplement the fraction used for hæmoglobin formation is increased. Cu has no effect on Fe retention. J. B. B.

Biology of the placenta. III. Permeability for adrenaline. IV. Permeability for amino-acids. H. SCHLOSSMANN (Arch. exp. Path. Pharm., 1932, 166, 74—80, 81—84).—III. In pregnant goats the intravenous injection of adrenaline into the mother has little effect on foetal blood-pressure, but permeability of the placenta for adrenaline is shown by injection into the umbilical artery, which produces a large increase in maternal blood-pressure.

IV. Slow intravenous injection of NH_3 -acids into the mother produces a rise in NH_3 -N in the foetus. J. B. B.

Resorption of dyes by the gastric mucous membrane. N. HENNING (Arch. exp. Path. Pharm., 1932, 166, 42—55).—A microscopical study, *in vivo*, of the mechanisms of uptake of acid and basic dyes by the gastric mucous membrane of the frog. J. B. B.

Toxicological identification of barbituric acid derivatives. K. BODENDORF (Arch. Pharm., 1932, 270, 290—291).—Zwicker's test (A., 1931, 1328) for barbituric acid derivatives is trustworthy with 1 mg. of substance. Colorimetric determination is possible by replacement of KOH-EtOH by piperidine. R. S. C.

Influence of intrarachidian injection of cocaine and similar substances on the cardio-vascular action of adrenaline. F. MERCIER (Compt. rend., 1932, 194, 1984—1986).—Introduction of cocaine into the spinal canal of chloralosed dogs in amounts sufficient to narcotise the cord results in an increase of intensity and duration of the pressor and vaso-constrictor action due to adrenaline, the central vasodilatatory action of which is suppressed by the anaesthesia. F. O. H.

Action of novocaine. Relation between hydrogen-ion concentration, potassium content, and headache in lumbal anaesthesia. B. BRANDI (Z. ges. exp. Med., 1931, 76, 760—779; Chem. Zentr., 1932, i, 3631).

Toxicological investigation of morphine and cocaine. L. W. RISING and E. V. LYNN (J. Amer. Pharm. Assoc., 1932, 21, 334—337).—The presence of EtOH, CH₂O, HgCl₂, As₂O₃, or embalmer's cavity fluid does not interfere with the determination of morphine or cocaine. The rates of decomp. in presence of tissue and the above substances are given; that of morphine is little affected in the presence of preservatives. Decomp. begins immediately and is complete in just over a year, but 50% can be recovered from the tissue after keeping for 7 months. Cocaine decomposes more rapidly; As₂O₃, HgCl₂, and EtOH retard the rate and 40% can be recovered at the end of 4 months. With cavity fluid 63% is recovered after the same period and with CH₂O only 18%. In every case the cocaine had disappeared completely after 7½ months.

E. H. S.

Effect of histamine on alkali-reserve and blood-sugar in man. R. F. HIESTAND and J. L. HALL (Arch. Int. Med., 1932, 49, 799—807).—The effect on blood-sugar of intramuscular injection of 0.75 mg. of histamine is negligible, whilst a similar quantity produces a very slight increase in the alkali-reserve.

P. G. M.

Effect of guanidine on metabolism. P. JUNKERSDORF and K. WEINAND (Arch. exp. Path. Pharm., 1932, 165, 462—481).—Subcutaneous administration of guanidine to dogs results in an immediate hyperglycæmia, followed by a marked hypoglycæmia. A marked rise in temp. accompanies the hypo- and hyper-glycæmia and convulsions set in during the hypoglycæmic period. The glycogen in the liver even of well-fed animals is practically completely eliminated during the period of guanidine administration, whilst muscle-glycogen is much reduced. The vol. and total N of the urine is increased.

W. O. K.

[Pharmacology of] theophylline monoethanolamine. A. L. CHEN (J. Pharm. Exp. Ther., 1932, 45, 1—5).—"Theophylline monoethanolamine," C₇H₈O₂N₄.OH.[CH₂]₂NH₂, has a diuretic action, toxicity, and other physiological effects attributable to the theophylline.

W. O. K.

Taste blindness. P. LEVENE and A. S. ANDERSON (Science, 1932, 75, 497—498; cf. A., 1931, 1186).—The percentage of individuals who fail to taste *p*-ethoxyphenylthiocarbamide is much lower among American Indians than among white population (6% as against 42%).

L. S. T.

Acceleration of autoxidation of mercaptans by organic catalysts. Explanation of the action of iodoacetic acid on glycolysis in muscle. T. BERSIN.—See this vol., 704.

Influence of "sarsaparilla extract" on experimental salyrgan nephritis. H. SCHLOSSMANN and F. SCHNEIDER (Arch. exp. Path. Pharm., 1932, 166, 62—73).—Treatment with a sarsaparilla extract cures severe salyrgan nephritis in dogs. The active substance is volatile in steam.

J. B. B.

Effect of cyanide on catalytic action in cellular oxygen consumption. E. S. G. BARRON and M. HAMBURGER, jun. (J. Biol. Chem., 1932, 96, 299—

305; cf. A., 1929, 460).—The O₂ consumption of cells deprived of hæmoglobin, in the presence of dyes, is scarcely affected by increasing concns. of KCN, showing that the action of dyes is not related to hæmin catalysis, but is due to direct oxidation of activated carbohydrates.

H. D.

Influence of the hydrogen halides on animal metabolism with special reference to hydrofluoric acid. V. GORLITZER (Arch. exp. Path. Pharm., 1932, 165, 443—461).—When HF is administered subcutaneously or percutaneously to white mice a fall in metabolism takes place which cannot be attributed either to the action of F⁻ in combining with and removing Ca or to the effect of the acid on the *p*_H of the tissues. HCl has a similar inhibiting action on metabolism only when much larger quantities are used, whilst HBr and HI raised the metabolism. HF (1—25,000 in distilled H₂O) strongly retards the development of tadpoles.

W. O. K.

Comparative study of the action of sodium and calcium acetates, after introduction into the stomach, on the composition of the urine and the alkali reserve of the blood. E. A. VLADIMIROVA and E. E. MARTINSON (Biochem. Z., 1932, 247, 153—160).—When NaOAc and Ca(OAc)₂ are introduced into the stomach of a starving dog the effects on the alkalinity of the urine and the alkaline reserve of the blood are dissimilar, Ca(OAc)₂ producing a much smaller basicity than NaOAc.

P. W. C.

Cadmium poisoning. II. L. PRODAN (J. Ind. Hygiene, 1932, 14, 174—196).—In cats inhalation of CdO fumes or of CdO or CdS dust produces marked pathological changes especially in the lungs. Cd compounds are less toxic when taken by mouth on account of the extensive vomiting which they induce. The industrial dangers arising from the fumes or dust are very considerable.

W. O. K.

Pharmacology of lead. VII. Resorption of the metal from the gastro-intestinal tract and the problem of retention. E. FEES (Arch. exp. Path. Pharm., 1932, 165, 583—593).—When a small amount of Pb(OAc)₂ containing a minute quantity of the isotope thorium-B is administered by mouth to white mice, the Pb (determined by radioactivity measurement) is rapidly absorbed from the gastro-intestinal tract, but is only slowly excreted, so that considerable retention takes place. The rate of resorption is not materially different in a fresh animal as compared with one previously treated with Pb and containing Pb in its tissues. No blood changes could be detected as the result of Pb administration.

W. O. K.

Detection of lead in urine. FISCHER and HUPPMANN (Süddeut. Apoth.-Ztg., 1931, 71, 603—604; Chem. Zentr., 1931, ii, 3642).—Schoorl's test is the most sensitive and certain test for Pb in urine. The brownish-black cubes of K₂CuPb(NO₃)₆ can be detected with 0.5 mg. of Pb per litre.

L. S. T.

Absorption, serum concentration, and narcotic effects of magnesium. I. NEUWIRTH and G. B. WALLACE (J. Pharm. Exp. Ther., 1932, 45, 109—112).—In dogs to which MgCl₂ has been administered

by mouth signs of depression appear when the Mg in the serum is 5—6 mg. per 100 c.c.; at about 14.0 mg. ataxia sets in, and complete anaesthesia at about 20 mg., whilst the lethal concn. is but slightly higher. Vomiting tends to decrease the level of serum-Mg reached after administration of a given dose of $MgCl_2$.
W. O. K.

Fate of free iodine on application to the unbroken animal skin. W. NYIRI and M. JAN-NITTI (J. Pharm. Exp. Ther., 1932, 45, 85—107).—I (in EtOH solution or in aq. colloidal solution) is absorbed through the skin of rabbits or dogs and appears in the urine as well as in the inner surface of the skin and in the efferent blood. The % absorption is the same whether the skin cells have a high or low vitality or are dead, and is independent of the direction of penetration. I perfused through the isolated rabbit ear or kidney is reduced to iodide.
W. O. K.

Mitogenetic radiation. III. Radiation of onions, carcinoma, and blood. H. SCHREIBER and M. NAKAIDZUMI (Biochem. Z., 1932, 247, 161—170).—Experiments designed for detection of action at a distance between different inductors and yeast gave negative results, although the conditions were favourable for the appearance of the mitogenetic effect.
P. W. C.

Enzyme action. J. E. NYROP (Protoplasma, 1932, 14, 622—628).—A theoretical discussion of the nature of catalysis and enzyme action. P. G. M.

Respiratory co-enzyme and adenylypyrophosphoric acid. I. BANGA and A. SZENT-GYORGYI (Biochem. Z., 1932, 247, 216—217).—The authors' respiratory co-enzyme of heart-muscle (A., 1931, 1448, 1454) is not adenylypyrophosphoric acid.
P. W. C.

Oxidation of proline and oxyproline by liver. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1932, 96, 325—330).—Proline and oxyproline are oxidised by a suspension of liver pulp at an optimum p_H of 8.0. One atom of O is used up to every 2 mols. of NH_2 -acid. Methylene-blue is also oxidised by liver, thus classing the catalyst responsible for the oxidation as a dehydrogenase.
H. D.

Action of colloidal sulphur on liver oxidations. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1932, 96, 331—339).—The behaviour of colloidal S on liver oxidations is that of the H_2S to which it is reduced, this reduction being accelerated by urethane. H_2S first accelerates and then inhibits the O_2 uptake of the liver, whilst urethane prevents the inhibition. The lactic and succinic dehydrogenases are inhibited only by the presence of both urethane and colloidal S.
H. D.

Catalase. II. Isoelectric point of catalase. K. G. STERN (Z. physiol. Chem., 1932, 208, 86—90; cf. this vol., 412).—The isoelectric point of catalase determined by the cataphoretic method with phosphate buffer is 5.58 (cf. A., 1913, i, 1008).
J. H. B.

Activator of catalase. A. K. BAILS and W. S. HALE (J. Amer. Chem. Soc., 1932, 54, 2133—2134).—Since the presence of -SH derivatives accelerates

proteolysis and that of S-S derivatives the decomp. of H_2O_2 , it seems that the position of the S-S — SH equilibrium determines whether the cell at the moment acts proteolytically or oxidatively.
C. J. W. (c)

Potato amylase. G. VON DOBY and J. BURGER (Fermentforsch., 1932, 13, 201—211).—The natural p_H of potato pulp increases on keeping the tubers from 5.8 to 6.4, thus approaching the optimum for the saccharogenamylase (6.95—7.00). The amylase action similarly increases on keeping, due to the change in p_H and to further production of the enzyme. Salts at concns. 0.001—0.1N increase the amylase activity in amounts varying with the ion and the concn. NaF stimulates at 0.0001N, but inhibits above this concn.; NH_4Cl strongly inhibits. The activation by cations at 0.01N is in the order $Na > K > NH_4$, by anions, $SO_4 > Cl > NO_3 > Br > F$. The amylase activity is favoured by autolysis, which is stimulated by certain salts (NaCl, KCl, NaF, K_2SO_4) at concns. of 0.001—0.1N.
J. H. B.

Amylase of sugar-beet leaves. G. VON DOBY and L. VON BRAZAY (Fermentforsch., 1932, 13, 212—227).—The p_H optimum of the saccharogenamylase of sugar-beet leaves at 30—60° using OAc' buffer is 6.0; the optimum temp. is 42° in a fresh leaf pulp, 53° in a dried prep. The temp. coeff. is low compared with other plant amylases. The amylase is completely inactivated in 60 min. at 60° in the pulp and at 70° in the dried prep. The heat inactivation coeff. increases more rapidly with rise of temp. in the pulp than in the dried prep. Amylase destroyed by heating at 100° for $\frac{1}{2}$ hr. could not be regenerated. Dialysis increases the activity of the amylase in 4—10 days by 32—74%. After 4 days' dialysis the amylase is further activated by certain salts, of which some (NaF, Na_2SO_4 , and KNO_3) displace the p_H optimum 0.2 on the acid side. NaF is most active. Autolysis at 38° scarcely affects the activity.
J. H. B.

"Biolase." E. GLIMM and I. VON GIZYCKI (Biochem. Z., 1932, 248, 449—473; cf. Pringsheim and Schapiro, A., 1926, 715).—Solid biolase consists of Na_2SO_4 (about 50%), NaCl (about 45%), and org. matter which contains much potato starch together with enzymes. These are chiefly amylases, but proteolytic enzymes and peroxidases are also present in small amount. Solutions of the solid prep. liquefy starch paste with great rapidity, producing first dextrin and then sugars, including glucose. No trisaccharide could be found. The other sugar obtained was not hygroscopic and gave no osazone. The prep. can be purified by dialysis, but adsorption (on Al_2O_3 , kaolin, C) and elution leads to reduction of the saccharifying power.
W. M.

Kinetics of invertase action *in vivo* and *in vitro*. J. M. NELSON, E. T. PALMER, and B. G. WILKES (J. Gen. Physiol., 1932, 15, 491—495).—The course of the hydrolysis of sucrose by yeast-invertase as determined by the const. vals. obtained for the const. in the Nelson-Hitchcock equation is found to be identical *in vivo* and *in vitro*.
A. L.

Specificity of invertases. II. H. PRINGSHEIM and F. LOEW (Z. physiol. Chem., 1932, 207, 241—

247; cf. this vol., 91).— α -Methylglucoside is hydrolysed even more rapidly than maltose by yeast maltase, but is not affected by malt extract. The enzymes of yeast hydrolyse maltosone, but not maltobionic acid (as Ca salt). The glucomaltase of *Aspergillus Wentii* is inactive towards maltosone, but hydrolyses Ca. maltobionate; taka-diastrase hydrolyses both substrates. J. H. B.

Emulsin. VII. B. HELFERICH, S. WINKLER, R. GOOTZ, O. PETERS, and E. GÜNTHER (Z. physiol. Chem., 1932, 208, 91—100; cf. this vol., 543).—Phenol- α -l-arabinoside (I), m. p. 153—155° (corr.), $[\alpha]_D^{20} +6.0^\circ$, was synthesised from acetobromoarabinose by way of the triacetate of (I), m. p. 87—89°, $[\alpha]_D^{20} +25.2^\circ$ in CHCl_3 . Different preps. of emulsin hydrolyse salicin, phenol- β -d-galactoside, (I), phenol- β -d-xyloside, and phenol- β -d-glucoside 6-bromohydrin (all *trans*-) at approx. the same rate. The β -glucosidase is thus insensitive to changes at C_4 and C_6 , but not to changes at C_1 . With purification emulsin loses its power of splitting (*cis*-) α -galactoside and (*cis*-) β -l-arabinoside, i.e., the *cis*- α -d-galactosidase is removed by purification. J. H. B.

Influence of prolonged aqueous maceration on emulsin from almonds. C. BOURDOUILL and H. YÜ (Bull. Soc. Chim. biol., 1932, 14, 645—648).—Continuous agitation of aq. emulsions of emulsin for 8 days at 30° in presence of PhMe does not markedly impair the action of the enzyme on salicin or β -methylglucoside. On keeping for some weeks after considerable dilution with H_2O , however, both the hydrolytic and synthetic actions on β -methylglucoside are diminished. F. O. H.

Myrosin. M. SANDBERG and O. M. HOLLY (J. Biol. Chem., 1932, 96, 443—447).—By the use of micro-methods to determine glucose (A., 1929, 1096) and S (A., 1931, 111) obtained by enzymolysis, in buffered solutions, of sinigrin (prep., A., 1928, 207) with myrosin (prep., Braecke, J. Pharm. Belg., 1928, 10, 481), the latter is shown to consist of a glucosidase and a thiosulphatase, both active over the range p_H 4.4—7.0, with no clearly defined p_H optimum. Contrary to von Euler (A., 1926, 542) both components act simultaneously on the substrate, but larger amounts of myrosin are necessary for the optimum fission of glucose (66% of the theoretical) than for the max. (100%) fission of S. J. W. B.

Lipase. I. Lipases from various organs of the carp (*Cyprinus carpio*). II. Hydrolysis of asymmetric aliphatic esters by lipase from the liver of the carp. J. C. KERNOT and H. W. WILLS (Z. physiol. Chem., 1932, 208, 33—39, 39—42).—I. Lipase is present in all organs of the carp examined. With Et *dl*-mandelate as substrate, the enzyme from carp's liver hydrolyses the *l*-form at first more rapidly, later more slowly, than the *d*-form, which is the reverse of pig's liver-lipase action. When the organ is kept in cold storage, the enzyme is quickly destroyed.

II. In the case of Et₂ *dl*-tartrate the *l*-ester is first hydrolysed by both carp's liver and ox-liver lipases. J. H. B.

Activation of lipases of different origin by polypeptides. E. ABDERHALDEN and W. GEIDEL

(Fermentforsch., 1932, 13, 156—159).—Various leucyl- and glycyl-polypeptides accelerate the action of pancreatic lipase. No relation between activity and structure was observed. Liver-, kidney-, and serum-lipases are not susceptible to activation by these polypeptides. J. H. B.

Enzymic formation of mandelic acid esters. P. RONA, R. AMMON, and H. I. TRURNIT (Biochem. Z., 1932, 247, 100—112).—The influence of strychnine, Na taurocholate, MgCl_2 , and CaCl_2 on the velocity of formation of Bu mandelate by preps. of human liver and pig's pancreas is investigated. Strychnine feebly inhibits and MgCl_2 greatly accelerates the synthesis. The products are always optically inactive. In the enzymic esterification of *dl*-mandelic acid with *dl*-phenylethylcarbinol, the *d*-carbinol is used more rapidly than the *l*-carbinol, whereas the *d*- and *l*-mandelic acids are utilised at the same rate. P. W. C.

Enzymic formation and hydrolysis of esters. P. RONA, E. CHAIN, and R. AMMON (Biochem. Z., 1932, 247, 113—145).—The prep. and properties of $\text{CHPhMe}\cdot\text{OH}$, b. p. 99°/15 mm. (*butyrate*, b. p. 119—123°/14 mm.), $\text{CHPhEt}\cdot\text{OH}$, b. p. 100—103°/13 mm. (*butyrate*, b. p. 122—127°/12 mm.), $\text{CHPhPr}\cdot\text{OH}$, b. p. 106—109°/12 mm. (*butyrate*, b. p. 130—140°/14 mm.), and $\text{CHPhBu}\cdot\text{OH}$, b. p. 139—145°/14 mm. (*butyrate*, b. p. 139—145°/13 mm.), by the Grignard method and by reduction of the corresponding ketones are described. The butyrates can all be prepared and hydrolysed enzymically. In the ester synthesis using pig's pancreas preps., the *d*-form is more quickly esterified. The *d*-form is more readily hydrolysed by pig's liver preps. P. W. C.

Action of thyroxine on serum-lipase. E. BACH, L. LOVAS, and L. NEUFELD (Arch. exp. Path. Pharm., 1932, 165, 614—620).—The tributyrase of rabbit's serum is reduced by 30—60% after subcutaneous injection of 0.5 mg. of thyroxine and returns to normal after 3—5 days. Continued daily administration of thyroxine leads to a reduction in blood-tributyrase which runs parallel with the fall in body-wt., but before death the tributyrase rapidly rises and may even exceed the normal. W. O. K.

Nuclein metabolism. XXVI. Nucleophosphatase. W. KLEIN. XXVII. Enzymic fission of thymus-nucleic acid with nucleotidase from intestinal mucosa. F. BIELSCHOVSKY and W. KLEIN. XXVIII. Specificity of Dische's colour reaction with diphenylamine and carbazole for the purine- and pyrimidine-nucleosides of thymus-nucleic acid. F. BIELSCHOVSKY and M. SIEFKEN-ANGER-MANN (Z. physiol. Chem., 1932, 207, 125—140, 202—209, 210—212; cf. A., 1930, 1464).—XXVI. A highly active nucleophosphatase was obtained from the intestinal mucosa of the calf. It was purified by pptn. with an AcOH-acetate mixture at p_H and redissolution in alkali. Glycerol extracts of the enzyme may be kept under PhMe without deterioration. Glycerol and phosphate and borate buffers inhibit the phosphatase. The p_H optimum is <9.2. Mg salts have an accelerating action on the enzyme in addition to furthering hydrolysis by

pptn. of MgNH_4PO_4 . Yeast-nucleic acid is much less readily hydrolysed than that of animal origin.

XXVII. The intestinal enzyme eliminates H_3PO_4 quant. from the nucleic acid mol. and partly hydrolyses the purine- and pyrimidine-nucleosides. Guanosine, thymosine, inosine, and cytidine were isolated from the reaction products. With large amounts of enzyme xanthosine was obtained in small yield.

XXVIII. Both the carbazole and NHPh . reactions of thymus-nucleic acid are due to thymosine; they are given by the free sugar and all the nucleosides. Differences in time of appearance are ascribed to differences in stability of the glucoside linking.

J. H. B.

Intestinal nucleotidase and polynucleotidase. P. A. LEVENE and R. T. DILLON (J. Biol. Chem., 1932, 96, 461—477).—The prep. of the enzyme from gastrointestinal juice of dogs and its properties are described, and the influence of p_{H} on activity towards glyceryl phosphate, adenylic acid, and thymus-nucleic acid is determined. An inhibitor is present in the original secretion. The ratio of nucleotidase to polynucleotidase activity is changed by dialysis, by fractional pptn. with COMe_2 , and by adsorption, but an attempt to separate the two enzymes was unsuccessful. The fraction adsorbed appears to be inactivated. Nucleotidase is probably a simple phosphatase.

J. B. B.

Influence of phosphatides on proteolytic enzymes. P. RONDONI (Z. physiol. Chem., 1932, 207, 103—110).—The process of activation by enterokinase of the tryptic enzymes proteinase and carboxypolypeptidase is inhibited by distearinlecithin, which, however, does not affect the already activated enzyme. Distearincephalin inhibits the proteinase, but is without action on carboxypolypeptidase. The phosphatides also inhibit dipeptidase, but not aminopolypeptidase. They accelerate cathepsin activated with H_2S or glutathione on a gelatin substrate, but not on clupein.

J. H. B.

Action of blood-serum, plasma, and some organ extracts on caseinogen and its degradation products. G. E. WIDMARK (Z. physiol. Chem., 1932, 207, 182—190).—When the proteolytic enzymes in serum, plasma, and organ extracts act on caseinogen and the protein is then pptd., the residual N in the filtrate frequently decreases, indicating a possible resynthesis from the fission products.

J. H. B.

Action of spleen enzymes on protein and its fission products. S. G. HEDIN (Z. physiol. Chem., 1932, 207, 213—234).—To show the presence of α -protease in calf spleen the spleen is treated with weak acid and the enzyme is obtained by extraction of the residue with aq. NaCl at slightly alkaline reaction at room temp. The acid destroys an enzyme capable of synthesising protein from its fission products at alkaline reaction. The spleen substance is also hydrolysed by the β -protease, rendering the extraction of α -protease easier. The synthesising enzyme can be obtained from a spleen untreated with acid by extraction with aq. NaCl. When caseinogen, NaCl, and fission products are added to the dialysed infusion, the protein pptd. at the isoelectric point decreases with time, probably owing

to synthetic action on a substance produced by alkali and NaCl on caseinogen. After 24 hr. at p_{H} 5—5.4 the infusion almost loses its synthetic power. With a caseinogen resistant to NaCl the synthesis appears after 4—5 days and the enzyme is more stable to acid. The synthesis can also be shown with spleen tissue in presence of NaCl and fission products of protein, without added caseinogen. The synthesis is clearer on addition of the synthesising enzyme.

J. H. B.

Production of ereptic action in "crepsin-free trypsin solutions." E. ABDERHALDEN and E. VON EHRENEWALL (Fermentforsch., 1932, 13, 262—290; cf. A., 1931, 766).—The development of the power of hydrolysing *dl*-leucylglycine by "crepsin-free" trypsin on addition of certain substrates is confirmed. The following are active in this manner: (a) glycerol + NH_2 -acids, either added as such or produced by the hydrolysis of complex compounds, (b) certain sugars + NH_2 -acids, (c) amino-hydroxy-acids (except *l*-tyrosine). Tyramine, tyrosineamide, thyroxine, quinine, and particularly chitosamine are also active. The presence of NH_2 and OH groups appears to be a decisive factor. Inactivated crepsin solutions also stimulate the ereptic action of trypsin.

J. H. B.

Physical and chemical properties of polypeptides containing glutathione (S-S) and their behaviour towards erepsin, trypsin-kinase, and cathepsin. E. ABDERHALDEN and W. GEIDEL.—See this vol., 762.

Dehydrodipeptidase. Enzymic fission of compounds of pyruvic acid and amino-acids. M. BERGMANN and H. SCHLEICH (Z. physiol. Chem., 1932, 207, 235—240).—Phenylpyruvic acid was isolated in 20% yield from the pancreatin hydrolysate of glycyldehydrophenylalanine. Kidney extracts do not hydrolyse glycineamide, which is therefore not an intermediate stage. Of pyruvoyl-glycine, *dl*-alanine, and *dl*-phenylalanine, only the last, probably owing to its higher dissociation const., is hydrolysed by pancreatin (optimum p_{H} 7.4). It is not attacked by the proteinase of trypsin.

J. H. B.

Urease. I. Separation of urease, its activity and kinetics. A. RUCHELMANN (Biochem. Z., 1932, 247, 89—99).—Urease separated by pptn. with EtOH and COMe_2 and by means of EtOH after previous pptn. of proteins with HCl is strongly active but preps. obtained by pptn. with AcOH are inactive. Removal of protein by adsorption on permutite removes also some of the enzyme. The action of urease on urea is catalytic. Changes of concn. of substrate affect the activity of urease, but not the velocity of reaction, changes of urease concn. affect the velocity, but not the activity, and changes of the amount of buffer (p_{H} 7.1) affect the activity and the velocity.

P. W. C.

Action of radiation on enzymes. H. B. COLLIER and H. WASTENEYS (Austral. J. Exp. Biol., 1932, 9, 89—112).—Ultra-violet radiation (200—313 $\text{m}\mu$) destroys impure urease, malt amylase, pepsin, and plasma-phosphatase, whilst the urease is also destroyed by infra-red radiation (750—1400 $\text{m}\mu$) and the phosphatase by visible radiation. Visible radiation

stimulates starch-amylase digests slightly and pepsin-ovalbumin digests strongly, although it has no effect on the enzymes alone. Probably the colloidal substrate of the digests absorbs the radiations, the energy of which is then degraded to the kinetic form with consequent increase in the rate of reaction. The rate of destruction of pepsin by ultra-violet radiation depends on the $[H^+]$ within the range p_H 1—7, the point of max. destruction coinciding with that of optimum activity of the enzyme. W. M.

Source of heat in anaerobic energy-producing reactions. C. NEUBERG and E. HOFMANN (Naturwiss., 1932, 20, 379—381).—Thermochemical data show that there is little energy change in the conversion of glucose into methylglyoxal, but that the dismutation of the latter into EtOH and CO_2 or lactic acid is responsible for the heat produced in alcoholic or lactic acid fermentation. A. C.

Stability of glycolase. C. NEUBERG and M. KOBEL (Austral. J. Exp. Biol., 1932, 9, 127—133).—Yeasts (37 preps. tested) which have been preserved for periods up to 20 years produce methylglyoxal from Mg hexosediphosphate but do not ferment sugar after addition of co-enzyme. W. M.

Adenosinetriphosphoric acid and cozymase. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1932, 208, 173—181).—Cozymase and adenosinetriphosphoric acid (as Ca salt) activate lactic acid formation in muscle juice to an approx. equal extent; in some cases the cozymase is superior, but never inferior, contrary to Lohmann's finding (A., 1931, 1449). The main action of the adenosinetriphosphate may be to shorten the induction period, cozymase probably being present as impurity. J. H. B.

Behaviour of l-histidine in yeast fermentation. W. KEIL (Z. physiol. Chem., 1932, 207, 275—276).—Added histidine disappeared rapidly in a yeast fermentation, but no histidol could be isolated. J. H. B.

Stimulation of yeast growth by thallium; a "bios" impurity of asparagine. O. W. RICHARDS (J. Biol. Chem., 1932, 96, 405—418).—The wide variations in the growth of yeast in a medium when different brands of asparagine were used is accounted for by the presence of Tl which in concns. of 0.001 mg. per c.c. of medium produces an increase of 80% in the yield of yeast; greater concns. are toxic. H. D.

Action at a distance of metals on bacteria and yeast. G. A. NADSON and C. A. STERN (Compt. rend., 1932, 194, 1597—1600).—The growth of certain bacteria and of yeast in Petri dishes is to some extent inhibited by the presence of certain metals near the surface of the medium, but not in contact with it, the order of activity being $Pb > Cu > Al$. W. O. K.

Chemical compounds lethal to yeasts and bacteria. W. NEWTON and H. I. EDWARDS (Sci. Agric., 1932, 12, 564—567).—Data for a number of substances are given. The higher $PhOH$ -coeff. of $KMnO_4$ offers an explanation of its action in increasing the fungicidal efficiency of S dusts. A. G. P.

Phenomenon of Boas [action of thiocyanate on micro-organisms]. P. LASSEUR, A. DUPAIX, and L. GEORGES (Compt. rend., 1932, 194, 1857—1859).—The fixation of Bordeaux B in presence and absence of KCNS by bacteria (*B. caryocyanus*) and by a basidiomycete (*Monilia albicans*) at various reactions was investigated (cf. A., 1926, 1276). With *B. caryocyanus* the bacterial vol. has a min. at p_H 3.6. Addition of KCNS induces a decrease in the swelling and in adsorption of the dye at any reaction. The min. of swelling corresponds with max. adsorption of dye whether KCNS be present or not. *M. albicans* has a min. vol. at p_H 3.0 and, in presence of KCNS, at p_H 3.4. In contradistinction to the bacteria, presence of KCNS increases the adsorption of dye over a range of p_H 2.4—8. The fixation of dye in various buffer solutions, with and without KCNS, indicates the importance of anions. F. O. H.

Soluble enzymes secreted by *Hymenomycetes*. Ketones, anthraquinones, and antioxygenic function. L. LUTZ (Compt. rend., 1932, 194, 1684—1686).—Various ketones were tested for antioxygenic activity on methylene-blue in presence of certain *Basidiomycetes* with negative results. Anthraquinone also exhibited no antioxygenic action, but a well-marked action was shown by hydroxyanthraquinones. F. O. H.

Reactions of Lindner's *Termobacterium mobile*. C. NEUBERG and M. KOBEL (Biochem. Z., 1932, 247, 246—248).—The bacterium converts $AcCHO$ and $BzCHO$ into the corresponding α -OH-acids, the yields being 87% of $d(-)$ -lactic and 86% of $d(-)$ -mandelic acids. Since isolation of the products is not quant., the dismutation must be asymmetric and almost complete (cf. this vol., 195). P. W. C.

Temperature characteristic of respiration of *Azotobacter*. H. LINEWEAVER, D. BURK, and C. K. HORNER (J. Gen. Physiol., 1932, 15, 497—505).—The crit. thermal increment of *A. vinelandii* has a const. val. of 19,330 between 20° and 30°. This val. is independent of p_H , O_2 pressure, and age of culture. The optimum temp. of respiration is 34—35° with limits at about 10° and 50°. A. L.

Thermophilic nitrite former. E. G. CAMPBELL (Science, 1932, 75, 23).—A new organism which oxidises NH_4 salts to nitrite at 55° in amounts from 1 to 5 parts of nitrite-N per million is described. At p_H 9.4 oxidation is at a max., at p_H 6.3 it is slight, and at p_H 4.8 it ceases. 1% of glucose added to the mineral salt medium completely inhibits nitrite formation, 0.5—0.25% retards it, but 0.1% has no effect; 1% of peptone checks oxidation temporarily. Free CO_2 from the atm. is necessary as the source of C. NH_4 salts are always used as a source of energy, except when starch is added to the inorg. salt medium. The suggested name is *Nitrosobacillus thermophilus*, Campbell. L. S. T.

Production of a cyanogen radical in peptone water cultures of cholera vibrio. C. L. PASRICHA and S. M. DAS-GUPTA (Indian Med. Gaz., 1931, 66, 551—552).— CN^{\cdot} was found after incubation for 72 hr. at 37°, acidification with tartaric acid, and distillation into KOH solution. Faeces from cholera.

when distilled, gave the AgNO_3 reaction of CN^- . *S. dysenteriae* (Flexner and Shiga), *E. typhi*, and *E. coli* gave negative results. CH. ABS.

B. caryocyaneus (Beijerinck-Dupaix) in a medium containing lithium. P. LASSEUR, P. VERNIER, A. DUPAIX, and J. MARCHAL (Compt. rend., 1932, 194, 1606—1608).—The presence of Li in a medium in which *B. caryocyaneus* is grown induces morphological changes associated with alterations in the permeability of the bacterial membranes and in the stability of suspensions of the bacteria in presence of cations or of agglutinating serum. W. O. K.

Nucleic acid of *B. diphtheriae*. R. D. COGHILL and D. BARNÉS (Anal. Fis. Quím., 1932, 30, 208—221).—A nucleic acid was obtained in 0.8% yield by extraction of *B. diphtheriae* with 2% NaOH (cf. A., 1931, 526). The approx. composition is N 14.5, P 8, guanine 9.5%, and it yields on hydrolysis guanine, adenine, cytosine, uracil, and thymine. It contains at least 13% of pentose, and 25% of nucleic acid of animal type is indicated by Widstrom's method (A., 1928, 1393). It is, therefore, either a new type or a mixture of plant and animal types. R. K. C.

Relation between toxicity and antigenic potency of diphtheria toxins. G. STODEL and A. BOURDIN (Compt. rend., 1932, 194, 1687—1688).—The relation of the antigenic potency (y) of a diphtheria toxin measured in definite units (A., 1924, i, 463) to the toxicity (x) measured in min. lethal doses for the guinea-pig is expressed by $y = Kx^2$, where K is a const.—6.3. F. O. H.

Cryptotoxic properties of sodium α -hydroxy- β -naphthoate and its selective action on diphtheria toxin. H. VINCENT and L. VELLUZ (Compt. rend., 1932, 194, 1697—1699).—The salt detoxicates tetanus toxin, injection of the cryptotoxin thus formed inducing complete immunity in the guinea-pig. It also neutralises diphtheria toxin, subcutaneous injection of diphtheria cryptotoxin being well tolerated by the guinea-pig, which is thereby rendered completely immune. Thus a guinea-pig injected with 5.5 c.c. of neutralised toxin can receive 12,500 times the min. lethal dose of toxin without the occurrence of abnormal symptoms. F. O. H.

Use of ethyl alcohol as precipitant in the concentration of anti-pneumococcus serum. L. D. FELTON (J. Immunol., 1931, 21, 357—373).—Practically all the protective substance is insol. in 15–20% EtOH at 0°. The H_2O -insol. protein is dissolved in NaCl solution and pptd. with 10% EtOH, giving a product in which the immune protein is approx. 80% of the total protein. Between p_{H} 5 and 9, if the ppt. is neutralised before dilution, the pneumococcus antibody is insol. in 20% EtOH. CH. ABS.

Gas metabolism of the tubercle bacillus. I. Oxygen consumption. H. DIECKMANN and G. MENZEL (Z. Hyg., 1932, 113, 709—734).—The O_2 -consumption of human strains was 20 cu. mm. per mg. dry wt. per hr., corresponding with 57.5 g.-cal. per g. N per 24 hr. In NH_4OAc -phosphate buffer suspension the O_2 -consumption was 3–4 times that in NaCl, Ringer, or phosphate buffer solutions without NH_4OAc . A. G. P.

Molecular weight of specific polysaccharides. M. HEIDELBERGER and F. E. KENDALL (J. Biol. Chem., 1932, 96, 541—558).—Staudinger's procedure for determining mol. wt. of the higher members of a series of polymerides by viscosity measurements is applied to the type III pneumococcus sp. polysaccharide, the lower polymerides being obtained by hydrolysis. The apparent mol. wt. varies with salt concn. of the solution, but correction for hydration gives a val. of approx. 1000. The diffusion method, assuming spherical particles and similarly corrected for hydration, gives 5600. Diffusion data are given for bovine tubercle bacillus polysaccharide, and it is concluded that the formula wts. of the sp. polysaccharides should be less than 10,000. J. B. B.

Resistance of guanidine and alkylated guanidines to bacterial guanidodeimidase and arginase. F. LINNEWER (Z. physiol. Chem., 1932, 207, 152—156).—Guanidine and alkylguanidines are not attacked by mixed cultures of putrefactive bacteria and are therefore resistant to guanidodeimidase and arginase. In boiling aq. solution guanidine carbonate forms urea. This may explain Ackermann's observation (A., 1909, i, 619).

J. H. B.

Bacterial multiplication. M. FAGUET (Compt. rend., 1932, 194, 1763—1764).—The growth of various bacteria in homogenous emulsions results in an increase of opacity which can be followed by utilisation of a photo-electric cell (this vol., 545). For the same experimental conditions the curves thus obtained are sp. for each distinct species.

F. O. H.

Biochemistry of the cortex of the suprarenal gland. I. Preparation and detection of the hormone of the suprarenal cortex. H. MAGISTRIS (Biochem. Z., 1932, 248, 39—54).—Two methods for preparing an aq. solution of the hormone are described, and the activity is demonstrated by maintaining suprarenalectomised rabbits alive. For the extract to be effective, it must be administered to the animals before extirpation of the glands. The hormone unit is suggested as the smallest amount which with daily subcutaneous injection is able to maintain suprarenalectomised rabbits alive for 1 week, the administration starting 2 days before the gland removal. P. W. C.

Hyperglycæmic activity of extracts of suprarenal cortex. M. T. REGNIER and H. SIMONNET (Bull. Soc. Chim. biol., 1932, 14, 614—622).—Suprarenal cortex is ground with H_2O and the paste extracted with 10 vols. of 95% EtOH. The extract is conc. to dryness in vac., the residue dissolved in PhMe, phosphatides are pptd. by COMe_2 , and the filtrate is again conc. to dryness. The oily residue dissolved in petrol is freed from adrenaline by washing with dil. alkali, dried, and evaporated to dryness, giving a residue sol. in olive oil. Injection into dogs of amounts equiv. to 2–20 g. of fresh gland produces a marked hyperglycæmia characterised by long duration of action which is not due to adrenaline. F. O. H.

Nervous mechanism of adrenaline action on muscle-glycogen. C. BRENTANO (Arch. exp. Path. Pharm., 1932, 165, 494—503).—In rabbits the muscle-glycogen disappears after administration of

adrenaline even though the mixed nerves proceeding to the muscles have previously been cut. Although this indicates that the action is not dependent on impulses passing down these nerves, it does not prove that the action is directly on the muscles themselves.

W. O. K.

Colloid-chemical basis of inflammation prevention by adrenaline. F. HINTEREGGER (Z. ges. exp. Med., 1931, 78, 374—381; Chem. Zentr., 1931, ii, 3623).—Addition of adrenaline hydrochloride to serum or to gelatin solution alters the viscosity only in so far as p_H is changed by the addition. The colloidal osmotic pressure of horse serum is also unchanged by adrenaline. A diminution of the swelling pressure of the serum-colloids cannot be assumed as the cause of the prevention of inflammation by adrenaline.

L. S. T.

Alleged increase in plasma-fat after injection of adrenaline. C. N. H. LONG and E. M. VENNING (J. Biol. Chem., 1932, 96, 397—404).—Injection of adrenaline does not produce an increase in plasma-fats in cats but an increase in blood-sugar. H. D.

Effect of adrenaline on the blood-cholesterol and -cholesteryl ester in relation to blood pressure and blood-sugar. K. GUGGENHEIM (Z. klin. Med., 1931, 116, 717—731; Chem. Zentr., 1931, ii, 3623).—A regular change in blood-cholesterol did not result from the injection of adrenaline. L. S. T.

Thymus and suprarenal medulla in regulation of blood-cholesterol. A. POLI (Arch. Farm. speriment., 1932, 54, 44—54).—Adrenaline and thymus extract have opposite effects on blood-cholesterol in rabbits. The former causes a rise, max. 2 hr. after injection, the latter a fall continuing 2—5 hr. after injection, whilst combined injections cause no change.

R. K. C.

Fat metabolism hormone of the anterior pituitary lobe. I. K. J. ANSELMINO and F. HOFFMANN. II. F. HOFFMANN and K. J. ANSELMINO (Klin. Woch., 1931, 10, 2380—2382, 2383—2386; Chem. Zentr., 1932, i, 962—963).—I. Substances present in the pituitary, when injected, increase the ketonic substances present in the blood. Anterior pituitary lobe, dehydrated with COMe_3 , was extracted with H_2O ; the centrifuged and ultra-filtered aq. extract is inactive. The hormone is insol. in Et_2O , CHCl_3 , and EtOH , but sol. in 50% EtOH . It is decomposed in aq. solution at 60° and sensitive towards alkalis, acids, and ultra-violet light. It is not adsorbable on C.

II. The hydroxybutyric acid is especially increased in man and the rat. In sufficient quantity, the hormone lowers the basal metabolism of man and increases the sp. dynamic action. The hormone can be detected in the blood after a meal of fat.

A. A. E.

Action of extracts of the posterior lobe of the pituitary on the glycogen content of liver and muscle. P. GOMORI and P. MARSOVSZKY, jun. (Arch. exp. Path. Pharm., 1932, 165, 516—519).—White rats treated subcutaneously with posterior pituitary extract show a decrease in liver-glycogen as compared with control animals, but the muscle-glycogen is unaltered.

W. O. K.

Correlative relations of the five hormone organs, pituitary, thyroid, thymus, gonad, adrenal, in healthy men and domestic animals by the interferometric method of the Abderhalden reaction. E. LENDEL and F. HOGREVE (Fermentforsch., 1932, 13, 244—261).—In domestic animals and man the strongest link exists between the thyroid and the gonad and their defence enzymes. Considerable differences are found between man and domestic animals in correlating the pituitary with the gonad.

J. H. B.

Purification and properties of insulin. T. D. GERLOUGH and R. W. BATES (J. Pharm. Exp. Ther., 1932, 45, 19—51).—The method of Scott and of Best and Scott (A., 1925, i, 617; 1926, 97) for the purification of crude insulin has been slightly modified so that insulin of activity practically equal to that of cryst. insulin is obtained. The modification depends on the relative solubilities of insulin and its impurities in dil. EtOH in presence of Na_2SO_4 . Sulphates displace the p_H at which solubility of insulin in aq. EtOH is min., but chlorides and acetates do not markedly alter the pptn. zone. The highly potent insulin obtained by fractional pptn. with EtOH contained less than 0.1% of tryptophan. Modified methods are given for the crystallisation of insulin. Cryst. insulin prepared from material previously coagulated by heat in acid solution had approx. the same activity as cryst. insulin prepared from uncoagulated material. No conclusive evidence was obtained that highly purified insulin coagulates in acid solution at 70 — 100° more rapidly than crude preps., but the rate of coagulation was retarded by CH_2O and certain proteins. Coagulation, which followed the course of a first order reaction, was min. between p_H 2.6 and 3.3. The coagulated insulin which is inactive regains its activity, although not instantaneously, when dissolved in NaOH solution at p_H 12.0.

W. O. K.

Relation of the duodenal mucosa to the internal secretion of the pancreas. N. B. LAUGHTON and A. B. MACALLUM (Proc. Roy. Soc., 1932, B, 111, 37—46).—Moist duodenal mucosa of cattle is rapidly desiccated, extracted with EtOH-HCl , EtOH distilled from the extract, and the fatty residue extracted with 1% aq. HCl . Pptn. of $\text{Ca}_3(\text{PO}_4)_2$ at p_H 7.8—8.0 in the extract yields a material containing the greater part of the active principle, which may be extracted from the adsorption complex by 0.3% aq. HCl . The prep. induces neither hypo- nor hyperglycaemia in rabbits, but when subcutaneously injected it considerably reduces the hyperglycaemia due to intravenous administration of glucose. This action persists for some time after injection and is even more marked in the partly depancreatized dog, whilst in the totally depancreatized dog no reduction of alimentary hyperglycaemia occurs.

The substance has no action on the blood-pressure nor on the flow of pancreatic juice, and hence is entirely distinct from secretion. It occurs in the duodenal mucosa of rabbits, dogs, and hogs. The theory is advanced that the active principle is a hormone stimulating the islets of Langerhans to secrete insulin.

F. O. H.

Hormono-vagal effect of thyroidectomy on carbohydrate metabolism, reactivity to adrenaline and insulin, and thermo-regulation. R. MESSINA (Arch. Farm. speriment., 1932, 54, 14—43).—In five rabbits the blood-sugar was diminished after thyroidectomy, there was a lowered capacity for assimilating glucose, due to lowered oxidative metabolism, a hypersensitivity followed by hyposensitivity to adrenaline, and an intensified insulin hypoglycaemia. The temp. fell and thermo-regulation was interfered with, the effect of glucose, adrenaline, and insulin being intensified. R. K. C.

Action of antithyroidin on the gas exchange of the rat. K. OBERDISSE and S. THADDEA (Arch. exp. Path. Pharm., 1932, 165, 538—552).—The metabolic rate of white rats, normal or treated with thyroxine, as measured by the CO_2 produced, is depressed by the oral administration of "antithyroidin-Mobius" (serum of thyroidectomised sheep), whilst the feeding of desiccated normal sheep or horse serum is without appreciable effect.

W. O. K.

Distribution and character of adipose tissue in the rat. II. Effect of ovariectomy and of feeding with thyroxine. L. L. REED, W. E. ANDERSON, and L. B. MENDEL (J. Biol. Chem., 1932, 96, 313—323).—Ovariectomy produces a negligible increase in the percentage of fat, whilst its quality, as indicated by its I val., is unchanged. Feeding with thyroxine leaves the distribution of fat unchanged, whilst the total quantity is halved and the I val. is increased by 10—15 units. H. D.

Isolation of the testicular hormone. (a) and (c) B. FRATTINI and M. MAINO; (b) and (d) A. BUTENANDT (Angew. Chem., 1932, 45, 324—326).—(a) A claim for priority (A., 1931, 398) over Butenandt (this vol., 96). The hormone has m. p. 210° and 1 fowl unit = 0.5 mg.

(b) The prep. of Frattini and Maino is insufficiently characterised, differs in chemical and physical properties from Butenandt's prep. (m. p. 178°), and has only 0.02% of the activity of the latter. It is probably an inactive material contaminated with traces of hormone.

(c) A reply.

(d) A reply. New results of assay are given.

R. K. C.

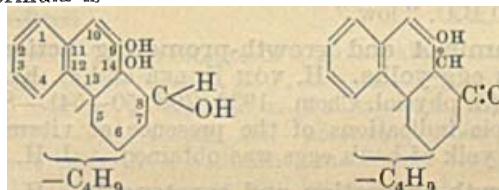
Female sexual hormone. VII. Isomeric follicular hormones. A. BUTENANDT and I. STORMER.

VIII. Constitution of the follicular hormone. I. A. BUTENANDT, I. STORMER, and U. WESTPHAL (Z. physiol. Chem., 1932, 208, 129—148, 149—172; cf. A., 1931, 1195).—VII. The original hydroxyketone, $\text{C}_{18}\text{H}_{22}\text{O}_2$, now termed the α -hormone, has the following properties: m. p. 255° , $[\alpha]_D +156$ — 158° , absorption max. at 280—285 $\text{m}\mu$, activity 8—10 and 40 million mouse units per g. for single and repeated dosage (benzoate, m. p. 217.5°). Other derivatives are doubtful as possibly being obtained from isomerides. With some derivatives, particularly the benzoate, the physiological activity is more protracted than with the free hormone. The hydrate forms mixed crystals with the hormone, hence the apparently varying activity; the pure

hydrate, $\text{C}_{18}\text{H}_{24}\text{O}_3$, has m. p. 279— 280° , $[\alpha]_D +30^\circ$, absorption max. 280—285 $\text{m}\mu$, activity 75,000 mouse units per g. characteristically protracted (Ac_3 derivative, m. p. 126° ; Me ether, m. p. 159— 160° , $[\alpha]_D +32^\circ$).

The elimination of H_2O from the pure hydrate by distillation over KHSO_4 yields isomeric hormones forming mixed crystals; the yield of β - is increased at the expense of the α -hormone by a rapid distillation at 200° . The β -hormone has m. p. 257° , $[\alpha]_D +165$ — 166° in CHCl_3 , absorption max. at 283—285 $\text{m}\mu$, physiological activity 1.25 and 8 million units per g. for single and repeated doses [benzoate (2 forms), m. p. 205 and 220.5°]. The β -form only was isolated from the urine of pregnant mares. The $\alpha\beta$ -isomerism may be due to a *cis-trans*-isomerism at the *tert.* OH.

VIII. Follicular hormone (I), m. p. 250° , forms a semicarbazone (II), m. p. 257— 258° (decomp.), probably containing 0.5 H_2O , and a Me ether (III), m. p. 168.5— 169° [semicarbazone, m. p. 267° (decomp.)]. The hormone hydrate gives with diazomethane a Me ether, m. p. 159— 160° , $[\alpha]_D +30.2^\circ$ in pyridine, which when heated with KHSO_4 in vac. forms (III). When heated with NaOEt , (I) gives deoxyfollicular hormone, m. p. 129— 129.5° [Me ether (IV), m. p. 71.5°]. Reduction of (III) with Zn-Hg and HCl affords (IV). With Zn-Hg in AcOH-HCl , (I) gives dihydrodeoxyfollicular hormone, m. p. 129° (benzoate, m. p. 166— 167°), physiologically inactive. The hormone hydrate, when catalytically reduced, yields hexahydrohormone hydrate (V), m. p. 255— 256° (Ac_3 derivative, m. p. 135°). A keto-derivative of (V) was not obtained. (III) and the hydrate acetate are not attacked by BzO_2H . The most probable type of formula is



for the hydrate and hormone respectively (or a similar arrangement with the substituents at C_8 and C_{14} occupying positions 5 and 13). The C^* atom could then give rise to diastereoisomerides. J. H. B.

Appearance of menformone in the blood of male dogs after radium irradiation. P. ENGEL (Wien. klin. Woch., 1931, 44, 671—672; Chem. Zentr., 1931, ii, 3622).—24 hr. after irradiation with Ra the blood of the male dogs contained considerable amounts of the female sexual hormone (3500—10,000 mouse units per litre); 1000 units per litre could be detected even after 14 days. Irradiation of blood *in vitro* produced no formation of hormone. Hence the female sexual hormone is not a sp. product of female sex glands, but it can be produced from other epithelial cells. L. S. T.

Probability of the presence of a sex antagonistic substance in urine. C. FUNK and P. F. ZEFIROW (Science, 1932, 75, 564—565).—Extracts from mixed male and female human urines inhibit the development of the sex organs in male and retard development in female rats. L. S. T.

Relative vitamin-A and vitamin-D content of samples of cod-liver oil. (Miss) K. H. COWARD, F. J. DYER, and (Miss) B. G. E. MORGAN (Analyst, 1932, 57, 368—372).—The "blue colour val." of cod-liver oil is no indication of its vitamin-D potency. A high "blue val." is, in general, an indication of a high vitamin-A content, but not of its abs. val., since oils of the same colour val. may differ in vitamin val. by as much as 400%. Vitamin-D vals. are not proportional to vitamin-A vals. M. S. B.

Vitamin-A of the liver of *Hippoglossus hippoglossus*. P. KARRER, E. KLUSMANN, and H. VON EULER (Arkiv Kemi, Min., Geol., 1932, 10, B, No. 16, 4 pp.).—Halibut livers (7 kg.) were minced, mixed with Na_2SO_4 , and extracted with Et_2O , yielding 3 kg. of oil, 1 g. of which had 192 cod-liver oil units of vitamin-A. The oil showed absorption max. at 315, 328, and 368 μ (cf. A., 1930, 1321; 1931, 529). The unsaponifiable fraction was freed from sterols by COMe, followed by treatment with digitonin, 250 g. of liver-oil yielding 420 mg. of sterols. The concentrate had a potency 1200 times that of cod-liver oil. One of 10,000 units has been prepared. The concentrates had absorption bands at 315 and 328 μ which were stronger than those of the original oil. Distillation of vitamin-A may be carried out at high vac. (0.01 mm. Hg). F. O. H.

Assessment of food and medicaments in regard to their vitamin-A content. A. JUNG (Z. Vitaminforsch., 1932, 1, 105—115).—200 B.U. (20 C.L.O.) is considered the min. daily requirement of vitamin-A and foods supplying more than 1000 B.U. daily may be classified as "very good," those giving 200—1000 B.U. "good," 50—200 B.U. "moderate," 10—50 B.U. "low." A. L.

Vitamin-A and growth-promoting action of bird's egg-yolks. H. VON EULER and E. KLUSMANN (Z. physiol. Chem., 1932, 208, 50—54).—Spectroscopic indications of the presence of vitamin-A in the yolk of hen's eggs was obtained. J. H. B.

Growth-promotion and carotenoids. H. VON EULER and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1932, 10, B, No. 20, 1—6).—Rats fed a vitamin-A-free diet together with carotene and thyroxine experience a wt.-increase significantly lower than that of rats receiving carotene alone, whilst controls receiving thyroxine suffer loss in wt. and ultimately die. Hence loss in wt. due to thyroxine is compensated by administration of carotene. The liver-fat of the carotene rats gives 2 Lovibond blue units per g. with CHCl_3 - SbCl_3 , whilst that from the carotene+thyroxine rats gives a negative response. This inactivating action of thyroxine applies to carotenoids and vitamin-A occurring in the serum or stored in various organs. Xanthophyll is not only a growth-promoting- and reserve-factor in plants, but is also related to propagation; thus it is isolated from the wheat-grain by extraction with CS_2 . The absorption spectra of various carotenoids are determined and their relation to constitution is discussed. F. O. H.

Vitamin of growth. III. *iso*Carotene. R. KUHN and E. LEDERER (Ber., 1932, 65, [B], 637—640; cf. A., 1931, 959, 1097).—*iso*Carotene is derived

exclusively from optically inactive β -carotene; an analogous dye is not obtained from α -carotene under analogous conditions. Carotene tetraiodide in MeOH or EtOH is converted by $\text{Na}_2\text{S}_2\text{O}_3$ mainly into β -carotene; *isocarotene* is not obtained from the solution in pyridine. If the tetraiodide is dissolved in C_6H_6 , CS_2 , or COMe_2 and the solution is treated after some time with $\text{Na}_2\text{S}_2\text{O}_3$, *isocarotene*, m. p. 180—181° (corr., Berl), is obtained; since immediate treatment regenerates β -carotene, the success of the reaction depends on a previous isomerisation of the tetraiodides which does not occur in MeOH, EtOH, COMeEt , although taking place in COMePh . *iso*-Carotene, $\text{C}_{40}\text{H}_{56}$ or possibly $\text{C}_{40}\text{H}_{54}$, is spectroscopically closely related to lycopene, like which it absorbs 13 mols. of H_2 . The blue coloration of *isocarotene* with SbCl_3 in CHCl_3 is very persistent, whereas that of lycopene is fugitive. Unlike lycopene, *isocarotene* does not afford COMe, when degraded with O_3 .

H. W.
Effects of carotene and vitamin-A on oxidation of linoleic acid. B. R. MONAGHAN and F. O. SCHMITT (J. Biol. Chem., 1932, 96, 387—395).—*In vitro* carotene and vitamin-A inhibit the oxidation of linoleic acid; oxidised carotene and oxidised vitamin-A do not inhibit this reaction. The significance of these results with reference to the metabolism of phospholipins is discussed. H. D.

Crystalline vitamin- B_1 obtained from yeast and rice polishings. A. G. VAN VEEN (Z. physiol. Chem., 1932, 208, 125—128).—The author's prep. based on Jansen and Donath's method agrees in m. p. (no depression on mixing), chemical properties, and antineuritic activity with the prep. of Windaus *et al.* (this vol., 310). The most probable formula for the hydrochloride is $\text{C}_{12}\text{H}_{20}\text{O}_2\text{N}_4\text{S}_2\text{HCl}$.

J. H. B.
Vitamin- B_1 and - B_2 in yeast. J. C. DRUMMOND and J. M. WHITMARSH (J. Inst. Brew., 1932, 38, 264—272).—Brewers' and bakers' yeast grown in natural media contains vitamin- B_1 and - B_2 . Brewing yeast (*S. cerevisiae*) grown in a purified sugar-salts medium supplemented by a small amount of "bios" shows a definite falling off in the content of - B_1 , but discloses no parallel reduction in - B_2 activity. Accordingly, vitamin- B_1 is not synthesised, but is absorbed from the medium by the yeast, whilst the evidence, although unconvincing, supports the view that - B_2 is synthesised. Certain other yeasts such as *S. logos* grown in an artificial medium undoubtedly synthesise both - B_1 and - B_2 . C. R.

Existence of a third vitamin-B growth-factor for the rat. N. HALLIDAY (J. Biol. Chem., 1932, 96, 479—486).—A factor, probably vitamin- B_4 , appears to exist in whole wheat, supplementing vitamins- B_1 and - B_2 . J. B. B.

Carbohydrate tolerance in general avitaminosis and avitaminosis-B. O. KAUFFMANN-COSLA, O. VASILCO, and S. OERIU (Z. physiol. Chem., 1932, 207, 113—124).—Administration of 6—8 g. of glucose per kg. of body-wt. to a dog receiving a complete diet produces no metabolic disturbance or increases in the C/N ratio of the urine. With full or B-avitaminosis, metabolic disturbances are ob-

served on glucose feeding; carbohydrate tolerance decreases and may become negative, and the MeCHO and $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ contents of the urine are increased. These changes gradually diminish on administration of insulin. J. H. B.

Varying value of the ratio vitamin-B : carbohydrate with the constitution of the latter in certain equilibrium conditions of nutrition. L. RANDOIN and R. LECOQ (Compt. rend. Soc. Biol., 1931, 108, 1041—1043; Chem. Zentr., 1932, i, 968).—The vitamin-B requirement differs with the kind of carbohydrate administered, and it is the higher the more rapidly the sugar is utilised by the organism. With glucose it is double that with maltose, sucrose being intermediate. A. A. E.

Narcotine and vitamin-C. O. RYGH (Z. Vitaminforsch., 1932, 1, 134—138).—Extraction of alkaline orange juice with Et_2O , after preliminary Et_2O extraction of the untreated material, gives narcotine and an oil possessing antiscorbutic action, the yield of both products, especially the former, decreasing as the fruit ripens. Demethylation of the narcotine gives an *o*-diphenol having an antiscorbutic action, this property being also shown to a smaller degree by anhydrocotarninephthalide and methylornarcotine. Other derivatives of narcotine examined were without antiscorbutic action. A. L.

Vitamin-C. O. RYGH (Angew. Chem., 1932, 45, 307—309).—A review, particularly of narcotine chemistry (cf. this vol., 310). Pure methylornarcotine has been synthesised and will be tested biologically. R. K. C.

Content of vitamin-D in commercial preparations. W. HEUBNER and M. FRERICH (Arch. exp. Path. Pharm., 1932, 165, 553—570).—Biological testing of a considerable no. of commercial vitamin-D preps. led in general to confirmation of the potency claimed by the makers. The experimental error of the method of assay is considerable. W. O. K.

Stearin from cod-liver oil as source of vitamin-D. R. E. ROBERTS (Poultry Sci., 1930, 9, 102—106).—Stearin from cod-liver oil, at 1% or more of the ration, prevented visible signs of rickets in chicks up to 8 weeks; 1—2% did not retard growth or affect mortality, but 4% retarded growth. CH. ABS.

Antirachitic activation of ergosterol in absence of oxygen. H. H. BEARD, R. E. BURK, H. E. THOMPSON, and H. GOLDBLATT (J. Biol. Chem., 1932, 96, 307—312).—Distillation alone does not, whilst irradiation with ultra-violet light does, activate ergosterol antirachitically. H. D.

Autoxidation of irradiation products of ergosterol. H. H. INHOFFEN and H. HAUPTMANN (Z. physiol. Chem., 1932, 207, 259—266).—In irradiated ergosterol preps. there is present a substance (tachysterol) with absorption band at 280 $\text{m}\mu$, not identical with the vitamin, lumisterol, or suprasterols I and II. On oxidation this is replaced by a substance, *m. p.* about 100°, $[\alpha]_D^{25}$ —128.8°, with absorption band at 250 $\text{m}\mu$, which is in turn destroyed. The pure vitamin is stable, but becomes oxidisable in presence of the labile product. J. H. B.

Vitamin-D and spontaneous rickets in monkeys. A. HOTTINGER and A. NOHLEN (Z. Vitaminforsch., 1932, 1, 99—105).—Three cases of spontaneous rickets in monkeys are described. Large and prolonged dosages of irradiated ergosterol were required for cure, and no indications of hypervitaminosis were observed. A. L.

Effects of moderate overdosage of vitamin-D and of vitamins-A and -D together on the growth rate and longevity of the white mouse. T. B. ROBERTSON, H. R. MARSTON, M. C. DAWBARN, J. W. WALTERS, and J. D. O. WILSON (Austral. J. Exp. Biol., 1932, 9, 203—212).—Daily administration of moderate overdoses (not more than 1000 mouse units) of vitamin-D has a beneficial effect on the growth of white mice and no detrimental effect on their longevity. The beneficial effect on the growth of 50 rat units daily of vitamin-D is not sustained when accompanied by a moderate overdosage of vitamin-A. W. M.

Vitamin-E requirements of poultry. L. E. CARD (Poultry Sci., 1929, 8, 328—334).—Addition of 2% of wheat-germ oil to a ration of yellow maize 60, wheat bran 15, wheat flour middlings 15, meat scrap 9, NaCl 1% did not improve the fertility or hatching power of the eggs. CH. ABS.

Vitamin-E. F. VERZÁR (Z. Vitaminforsch., 1932, 1, 116—134).—A review. A. L.

Is the chief value of milk for feeding poultry due to the presence of a new vitamin? L. C. NORRIS, G. F. HEUSER, and H. S. WILGUS, jun. (Poultry Sci., 1930, 9, 133—140).—The presence of a substance which prevents paralysis of the legs and feet and is indirectly growth-promoting is postulated. CH. ABS.

Occurrence in chicks of a paralysis of nutritive origin. L. C. NORRIS, G. F. HEUSER, H. S. WILGUS, jun., and A. T. RINGROSE (Poultry Sci., 1931, 10, 93—97).—The factor (cf. preceding abstract) is present also in a vitamin concentrate from milk, yeast, autoclaved yeast, and lucerne meal. CH. ABS.

Respirometer vessel for study of metabolism of seeds. P. S. TANG (J. Gen. Physiol., 1932, 15, 571—574).

Respiratory quotient of *Lupinus albus* as a function of temperature. P. S. TANG (J. Gen. Physiol., 1932, 15, 561—569).—The ratio $\text{R.Q. } 18^\circ/\text{R.Q. } 8^\circ$ for germinating seeds of *L. albus* agrees with the theoretical val. A. L.

Intake of carbon dioxide by higher plants in an atmosphere rich in carbon dioxide and continuously illuminated. P. JACCARD and O. JAAG (Ber. deut. bot. Ges., 1932, 50, 167—177).—Relations between respired CO_2 and the intake of CO_2 by photosynthesis in a no. of plants are examined in continuous and intermittent light, and discussed in relation to photosynthetic activity and the rate of translocation of carbohydrates. A. G. P.

Plants as electrical conductors. J. O. MUCCO (Z. Pflanz. Dung., 1932, 24A, 334—341).—A difference of potential exists between the leaves of

plants and the soil in the neighbourhood of the roots. Variations in this p.d. are largely controlled by changes in temp. The passage of ions from soil to plant tissues increases with rise of temp. and the proportion of cations and anions in the plant depends on temp. and the nature of the charge on the soil. A. G. P.

Suction force measurements in cereals. F. BERKNER and W. SCHLIMM (Landw. Jahrb., 1932, 75, 499—530).—The suction force of cereals varies with the origin of the seed and is closely related to the sugar content. High suction force is associated with high yielding power, low transpiration coeff., and, in the case of spring wheat, with drought-resistance. A. G. P.

Catalase activity in relation to the growth curve in barley. M. N. POPE (J. Agric. Res., 1932, 44, 343—355).—Catalase activity, as measured by the evolution of O_2 from an intimate mixture of plant tissue and H_2O_2 , is approx. proportional to the reciprocal of the growth rate, maxima occurring during early germination, during development of the crown roots, and during early jointing. Three explanations are suggested. W. G. E.

Acceleration of the sprouting of potato tubers. K. SNELL (Ber. deut. bot. Ges. (Festschr.), 1932, 50A, 146—161).—Storage of tubers for four-day periods at 32°, 1°, and 32° in order, caused more rapid sprouting than storage at 20° throughout. At 1° the transition of sugars to starch becomes more rapid. A. G. P.

Effect of mercury salts on germination of seeds. J. BODNAR and L. E. RÓTH (Biochem. Z., 1932, 248, 375—382).—The toxic action of Hg salts on the germination of seeds (wheat) depends, not on the Hg ion, but on the solubility in lipins and hence the salts which ionise readily [$Hg(NO_3)_2$, $HgSO_4$, $Hg(OAc)_2$] have scarcely any action, whereas the less readily ionised salts [$HgCl_2$, $HgBr_2$, $Hg(CN)_2$], which are more sol. in lipins, are rather toxic. The same reason explains why $HgBr_2$ is more toxic than $HgCl_2$, why the addition of alkali halides reduces the toxicity of Hg salts, why K salts act more powerfully than Na salts, and why the toxic action of $Hg(OAc)_2$ is increased by addition of a little NaCl, but decreased by that of more NaCl. The degree of solubility of Hg salts in lipins is deduced from the extent to which Et_2O extracts them from aq. solutions. The results conflict with the theory of Kronig and Paul (Z. Hyg., 1897, 25, 1). W. M.

Stimulative effects of illuminating gas on trees. C. G. DEUBER (Science, 1932, 75, 497).—The marked responses to stimulation by a mixture of coke-oven gas and water-gas are described for several trees. L. S. T.

Wheat germ. O. DE A. COSTA (Rev. brasil. chim., 1931, 2, 457).—The germ (1% of grain) contains H_2O 17.60, N-substances 31.50, fat 9.44, reducing sugar (as glucose) 2.00, dextrin 22.50, starch and cellulose 13.50, ash 3.90%; P (present as phytin; as P_2O_5) 2.15%. CH. ABS.

Composition of *Ipomœa pandurata*. E. M. STEVENS and A. S. WHEELER (J. Elisha Mitchell

Sci. Soc., 1932, 47, 16).—The powdered roots contained H_2O 71.50, invert sugar 0.36, sucrose 0.29, starch 10.10, cellulose and ash 12.47, resins 4.69%.

CH. ABS.

Membranes of spores and pollen. IX. Thermal behaviour of sporopollenins. X. Temperature of formation of coal. F. ZETTSCHKE and O. KALIN (Helv. Chim. Acta, 1932, 15, 670—674, 675—680; cf. this vol., 665).—IX. Recent and fossilised sporopollenins lose wt. considerably when heated in H_2O , paraffin, or glycerol, with or without KOH or H_3PO_4 , and become smaller. Sporopollenins in coal are little affected by this treatment. There is no relation between the amounts of bitumen sol. and insol. in C_6H_6 or pyridine contained in coal.

X. Sporopollenins from coal are thermolabile above 100°, and it is therefore concluded that the coals were formed below this temp. R. S. C.

Anatomy and microchemistry of the cotton seed. R. G. REEVES and C. C. VALLE (Bot. Gaz., 1932, 93, 258—277).—In addition to oil and protein, traces of starch occur occasionally in both young and mature embryos of cotton seed. Pentosans are located in the resin glands. Cell-walls consist chiefly of cellulose. In the endosperm tissue, starch, oil, and protein are present and cell-walls are largely of cellulose. Considerable proportions of starch exist in the two integuments of the developing ovule, but disappear before maturity. The cell-wall of the perisperm and the colourless layer become lignified before maturity and those of the pigmented layer are of lignocellulose. The palisade layer of the seed-coat contains cellulose and lignocellulose.

A. G. P.

Chemistry of the fruit from the white cedar tree (*Melia Azedarach*, L., var *australasica*, C.DC.); reputed toxicity. F. R. MORRISON (J. Proc. Roy. Soc. N.S.W., 1932, 65, 153—177).—The whole fruit (H_2O 18—29%) grown in 1922 contains about 3% of oil having d_{20}^{25} 0.9735, n_D^{20} 1.4930, acid val. 9.1, sap. val. 150.6, and I val. 145.05, and from this was isolated a resin (m. p. 102°, acid val. 17.7, sap. val. 155.82, I val. 117.6, d when fused 1.1533) containing a basic alkaloidal substance. Glucose, a meal (4% and largely starch), and seeds were also present in the fruit. The seed oil has d_{20}^{25} 0.9534, n_D^{20} 1.4787, acid val. 71.5, sap. val. 194.9, and I val. 128.1. Feeding tests of the fruits from at least one variety of the species on guinea-pigs showed toxic symptoms similar to those shown with strychnine. The toxic substance is present in the resin, but the alkaloid alone is not poisonous. E. H. S.

Do tomatoes contain oxalic and glycollic acids? A. BORNTRAEGER (Z. Unters. Lebensm., 1932, 63, 447—448).—Oxalic and glycollic acids occur in tomatoes only in exceptional cases. The former (cf. B., 1926, 105; 1928, 543) is sometimes found (0.0016%) in extremely unripe fruits, or in the presence of bacteria or moulds. The presence of the latter has not been established. J. G.

Tectoquinone, the volatile principle of teak wood. K. KAFUKU and K. SEHE (Bull. Chem. Soc. Japan, 1932, 7, 114—127).—Teak wood contains tectoquinone (I) (J.C.S., 1887, 51, 869) (0.5%) and

2-methylanthracene [oxidised to anthraquinone-2-carboxylic acid (II)]. (I), m. p. 195—196°, b. p. 215—220°/4 mm., is proved to be 2-methylanthraquinone by conversion by the appropriate reagents into tectonic acid [= (II)] (acid chloride, amido, Me and Et ester), anthraquinone, hydrotectonic acid [=anthracene-2-carboxylic acid] (amide, Et ester), tectonene (=2-methylanthracene) (mesodibromide), anthracene, 2-methylanthrone, diacetyl-2-methylanthrahydroquinone, and 1-nitro-2-methylanthraquinone.

R. S. C.

Occurrence of saponins in some *Polygalaceæ*. E. GILGUD and P. N. SCHURHOFF (Arch. Pharm., 1932, 270, 276—283).

Poisons of *Amanita phalloides*. H. A. RAAB (Z. physiol. Chem., 1932, 207, 157—181).—The thermostable *Amanita* toxin of Abel and Ford (A., 1908, ii, 1061) was extracted with H₂O from the dried fungus and purified by various methods; the toxicity was followed by injection into guinea-pigs, the min. lethal dose producing death in 5—7 days. Impurities were removed by pptn. with Pb(OAc)₂ and then with MeOH. The best precipitant for the toxin was Hg(OAc)₂, which after H₂S treatment gave a highly active fraction which was further purified by pptn. with K Bi iodide. The activity of the toxin is reduced to $\frac{1}{2}$ with 0.3N-Ba(OH)₂ in 2 hr. It is not depressed by 2N-H₂SO₄ in 24 hr.

J. H. B.

Spectrometric measurements on alcohol extracts of the leaves of chlorophyll-mutants of barley. H. VON EULER and H. HELLSTROM (Z. physiol. Chem., 1932, 208, 43—49).—EtOH extracts from the leaves of four strains of chlorophyll-defective mutants were examined spectroscopically, and found to arrange themselves in two groups: (1) albina 1 and 3, (2) albina 2 and 7. In the leaves of 1, 3, and 7, a band at 320 m μ corresponding with vitamin-A max. was observed. There is about $\frac{1}{2}$ the normal amount of hæmochromogen in the chlorophyll-defective leaves.

J. H. B.

Pigment of marigold (*Calendula officinalis*). **Lycopene of blossoms.** L. ZECHMEISTER and L. VON CHOLNOKY (Z. physiol. Chem., 1932, 208, 26—32).—The pigment of *C. officinalis* contains approx. 0.02% of lycopene, 0.1% of carotene, 0.1% of violaxanthin, and 0.1% of other xanthophylls in the dried petals. A phytosterol is also present as shown by Wirth.

J. H. B.

Distribution and nature of carotenoids in berries. A. WINTERSTEIN and U. EHRENBERG (Z. physiol. Chem., 1932, 207, 25—34).—By pretreatment of the berries with MeOH or COMe₂, the following carotenoids were isolated: carotene, lycopene, and xanthophyll from *Convallaria majalis*, lycopene from *Solanum dulcamara*, physalien from *Hippophae rhamnoides*, *Solanum Hendersonii*, and asparagus.

J. H. B.

Determination of carotenoids. R. KUHN and H. BROCKMANN (Z. physiol. Chem., 1932, 206, 41—64).—A scheme for separation of the carotenoids depends on their distribution between C₆H₆ and 90% aq. MeOH. The hydrocarbons and xanthophyll

esters are found in the C₆H₆ layer, the xanthophylls in the MeOH. The xanthophyll esters are then hydrolysed. Certain carotenoid carboxylic acids and chlorophyll, which behave like the xanthophylls, may be separated by treatment with NaOH. Further separation of individuals in the groups is attained by selective adsorption (e.g., lycopene and carotene). Colorimetric determinations are made against an azobenzene standard (14.5 mg. in 100 c.c. of 96% EtOH). *Physalis Franchetti* contains zeaxanthin dipalmitate exclusively in the ripe sepals and berries. Green leaves of deciduous trees contain only traces of xanthophyll esters, but these are formed in considerable amounts in the yellow autumn leaves at the expense of the free xanthophylls (lutein and violaxanthin). Attempts at enzymic hydrolysis of physalien were unsuccessful, although such hydrolysis occurs in the rat's digestive tract (since physalien feeding leads to excretion of zeaxanthin) and in the hen's organism where physalien yields eggs with yolks containing free zeaxanthin. The carotene/xanthophyll ratio in human placenta decreases with development; the abs. amount of carotene (0.2 mg.) is practically const. after the 4th month.

The cow's corpus rubrum contains 0.12% of β -carotene.

J. H. B.

Drying and fermentation of tobacco. I. **Changes of hydrogen-ion concentration in tobacco during drying and fermentation.** J. BODNAR and L. BARTA (Biochem. Z., 1932, 247, 218—223).—The [H⁺] of tobacco decreases during drying and increases during fermentation, the amount of acid formed in the latter process being closely related to the NH₃ liberated.

P. W. C.

Hydrogen-ion concentration and buffering in the press-juice of tobacco leaves in relationship to the nutrition and development of the plant. I. K. BONING and E. BONING-SEUBERT (Biochem. Z., 1932, 247, 35—67).—The nutrition of plants exerts only a limited influence on the actual p_H of the leaf-juice, but does exert considerable influence on the buffering. A series of 11 buffer index curves obtained by titration of the press-juice of tobacco leaves shows the effect of nutritions rich and poor in K, Ca, NO₃⁻, P, SO₄²⁻, Cl⁻, and Mg. Lack of Ca leads to a high p_H and low buffering power, excess of Ca to increased acidity and buffering, lack of K and P to high buffering power, and excess of inorg. anions to enfeebled buffering.

P. W. C.

Bromine normally present in plants: edible plants and fruits. A. DAMIENS and S. BLAIGNAN (Compt. rend., 1932, 194, 2077—2080; cf. this vol., 205).—The ratio Br/Cl in 48 varieties of vegetables, fruits, and fungi is low, particularly in the fruits, many of which contain no Br.

W. S.

Berries rich in calcium. E. YANOVSKY, E. K. NELSON, and R. M. KINGSBURY (Science, 1932, 75, 565—566).—The H₂O-free, ripe fruit of blackberries (*Celtis occidentalis*, L.) contained reducing sugar 32—36%, pentosans and hemicelluloses 2—4%, crude fat 2.8%, crude protein 11.6%, and ash 29% (CaO 13.9%, Al₂O₃+Fe₂O₃ 1.2%, SiO₂ 2.4%). The Ca is present mainly as CaCO₃, but Ca salts of malic, citric,

and oxalic acids, of a gum acid, and an unsaturated acid are also present.

L. S. T.

Water balance of Mediterranean woods in midsummer. H. R. OPPENHEIMER (Ber. deut. bot. Ges. (Festschr.), 1932, 50A, 185—245).—Measurements of various physical factors concerned in controlling the H_2O economy of plants are recorded and correlated with ecological observations. A. G. P.

Adaptation of halophytes to concentrated salt solutions. W. S. ILJIN (Planta [Z. wiss. Biol.], 1932, 16, 352—366).—Plants exhibit physiological powers of adjustment to the salt concn. of nutrient media. Different species vary in their resistance to high concn. of individual cations. In general K^+ and Ca^{++} are less injurious than Na^+ . Resistance to Na^+ and sensitiveness to Ca^{++} are characteristic of halophytes, whereas glycophytes withstand high proportions of Ca^{++} and are sensitive to Na^+ .

A. G. P.

Influence of sulphurous acid on *Elodea canadensis*. M. ROSEN and W. DORRIES (Ber. deut. bot. Ges., 1932, 50, 53—58).—Preliminary experiments with *E. canadensis* indicate that phaeophytin formation precedes bleaching of chlorophyll by dil. H_2SO_3 .

W. G. E.

Permeability of plant protoplasts to non-electrolytes. W. WILBRANDT (Pflüger's Archiv, 1931, 229, 86—99; Chem. Zentr., 1932, i, 537).—The permeabilities of glycerol, glycol, biuret, pinacone hydrate, succinimide, NH_4Ac , methylcarbamide, and urea have been compared.

A. A. E.

Autumnal frosts, oxidising enzymes, and decline of plants in full vegetation. GARD (Compt. rend., 1932, 194, 1184—1187).—Extracts made from the organs of various plants which have been subjected to temp. considerably below zero show an increase in the peroxidase and tyrosinase activity as compared with extracts of normal plants, whilst the oxidase activity tends to be subnormal. This alteration is associated with various physical changes in the plant such as loss of turgescence and decay.

W. O. K.

Causes of the death of [plant] cells in anaerobiosis. G. GRUNBERG (Planta [Z. wiss. Biol.], 1932, 16, 433—466).—Death of plant cells maintained under anaerobic conditions results from the loss of active energy and the accumulation of toxic metabolic products. The $[H^+]$ of the cell-sap is an important factor in the operation of these two causes. Exposure to light of neutral-sap plants after a period of darkening retards the death of cells, but accelerates this in acid-sap plants, since a toxic concn. of acid enhanced by carbohydrate formation is attained earlier. Relationships between this phenomenon, the formation of org. acids, the presence of various carbohydrates, and respiratory activities are examined.

A. G. P.

Pathology of peach canker. K. TOGASHI (Bull. Imp. Coll. Agric. Forestry, Japan, 1931, 16, 178 pp.).—Both *Leucostoma persoonii* and *Valsa japonica* make mycelial growth on hemicellulose, pectin,

starch, and cellulose-dextrin media, but not on sucrose, maltose, or amygdalin. Both secrete diastase, invertase, maltase, emulsin, hemicellulase, pectinase, and cellulase.

CH. ABS.

Microchemical detection of volatile fatty acids in plants. G. KLEIN and H. WENZL (Mikrochem., 1932, 11, 73—130; cf. this vol., 203).—Characterisation of fatty acids by means of their metallic salts is not restricted (as is that which depends on conversion into org. derivatives) to single acids, and is possible with far smaller quantities. Ce^{III} , Zr, Th, Hg^I , Ag, Cu^{II} , Zn, Pb, Co, and Ni salts of the fatty acids C_1 to C_8 and of lactic acid have been examined, and the limits of detectability ascertained. All the acids mentioned can be identified in quantities of 0.1 mg. or less. Tables and photomicrographs are given. Procedure in dealing with raw plant material is described. Among a no. of flowers examined, HCO_2H and $AcOH$ have been found in all, Bu^iCO_2H in a few, and $PrCO_2H$ in none.

F. L. U.

Determination of residual nitrogen by direct Nesslerisation. A. LUBLIN (Z. physiol. Chem., 1932, 206, 282—284).—A reply to Stohr (this vol., 438). The N content of "perhydrol" (Merck) has in practice no effect on the determination.

J. H. B.

Acetone as a substitute for alcohol [in vegetable histology]. J. E. SASS (Stain Tech., 1932, 7, 65—66).— $COMe_2$ can be used instead of $EtOH$ as a killing and dehydrating agent.

H. W. D.

Heidenhain's hæmatoxylin in the smear technique [for staining pollen mother-cells]. W. C. BARRETT, jun. (Stain Tech., 1932, 7, 63—64).—Hæmatoxylin is superior to aceto-carmin for staining the meiotic chromosomes.

H. W. D.

Colorimetric determination of phosphorus. E. J. KING (Biochem. J., 1932, 26, 292—297).—The method is based on the combination of Robison and Martland's modification of Briggs' method and of Fiske and Subbarow's method. The org. matter is destroyed by heating with $HClO_4$.

S. S. Z.

Micro-determination of iodine. A. W. ELMER (Biochem. Z., 1932, 248, 163—167).—The method, which depends on the destruction of org. matter by carbonising in a porcelain crucible, ashing in a combustion tube, extracting the I in a micro-apparatus with $EtOH$, and determining it either by titration or colorimetrically, can be carried out on 5 c.c. blood in about 2—2.5 hr.

P. W. C.

Elimination of phosphate in the determination of sodium by the uranyl magnesium acetate method. J. BOUGAULT and E. CATTELAÏN (Bull. Soc. Chim. biol., 1932, 14, 275—277).—The PO_4^{3-} is first pptd. by the addition of aq. $Pb(OAc)_2$ in the presence of $AcOH$.

A. L.

Determination of arsenic in physiological materials. W. DECKERT (Z. anal. Chem., 1932, 88, 7—16).—A colorimetric method, based on Gutzeit's method but employing $HgBr_2$ test-papers, would make a suitable and simply operated standard method.

M. S. B.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1932.

General, Physical, and Inorganic Chemistry.

Resonance spectrum of hydrogen. K. R. RAO (Nature, 1932, 129, 869). L. S. T.

Theory of some electron levels in H_2 . J. K. L. MACDONALD (Proc. Roy. Soc., 1932, A, 136, 528—537).—Mathematical. The electron energies for 2- and 3-quantum levels in H_2 are calc., using the variation method, based on H_2^+ and at. H functions. The sequence of levels is the same as that found experimentally. L. L. B.

Lower limit for the ground state of the helium atom. D. H. WEINSTEIN (Physical Rev., 1932, [ii], 40, 797—799).—Mathematical. The calc. and experimental vals. are $-6.2R$ and $-5.818R$, respectively. N. M. B.

Second spark spectrum of sodium, Na III, in the extreme ultra-violet. J. SODERQVIST (Z. Physik, 1932, 76, 316—318). A. B. D. C.

Plane waves of light. III. Absorption by metals. T. C. FRY (J. Opt. Soc. Amer., 1932, 22, 307—332).—Theoretical. The absorption of light by thin films of alkali metals deposited on glass or Pt is investigated. A. J. M.

Variations in wave-length of copper lines in a very intense arc. J. GILLES (Compt. rend., 1932, 194, 2200—2202).—A steady Cu spectrum in a very intense arc is obtained with brass anode and graphite cathode. Diminutions of wave-length occurred at the cathode and increases at the anode. C. A. S.

Arsenic spectrum. L. WINAND (Bull. Acad. roy. Belg., 1932, [v], 18, 422—436).—The extinction coeff. of As vapour has been measured at various temp. and over the wave-length range 3000—3900 Å. The emission spectrum of As vapour shows a group of bands in the region 2700—4200 Å., which are attributable to As_2 , whilst several lines in the region 2148—3047 Å. appear to be due to As atoms. No As fluorescence spectrum could be obtained. J. W. S.

Fine structure in the arc spectra of bromine and iodine. S. TOLANSKY (Proc. Roy. Soc., 1932, A, 136, 585—604).—An examination has been made of 29 Br lines and 16 I lines. The nuclear spin found for Br is $3/2$, both the isotopes (79, 81) having the same spin. A simple mass isotope displacement is observed, of the same order as that calc. The nuclear spin for I is $9/2$. The fine structure interval factors for 24 terms in Br and 17 in I are calc. L. L. B.

Shift of the transmission band of silver by cold working. H. MARGENAU (Physical Rev., 1932, [ii], 40, 800—801; cf. A., 1929, 972).—The shift can be

explained on Kronig's theory of metallic dispersion due to change in lattice const. N. M. B.

Magnetic quenching of iodine fluorescence and Λ -doubling in $^3\Pi_0$ states. J. H. VAN VLECK (Physical Rev., 1932, [ii], 40, 544—568).—Turner's proposal that the magnetic quenching of I fluorescence is a predissociation phenomenon is developed theoretically (cf. A., 1931, 1). N. M. B.

Conditions of origin of forbidden lines in the spectrum of Hg II. S. SAMBURY (Z. Physik, 1932, 76, 266—267). A. B. D. C.

Hyperfine structure of mercury. V. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 177—190; cf. this vol., 552).—Data are recorded and interpreted for λ 5791, 3663, 3662, 3654, 4046, 4077, 4358, 5460, 4339.23, and 3650.15. The components of even isotopes in λ 5461 emit only 74% of their theoretical intensity. N. M. B.

Mean lives of mercury lines λ 2537 and λ 1849. P. H. GARRETT (Physical Rev., 1932, [ii], 40, 779—790).—The mean life of λ 2537 measured by a photo-electric method was 1.08×10^{-10} sec. accurate to 1%, and that of λ 1849 by an absorption method was 2.9×10^{-10} sec. accurate to 25%. N. M. B.

Hyperfine structure of lead. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 191—204).—Data are recorded and interpreted for λ 3639, 3683, 4019, 4057, 4062, and 4168 of Pb I. and for 3786, 4386, 4244, 4579.15, 5372, 5608, and 6660 of Pb II. The abundance ratios of isotopes are $Pb^{208}, ^{207}, ^{206} = 47.7 : 25.9 : 26.4$. N. M. B.

Hyperfine structure of lead. J. L. ROSE and L. P. GRANATH (Physical Rev., 1932, [ii], 40, 760—778).—Data for 13 lines of Pb I and 5 lines of Pb II are reported. Isotope displacements of Pb^{206} and Pb^{207} with respect to Pb^{208} were found; vals. for Pb II were much larger than for Pb I. N. M. B.

Plasma vibrations and selective optical reflexion by metals. M. STEENBECK (Z. Physik, 1932, 76, 260—265).—Theoretical. A. B. D. C.

Processes of excitation and ionic motions in the luminous arc. R. MANNKOPFF (Z. Physik, 1932, 76, 396—406).—A spectroscopic study of the arc current before and after breaking the circuit reveals that 75% of the excitation is thermal. A. B. D. C.

Origin of coronal lines. R. FRERICH (Nature, 1932, 129, 901—902). L. S. T.

Origin of coronal lines. H. DINGLE (Nature, 1932, 129, 902). L. S. T.

Scattering of X-rays by monatomic gases. Y. H. WOO (Sci. Rep. Nat. Tsing Hua Univ., 1932, A, 1, 135—143).—Wollan's results (A., 1931, 781, 1106) on the intensity of X-ray scattering by inert gases are compared with theoretical vals. deduced from a modified Raman-Compton formula.

W. R. A.

Absorption and scattering of X-rays by argon. S. H. YU (Sci. Rep. Nat. Tsing Hua Univ., 1932, A, 1, 155—157).—The scattering is calc. from the Compton formula.

W. R. A.

Structure of absorption edges of light elements. H. GEIGER (Z. Physik, 1932, 76, 420).—Neufeldt's results (A., 1931, 781, 1206) could not be reproduced.

A. B. D. C.

Origin of the X-ray non-diagram lines in the K series. M. SAWADA (Mem. Coll. Sci. Kyoto, 1932, A, 15, 43—56).

A. R. P.

Wave-lengths of the tungsten K series spectrum with the double spectrometer. J. H. WILLIAMS (Physical Rev., 1932, [ii], 40, 791—796).—Experimental.

N. M. B.

Two-crystal analysis of L-absorption limits of mercury. H. L. HULL (Physical Rev., 1932, [ii], 40, 676—683).

N. M. B.

Relative excitation of the three X-ray L levels with cathode rays of different velocities. D. COSTER and J. VAN ZUYLEN (Nature, 1932, 129, 942—943).

L. S. T.

Displacement in the N lines of tungsten and tantalum. F. C. CHALKLIN and L. P. CHALKLIN (Nature, 1932, 129, 905—906).—Lines at 55.58 and 58.42 Å. have been obtained from W sputtered on to a H₂O-cooled anticathode. With an incandescent anticathode of W sheet the lines are displaced to 55.29 and 58.09, respectively, representing an increase of 1.2 electron volts in the energies for each line. The O_{II}, III level is concluded to be 1.2 volts deeper within the atom for cold W than for hot, and the shift is attributed to measurements for hot W being due to the metal and for the cold measurements to oxidised W.

L. S. T.

Absorption of scattered X-rays. S. R. KHASTGIR (Phil. Mag., 1932, [vii], 14, 99—112; cf. A., 1931, 1105).—Additional evidence is adduced in support of the existence of the J phenomena.

H. J. E.

Scattering of cathode rays at crystal surfaces. F. KIRCHNER and H. RAETHER (Physikal. Z., 1932, 33, 510—513).

A. J. M.

Compound photo-electric effect of X-rays in light elements. G. L. LOCHER (Physical Rev., 1932, [ii], 40, 484—495; cf. Compton, A., 1930, 138).—The K fluorescence yields of O₂, Ne, and Ar are 8.2, 8.3, and 14.9%, respectively, for 0.709 Å. X-rays. These vals. are related with available data for 47 elements. A new type of double track attributed to metastable Kr atoms, and having components of similar energy but producing unequal ionisation, was observed. 15 parts of Kr in 10⁵

of O₂, or 50 parts of Xe in 10⁵ of O₂, can be detected by the cloud method.

N. M. B.

Anomalies in radiographs produced by means of resistance cells. G. REBOUL (Compt. rend., 1932, 194, 2304—2405; cf. this vol., 446).

C. A. S.

Photo-electric microphotometer for X-ray work. W. BUSSEM and B. LANGE (Z. Krist., 1932, 82, 474—476).—The instrument makes use of Lange's new photo-cell (cf. A., 1931, 9).

C. A. S.

Multiple interference spectroscopy compared with other interference spectroscopes. E. LAU and E. RITTER (Z. Physik, 1932, 76, 190—200).

A. B. D. C.

Measurements with liquid helium. XVIII. Behaviour of superconducting tin on bombardment with slow electrons. W. MEISSNER and K. STEINER (Z. Physik, 1932, 76, 201—212).—Electrons of the velocity of conductivity electrons do not pass through Sn foil when this is superconducting.

A. B. D. C.

Determination of potential curves for diatomic molecules with the aid of spectral terms. O. KLEIN (Z. Physik, 1932, 76, 226—235).—Theoretical.

A. B. D. C.

Ionisation potential of molecular hydrogen. W. BLEAKNEY (Physical Rev., 1932, [ii], 40, 496—501; cf. A., 1930, 969).—A mass spectrograph for use with gases at pressures of the order 10⁻⁶ mm. is described, and gives 15.37±0.03 volts for the ionisation potential of mol. H₂. Previous vals. are critically reviewed.

N. M. B.

The Hume-Rothery relationship between ionisation potentials of elements and their atomic number. H. YAGODA (Phil. Mag., 1932, [vii], 13, 1163—1171; cf. A., 1930, 1233).—A more exact relationship for elements in any one periodic group is $\log n - V - a \log z + b$. This is also valid for singly-ionised atoms.

H. J. E.

Photo-electric effect at surfaces of magnesium. H. GERDING and R. GERDING-KROON (Rec. trav. chim., 1932, 51, 612—618; cf. A., 1931, 138).—As with Al, the photo-electric current is increased by scraping in a vac., and diminishes on keeping, more rapidly in presence of air. The photo-electric threshold is displaced by scraping from about 3126 Å. to 4900 Å. The effect of air is due to the retarding action of the contact potential between O₂ and Mg.

F. L. U.

Depth of origin of photo-electrons. H. E. IVES and H. B. BRIGGS (Physical Rev., 1932, [ii], 40, 802—812).—In the earliest development of Na or Cs films on Ag the photo-emission is characteristic, at first, of the light absorption in Ag, and, as the film builds up, of energy above the Ag, indicating that the photo-electrons originate partly in the Ag and partly in the film, the proportion varying with the film thickness.

N. M. B.

Resemblance between longitudinal asymmetry of the classical field of an accelerated electron and distribution of scattered photo-electrons. L. SIMONS (Phil. Mag., 1932, [vii], 14, 148—158).—Theoretical.

H. J. E.

Influence of salts on minimum potential. W. GRAWE (Physikal. Z., 1932, 33, 483—488).—The min. discharge potential of a negatively-charged wire is lowered by inorg. salts, the effect increasing with increasing quantity of salt and with rising temp. The emission from positively-charged wires is not affected. H_3BO_3 and H_3PO_4 do not lower the min. potential, but their salts do so; electron emission is due, therefore, to the metal ion.

E. S. H.

Photo-electric and thermo-electric effect of palladium-silver and palladium-gold alloys charged with hydrogen. J. SCHNIEDERMANN (Ann. Physik, 1932, [v], 7, 761—779).—The absorption of H_2 by Pd and its alloys with Ag and Au increases linearly with the quantity of Ag or Au added. The photo- and thermo-electric effects are increased by the absorbed H_2 . There is a max. for alloys with 40% Ag or Au.

A. J. M.

Photo-electric properties of films of beryllium, aluminium, magnesium, and thallium. H. DE LASZLO (Phil. Mag., 1932, [vii], 13, 1171—1178).—The photo-electric response for films of these metals has been studied in monochromatic light between 5000 and 2400 Å. Mg is specially suitable for the construction of ultra-violet photo-cells.

H. J. E.

Polarisation of electrons by scattering. E. G. DYMOND (Proc. Roy. Soc., 1932, A, 136, 638—651).—Electrons of max. velocity 70 kv. were scattered successively through 90° by thin Au foils, and a small change in intensity was noted as the azimuth of the second scattered beam was altered. The polarisation effect was found to be $1.7 \pm 0.3\%$, that predicted by Mott being 10%.

L. L. B.

Electron polarisation. G. O. LANGSTROTH (Proc. Roy. Soc., 1932, A, 136, 558—568).—Electrons are scattered twice at approx. 90° from thick W targets, and results indicate that the intensities scattered at 0° and 180° of the azimuth do not differ by more than 1%, the experimental error, for primary electron energies up to 10 kv.

L. L. B.

Scattering formulæ for electrons of relativity velocities. H. BETHE (Z. Physik, 1932, 76, 293—299).—Theoretical. Energy loss per cm. reaches a min. at 96% the velocity of light.

A. B. D. C.

Radius of electrons. E. GUTH (Naturwiss., 1932, 20, 470—471).

W. R. A.

Electron radius and molecular recoil. E. GUTH (Naturwiss., 1932, 20, 490).—Polemical.

W. R. A.

Expulsion of electrons from a negative probe by excited atoms or positive ions. F. LUDI (Z. Physik, 1932, 76, 319—321).—Attention is directed to work of Kobel (Brown-Boveri-Mitt., Feb. 1930).

A. B. D. C.

Diffraction of low-speed electrons by single crystals of copper and silver. H. E. FARNSWORTH (Physical Rev., 1932, [ii], 40, 684—712; cf. A., 1929, 1212).—Data for classes of diffraction beams and related refractive indices are reported. Intensities as a function of angle of incidence, and regular reflexion of electrons from crystal planes were investigated. The change in structure with

thickness of a surface gas lattice gives rise to characteristic beams.

N. M. B.

Angular distribution of electrons scattered elastically and inelastically in mercury vapour. J. T. TATE and R. R. PALMER (Physical Rev., 1932, [ii], 40, 731—748).—Experimental.

N. M. B.

Motion of electrons in the static fields of hydrogen and helium. J. McDUGALL (Proc. Roy. Soc., 1932, A, 136, 549—558).—Mathematical.

L. L. B.

Examination of a thin layer of paraffin with electronic radiation. J. GARRIDO and J. HENGSTENBURG (Z. Krist., 1932, 82, 477—480).—A stream of electrons passed through a thin film of the paraffin $C_{21}H_{44}$ gives a sharp diffraction diagram. It indicates that the film consists of crystallites the c axes of which coincide with the length of the mols.

C. A. S.

Ratio h/e by means of electron diffraction. R. VON MEIBOM and E. RUFF (Ann. Physik, 1932, [v], 13, 725—731).—From direct measurement of electron velocity by the Wiechert-Kirchner method and from the estimated wave-lengths of fast electrons diffracted by Au a val. for $h/e = 1.3798 \times 10^{-17}$ was obtained from the de Broglie relation.

W. R. A.

Transference of slow positive particles through canal rays. J. KOENIGSBERGER (Ann. Physik, 1932, [v], 7, 780—782).—A discussion.

A. J. M.

Formation, detection, and absorption of slow neutral rays. H. KALLMANN, V. LASAREV, and B. ROSEN (Z. Physik, 1932, 76, 213—225).—Homogeneous neutral rays of 30 to 800 volts were obtained, and their relative intensity was measured by their emission of electrons from metals. Absorption curves are given for neutral rays in other gases.

A. B. D. C.

Absolute values of the mobility of gaseous ions in pure gases. N. E. BRADBURY (Physical Rev., 1932, [ii], 40, 508—523).—The abs. method of Tyndall and Grindley (cf. A., 1926, 219), with improved resolving power, was used for highly-purified gases. Mobilities in cm./sec. per volt/cm. are, for air, positive ion 1.6, negative ion 2.21; for O_2 from $KClO_3$, negative ion 2.65 (anomalously high); for O_2 from $KMnO_4$ and a commercial source, positive ion 1.58, negative ion 2.18; for N_2 (commercial), no negative ions, positive ion 2.09; for H_2 , no negative ions, positive ion 8.2, and indications of 13.1; for He, no negative ions, positive ion 17.0.

N. M. B.

Mobility experiments in gaseous mixtures and ageing experiments in pure gases. N. E. BRADBURY (Physical Rev., 1932, [ii], 40, 524—528; cf. preceding abstract).—Vals. for the positive ion mobility in H_2-NH_3 and N_2-NH_3 mixtures were 9.4 (at 0.15 mm. partial pressure of NH_3) and 1.83 (in addition to 2.09 for the normal positive ion in pure N_2), respectively. A continuation of experiments on ageing is reported (cf. A., 1931, 889).

N. M. B.

High-velocity positive ions. I. Method of obtaining high-velocity positive ions. J. D. COCKCROFT and E. T. S. WALTON (Proc. Roy. Soc., 1932, A, 136, 619—630).—To obtain large steady potentials for the acceleration of protons, a method is

developed by which the voltage of a transformer can be rectified and multiplied several times by an arrangement of valves and condensers. L. L. B.

At. wts. of H^2 and Be^9 . N. S. GRACE (J. Amer. Chem. Soc., 1932, 54, 2562—2563).—The at. wts. 2.0113 ± 0.0012 and 9.005 ± 0.002 are theoretically deduced for H^2 and Be^9 , respectively. The existence of H^2 nuclei and neutrons suggests that all known at. nuclei may originate from protons and electrons by a succession of two-body collisions, e.g., two H^2 nuclei form an α -particle. C. J. W. (c)

Hydrogen isotope of mass 2. H. KALLMANN and W. LASAREV (Naturwiss., 1932, 20, 472).—From an examination of distilled H_2 by a mass spectrograph it is concluded that H^2 is present. This isotope seems to be bound in the H_3 ion. W. R. A.

Separation of gaseous isotope mixtures. G. HERTZ (Naturwiss., 1932, 20, 493—494).—A method for separating the isotopes of Ne is described. Ne^{21} and Ne^{23} were found by the mass-spectrograph method, but are not encountered in optical spectra. These isotopes occur in the ratio 1 : 2000 in normal Ne. W. R. A.

Existence of isotopes of selenium and tellurium deduced from the examination of the resonance multiplets of Se_2 and Te_2 . P. SWINGS and Y. CAMBRESIER (Bull. Acad. roy. Belg., 1932, [v], 18, 419—421).—The rotation quantum nos. of Se_2 and Te_2 mols. in the excited state have both odd and even vals. Consequently these elements must each exist in at least two isotopes (cf. A., 1931, 1348). J. W. S.

Radioactive transformations. L. WERTENSTEIN (Compt. rend., 1932, 194, 2305—2307).—Theoretical. A discussion of the modifications of the views as to the mechanism of radioactive transformations, and the nature and origin of the radioactive elements consequent on the idea of demihelions (cf. this vol., 556). C. A. S.

Existence of a neutron. J. CHADWICK (Proc. Roy. Soc., 1932, A, 136, 692—708).—When Be (or B) is bombarded by α -particles from Po a very penetrating radiation is produced which effects long-range particles from H_2 and many light elements. The results are consistent with the view that the radiation consists of neutrons, a neutron being a proton and an electron in close association, the binding energy being 1 to 2×10^6 electron volts, the mass 1, and the charge 0. Experiments on the passage of neutrons through matter give information on the frequency of their collisions with at. nuclei and electrons. L. L. B.

Attempts to detect the interaction of neutrons with electrons. P. I. DEE (Proc. Roy. Soc., 1932, A, 136, 727—734).—From experiments in a Wilson cloud track chamber it is concluded that the probability of an interaction of a neutron with an electron with production of a recoil electron track is less than 1% of the probability of a similar interaction with a N nucleus. L. L. B.

Collisions of neutrons with nitrogen nuclei. N. FEATHER (Proc. Roy. Soc., 1922, A, 136, 709—727).—Neutrons obtained from Be, by α -particle

bombardment, give rise to tracks in an expansion chamber after collision with N nuclei and are shown to be emitted with energies distributed over a wide range. Two types of inelastic collision resulting in disintegration are found, one in which a neutron is captured and an α -particle liberated, and another in which a neutron is not captured but a proton is probably liberated. L. L. B.

Demihelions. F. PERRIN (Compt. rend., 1932, 194, 2211—2213; cf. this vol., 556).—It is suggested that the single anomalous forked track observed by Blackett (cf. this vol., 672) is due to expulsion of a demihelion, composed of one proton and one neutron, of at. wt. 2.0115 ± 0.0005 . C. A. S.

Radiations excited in light atoms by α -particles. (MME.) I. CURIE, F. JOLIOT, and P. SAEV (Compt. rend., 1932, 194, 2208—2211; cf. this vol., 555, 672).—The neutrons projected from Be by α -particles in the same direction as that of the α -particles eject from paraffin a main group of H-particles of path 28 cm. in air and a small group of max. path about 70 cm. Neutrons projected backward (at 120° — 180°) eject H-particles of path 23 cm. The velocities of the two main groups are 3.84 and 2.94×10^8 cm./sec. respectively; they possibly result from the reactions $Be^9 + \alpha = C^{12} + n$ and $Be^9 + \alpha = C^{12} + n + \gamma$, respectively, which gives as at. wt. of Be^9 9.006. Neutrons projected backwards are diffused more by Pb than by Cu. Po+Li radiation is similarly dissymmetric; the ratio of the ionisation produced by the forward radiation to that produced by γ -rays of Po in H_2 , N_2 , and A is, respectively, 0.55, 0.31, and 0.25; it is absorbed equally by 1 g. per sq. cm. of paraffin or 4 g. of Pb. This radiation is also probably neutrons, due possibly to the reactions $Li^6 + \alpha + \text{electron} = Be^9 + n$ or $Li^7 + \alpha = B^{10} + n$. C. A. S.

Disintegration constant of uranium by the method of counting α -particles. A. F. KOVARIK and N. I. ADAMS, jun. (Physical Rev., 1932, [ii], 40, 718—726).—More than 100,000 counts of α -particles emitted from thin films of pure U_3O_8 gave 1.53×10^{-10} year⁻¹ for the disintegration const., 3.40×10^{-7} for the Ra-U ratio, and 0.96—0.97 for the branching ratio. N. M. B.

Anomalous scattering of α -particles by H_2 and He. H. M. TAYLOR (Proc. Roy. Soc., 1932, A, 136, 605—618).—Mathematical. In H_2 and He the scattering at small angles of α -particles can be explained by the same field as that for large angles, and the results are independent of the form of the potential energy curve assumed for one particle in the field of the other, as long as the energy is Coulombian for distances greater than 5×10^{-13} cm. L. L. B.

Magnetic spectrum of β -rays of Th-C+C'+C''. S. V. SZE (Compt. rend., 1932, 194, 2206—2208; cf. this vol., 442, 443).—The intensities, H_p , and energies of 56 (18 new) β -rays in this magnetic spectrum, referred to H_p 1398 as standard, have been determined. 12 of these rays are considered to be due to γ -rays converted in the atom of Th-C'' (cf. A., 1926, 6). C. A. S.

Close collisions of fast β -particles with electrons, photographed by the expansion method. F. C. CHAMPION (Proc. Roy. Soc., 1932, A, 136, 630—637).—In a no. of collisions of fast β -particles and electrons, in all cases except one momentum and energy were conserved and results predicted by the principle of restricted relativity verified. L. L. B.

Gamma-radiation and its relation to nuclear structure. P. G. KRUGER (Physical Rev., 1932, [ii], 40, 727—730).—The calc. wave-lengths of γ -radiation from the nucleus for 14 radioactive elements are in moderate agreement with observed vals.

N. M. B.

Interaction between γ -radiation and the atomic nucleus. L. H. GRAY and G. T. P. TARRANT (Proc. Roy. Soc., 1932, A, 136, 662—691).—Elements of high at. no. absorb the hard γ -rays of Th-C' and Ra-C, and emit a secondary radiation quite unlike that scattered by the electronic system of the outer atom. The absorption curves of the characteristic radiations of Pb, Sn, Fe, and O₂ are very similar. The results indicate that the absorption process is an excitation of the nucleus which subsequently emits characteristic radiations.

L. L. B.

δ -Rays and the relation between range and velocity for slow electrons. T. ALPER (Z. Physik, 1932, 76, 172—189).—The lengths of δ -ray tracks were measured at different points along an α -ray track in a Wilson chamber, and a relation was obtained connecting range and velocity of electrons of 200 to 4500 volts.

A. B. D. C.

Structure of atomic nuclei. (Proc. Roy. Soc., 1932, A, 136, 735—762).—(LORD) RUTHERFORD. Progress in certain fields of research bearing on this problem is reviewed, with special reference to optical methods (*e.g.*, the relative intensities of lines in band spectra of light elements), applications of wave-mechanics, Gamow's theory of a high potential barrier surrounding the nucleus, the origin of γ -rays, the conception of energy levels in the nucleus, the excitation of nuclei by γ -rays, the artificial transmutation of the elements, and the scattering of α -particles.

J. CHADWICK reviewed the evidence for the existence of the neutron.

C. D. ELLIS discussed α - and β -ray spectra.

R. H. FOWLER discussed the question of nuclear spin.

J. C. MCLENNAN described the data obtainable from a study of the fine structure of spectral lines, from which can be calc. the mechanical moments and the ratio of magnetic to mechanical moments for a no. of at. nuclei.

F. A. LINDEMANN indicated difficulties in the conception of free electrons in the nucleus and the idea of the neutron.

N. F. MOTT described the application of quantum mechanics to the problem of the anomalous scattering of α -particles.

L. L. B.

Wave-mechanical calculation of the polarisability of the hydrogen molecule. B. MROWKA (Z. Physik, 1932, 76, 300—308).

A. B. D. C.

Pressure effect in radiationless dissociation. K. WURM (Z. Physik, 1932, 76, 309—315).—The pre-

dissociation system of AlH bands was obtained by temp. emission; the band lines become sharp near 2 mm. pressure.

A. B. D. C.

Destruction of matter by ultra-radiation. E. G. STEINKE and H. SCHINDLER (Naturwiss., 1932, 20, 491—493).

W. R. A.

Ultra-violet transmission of thin blown glass windows. H. KLUMB and T. HAASE (Z. Physik, 1932, 76, 322—327).—A method of making and using windows 10 μ thick is described.

A. B. D. C.

Spectroscopic determination of electron affinities of the pseudo-halogens OH and CN. E. LEDERLE (Z. physikal. Chem., 1932, B, 17, 362—368).—Available data show that for the halides of a given metal the graphs of the electron affinity of the halogen against the heat of dissociation of the halide and against the energy level of the ultra-violet absorption max. are often rectilinear, deviations from this rule being associated with differences in crystal form. By means of this relation the following data have been obtained: electron affinities of OH and CN, 88 ± 1 and 92 ± 2 , respectively; heat of dissociation (CN)₂ = 2CN, 61 ± 3 ; splitting of aromatic C-Br linking, 75 kg.-cal.

R. C.

Determination of electron affinities of halogens from continuous absorption spectra of alkali halide vapours. E. LEDERLE (Z. physikal. Chem., 1932, B, 17, 353—361).—From the energy levels of the ultra-violet absorption maxima of alkali halide vapours (A., 1925, ii, 1025) and the heats of dissociation (A., 1924, ii, 434) the electron affinities of Cl, Br, and I have been calc. to be 90 ± 1 , 82 ± 1 , and 73 ± 1 kg.-cal., respectively. By extrapolation the electron affinity of F has been found to be 95 ± 2 and the heat of dissociation 60.8 ± 0.5 kg.-cal.

R. C.

Predissociation in the spectrum of iodine chloride. W. G. BROWN and G. E. GIBSON (Physical Rev., 1932, [ii], 40, 529—543).—The 17,446, 17,664, and 17,828 cm.⁻¹ bands lying just beyond the convergence of the visible absorption bands are analysed, and reveal a case of predissociation due to interaction with a repulsive O⁺ state derived from two normal atoms.

N. M. B.

Increase of predissociation by collision and Beer's law. V. KONDRATIEV and L. POLAK (Z. Physik, 1932, 76, 386—389).—Observations of absorption by Br and NO₂ showed that Beer's law does not hold for regions of predissociation, and deviations increase with increasing pressure of the original or foreign gas.

A. B. D. C.

Simple relations between molecular spectra and structures. H. DESLANDRES (Compt. rend., 1932, 194, 2093—2097; cf. this vol., 444).—Further examples are given.

C. A. S.

Theory of the relationships between absorption of light and constitution. A. BURAWOY (Ber., 1932, 65, [B], 941—947).—The author's views (A., 1931, 144, 544, 1052) are developed further and the results are applied to the elucidation of the chemical valency problem of unsaturated compounds. It is shown that the unsaturated nature of double linkings is due to equilibria between saturated mols. and those

with free valencies. Addition to compounds containing neighbouring double linkings invariably occurs in such a manner that a new conjugated system results. Addition in the 1 : 2 position is ascribed to the presence of mols. in which conjugated systems are not present but which contain their electron-isomeric forms with free valencies in 1 : 2 position. H. W.

Absorption of light and constitution. IV. A. BURAWOY (Ber., 1932, 65, [B], 947—949; cf. A., 1931, 144, 544, 1052).—A reply to Dilthey (A., 1931, 955). H. W.

Rotational structure of the ultra-violet absorption bands of formaldehyde. G. H. DIEKE and G. B. KISTIAKOWSKY (Proc. Nat. Acad. Sci., 1932, 18, 367—372).—Rotational fine structure of bands at 3520, 3430, and 3390 Å. was investigated, and moments of inertia in upper and lower states are deduced. A. B. D. C.

Ultra-violet bands of formaldehyde and their presence in the solar spectrum. N. R. DHAR (Z. anorg. Chem., 1932, 206, 270—272).—Some lines of the absorption spectrum of CH_2O vapour correspond with lines in the solar spectrum of which the source has not hitherto been determined. Especially notable are those bands of which the strongest parts of the central max. are at 3035.8, 3088.7, 3143.4, 3170.4, and 3389.3 Å. M. S. B.

Absorption of ultra-violet light by glyoxaline and some of its derivatives. C. S. HICKS and H. F. HOLDEN (Austral. J. Exp. Biol., 1932, 10, 49—52).—Glyoxaline-4 : 5-dicarboxylic acid has an absorption band at approx. 251.0 m μ whilst histidine, glyoxaline, methylglyoxaline, and histamine have no bands but only increasing absorption on approaching the region 220 m μ . W. O. K.

Ultra-violet absorption spectrum of histidine. F. ELLINGER (Biochem. Z., 1932, 248, 437—448; cf. A., 1929, 98; 1930, 1048).—An unknown Fe compound (probably of protein) sensitises the absorption by histidine hydrochloride of long ultra-violet rays and promotes the production of a histamine-like substance. FeCl_3 acts in the same way but to a smaller extent. The biological significance of the results is discussed. W. M.

Attempt at co-ordinating infra-red absorption bands of some ring hydrocarbons. J. LECOMTE (Compt. rend., 1932, 194, 2037—2040).—The frequencies of the infra-red (λ 6—16 μ) absorption bands of C_6H_6 , C_7H_8 , C_8H_{10} , and C_{10}H_8 are classified into several series expressed by $\nu = a + bn + cn$, n being an integer. C. A. S.

Intensity of infra-red absorption bands. L. A. MATHESON (Physical Rev., 1932, [ii], 40, 813—828).—The abs. intensities of infra-red absorption bands in CO and a band analysis were obtained by measuring the absorbed energy directly by the vol. change in the gas due to the heat evolution in it. N. M. B.

Absorption spectrum of water vapour beyond 10 μ . L. R. WEBER and H. M. RANDALL (Physical Rev., 1932, [ii], 40, 835—847).—Using a new type spectrometer of high dispersion (cf. A., 1931, 1387)

the highly complex spectrum in the region 10—25 μ was re-measured. N. M. B.

Cabannes-Daure effect and molecular field. A. ROUSSET (Compt. rend., 1932, 194, 2299—2301; cf. A., 1928, 1310; 1929, 752).—It is shown that the intensity of laterally scattered light depends on the anisotropy and refractive index of the liquid concerned, and that dissymmetry in the Cabannes-Daure effect is confined to anisotropic liquids. Experimental results with C_6H_6 , AcOH , CCl_4 , and EtOH are in agreement. C. A. S.

Intensity measurements in Raman spectra. A. CARRELLI and J. J. WENT (Z. Physik, 1932, 76, 236—249).—Quant. measurements of the intensity of Raman displacements must allow for these being bands, not lines, and each Raman band has a characteristic form. The degree of polarisation is not const. throughout the band. CCl_4 showed no continuous spectrum, whilst C_6H_6 did so. A comparison of the intensity of Raman bands and Rayleigh radiation gave the ratio of the scattering moments of the mol. for displaced and undisplaced radiation. A. B. D. C.

Scattering of light by liquid helium. J. C. McLENNAN, H. D. SMITH, and J. O. WILHELM (Phil. Mag., 1932, [vii], 14, 161—167).—No Raman lines were observed with liquid He, but certain Hg lines had "wings," interpreted as due to rotational Raman transitions in loosely-bound He mols. in the liquid. Surface tension measurements also indicate association. H. J. E.

NO_3 frequency in organic nitrates. A. S. GANESAN and V. N. THATTE (Nature, 1932, 129, 905).—The characteristic inactive frequency at 9.5 μ appears as a Raman line in EtOH solutions of organic nitrates. Raman lines for MeNO_2 are recorded. L. S. T.

Raman effect of polyatomic molecules. J. WEIGLE (Arch. Sci. phys. nat., 1932, 14, 82—95).—A descriptive survey of the principle and some applications of the phenomenon. N. M. B.

Polarisation of Raman lines in crystals. J. CABANNES (Compt. rend., 1932, 194, 2134—2136; cf. this vol., 212).—It is shown, with a crystal of type C_{2v} , as example, that when the vibrations of the incident polarised ray are parallel to an axis of symmetry of the crystal depolarisation of light diffused perpendicularly to the incident ray is zero for rays symmetrical relative to the axis of symmetry, complete for rays antisymmetrical thereto, or degenerate (cf. A., 1930, 397; 1931, 893). C. A. S.

Raman effect and molecular anisotropy. J. WEILER (Physikal. Z., 1932, 33, 489—498).—A summary of work on the connexion between the width of the primary lines and mol. anisotropy. A. J. M.

Raman bands of water. S. RAFALOVSKI (Bull. Acad. Polonaise, 1931, A, 623—628; cf. A., 1931, 1353).—Details are given of results described previously. Support is given to the view that Raman bands for H_2O have a threefold structure. J. W. S.

Raman spectra of a series of octanols. G. COLLINS (Physical Rev., 1932, [ii], 40, 829—834).—Data are reported for 19 octanols differing only in the relative position of a Me and OH group along a chain of 7 C atoms, using $Hg\lambda$ 4358 as the exciting line. Results are interpreted by comparison with mol. structure. N. M. B.

Polarisation of Raman lines in liquids. S. BHAGAVANTAM (Indian J. Physics, 1932, 7, 79—86).—Results are reported for C_5H_{12} , CS_2 , HCO_2H , thiophen, CCl_4 , $SiCl_4$, $TiCl_4$, and $SnCl_4$. N. M. B.

Raman spectrum of quinoline, and the carbon-nitrogen linking. G. B. BONINO and P. CELLA (Atti. R. Accad. Lincei, 1932, [vi], 15, 385—389).—The Raman spectrum is described. A line at 1433 cm^{-1} is attributed to the C:N linking, since a line of approx. the same frequency occurs also in the spectrum of pyridine and various thiocarbimides. The double nucleus gives rise to a line at 1375 cm^{-1} . H. F. G.

Raman spectra of piperidine, ethyl alcohol, and acetone. S. C. SARKAR (Indian J. Physics, 1932, 7, 61—78).—Full data and comparisons with infrared absorption curves are reported. Piperidine shows 14 new lines; EtOH shows new lines at 2709 and 2743 \AA , and the older line 925 of CO_2 is corrected to 2689 cm^{-1} . N. M. B.

Lateral radiation and the nature of the colouring substance in rock-salt. M. KAHANOWICZ (Z. Physik, 1932, 76, 283—292).—An investigation of the blue and violet fluorescence of rock-salt revealed that the emitted radiation is identical with the fluorescent bands of Na_2 , and the source of the rock-salt emission is impurities of small Na crystals; transition from the Na crystals to colloidal Na is accompanied by change from fluorescence to Rayleigh scattering. A. B. D. C.

Extinction curve of scintillation of zinc sulphide. J. STALONY-DABROWSKI (Rocz. Chem., 1932, 12, 299—310).—The duration of scintillation of ZnS excited by α -particles is 0.125 sec.; the most intense luminescence is emitted during the first 0.00003 sec., during which 7% of the total energy is dissipated. The light intensity then falls sharply to 19% of the original val., after which it continues to diminish progressively, at first rapidly, and then more slowly. R. T.

Relation between certain types of luminescence. E. L. NICHOLS and F. G. WICK (J. Opt. Soc. Amer., 1932, 22, 357—368).—Experiments in support of the view that in cathodo- and cathodoluminescence there is the same process are described. A. J. M.

Luminescence of glass and fluorite. T. LYMAN (Physical Rev., 1932, [ii], 40, 578—582). N. M. B.

Phosphorescent sulphides: extinguishing action of metals of the iron group. M. CURIE and J. SADDY (Compt. rend., 1932, 194, 2040—2042; cf. this vol., 560).—The addition, at the time of prep., of small amounts of $CoCl_2$, $FeCl_2$, or $PbCl_2$ to a phosphorescent ZnS causes large (Co), moderate (Fe), or no (Pb) diminution in its conductivity and luminescence. C. A. S.

Electrostatic potential of some cubic crystal lattices. T. S. WHEELER (Phil. Mag., 1932, [vii], 14, 56—66).—A method for calculating the electrostatic potential of a cubic lattice with regard to the central lattice point is developed and applied. H. J. E.

Dependence of ionisation number on field strength and the mean "ionisation field strength" in liquids. A. NIKURADSE (Ann. Physik, 1932, [v], 7, 851—873).—Mean "ionisation field strength" depends on the nature of the liquid. A. J. M.

Ionisation phenomena in benzene [vapour]. E. FRIEDLANDER and H. KALLMANN (Z. physikal. Chem., 1932, B, 17, 265—275; cf. A., 1930, 514).—The principal intensity maxima in the mass spectrograph of C_6H_6 vapour bombarded with electrons of variable velocity correspond with the ions $C_6H_6^+$, $C_6H_4^+$, and $C_2H_2^+$. Other ions are formed either by direct ionisation of the C_6H_6 or from products of its thermal decomp. The ionisation voltages have been determined. By collision with a gas mol. the $C_6H_6^+$ ion may be dissociated into $C_2H_4^+$ and a residue, or $C_4H_2^+$ and a residue. R. C.

Outer photo-electric effect for liquids. Determination of the long-wave limit for water. P. GORLICH (Ann. Physik, 1932, [v], 7, 831—850).—The long-wave photo-electric limits for H_2O and conc. solutions of $AgNO_3$, $K_4Fe(CN)_6$, Na_2SO_4 , and $NaCl$ were determined. The val. for H_2O is 203—204 m μ . Solutions have the same limit as the solvent. The spectral photo-electric distribution for H_2O was also found. An absorption max. occurs at 185 m μ . A. J. M.

Photo-cells and light elements. F. VON KOROSY and P. SELENYI (Ann. Physik, 1932, [v], 13, 703—724).—Experimental methods are developed for determining the characteristics of the unidirectional layer of a Cu-Cu₂O photo-cell. W. R. A.

Nature of electrical conductivity of cuprous oxide. H. DUNWALD and C. WAGNER (Z. physikal. Chem., 1932, B, 17, 467—470).—At 800—1000° and under such O_2 pressures that neither Cu nor CuO can be present as a second solid phase the conductivity of Cu₂O plates, κ , is approx. given by $\kappa = p_{O_2}^{1/2}$, const. The thermo-e.m.f. Pt|Cu₂O has been measured at 900—1000°. R. C.

Becquerel effect for cuprous oxide as a boundary layer photo-effect. F. WAIBEL (Z. Physik, 1932, 76, 281—282). A. B. D. C.

Dielectric behaviour of colloidal particles with an electric double layer. J. B. MILES, jun., and H. P. ROBERTSON (Physical Rev., 1932, [ii], 40, 583—591).—Mathematical. N. M. B.

Dielectric constant of nitrogen up to 150 atmospheres at 25°, 75°, and 125°. A. MICHELS and C. MICHELS (Phil. Mag., 1932, [vii], 13, 1192—1196).—The experimental details and results are recorded. H. J. E.

Inorganic halides and their molecular compounds. VI. Dipole moments of titanium and tin tetrachlorides. H. ULLICH, E. HERTEL, and W. NESBITAL (Z. physikal. Chem., 1932, B, 17, 369—

379; cf. this vol., 676).—Solid and liquid halides and solutions in CCl_4 have zero dipole moment. In C_6H_6 solution the moment of SnCl_4 is 0.80, perhaps due to the formation of a mol. compound. Bergmann and Engel's experimental methods (A., 1931, 999, 1000) are criticised. R. C.

Dielectric constant of liquids. VII. Dielectric constant and electric moment in aqueous solution. G. DEVOTO (Atti R. Accad. Lincei, 1932, [vi], 15, 471—473; cf. A., 1930, 1358).—Vals. of the dielectric constant—concn. coeff., de/dc , for $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ and its homologues are given. If the increase in the length of the chain per CH_2 group is 1.3 Å., as with the fatty acids, the calc. increase of de/dc per CH_2 group is 11—12 units, in agreement with experiment. O. J. W.

Electric moments of 1-halogeno-2:4-dinitrobenzenes. H. LUTGERT (Z. physikal. Chem., 1932, B, 17, 460—462).—The moments have been determined by measurements with C_6H_6 solutions and have made it possible to calculate the direction of the moment produced by the two groups in the *o*-position. R. C.

Electric moment and molecular structure. VII. Carbon valency angle. C. P. SMYTH and W. S. WALLS (J. Amer. Chem. Soc., 1932, 54, 1854—1862).—Determinations of the moments of several CH_2Ph and *p*-substituted CH_2Ph compounds have given vals. for the C valency angle differing from the theoretical tetrahedral angle by no more than the probable error. H. F. J. (c)

Calculation of "angular values" from dipole moments of aromatic compounds. K. L. WOLF (Z. physikal. Chem., 1932, B, 17, 465—466).—Polemical against Bergmann (cf. this vol., 677). R. C.

Molecular area and volume in films: application to determination of molecular mass. D. G. DERVICHAN (Compt. rend., 1932, 194, 2294—2296).—Deviations from the thickness of the film at the "vaporisation point" being exactly $V^{1/3}$ are due to the orienting effect of the liquid surface. The mol. mass of the film substance, $M = d(SRT/S'P)^{3/2}/N^{1/2}$, where S is the area of the film at the vaporisation point, S' the corresponding area when the relation $P_s = RT$ holds (s being the surface per g.-mol.), d density, and R , T , N , and P have their usual meanings. The formula, which gives M for oleic acid—190, would be useful in microchemical analysis as 10^{-6} g. gives a measurable film. C. A. S.

Kerr effect, optical anisotropy, and molecular structure. Structure of molecules of stannic chloride, propyl chloride, and nitrous oxide. H. A. STUART and H. VOLKMAN (Z. physikal. Chem., 1932, B, 17, 429—456; cf. A., 1929, 872).—The Kerr consts. of the vapours of SnCl_4 , C_6H_6 , CHCl_3 , $\text{C}_2\text{H}_4\text{Cl}_2$, *cis*- and *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$, PrCl , and COMeEt have been determined and the polarisation ellipsoids calc. The data for SnCl_4 agree with a tetrahedral structure of the mol. and not with a pyramidal structure, and the N_2O mol. has the form $\text{N}:\text{N}:\text{O}$, not In PrCl the linking holding the Et group has considerable or

total freedom of rotation, and the mol. has no fixed plane configuration, such as a zigzag. The optical anisotropy and thence the structure of a mol. may be determined in cases where the Kerr effect and the scattering of light give no assistance by means of an examination of the rotational fine structure of Raman and Rayleigh lines and the polarisation relations of Raman lines (cf. A., 1930, 840; 1931, 893). R. C.

Explanation of a magneto-optic effect. M. CAU (Compt. rend., 1932, 194, 2042—2045).—The modification of the magnetic rotation caused by a thin layer of Fe due to its being in contact with one of Pt is explicable as due to multiple reflexions at the Fe-Pt surface. C. A. S.

Variation of Faraday effect with concentration. P. K. PILLAI (Indian J. Physics, 1932, 7, 87—90).—The rotation of $\text{Ce}(\text{NO}_3)_3$ at 10 different concns. plotted against concn. gave a straight line relation. Variations of Verdet's const. for FeCl_3 are discussed. N. M. B.

Magnetic rotations of liquid mixtures. R. N. MATHUR and A. N. KAPUR (Indian J. Physics, 1932, 7, 15—18).—The max. differences between the experimental and calc. vals. for $\text{CHCl}_3\text{-COMe}_2$, $\text{Et}_2\text{O-CHCl}_3$, and $\text{Et}_2\text{O-COMe}_2$ mixtures are of the order 1% (cf. Trew and Spencer, A., 1931, 676). N. M. B.

Thermal variation of magnetic rotatory power of nickel chloride. H. OLLIVIER, (Mlle.) J. PERNET, and J. LESNE (Compt. rend., 1932, 194, 2301—2303; cf. A., 1930, 1095).—The sp. magnetic rotation of anhyd. NiCl_2 , as deduced by the additive law from its aq. solutions, is independent of the concn. It is also independent of temp. for moderately conc. solutions, but for dil. solutions diminishes as temp. rises, but less than required by the Curie-Weiss law. C. A. S.

Influence of temperature on the natural and magnetic rotation of *d*- and *l*- α - and *l*- β -pinene. C. SALCEANU (Compt. rend., 1932, 2136—2138; cf. A., 1931, 148).—The ordinary and magnetic rotations of these liquids have been determined at various temp. $> 141.5^\circ$ for λ 5780, 5460, and 4360, and the dispersion is discussed (cf. A., 1911, ii, 352). C. A. S.

Influence of solvents and other factors on the rotation of optically active compounds. XXIX. Rotation-dispersion of camphor, camphoroxime, isonitrosocamphor, and oxymethylenecamphor. T. S. PATTERSON, E. F. M. DUNN, C. BUCHANAN, and J. D. LOUDON. XXX. Rotation-dispersion of various derivatives of camphor. T. S. PATTERSON and J. D. LOUDON (J.C.S., 1932, 1715—1725, 1725—1744).—XXIX. The rotation of camphor is influenced by the solvent, being a max. in $\text{C}_2\text{H}_4\text{Br}_2$, and a min. in PhOH , among the org. solvents used. Conc. H_2SO_4 depresses the rotation to -75.6° .

XXX. Conc. H_2SO_4 depresses the rotation of a no. of camphor derivatives, particularly camphor-10-sulphonic acid. A method for the esterification of this acid and its α -Cl- and α -Br-derivatives is described. The rotations of these esters and their corresponding amides, except camphor-10-sulphonamide where the anhydramide was used, and of α -chloro- and α -bromocamphor have been investigated in different solvents.

Camphor-10-sulphonic acid may possibly have a laevo-configuration, and the α -halogen derivatives dextro-configurations. A. J. M.

Molecular structure and physical properties of hydrocyanic acid. I. Refractive dispersion of hydrocyanic acid and its homologues. T. M. LOWRY and S. T. HENDERSON (Proc. Roy. Soc., 1932, A, 136, 471—487).—With an improved method, mean deviation 5 units in the 5th decimal place, measurements have been made of the vals. of n of HCN and the homologous MeCN (I), EtCN (II), MeNC (III), and EtNC (IV) for 26 wave-lengths in the visible spectrum and up to 2473 Å. in the ultra-violet. The results are expressed by equations of the Ketteler-Helmholtz type, the characteristic frequencies being at 978, 994, 994, 1085, and 1067 Å. for HCN, (I), (II), (III), and (IV), respectively. A comparison of the mol. refractions of cyanides and carbylamines with HCN shows that the liquid acid is almost completely HCN. L. L. B.

Attack of oxygen molecules on highly crystalline graphite. E. N. GREER and B. TOPLEY (Nature, 1932, 129, 904—905).—The brilliant reflexion from the surface of a flake of Ceylon graphite remains unimpaired during oxidation at 900° in O₂ at 1 mm. pressure. The C atoms appear to be removed layer by layer without pitting. The holes which finally appear have a well-defined hexagonal form. L. S. T.

Quantum theory and chemistry. E. A. HYLLE-RAAS (Tids. Kjem., 1932, 12, 89—94).—Theoretical. H. F. H.

Theory of induced polarities in benzene. E. HÜCKEL and W. HÜCKEL (Nature, 1932, 129, 937—938).—A reply to Lapworth and Robinson (this vol., 324). L. S. T.

Structure of complex salts containing various co-ordinated atoms or groups. I. Complexes of co-ordination number 6: (NH₄)₃[VF₆] and Ti₂[VF₆(H₂O)]]. II. (NH₄)₃[CrF₆] and Rb₃[CrF₆(H₂O)]. L. PASSERINI and R. PIRANTI (Gazzetta, 1932, 62, 279—288, 289—295).—I. (NH₄)₃[VF₆] and Ti₂[VF₆(H₂O)] form cubic crystals. The former has a 9.04±0.005 Å., d_{calc} 1.97, 4 mols. in unit cell; the latter a 8.45±0.005 Å., c 6.29, 4 mols. in unit cell, and the 5 F⁺ ions and the H₂O group occupy equiv. positions with regard to the V atom. It is therefore possible for a neutral mol. (H₂O) to replace an ion (F⁺) without change of structure provided that the two are of similar vol.

II. (NH₄)₃[CrF₆] forms cubic crystals; a 9.01±0.005 Å., 1.997, 4 mols. in unit cell. Rb₃[CrF₆(H₂O)], prepared by evaporation of a solution containing RbNO₃ and CrF₃, forms sparingly sol. light green cubic crystals, a 8.38±0.005 Å., 3.79, 4 mols. in unit cell; the H₂O group occupies a position equiv. to those of the F ions, in confirmation of the view expressed above. H. F. G.

Magnetic susceptibility of sulphur vapour. L. NEEL (Compt. rend., 1932, 194, 2035—2037).—The magnetic susceptibility, χ_s , of S₂ has been deduced from determinations made on the vapour in sealed quartz tubes, corrected for the diamagnetism of S₈ and S₆ (cf. A., 1909, ii, 977). $\chi_s \times 10^6$ decreases from

12.2 at 600° to 8.40 at 800°, or thrice as rapidly as required by the Curie law, indicating variable magnetic moment. C. A. S.

Diamagnetic susceptibilities of some beryllium compounds. W. R. ANGUS and J. FARQUHARSON (Proc. Roy. Soc., 1932, A, 136, 579—584).—The diamagnetic susceptibilities of basic Be acetate, propionate, pivalate, and acetylacetonate were measured on a Curie-Cheneveau torsion balance. Pascal's method was used to calculate the susceptibilities of the org. groups; the ions were calc. by the Angus-Slater method. L. L. B.

Ionic diamagnetic susceptibilities. W. R. ANGUS (Proc. Roy. Soc., 1932, A, 136, 569—578).—The ionic or at. susceptibilities of 76 atoms or ions having completed groups and sub-groups are evaluated by Slater's method and by a modification. Vals. for the ionic susceptibilities of 24 ions with incomplete groups or sub-groups have been calc. by the same methods. L. L. B.

Magnetic behaviour of compounds. V. Ferric dibutyldithiocarbamate. L. CAMBI, L. SZEGO, and A. CAGNASSO [with C. JACINI] (Atti R. Accad. Lincei, 1932, [vi], 15, 329—335).—The following compounds are described: NHBu^{sec}.Bu^{sec}, b.p. 150°; NHBu^{sec}.Bu, b.p. 147°; NHBu^{sec}.CS₂, b.p. 137°;

Fe(NBu^{sec}.CS₂)₃; Fe[NBu^{sec}.Bu^{sec}.CS₂]₃; Fe[Nsec.Bu^{sec}.CS₂]₃; Fe[NBu^{sec}.Bu^{sec}.CS₂]₃; and Fe[NBu^{sec}.Bu^{sec}.CS₂]₃. The susceptibilities of the Fe derivatives and of Fe(NBu^{sec}.CS₂)₃ have been determined at temp. between 84° and 350° abs., and the results are discussed in relation to those previously obtained for the analogous Pr derivatives. H. F. G.

Magnetic properties of iron, nickel, cobalt, and some alloys at high temperatures. H. KUHLEWEIN (Wiss. Veroff. Siemens-Konz., 1932, 11, No. 1, 124—140).—Magnetic measurements confirmed Forrer's observation (A., 1930, 529) that some metals and alloys have two Curie points. For Ni with 1% Mn the paramagnetic point, Θ_p , is 436° and the ferromagnetic point, Θ_f , 378° on heating; on cooling, Θ_p occurs at 394° and Θ_f at 340°. For Fe Θ_p is 830° and Θ_f 790°.

In Co-Fe alloys with 20—70% Co the magnetic transformation is identical with the A3 change, and $\Theta_p > \Theta_f$. A. R. P.

Direct measurement of magnetic susceptibility of liquids by the Curie-Cheneveau magnetic balance. C. COURTY and C. CHENEVEAU (Compt. rend., 1932, 194, 2197—2198; cf. this vol., 216).—The balance is further improved by replacing the cylindrical tubes by vessels resembling sp. gr. flasks. The coeffs. of magnetisation and susceptibility ($\times 10^6$) of C₆H₆ are 0.713 and 0.628, respectively; of CCl₄ 0.427 and 0.697; CHCl₃ 0.488 and 0.742; EtOH 0.744 and 0.595; and of pyridine 0.622 and 0.610. C. A. S.

Diamagnetism and structure of some compounds of ethylene, carbon tetrachloride, and titanium tetrachloride. V. I. VAIDYANATHAN and B. SINGH (Indian J. Physics, 1932, 7, 19—26).—The magnetic susceptibilities of C₂H₄, C₂H₄(OH)₂, C₂H₄(NH₂)₂, C₂H₄Cl₂, C₂H₄Br₂, C₂H₄I₂, CCl₄, and

TiCl₄ are reported. Deviations from additivity were found; interpretation from the nature of the valency linkings is discussed. N. M. B.

Ethyl palmitate. Its density, surface tension, parachor, and Eotvos-Ramsay-Shields coefficient. C. P. ELLIS (J.C.S., 1932, 1697—1699).—The determination of the density and surface tension of Et palmitate over a temp. range of 20—150° gives the parachor as 785.7 and the Eotvos-Ramsay-Shields coeff. —3.45. A. J. M.

“Back-reflecting” [camera to obtain] Laue interference figures. L. CHROBAK (Z. Krist., 1932, 82, 342—347). C. A. S.

Precision comparison of calculated and observed grating constants of crystals. Y. TU (Physical Rev., 1932, [ii], 40, 662—675).—Calc. values based on density measurements and observed vals. obtained from the angles of reflexion of the Mo K α_1 line by two methods for calcite, rock-salt, artificial KCl, and diamond, using calcite as standard, agree within experimental error. No evidence of Zwicky’s “secondary structure” was found (cf. A., 1930, 660). Measurements on two quartz crystals showed variation of internal structure. N. M. B.

Measurement of reflecting power of absorbing crystals, especially of ores. III. Methods of standardising reflecting power. A. CISSARZ (Z. Krist., 1932, 82, 438—450; cf. A., 1931, 587, 703). C. A. S.

X-Ray studies of the thermal expansion of bismuth single crystals. A. GOETZ and R. C. HERGENROTHER (Physical Rev., 1932, [ii], 40, 643—661; cf. this vol., 681).—The vals. of thermal lattice expansion α , calc. from measurements of the temp. shift of Bragg reflexions between liquid air temp. and the m.p. of the metal show wide divergence from those of macroscopic crystal measurements. The discontinuity in macroscopic expansion at 75° was not found by the X-ray shift method. N. M. B.

Crystallisation surface of supercooled liquids. H. E. VON GRONOW and W. WEYL (Z. anorg. Chem., 1932, 206, 224—226).—Theoretical. A formula is derived for the vol. of super-cooled liquid cryst. in a given time and a space diagram is constructed showing how time, vol. of crystals formed, and degree of super-cooling may be connected. It is calc. from available data (A., 1931, 1360) that isothermal crystallisation of piperine occurs most rapidly for supercooling of 55°. M. S. B.

Very thin crystals with curved boundaries. L. KOWARSKI (Compt. rend., 1932, 194, 2126—2129).—The process of the growth and disappearance of crystals of *p*-toluidine about 1 μ thick (cf. A., 1930, 1111, 1336) is described and figured. C. A. S.

Structural relations of silicon compounds on assumption of tetrahedral domains of the atoms. Geometrical derivation of cubic crystals as a guide to structure determination. R. REINICKE (Z. Krist., 1932, 82, 394—418, 419—437).—The domain of influence of Si is represented as a tetrahedron, similar to that of C, and also, with certain modifications, the domains of O, N, F, and Ne. The structures of SiC and of the various varieties of SiO₂

are deduced, and then, regarding silica as Si(SiO₄), those of the silicates, leading to results differing from Bragg’s (cf. A., 1927, 501). Extending the assumption of tetrahedral domains the co-ordinate relations of a cubic body-centred lattice are deduced, and a general method for deducing the positions of the atoms in any cubic substance when the no. of mols. in the unit cube is known. C. A. S.

Stereochemistry of crystal compounds. VIII. Geometrical derivation of structure-types AB₃. W. NOWACKI (Z. Krist., 1932, 82, 355—378; cf. this vol., 682). C. A. S.

X-Ray investigations of solid nitrogen and oxygen. M. RUHEMANN (Z. Physik, 1932, 76, 368—385).—Above 35° abs. β -N₂ forms crystals of hexagonal spherical packing, with 2 mols. per cell and with a 4.03 Å., c/a 1.63. At lower temp. α -N₂ crystallises in cubic form with side 5.67 Å. The modifications of solid O₂ show little difference in their X-ray patterns, but these do not agree with the rhombohedral structure of McLennan and Wilhelm (A., 1927, 297). A. B. D. C.

Crystal [structure] of zinc coating [produced by hot-dipping on] the surface of iron plate. Y. MATSUNAGA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 263—265).—The deposit consists of single-crystal Zn with the (0001) plane inclined at 18° to the surface of the Fe. A. R. P.

Arrangement of micro-crystals in compressed single-crystal plates of aluminium. IV. Y. FUKAMI (Mem. Coll. Sci. Kyoto, 1932, A, 15, 23—30; cf. A., 1931, 1358).—The relation between the initial orientation of the crystallites in Al and the type of fibrous arrangement produced by compression is shown by the aid of the crystallographic globe. A. R. P.

Arrangement of the micro-crystals in the film of molybdenum obtained by deposition [from electronic bombardment of a molybdenum anode]. T. FUJIWARA (Mem. Coll. Sci. Kyoto, 1932, A, 15, 31—33).—In most of the crystals the (110) plane is parallel to the surface of the film and a cube edge is parallel to the longitudinal direction, but the larger crystals are arranged in fibres about the (110) axis which is normal to the flat surface of the film. A. R. P.

Effects of the direction of drawing on the arrangement of the micro-crystals in aluminium wire and on its tensile strength and broken fracture. T. FUJIWARA (Mem. Coll. Sci. Kyoto, 1932, A, 15, 35—42).—In wire drawn continuously in one direction micro-crystals with their (111) axes inclined to the direction of drawing predominate. In wire drawn alternately in reverse directions the (111) axes of the crystals in the outer layers are inclined to the wire axis on both sides. In the first case the wire is harder and more brittle. A. R. P.

Structure of steel explained by the form of the lattice. H. HANEMANN (Arch. Eisenhüttenw., 1931—1932, 5, 621—624).—The microstructure of steel depends on the rate of movement of the C atoms; in the γ -phase movement of C takes place at a high rate by perfusion (cf. A., 1931, 301), and in the α -phase at

a much lower rate by true diffusion. The ferrite in steel with a very coarse Widmannstätten structure is distributed as thin plates along octahedron planes and occasionally along cube planes, but never in any other direction. A. R. P.

Lattice distortion and carbide formation in tungsten magnet steels. W. A. WOOD and C. WAINWRIGHT (Phil. Mag., 1932, [vii], 14, 191—198).—In a 6% W magnet steel in the spoiled state the W and C have been ejected from the parent lattice to form $\text{Fe}_4\text{W}_2\text{C}$ and WC, thus releasing the lattice strain. In the normal and recovered state W and C dissolve in the lattice producing distortion, with enhanced coercive force and hardness. H. J. E.

Molecular process of crystal growth in hexagonal metals. Deposition upon monocrystalline hemispheres of zinc. P. A. ANDERSON (Physical Rev., 1932, [ii], 40, 596—606).—A monocryst. hemisphere formed from a small orifice into a mass of molten Zn is bombarded uniformly by Zn vapour, and the variation of depositional rate with crystal surface structure is studied. The macroscopically observed growth is interpreted in terms of atom-by-atom deposition. N. M. B.

Precision determination of lattice constants of beryllium. M. C. NEUBURGER (Z. physikal. Chem., 1932, B, 17, 285—292).—The vals. 2.2680 ± 0.0002 and 3.5942 ± 0.0003 Å. have been obtained for a and c , respectively. R. C.

Crystal structure of gallium. F. LAVES (Naturwiss., 1932, 20, 472).—Ga seems to have a pseudo-tetragonal crystal structure, space-group V_1^{18} , a 0.159, c 0.080; $a=b=4.51$, c 7.64 Å. W. R. A.

γ - γ -Martensite as a Widmannstätten structure. H. HANEMANN (Arch. Eisenhüttenw., 1931—1932, 5, 625—626).—Crystallographic measurements of two sections of γ - γ -martensite cut at right angles to one another from the same crystal show that the γ -needles lie on corresponding octahedron or cube planes and that, therefore, the γ - γ -martensite structure is a true Widmannstätten structure. A. R. P.

Crystal structure of nitrogen tetrasulphide and tetrahydronitrogen tetrasulphide. F. M. JAEGER and J. E. ZANSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 782—807).—Small orange-yellow dichroic crystals of N_4S_4 were obtained by slow evaporation of a C_6H_6 solution. Calc. axial ratios, $a:b:c=1.039:1:0.842$, are in good agreement with those derived from X-ray examination, $a:b:c=1.0472:1:0.8512$. Other crystallographic data are given. Powder spectrograms were made, using Cu- α and - β radiation at 50,000 volts. The principal and accessory spectra from rotation spectrograms about (100), (010), and (001) are given. The val. of ρ is 2.23. The lattice parameters from powder spectrograms are a_0 8.76, b_0 8.44, c_0 7.11 Å., whilst the identity distances calc. from the rotation spectrograms are I_a 8.37, I_b 8.47, I_c 7.21 Å. From the reflexions the space-group is V_1^4 . The simple orthorhombic cell contains 16 S and 16 N atoms for which parameters have been assigned so as to give good agreement between calc. and observed intensities. The symmetry of each N_4S_4 mol. is C_{2v} .

The arrangement of N_4S_4 mols. within the elementary cell is discussed.

Crystals of $\text{H}_4\text{S}_4\text{N}_4$ are orthorhombic. The axial ratios are $a:b:c=1.8202:1:1.1723$ whilst the ratios calc. from X-ray measurements are $a:b:c=1.7869:1:1.1582$. The val. of ρ is 1.88. Principal and accessory spectra of the rotation spectrograms about the (001), (100), and (010) faces give I_a 12.08, I_b 6.76, I_c 7.86 Å., and indicate that there are 4 mols. in the unit cell. The structure has the symmetry C_{2v} of the space-group V_1^4 as for N_4S_4 . The powder spectrograms of the two mols. have not much in common. W. R. A.

Density and crystal structure of magnesium nitride. G. HAGG (Z. Krist., 1932, 82, 470—472).—Magnesium nitride prepared by the action of NH_3 on Mg contains varying amounts of NH_3 only removed by heating to 400° ; this explains the varying density of the product, which with greatest content of NH_3 , corresponding approx. with $\text{Mg}_3\text{N}_2 \cdot 2\text{NH}_3$, is 1.75. The pure product prepared thus or by the direct action of N₂ on Mg has d 2.72. This (cf. A., 1931, 549) gives 16 mols. to the unit cell, indicating that the Mg atoms are not all equiv., or that the constituent atoms are ionised. C. A. S.

Transition of silver oxide under pressure. P. W. BRIDGMAN (Rec. trav. chim., 1932, 51, 627—632).—The change of vol. of Ag_2O when subjected to a pressure of 12,000 kg. per sq. cm., after allowance is made for the true compressibility, shows a residual effect which is attributed to a transition to a new phase. No new lines were observed in an X-ray powder diagram of a specimen which had been maintained at a pressure of 20,000 kg. per sq. cm. for four days. The p - v curves show wide hysteresis loops. F. L. U.

Structure of thin films of certain metallic oxides. W. L. BRAGG and J. A. DARBYSHIRE (Trans. Faraday Soc., 1932, 28, 522—529; cf. A., 1931, 1207).—The electron diffraction spectra of the oxide films formed on the surface of Pb and Sn by heating correspond with the rutile structure for PbO_2 and SnO_2 . The film of ZnO formed on molten Zn corresponds with a hitherto unrecorded cubic modification of which the unit cell of side 4.62 Å. contains 4 mols. J. G. A. G.

Needle-shaped crystals of sodium chloride obtained by percrystallisation. H. TAUBER and I. S. KLEINER (J. Amer. Chem. Soc., 1932, 54, 2392—2393; cf. A., 1917, ii, 295).—By evaporation of aq. NaCl in air as it diffuses through a collodion bag, needle-shaped crystals of the regular cubic system are obtained. F. D. S. (c)

Structure of dihalides of mercury and of lead. J. M. BIJVOET and H. J. VERWEEL (Rec. trav. chim., 1932, 51, 605—611; cf. this vol., 450).—Reasons for the differences between the structure of the chlorides and bromides of Hg^{II} and Pb and that of their fluorides and iodides are discussed. F. L. U.

Crystalline structure of tetramminoplatinous chloride. E. G. COX (J.C.S., 1932, 1912—1920).—X-Ray investigation shows that the four Pt covalencies in the complex $[\text{Pt}(\text{NH}_3)_4]$ are coplanar and

directed to the corners of a square. The general configuration of complexes of the form $[PtX_2Y_2]$ is discussed.
A. J. M.

Lattice dimensions of spinels. G. L. CLARK (Z. physikal. Chem., 1932, B, 17, 463—464).—Comments on Hauptmann and Novak's paper (this vol., 326).
R. C.

Structure of kernite. J. GARRIDO (Z. Krist., 1932, 82, 468—470; cf. A., 1928, 1349).—Kernite, $Na_2B_4O_7 \cdot 4H_2O$, is only pseudo-rhombic, really monoclinic, with a 15.65, b 9.07, c 7.01 Å., β $108^\circ 52'$; the unit cell contains 4 mols.; space-group C_{2h}^2 .
C. A. S.

Structure of asbestos. B. E. WARREN (Ind. Eng. Chem., 1932, 24, 419—422).—The unit cell of diopside, $CaMg(SiO_3)_2$, contains 4 mols.; each Si atom is surrounded tetrahedrally by 4 O atoms and such tetrahedra are linked in chains. A similar stronger type of Si—O chain is responsible for the fibrous structure of asbestos. The crystal is monoclinic, a 9.71, b 8.89, c 5.24 Å. The structure of mica is "two-dimensional asbestos."
C. I.

Rotation of molecules in crystals. J. D. BERNAL (Nature, 1932, 129, 870).—Further cases of rotating and fixed mol. forms in aliphatic compounds are reported. $C_{12}H_{25}OH$ has a hexagonal rotating form between 16° and 24° with 4.76 Å. between the chains. The low-temp. form differs by being monoclinic with inclined chains corresponding with the high-temp. form of the monobasic acids. The transitions between the forms can be followed in single crystals in the polarising microscope. $C_{13}H_{27}NH_2 \cdot HCl$ has a non-rotating form which is orthorhombic with a base 5.2×5.15 Å. Four layers per cell in alternate pairs inclined at approx. 48° to the c plane produce a negative birefringence unlike that of all other long-chain compounds.
L. S. T.

Determination of the mol. structure of acetone and formic acid by means of electron diffraction [measurements]. J. HENGSTENBERG and L. BRU (Anal. Fis. Quim., 1932, 30, 341—358).—Debye's theory of the diffraction of electrons by gases is outlined, and a form of apparatus is described. Measurements with $COMe_2$ give the distance between the 2 C atoms 1.57 ± 0.04 Å. Interpretation of the diffraction diagram obtained with HCO_2H requires the assumption that the linkings C—O and C=O are of the same length; the most probable configuration is that in which the O atoms are situated at the corners of a tetrahedron. The calc. distance between the C and O atoms is 1.24 ± 0.04 Å.
H. F. G.

X-Ray analysis of crystals of the 1:4-cyclohexanediol with the m.p. 139° (*trans*-quinitol). E. HALMÖY and O. HASSEL (Z. physikal. Chem., 1932, B, 17, 258—264; cf. A., 1931, 1219).—This compound has the space-group C_{2h} and a 6.31, b 21.00, c 7.26, and d 9.18 Å.
R. C.

X-Ray analysis of the structure of diphenyl. J. DHAR (Indian J. Physics, 1932, 7, 43—60).—The two Ph rings in each mol. are flat regular hexagons lying in one plane. The distance between the consecutive C atoms in each ring from centre to centre is

1.42 Å.; the length of the C—C linking connecting the two rings is 1.48 Å.
N. M. B.

Crystal form of ethyl fluorene-9:9-dicarboxylate. G. SCHAFER (Z. Krist., 1932, 82, 472—473; cf. this vol., 614).—This compound is monoclinic, $a:b:c=0.8224:1:0.8346$, β 114.46° ; dispersion strong, $p > v$.
C. A. S.

Relations between hydrated 10-bromophenanthrene-3(or 6)-sulphonic acid and paracrystalline structures in organisms. F. RINNE (Z. Krist., 1932, 82, 379—393).—X-Rays show anhyd. 10-bromophenanthrene-3(or 6)-sulphonic acid (cf. A., 1916, ii, 556) to be cryst. Addition of a little H_2O transforms it into a paste showing a nematic phase where there is more H_2O , passing into a smectic phase where there is less. The addition of H_2O causes a loosening of the crystal lattice (d increasing from 3.40 to 3.47 Å.). Slow drying reverses the change. The phenomena are discussed in their bearing on biological products (cf. A., 1931, 1081). The effect of H_2O is attributed to its high dielectric const. and the presence of the SO_3H group.
C. A. S.

X-Ray evidence of structure of the furanose and pyranose forms of α -methylmannoside. E. G. COX and T. H. GOODWIN (J.C.S., 1932, 1844—1855).—The mols. of the two forms in the cryst. state have the constitutions assigned by Haworth (A., 1928, 156; 1930, 748), the form m.p. 193° having a C_5O ring, and that m.p. 118° having a C_4O ring. Hence methylation in this case is not accompanied by changes in ring structure. The side-chain in the furanose mol. lies in approx. the same plane as the ring, and Me groups, when present, are also in this plane.
A. J. M.

Polymorphic system of the natural triglycerides. C. WEYGAND and W. GRUNTZIG (Z. anorg. Chem., 1932, 206, 304—312).—The fats tristearin (C_{18}), tripalmitin (C_{16}), trimyristin (C_{14}), and trilaurin (C_{12}) may each be obtained in 7 polymorphic forms with definite m.p. Each group of polymorphs shows a periodicity, since it may be divided into 3 sub-groups of 3, 3, and 1, in which the m.p. varies to a small extent only, beginning with the forms of highest m.p. A similar periodicity was found for p' -methylchalcone (A., 1929, 815), but there the grouping was 1, 3, and 3. The m.p. increment for the increase of the mol. by $6CH_2$ diminishes with increasing mol. wt. The m.p. range is as follows: (C_{18}) $71-55^\circ$; (C_{16}) $65-45.5^\circ$; (C_{14}) $56.5-32^\circ$; (C_{12}) $46.5-18^\circ$.
M. S. B.

Structure of highly-nitrated cellulose nitrate films. DESMAROUX and MATHIEU (Compt. rend., 1932, 194, 2053—2054; cf. this vol., 218).—Using cellulose nitrate of N 13.13%, films obtained from $COMe_2$ solutions show structures passing from amorphous in films from dil. (0.5%) solutions to cryst. from conc. solutions. This decrease in crystallinity with increased dispersion indicates progressive separation of the elementary fibres composed of chains of glucose residues.
C. A. S.

X-Ray diffraction photographs of vegetable and animal fibres. W. T. ASTBURY (Phot. J., 1932, 72, 318—323).—A lecture.
A. J. M.

Improvement of the zinc-aluminium alloy, Al,Zn. H. MEYER (Z. Physik, 1932, 76, 268—280).—A study of the effect on electrical resistance, for d.c. and a.c., of the drop in temp., time of maintenance at the higher temp., and mean temp. of the temp. interval. A. B. D. C.

Dependence of the piezo-electric constant of quartz on temperature. V. FRÉDERICKSZ and G. MICHAŁOW (Z. Physik, 1932, 76, 328—336).—The piezo-electric const. of quartz begins to diminish at 500°. A. B. D. C.

Effect of mechanical and electrical fields of force on the double refraction of quartz. N. GÜNTHER (Ann. Physik, 1932, [v], 7, 783—801). A. J. M.

Cohesion limits for synthetic potassium halide crystals. W. SCHÜTZE (Z. Physik, 1932, 76, 135—150). A. B. D. C.

Dependence on orientation of cohesion limits of synthetic potassium chloride crystals. W. SCHÜTZE (Z. Physik, 1932, 76, 151—162). A. B. D. C.

Properties of pure silicon. R. L. TEMPLIN (Metals and Alloys, 1932, 3, 136—137, 150).—Young's modulus for cast Si (99.41%) is 16,350,000 lb. per sq. in. Failure occurs suddenly in the form of general fragmentation at 13,470 lb. per sq. in. E. S. H.

Cathodic evaporation in a magnetic field. O. GOCHÉ (Bull. Acad. roy. Belg., 1932, [v], 18, 412—418; cf. A., 1926, 693; 1927, 118; 1931, 407; this vol., 211).—The cathodic evaporation of hydride-forming elements (Sb, Bi, and Te) is mainly of the "directed" type, but not to the same degree as that of C. The evaporation of Pt is almost entirely directed, so it is concluded that, except in the case of C, chemical reaction between the cathode and gas must play at most only a secondary role in the phenomenon. Au, Ag, and Cu show mixed directed and undirected evaporation. J. W. S.

Allotropy in liquids. III. A. SMITS and H. GERDING [with F. W. BROEKMAN and W. C. STAPPER] (Z. physikal. Chem., 1932, 160, 231—244; cf. this vol., 683).—Dilatometric measurements with liquid PhNO₂ between 6° and 11° and AcOH between 15° and 19° and the heating curve of H₂O between 3° and 5° give no evidence of the existence of transition points (cf. this vol., 329). A thermoregulator by means of which the temp. of a thermostat may be kept const. to within 0.0005° is described. R. C.

Measurements with liquid helium. XVII. Resistance of lead in a magnetic field below the transition temperature. W. MEISSNER (Ann. Physik, 1932, [v], 13, 641—648).—The resistance below the transition temp. for pure Pb was determined by extrapolation to zero field. Agreement with the T² law was obtained. W. R. A.

Thermal diffusivity of nickel. R. H. FRAZIER (Physical Rev., 1932, [ii], 40, 592—595; cf. this vol., 442).—Further results, accurate to 0.06%, are reported. N. M. B.

New optical properties produced in liquids by high-frequency sound waves. R. LUCAS and P.

BIGUARD (Compt. rend., 1932, 194, 2132—2134).—Parallel light passed through H₂O subjected to high-frequency sound waves shows diffraction effects similar to those produced by passing perpendicularly through a grating. C. A. S.

Heat of dissociation of nitrogen. A. K. DATTA (Nature, 1932, 129, 870).—The absorption spectrum of N₂O is continuous with no trace of bands. Absorption begins at 2740 Å. corresponding with 104.4 kg.-cal. Assuming a photochemical decomp. into NO and N, the calc. val. of the heat of dissociation of N₂ is 203 kg.-cal. L. S. T.

Surface energy and heat of vaporisation of liquids. L. S. KASSEL and M. MUSKAT (Physical Rev., 1932, [ii], 40, 627—632; cf. Margenau, A., 1931, 1114).—An approx. calculation of the total surface energy and heat of vaporisation of He, Ne, A, N₂, Cl₂, and O₂ is made by quantum mechanics. N. M. B.

Alternating m.p. in homologous series. C. WEYGAND and W. GRÜNTZIG (Z. anorg. Chem., 1932, 206, 313—316).—By comparing the polymorphic forms of the fats (C₁₄), (C₁₆), and (C₁₈) (cf. this vol. 798) containing even nos. of C atoms with the odd members (C₁₅) and (C₁₇), it is found that no alternation of m.p. is observed, provided corresponding modifications are compared, but only a regular rise in m.p. with increase in mol. wt. (C₁₅) and (C₁₇) have each 4 modifications, of m.p. ranging from 40° to 52° and 49.5° to 57.5°, respectively. M. S. B.

Effect of particle size on m.p. N. SCHOORL (Z. physikal. Chem., 1932, 160, 158—160).—The m.p. depression exhibited by certain solids when finely powdered (A., 1910, i, 740) seems to be caused by products of devitrification of the walls of the m.p. tube, or by impurities on the surface of larger crystals. R. C.

Specific heat of gases at high temperatures. W. T. DAVID (Nature, 1932, 129, 942).—Incomplete combustion at the moment of max. pressure in closed vessel explosions is generally so large that the explosion method as usually employed is untrustworthy for sp. heat determinations. Data for H₂-O₂ and CO-air explosions in large and small vessels support this view. L. S. T.

Permeability of glass and fused quartz to ether, alcohol, and water at high pressure. T. C. POULTER and R. O. WILSON (Physical Rev., 1932, [ii], 40, 877—880).—Pressures of the order 15,000 atm. for 5—15 min. caused considerable penetration and a weakening effect. With non-penetrating liquids higher pressures could be used. N. M. B.

Physical properties of compressed gases. III. Hydrogen. W. E. DEMING and (Miss) L. E. SHUPE (Physical Rev., 1932, [ii], 40, 848—859; cf. A., 1931, 553; this vol., 220).—Complete data for sp. vol., density, temp. and pressure expansion coeffs., fugacity, C_p, C_p—C_v, C_v, and α are obtained from available compressibility data for the temp. range —215° to 500° and up to 1200 atm. pressure. N. M. B.

Entropy, strain, and the Pauli exclusion principle. W. S. KIMBALL and G. BERRY (Phil. Mag., 1932, [vii], 13, 1131—1143).—Theoretical. H. J. E.

Salts of low m.p. VII. Density, conductivity, and viscosity of molten mixtures of picrates. P. WALDEN and E. J. BIRR (*Z. physikal. Chem.*, 1932, 160, 161—193; cf. this vol., 685).—The d , mol. conductivity, viscosity, η , and val. of $\lambda\eta$ for a molten mixture of tetra-alkylammonium picrates (I) are additively constituted of the vals. for the constituents, but the mol. vol. < the additive val. For mixtures of (I) with di- (II) or mono-alkyl salts (III) the val. of $\lambda\eta$ < the additive val., which is traced to diminution in the degree of dissociation, α , of (III) or (II) by (IV). This diminution, which is the greater the lower is the temp. and the higher is the concn. of (I), is accompanied by a proportionate decrease of η below the additive val., which shows that in molten (III) and (II) the cations have an envelope of undissociated mols., which are released when the ions combine. Such solvation is more marked with (III) than with (II). On mixing (II) with (I) or tri-alkyl salts (IV) α diminishes for both constituents. No appreciable change in α occurs when (I) and (IV) are mixed. The above observations are supported by mol. vol. data, the contraction in vol. on mixing being abnormally small when repression of ionisation occurs. R. C.

Critical constants and vapour pressure of boron trifluoride. H. S. BOOTH and J. M. CARTER (*J. Physical Chem.*, 1932, 36, 1359—1363).—The crit. temp. is $-12.25 \pm 0.03^\circ$ and the crit. pressure 49.2 ± 0.1 atm. From 10 to 50 atm. $\log p = 5.1009 - 0.8896 \times 1000/T$, where p is the v.p. The mol. heat of vaporisation calc. from p is 4057 g.-cal. At about -50° and 13 atm. the viscosity becomes appreciable, suggesting association. Dry BF_3 does not attack Hg, Cr plating, or glass over long periods even at high pressure. A. L. H. (c)

Calculation of the effect of a solid wall on the state of aggregation of a liquid from viscosity determinations. M. REINER (*Physikal. Z.*, 1932, 33, 499—502).—Theoretical. A. J. M.

Coefficient of viscosity of liquid sodium amalgams. G. R. PARANJPE (*Indian J. Physics*, 1932, 7, 95—97).—The viscosity of liquid Na amalgams decreased continually with time, the initial val. being restored by mechanical agitation. N. M. B.

Critical temperatures and pressures of the three two-component systems composed of carbon dioxide, methyl ether, and propylene. C. A. WINKLER and O. MAASS (*Canad. J. Res.*, 1932, 6, 458—470).—The crit. phenomena associated with the three separate pairs of binary mixtures have been examined in detail. Above the "crit. contact temp." liquefaction is impossible, whatever pressure is applied. At temp. below the plait point condensation is regular; between the plait point temp. and the crit. contact temp. the amount of liquid increases as the pressure is increased. A single crit. point cannot be ascribed to a mixture, but the plait point temp. and the crit. contact temp. are regarded as the limits of a crit. region. No evidence of compound formation in any of these systems was obtained. E. S. H.

Viscosity of potassium-sodium alloys in the liquid state. R. KREMANN, M. PESTEMER, and

H. SCHREINER (*Rec. trav. chim.*, 1932, 51, 557—563).—Viscosities of K-Na alloys with 0—100% K have been measured at 125° . The viscosity-composition curve shows a sharp max. at 66.7 at.-% K, indicating the existence of the compound K_2Na in the liquid state. F. L. U.

Theory of formation and state of glass. E. BERGER (*Kolloid-Beih.*, 1932, 36, 1—42).—The formation of glass differs from crystallisation in consisting in the transformation of the viscous, undercooled liquid into the brittle state. At a certain temp. the temp. coeff. of this change increases suddenly, thus providing a transformation point. The transformation is influenced by the thermal history of the material; this effect is not due to mechanical strain, but to a change in state of aggregation, which proceeds more slowly as the transformation point is approached and is completely inhibited at lower temp. Measurements of viscosity and electrical resistance between 1300° and 300° show clearly the difference between the viscous and brittle states, and indicate that below the transformation point glass is not simply an undercooled liquid. The mol. kinetics of the transformation point and the structure of the brittle state are considered theoretically. Regarding the system as composed of secondary aggregates dispersed in a medium consisting of primary particles and single mols., the transformation point is analogous to the sol-gel transformation. E. S. H.

Diffusion of zinc in copper and its alloys. Y. YAMAUCHI (*Mem. Coll. Sci. Kyoto*, 1932, A, 15, 67—95).—The rate of absorption of Zn vapour per unit area of Cu (ΔW) in an atm. of H_2 at 400 — 655° is given by $\Delta W = Ae^{-B/T}$ where A and B are consts. ΔW for rolled Cu is lower than for cast Cu at temp. below the recryst. point. The Zn loss from α -brass on heating varies with the Zn content (C) of the brass according to the equation: $\Delta W = ae^{bC}$ where a and b are consts. Brass containing β or $\alpha + \beta$ loses Zn on heating according to the same law as that which controls absorption of Zn by Cu. Addition of Pb, Fe, Mn, and especially Sn increases the rate of Zn loss from brass on heating, whereas addition of Al appreciably reduces this rate. A. R. P.

Lattice dimensions in copper-silver alloys. (Miss) H. D. MEGAW (*Phil. Mag.*, 1932, [vii], 14, 130—142).—The variation of spacing with composition in Ag-rich and Cu-rich alloys subjected to varied heat-treatment has been examined. The spacings for pure Ag and Cu are 4.0774 and 3.6090 Å. respectively. H. J. E.

Gold-silver alloys as a type of continuous solid solutions. W. BRONIEWSKI and E. WESOLOWSKI (*Compt. rend.*, 1932, 194, 2047—2049; cf. this vol., 566).—Further observations show that the alloys form a typical series of solid solutions free from any discontinuity. C. A. S.

Superconductivity of alloys containing gold and silver. J. C. McLENNAN, J. F. ALLEN, and J. O. WILHELM (*Phil. Mag.*, 1932, [vii], 13, 1196—1209).—Au and Ag lower the superconducting temp. of Pb and Sn, whereas Bi, Sb, and As raise it. The phase relations in the systems Ag-Sn, Au-Sn, Au-1) have been studied. H. J. E.

β -Transformations in copper- and silver-zinc alloys. M. STRAUMANIS and J. WEERTS (Metall. Wirt., 1931, 10, 919—922; Chem. Zentr., 1932, i, 629).—Results of X-ray study of the crystal structure at 100—300° are described. A. A. E.

Equilibrium diagram of the binary system, nickel-zinc. K. TAMARU (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 90).—Thermal and dilatometric analysis and electrical resistance measurements on Ni-Zn alloys show that the α -phase extends to 61.61% Ni at 1403° and the β -phase to 37.5% Ni at the eutectic point. The eutectoid transformation in β extends from 45.5 to 24.4% Ni and occurs at 700° on heating and at 640° on cooling. The δ -phase is homogeneous between 49 and 45.5% Ni and the compound NiZn₃ dissolves up to 1.4% Ni. The reaction $\alpha + \beta \rightleftharpoons \delta$ takes place at 804° and the peritectic reaction near NiZn₃ previously reported does not take place. The α -phase is face-centred cubic, the β - and δ -phases are hexagonal, and the γ -phase has an α -Aln structure. A. R. P.

X-Ray determination of the solubility of manganese in magnesium. E. SCHMID and G. SIEBEL (Metall. Wirt., 1931, 10, 923—925; Chem. Zentr., 1931, ii, 629—630).—Accurate determinations of the lattice consts. by the reflexion method have been used to find the effect of temp. on the saturation concn. of the α -mixed crystals. The solubility falls rapidly from 3.4% at the eutectic temp. (645°) to zero at 200°. L. S. T.

System iron-cobalt-molybdenum. W. KOSTER and W. TONN (Arch. Eisenhüttenw., 1931—1932, 5, 627—630).—The system has been investigated up to a Mo content corresponding with that of the CoMo-Fe₃Mo₂ section using thermal, dilatometric, and micrographical methods. CoMo and Fe₃Mo₂ form a continuous series of δ -solid solutions. The eutectic points in the Fe-Mo and Co-Mo systems and the peritectic point in the Fe-Co system are all lowered by the addition of the third constituent and eventually merge at 1300° into the 4-phase equilibrium: liquid + $\alpha \rightleftharpoons \gamma + \delta$. From this point two lines of 3-phase equilibrium extend, viz., (a) liquid = γ + CoMo and (b) α = γ + δ . Equilibrium diagrams are given for ternary alloys with 10, 20, 30, and 45% Mo showing particularly the changes which occur in the shape of the α - γ curve. Many of the alloys show pptn.-hardening phenomena with suitable heat-treatment. A preliminary examination of the section Mo-CoMo-Fe₃Mo₂ indicates that FeMo forms solid solutions with CoMo and with Fe₃Mo₂, both of which are of the γ type. A. R. P.

Active oxides. L. Change of the catalytic, magnetic, and X-ray spectroscopic properties during the formation of spinel in mixtures of zinc oxide and chromic oxide. G. F. HUTTON, H. RADLER, and H. KITTEL (Z. Elektrochem., 1932, 38, 442—449).—The catalytic activity, ϕ , in the decomp. of MeOH at 300°, the magnetic susceptibility, χ , the solubility in 0.28M-KOH, and the X-ray diagrams of various mixtures of ZnO and Cr₂O₃ of different origins have been determined, and the effect of heating the mixtures up to about 1150° has been studied. Heating at 300—400° does not cause spinel

formation, but ϕ increases 7-fold, and χ also increases; subsequent heating at 400—500° causes a gradual reduction of ϕ and χ , and at 500° spinel formation commences. A mixture of Cr₂O₃ with ignited ZnO does not catalyse the decomp. of MeOH. The results may be interpreted in part in terms of reaction at the ZnO-Cr₂O₃ interface. H. F. G.

Physical properties of mixtures of acetone and bromoform. V. C. G. TREW (Trans. Faraday Soc., 1932, 28, 509—514).—The density, viscosity, refractive index, heat of mixing, and sp. heat of COMe₂-CHBr₃ mixtures show deviations from the simple mixture rule which resemble those found for COMe₂-CHCl₃ mixtures. Mol. compound formation is indicated. J. G. A. G.

Measurement of small vapour pressures. Pressure of water vapour over various concentrations of sulphuric acid. W. VON MEYEREN (Z. physikal. Chem., 1932, 160, 272—278).—The v.p. at 0—40° has been determined with the aid of Gaede's vacuscope. The latter operates on the McLeod gauge principle, and enables v.p. of 0.01—5 mm. to be measured. R. C.

Theory of conjugate solutions. P. BRUN (J. Chim. phys., 1932, 29, 184—191).—The system H₂O-MeOH-isoamyl alcohol has been examined with reference to the theory of Antonov (A., 1928, 593). W. R. A.

Critical liquid mixtures as colloidal emulsions. W. OSTWALD (Austral. J. Exp. Biol., 1932, 9, 83—88).—Crit. liquid mixtures (C₆H₁₄-MeOH and PrⁿCO₂H-H₂O) possess structural viscosity, do not obey Poiseuille's law at low pressures, and show large increases in viscosity at low rates of flow. In these respects they resemble gelatin solutions. W. M.

Equilibria in the systems: alcohol-benzene-water and alcohol-toluene-water. D. N. TARASENKOV and E. N. POLOSHINCEVA (J. Gen. Chem. Russ., 1932, 2, 84—88).—Miscibility data are shown in the form of equilibrium diagrams. R. T.

Isobars of the system isobutyl alcohol-water. T. BYLEWSKI (Rocz. Chem., 1932, 12, 311—326).—The b.p. mixtures have been determined at pressures at which the b.p. of H₂O is 100°, 110°, 120°, and 130°. The v.p.-temp. curves of BuⁿOH and H₂O do not intersect but approach each other most closely at 117°. At high pressures the mixtures change from the heteroazeotropic to the azeotropic type. R. T.

Solubility of potassium perchlorate in water, and certain physicochemical constants of its solutions. N. A. PUSHIN and D. KOVATSCHEV (Bull. Soc. Chim. Yougoslav., 1931, 2, 25—31).—The eutectic point is at -0.060° and 0.343% of KReO₄. The solubility rises from 0.35% at 0° to 3.08% at 50° and 9.44% at 100°. The d and n increase with concn., whilst the viscosity decreases slightly. R. T.

Solubility relations of silver chloride in aqueous solutions of strong electrolytes. E. W. NEUMAN (J. Amer. Chem. Soc., 1932, 54, 2195—2207).—The solubility at 25° in aq. solutions of H, K, Ca, Mg, and La sulphates, and K, Ba, and La nitrates has been determined. The solubility in H₂O is $1.273 \times 10^{-5} M$,

and the activity coeff. 0.9985. There are marked deviations from the Debye-Hückel limiting law. The Gronwall and La Mer extensions agree with the data for symmetrical compounds. Neither accounts for the sulphates of unsymmetrical valency type.

G. M. P. (c)

Solubility of thallous chloride in presence of edestin nitrate. C. F. FAILEY (J. Amer. Chem. Soc., 1932, 54, 2367—2371; cf. this vol., 457).—The negative logarithm of the activity coeff. of TiCl_3 obtained from solubility determinations in HNO_3 containing 0—5% of edestin, is approx. proportional to the edestin concn. Other data for the activities of salts in protein solutions are collected and compared.

H. A. B. (c)

Dichloroethylene as a solvent. D. MANN (Chem. Ztg., 1932, 56, 452).— $\text{C}_2\text{H}_2\text{Cl}_2$ is found to be more selective than Et_2O as a solvent for chemically similar substances.

J. G.

Increase in the solubility of sparingly soluble materials in the presence of hydrophilic colloids or surface-active materials. H. BRINTZINGER and H. G. BEIER (Naturwiss., 1932, 20, 254—255).—The solubility of many sparingly sol. acids, bases, and salts is increased by the presence of hydrophilic colloids, such as gelatin, albumin, and gum arabic, or of active charcoal, SiO_2 gel, clay, $\text{Al}(\text{OH})_3$, hydrated SnO_2 , etc. This is due to the adsorption of one of the ions on the added material, causing a disturbance of the ionisation equilibrium and consequently of the equilibrium between solid and dissolved material.

J. W. S.

Mechanism of dissolution of organic substances in non-aqueous solvents. III. Cellulose nitrate in cyclohexanone, *p*-methylcyclohexanone, fenchone, and *m*-xylene. T. TOMONARI, C. TROGUS, and K. HESS (Z. physikal. Chem., 1932, B, 17, 241—257; cf. this vol., 568).—The formation of compounds has been demonstrated by the methods previously described. The proportions in which combination occurs with ketones depend on the nature of the ketone, and are changed by even slight variations of the structure of the latter. It is probable that compound formation between cellulose esters and org. substances follows the principles of the co-ordination theory, the C_6 group serving as a centre at which addition occurs in the ratio 1:1 or 1:3. Cellulose nitrate combines with *m*-xylene only in presence of a ketone, which, however, does not enter into the composition of the compound formed. The "constancy of the fibre period of cellulose in its derivatives" is illusory.

R. C.

Formation and properties of precipitates. Theory of co-precipitation. III. I. M. KOLTHOFF (Chem. Weekblad., 1932, 29, 332—338).—Largely a review of recent work. The Paneth-Fajans adsorption law has been extended by the statement that when a crystal lattice has adsorbed one type of ion, an equiv. quantity of a different ion will be found on the surface ("secondary adsorption"). Preferential adsorption of ions occurs when these secondary ions carry a large charge of sign opposite to that of the ions adsorbed on the lattice, or

when they form with the adsorbed ions a sparingly sol. or only slightly dissociated compound.

H. F. G.

Formation and properties of precipitates. Theory of co-precipitation. IV. I. M. KOLTHOFF (Chem. Weekblad., 1932, 29, 346—348).—Fineness of subdivision increases the solubility of BaSO_4 and CaSO_4 , and the fact that a mixture of fine and coarse particles dissolves to an extent which corresponds with the solubility of the coarse particles is explained by the relatively greater effect of ionic charges in the case of fine particles. The conception of supersaturation in connexion with rate of formation of ppts. has no exact significance.

S. I. L.

Formation and properties of precipitates. Theory of co-precipitation. V, VI. I. M. KOLTHOFF (Chem. Weekblad., 1932, 29, 362—363, 378—380).—V. An explanation of the fact that many finely divided ppts. become more easy to filter after being allowed to remain for a time in contact with the solution.

VI. Weimarn's theory of the formation of ppts. is based on unjustifiable assumptions and the term "amorphous modification" has no real significance. The rate of formation of nuclei is not governed solely by the abs. concn. of the reacting ions, since adsorbed ions may exert considerable influence on the rate of growth of the particles.

H. F. G.

Formation and properties of precipitates. Theory of co-precipitation. VII. I. M. KOLTHOFF (Chem. Weekblad., 1932, 29, 395—400).—The relation between adsorption, crystal growth, and the separation of metastable modifications is discussed. Crystal formation in a ppt. is less complete as co-pptn. of foreign ions increases.

S. I. L.

Carrying down of polonium by crystalline oxalates in nitric acid solution. SERVIGNE (Compt. rend., 1932, 195, 41—43).—Observations have been made with La, Sc, Ca, and Sr salts.

C. A. S.

Supersaturation. J. R. PARTINGTON (J. Physical Chem., 1932, 36, 1853—1854).—A claim for priority over Kolthoff (cf. this vol., 457).

G. M. M. (c)

Some solvent properties of soap solutions. II. E. L. SMITH (J. Physical Chem., 1932, 36, 1672—1684; cf. this vol., 687).—The distribution ratio, K , of *p*-dimethylaminoazobenzene (I) between Et_2O and aq. soap solution at room temp. decreases with increasing soap concn. and concn. of excess alkali in the soap solution, whilst with gradual addition of MeOH it passes through a max. If the colloidal soap is regarded as a third phase, the results are in semi-quant. agreement with the theory that I is distributed between the Et_2O and the non-colloidal aq. phase according to the partition law and between the non-colloidal and colloidal aq. phases according to an adsorption law. MeOH greatly increases the solubility of I in the aq. phase, thus increasing K , but diminishes the proportion of soap in the colloidal form, tending to reduce K . In the partition of NH_2Ph between EtOAc and aq. Na oleate at 25° K is decreased considerably by increase in the soap concn. and slightly by addition of NaCl, but is almost independent of the NH_2Ph concn.

O. T. Q. (c)

Partition of iodine between carbon disulphide and water. J. LANZA (Anal. Fis. Quim., 1932, 30, 372—376).—Herrero's work (this vol., 118) is criticised. The view is re-affirmed that the I in the H_2O phase is introduced by dissolution of CS_2 in the H_2O .
H. F. G.

Sorption of gases by iron. A. F. BENTON and T. A. WHITE (J. Amer. Chem. Soc., 1932, 54, 1820—1830; cf. this vol., 689).—The sorption of N_2 , CO , and H_2 on reduced Fe has been studied at -195° to 400° . At the low temp., sorption consists solely of physical adsorption. Activated adsorption takes place at higher temp., the rate being greatest for CO and least for N_2 . With H_2 at 110° and above, dissolution probably occurs. A stepwise increase in the adsorption at low temp. suggests the accumulation of molecular layers.
H. F. J. (c)

Active charcoal. I. Adsorption isotherms of organic acids on ash-free charcoals. C. OCKRENT (J.C.S., 1932, 1864—1875; cf. this vol., 332).—Adsorption data agreeing with Langmuir's equation, $k\Gamma = C(I - \Gamma/\Gamma_{max})$, were obtained with 4 specimens of charcoal, for aq. HCO_2H , $AcOH$, $CH_2Cl \cdot CO_2H$, $CHCl_2 \cdot CO_2H$, and $CCl_3 \cdot CO_2H$, salicylic acid, and $BzOH$. Each acid gives the same k for all the charcoals, showing that they have the same structure, in agreement with X-ray data (this vol., 16), but differ in Γ_{max} , which also depends on the size of the adsorbed mols. The effects of grinding and activation are explained by the assumption that active charcoal is an assembly of ultrapores of mol. dimensions. Grinding increases Γ_{max} for large mols. and decreases it for small mols.
D. R. D.

Adsorption of weak electrolytes on charcoal. R. A. PETERS and H. J. PHELPS (Nature, 1932, 129, 939).—The adsorption of weak electrolytes by highly purified C is essentially a process different from the adsorption of strong electrolytes under the same conditions.
L. S. T.

Surface effect and exchange adsorption of pyrophosphate by charcoal. F. AXMACHER (Kolloid-Z., 1932, 59, 298—305).— $Na_4P_2O_7$ is taken up by pure animal charcoal in accordance with the adsorption isotherm. The amount of PO_4''' given up by blood C of high ash content is greater in $Na_4P_2O_7$ solution than in H_2O ; the influence of time, temp., and relative amounts of the adsorbent and electrolytes has been studied. The exchange of PO_4''' is also effected by other anions in the order $P_2O_7 > F > C_2O_4 > tartrate > OAc > SO_4 > NO_3 > Cl$, but there is no evidence of exchange adsorption of Cl' .
E. S. H.

Adsorptive power and graphite structure of carbon. P. M. WOLF and N. RIEHL (Angew. Chem., 1932, 45, 400—401).—Photographic records show that the adsorption of Rn by a large graphite crystal occurs mainly at the prism faces, thus supporting the view that the linkings between the hexagonally-disposed C atoms are essentially different from those between the basal planes (cf. this vol., 16). The result suggests also that the adsorptive power of C depends not only on the particle size of the crystallites of graphite but also on their development of prism faces.
E. S. H.

Adsorption of nitrogen peroxide by colloidal silicic acid. II. A. P. OKATOV and I. A. CHAINSKI (J. Gen. Chem. Russ., 1931, 1, 1181—1192).—Colloidal SiO_2 is a satisfactory adsorbent for NO_2 at 20° . The data agree with Freundlich's equation.
R. T.

Adsorption of radium emanation by silica gel in relation to state of dehydration. M. FRANCIS (Kolloid-Z., 1932, 59, 292—298).—Measurements of the adsorption of Rn by SiO_2 gel show a max. for specimens dehydrated at 800° (1.2% H_2O) and at 150° (5.5% H_2O), indicating structural differences in the gels. Ageing of the gel has a differential influence on the adsorption of Rn and air.
E. S. H.

Displacement of chemical equilibria due to selective adsorption of hydroxides by silica gel. BERTHON (Compt. rend., 1932, 195, 43—45).— SiO_2 gel (Patrick's) adsorbs Na ions only from a solution of NaCl containing NH_3 . The order of the effect for the alkali metals as chlorides is the reverse of that for the free bases (cf. A., 1929, 757); for the alkaline-earth metals the order is the same as that of the lyophilic series. Fe^{III} tartrate behaves similarly to NaCl.
C. A. S.

Adsorption at the surface of a solution. W. F. K. WYNNE-JONES (Phil. Mag., 1932, [vii], 14, 203—204; cf. this vol., 458).—Polemical.
H. J. E.

Height of liquid between parallel plates. S. RAY (Kolloid-Z., 1932, 59, 280—283).—The observation of Schultze (A., 1931, 679) is explained in terms of the colloidal theory of surface tension (A., 1928, 702).
E. S. H.

Determination of relative surface tension (capillary activity): use for characterising essential oils and related substances. A. MÜLLER (J. pr. Chem., 1932, [ii], 134, 158—166).—The liquid is allowed to drop from a capillary tube (a series is used for liquids of varying viscosity) on to a sheet of filter-paper placed at a definite distance beneath. The area of the spreading drop is measured at definite intervals. The results are comparable with those given by Traube's stagonometer (B., 1928, 111), and are of val. in the characterisation of essential oils.
H. A. P.

Dependence of the angle of contact on the constitution of adsorbed organic compounds. A. B. COX, E. E. WARK, and I. W. WARK (Nature, 1932, 129, 871).—A trace of K Et xanthate in H_2O gives an angle of contact in the system mineral- H_2O -air which is independent of the concn. of the xanthate and the nature of the mineral. Na Et_2 dithiophosphate and other Et compounds containing an SH group give the same angle $60^\circ \pm 2^\circ$. Each alkyl or aryl group shows a characteristic angle of contact which is apparently independent of the nature of the polar group of the adsorbed mol.
L. S. T.

Conductance of some sodium oleate solutions in relation to interfacial adsorption. R. F. NICKERSON and P. SEREX (J. Physical Chem., 1932, 36, 1585—1593).—The conductivity-concn. relation of Na oleate at 25° changes abruptly at 0.002N, which coincides with the min. of surface tension, γ , and loss of foaming power. Between 0.059 and 0.002N γ

varies inversely as the hydrolysis. More acid oleate is adsorbed at the oil-solution than at the vapour-solution interface of a Na oleate solution. Foaming is attributed to a hydrolytic equilibrium between a saturated surface and an excess of colloidal and crystalloidal oleate. Oils differ in their adsorbent capacity for acid Na oleate. S. L. (c)

Electrokinetic potentials. XI. Effect of soaps on the electric moment of the double layer at an aqueous cellulose interface. H. B. BULL and R. A. GÖRTNER (Physics, 1932, 2, 21—32).—Aq. Na formate, acetate, propionate, butyrate, octoate, oleate, and oxalate were investigated by a streaming-potential method. The electric moment of the double layer is practically const. after the fourth C atom. Long-chained soaps give a val. independent of the concn. The max. val. is 2×10^{-14} N. CH. ABS.

Electrocapillary effect of capillary-active organic molecules. A. W. DAVIS (Phil. Mag., 1932, [vii], 13, 1188—1192).—The max. in the electrocapillary curve for aq. KI is depressed by MeOH. The effect is compared with that for aq. KCl and MeOH. H. J. E.

Capillary activity of normal aliphatic dicarboxylic acids. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1932, 7, 168—176).—The depression of the surface tension of aq. solutions of the acids $(CH_2)_n(CO_2H)_2$ ($n=0-7$) is proportional to the concn., and for solutions of equiv. concn. increases in the order $n=0 < 2 < 3 < 1 < 4 < 7 < 6$. Adsorption by animal charcoal increases in the same order. When n is even, the work needed to bring 1 mol. of acid from the surface into the solution increases by 620 g.-cal. for each CH_2 group. D. R. D.

Wetting and ultra-porosity. Adsorption and stabilisation of hydrophobic and hydrophilic carbons in solutions of dyes. B. V. ILJIN and S. G. PINSKER (Kolloid-Z., 1932, 59, 283—285).—Both hydrophobic and hydrophilic suspensions of C are stabilised by Me-violet, which is adsorbed thereby, in accordance with the view that hydrophilic C is characterised by ultra-porosity. E. S. H.

Heat of wetting of carbon and silica gel in mixtures of water and acetic anhydride. B. V. ILJIN, W. A. OSCHMANN, N. L. REBENKO, and N. K. ARCHANGELSKAJA (Z. anorg. Chem., 1932, 206, 174—176).—The heat of wetting of powdered hydrophobic C in mixtures of H_2O and Ac_2O shows a max. for a 50% mixture (glacial $AcOH$). With powdered hydrophilic C there is inversion, glacial $AcOH$ giving a min. heat of wetting. Similar results are obtained with powdered hydrophilic SiO_2 gel and thus confirm the view that the method may be employed for studying compound formation in solution (cf. A., 1930, 153). M. S. B.

Schaum's phenomenon. H. REIBSTEIN (Kolloid-Z., 1932, 59, 337—342).—The factors affecting the movements of small crystals at the interface $Hg/dil. H_2SO_4$ are discussed. E. S. H.

Influence on diffusion of salts through gels and of gases through membranes. H. EPPINGER and W. BRANDT (Biochem. Z., 1932, 249, 11—20).—The

permeability of gelatin for NaCl is increased by small and decreased by large amounts of caffeine and uric acid, increased by carbamide, strophanthin, digitalis, and saponin, and decreased by EtOH, Et_2O , and deoxycholic acid. The permeability of a soap film for H_2 is increased by addition of lecithin and deoxycholic acid and decreased by addition of strophanthin, caffeine, digitalis, Et_2O , EtOH, $CCl_3 \cdot CH(OH)_2$, histamine, cholesterol, saponin, and $CaCl_2$. The last three substances in min. doses cause a small increase of permeability. P. W. C.

Cryoscopic study of ether and acetone in solutions of potassium chloride. F. BOURION and E. ROUYER (Compt. rend., 1932, 194, 2050—2052; cf. this vol., 570).—Further f.-p. data are recorded. C. A. S.

Ebullioscopic experiments. M. CENTNERSZWER and M. ŁAŻNIEWSKI (Z. physikal. Chem., 1932, 160, 257—271).—By means of Świentosławski's ebullioscope (cf. A., 1931, 1388) the vals. of 26.42° and 38.02° have been obtained for the mol. b.-p. elevations of C_6H_6 and $CHCl_3$, referred to 100 g. of solvent, and the degrees of association of alkylammonium salts in $CHCl_3$ have been determined. R. C.

Variation with concentration of equivalent refraction of dissolved electrolytes. G. PESCE (Z. physikal. Chem., 1932, 160, 295—300; cf. A., 1931, 1122).—The apparent refraction of aq. $CaCl_2$, $SrCl_2$, and Na_2CO_3 at 25° from about 1M to saturation is a linear function of the concn. With $BaCl_2$ it falls more rapidly with increasing concn. than with $SrCl_2$, pointing to a greater tendency to ionic association. With Na_2CO_3 it rises with the concn. R. C.

Effect of concentration and of degree of ionisation on the optical refractivity of solutions of amino-acids, proteins, and other compounds. R. CRAIG and C. L. A. SCHMIDT (Austral. J. Exp. Biol., 1932, 9, 33—67).—The factors which govern the change of n of aq. solutions of NH_2 -acids on the addition of strong acid or strong base also operate with gelatin, edestin, and serum-albumin. In gelatin solutions the change from gel to sol causes a change in n . W. M.

Dispersion of air in aqueous solutions. N. A. ALEJNIKOV (Kolloid-Beih., 1932, 36, 82—122).—The methods available for the prep. of disperse systems of air in aq. solutions are reviewed, particularly in relation to their application to flotation processes. The systems formed by shaking a solution of a surface-active substance sparingly sol. in H_2O tend to a limiting mean degree of dispersion as the concn. of the surface-active substance is increased. The polydisperse system originally formed rapidly separates into two systems, viz., foam and emulsion. The time-stability of the emulsion tends towards a limiting val. with increasing concn. of surface-active substance, whilst that of the foam possesses a max. The pneumatic method of dispersion (leading the air into the solution through a capillary or porous diaphragm) is more suitable for the subsequent examination of the systems. Experiments on the pressure and stability of several such systems are described. E. S. H.

Making gold sol for [cerebro]spinal-fluid tests. B. S. LEVINE (Amer. J. Syph., 1932, 16, 103—109).—Carefully distilled H_2O is necessary; cleanliness of reaction vessels and concn. of reagents are important matters. The mixed reagents must not be exposed to the flame. Org. substances should be eliminated and some active O_2 must remain dissolved in the H_2O . Directions for the prep. of Au sol by treating a solution of $AuCl$ and K_2CO_3 with CH_3O and H_2O_2 are given. CH. ABS.

Diffusion of colloid particles. IV. Influence of charge on diffusion velocity and its alteration during coagulation. H. R. BRUNS (Kolloid-Z., 1932, 59, 263—266).—During the coagulation of amylum sols by electrolytes the rate of diffusion does not decrease, as expected, but increases in accordance with the electrical theory developed (A., 1931, 561). E. S. H.

Reproducibility and rate of coagulation of stearic acid smokes. H. S. PATTERSON and W. CAWOOD (Proc. Roy. Soc., 1932, A, 136, 538—548).—An apparatus for the production of reproducible uniform stearic acid smokes is described. For many smokes of the same wt. concn. the velocity of coagulation is const. within small limits. The measured velocities of coagulation agree with Smoluchowski's theory if account is taken of the fact that smokes originally homogeneous become heterogeneous during coagulation. L. L. B.

Colloidal systems. Peptisation of ferric hydroxide by ferric chloride. A. DUMANSKI and V. M. SIMONOVA (J. Gen. Chem. Russ., 1931, 1, 1229—1244).—The process of peptisation of $Fe(OH)_3$ by $FeCl_3$ is represented using triaxial co-ordinates. The coagulative action of anions diminishes in the order $SO_4^{2-} > F^- > Cl^-$ or Br^- , and of cations in the order $Li^+ > K^+$ or Na^+ , and $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. In high concns. sulphates produce complex peptisation, both $FeCl_3$ and SO_4^{2-} being adsorbed by $Fe(OH)_3$; no coagulation of the sols is observed in such cases. The action of $AlCl_3$ is antagonistic to that of $FeCl_3$. R. T.

Acclimatisation and sensitisation of colloidal ferric hydroxide. A. V. DUMANSKI and A. I. SOLIN (Kolloid-Z., 1932, 59, 314—324).—The coagulation of $Fe(OH)_3$ sols, prepared by different methods, by alkali halides with and without the addition of MeOH affords evidence of acclimatisation, particularly in the more dil. sols. In general, the dil. sols are the most stable. A connexion is established between acclimatisation and adsorption. No acclimatisation was observed with K_2SO_4 . The sols are sensitised towards coagulation by K_2SO_4 by adding MeOH, but to an extent which depends on the nature of the electrolyte produced simultaneously with the colloid. Sols of $Fe(OH)_3$ containing NaF do not show acclimatisation towards coagulation; the strongly coagulating power of NaF suggests the ion F_2^{2-} . E. S. H.

Silver ferrite. V. Ageing process of orthoferric hydroxide and the constitution of goethite ($\alpha-FeO \cdot H$). A. KRAUSE and A. LEWANDOWSKI (Z. anorg. Chem., 1932, 206, 328—336).—The ageing process of orthoferric hydroxide may be followed by

its decreasing ability to form Ag ferrite (this vol., 481), after an initial rise, and also from the nature of the insol. residue from the Ag ferrite. The rate increases with increasing concn. of OH^- . Ageing is the result of the following changes: orthohydroxide \rightarrow polyorthohydroxide \rightarrow ferrous acid \rightarrow goethite. It is also possible for hydrohamatite to be formed, depending on the OH^- concn. Ag ferrite becomes ferromagnetic after decomp. sets in at 250—280°, but on calcination it loses this property. The relationship between amorphous and cryst. $\gamma-FeO \cdot H$ is discussed, and also the constitution and mol. wt. of goethite. M. S. B.

Coagulation of colloids from the point of view of Smoluchowski's theory. III. Coagulation of arsenious sulphide sol by sulphuric acid solutions. S. S. JOSHI and G. R. PHANSALKAR (J. Indian Chem. Soc., 1932, 9, 157—161).—The results previously obtained (A., 1931, 1124) are amplified and confirmed. Contrary to Linder and Picton (J.C.S., 1905, 87, 1906), the rate of coagulation is increased by rise in temp. The influence of temp. depends on the colloid concn. when the concn. of coagulator is const. H. B.

Electrolyte coagulation of copper oxide sol in the presence of starch. H. BREINDL and K. SÖLLNER (Kolloid-Z., 1932, 59, 331—335).—The coagulation of CuO sols by K_2SO_4 has been followed by centrifuging the coagulate and determining Cu in the liquid. Small amounts of starch have practically no effect, but when a crit. concn. of starch is reached (increasing with increasing concn. of K_2SO_4) the velocity of coagulation is sharply reduced, further addition of starch causing little more change. The influence of starch is not reversible; subsequent dilution has little influence. E. S. H.

Influence of temperature on the coagulation of colloidal manganese dioxide. S. S. JOSHI and T. S. NARAYAN (Kolloid-Z., 1932, 59, 335—336).—In this system, with rising temp. the Smoluchowski factor β passes through a min. at 30°, and rises rapidly at 45°, reaching a const. val. at 50°. E. S. H.

Influence of salts on viscosity of hydrophilic colloids. E. H. BUTCHER (Rec. trav. chim., 1932, 51, 619—623).—Viscosities of sols of gum arabic, casein, ovalbumin, and glycogen in the presence of neutral Na salts of various acids have been measured at 25°. The viscosity of the two first-named substances is considerably lowered by small concns. of salt, and but little changed above $N/8$, whilst that of the other two is only slightly lowered at first and is subsequently raised until it is equal to or higher than that of the pure sol. The lyotropic effect of the salts used (sulphate, tartrate, bromide, thiocyanate) is much less marked in these experiments than in those on swelling and salting out. F. L. U.

Relation between coagulation and gelation points of sols. S. PRAKASH (J. Indian Chem. Soc., 1932, 9, 133—136).—Larger quantities of KCl , KBr , K_2CrO_4 , K_2SO_4 , $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$ are required to set a jelly than to coagulate the jelly-forming sol (Fe^{+++} and Cr^{+++} arsenates, Zr molybdate

and borate, and titanitic acid) in the same time. The ratio (R) of the gelation and coagulation concns. (of K_2SO_4) decreases towards unity with increasing purity of the sol (Fe^{+++} arsenate). R is greater for K_2SO_4 than for KCl with Fe^{+++} arsenate, Zr molybdate and borate, and titanitic acid sols. H. B.

Influence of charge on the sedimentation velocity of colloids, especially in the ultracentrifuge. A. TISELIUS (Kolloid-Z., 1932, 59, 306—309).—The sedimentation of colloidal particles is retarded as the charge on the particles is increased. The effect is due to an increase in friction, and becomes noticeable only when the particle size falls below a certain val., but the effect has an influence on the determination of particle size by ultracentrifugal sedimentation analysis. The relation $s' = s(1 - t_k)$ is derived, where s' and s are respectively the apparent and true sedimentation velocities, and t_k is the fraction of the total electrical conductivity (colloid + electrolyte) which is carried by the colloid ion. Experiments on the velocity of sedimentation of phycoerythrin have given results in accordance with the theory. E. S. H.

Cataphoretic measurements. A. J. RABINOVITSCH and E. B. FODIMAN (Kolloid-Z., 1932, 39, 310—314).—The technique of electrophoretic measurements is discussed, whence it appears that abs. quant. vals. cannot be obtained by present methods, particularly in view of the varying influence of the overlayer liquid. These difficulties have been studied experimentally with sols of $Fe(OH)_3$ and As_2S_3 . A sharp boundary is obtained only if the conductivity of the overlayer liquid is equal to or slightly $>$ that of the sol. Increasing the conductivity of the overlayer liquid relatively to that of the sol lowers the electrophoretic velocity; lowering the p_H of the overlayer liquid has the opposite effect. E. S. H.

Cataphoretic velocity in a concentrated suspension. S. KOMAGATA (Bull. Chem. Soc. Japan, 1932, 7, 137—143).—The electrode on which the colloid is deposited is suspended from a spring balance. The cataphoretic velocity is calc. from the change in wt. The results for suspensions of clay in aq. $NaOH$ agree well with those obtained by the U-tube method. D. R. D.

Colloidal charcoal. II. Cataphoresis. H. LACHS and K. GESTEL (Rocz. Chem., 1932, 12, 327—340).—The velocity of cataphoresis ζ of charcoal sols falls as the concn. of KCl rises to $0.04M$. ζ increases as the concn. of $K_4Fe(CN)_6$ rises to $0.01M$, above which it falls, at first rapidly and then more slowly. ζ is similarly increased by addition of KOH , and greatly reduced by even very small concns. of $ThCl_4$. The results obtained are discussed in relation to Stern's theory (Z. Elektrochem., 1924, 30, 508). R. T.

Physical properties of colloidal clay. C. LA ROTONDA (Kolloid-Beih., 1932, 35, 413—440).—Colloidal clay of particle size $< 0.1\mu$, obtained from acid soils, is converted by electrodialysis into H-clay and by treatment with alkalis into Na-, K-, Mg-, and Ca-clays. Viscosity measurements show a max. in H-clay, decreasing to a min. as the H^+ is replaced by other cations and afterwards rising to higher vals.

as saturation is approached. The electrophoretic velocity and ζ potential increase with the cation saturation of the clay. The "suspension effect" (a difference in p_H of the suspension and the ultrafiltrate) was observed in all the systems except the H-clay.

E. S. H.

Behaviour of clay gels under small pressures, and influence of the exchangeable base present. R. M. WOODMAN and G. W. CHAPMAN (J.S.C.I., 1932, 51, 175—178T).—A simple apparatus for measuring the swelling of clays under small excess pressures is devised. Swelling under pressure depends on (1) the total base-exchange capacity of the clay or the SiO_2/Al_2O_3 ratio, (2) the base saturating the clay, and (3) the age of the clay suspension used. A hysteresis effect in subsequent swelling probably occurs on reduction of the pressure to which a clay has been subjected.

Thixotropy of bentonite suspensions. H. FREUNDLICH, O. SCHMIDT, and G. LINDAU (Kolloid-Beih., 1932, 36, 43—81; cf. A., 1931, 1232).—Suspensions of H-bentonite are not thixotropic, but are made so by adding alkali-metal ions, Tl^+ , and to a smaller extent Ca^{++} and Ba^{++} . Al^{+++} , Th^{++++} , and org. bases do not induce thixotropy. The particles of H-bentonite are negatively charged; small concns. of alkali hydroxides raise the ζ potential, whilst higher concns. lower it; multivalent ions cause a reversal of charge. The phenomena of thixotropy, swelling, and electrophoresis in these systems are consistent with the view that the metal aluminosilicates are dissociated, the degree of dissociation depending on the nature of the metal cation. E. S. H.

Lyophilic colloids. XIII. Measurement of small elastic deformations of hydrophilic gels. Agar gel. H. G. B. DE JONG and J. P. HENNE-MANN (Kolloid-Beih., 1932, 35, 441—475).—Apparatus and technique for measuring elastic deformations ($< 1\%$ of the length of the specimen) of hydrophilic gels are described. The deformation of agar gel is reversible and consists of two partial deformations occurring with different velocities. These have been analysed and expressed by equations. During slow compression H_2O is expressed and is taken up during slow expansion; the process is strictly reversible, therefore, only when the gel is immersed in a liquid in equilibrium with it. E. S. H.

Formation of inorganic jellies. S. PRAKASH (Allahabad Univ. Studies, 1932, 8, Sci. Sect., 119—154).—A review of published work on jellies of inorg. oxy-acids, basic hydroxides, arsenates, phosphates, molybdates, tungstates, and borates.

E. S. H.

Viscosity anomalies of gelatin solutions. M. PICHOT (J. Phys. Radium, 1932, [vii], 3, 205—218).—A theory is developed, which describes the observed phenomena in terms of a viscosity coeff. and a coeff. of structure. Both coeffs. are functions of concn., temp., and treatment of the solution. A gelatin solution of given concn. obeys Poiseuille's law above a certain temp., θ . The decomp. of the solution is accompanied by a decrease in the viscosity coeff. to a limiting val., whilst the structure coeff. gradually falls to zero. At temp. below θ the theory is consistent

with the viscosity anomalies, provided that the solution is sufficiently far from gelation. Apparatus and technique for viscosimetry and the graphical determination of the two coeffs. are described.

E. S. H.

Swelling of gelatin. I. A. KARSEN and G. C. HERINGA (Rec. trav. chim., 1930, 51, 593—597).—A method of preparing isotropic gelatin is described. The total swelling of the latter in dil. AcOH is limited, proportional to the respective initial dimensions in different directions, and reversible. The rates of increase in the length and breadth of a rectangular strip of uniform thickness are equal until the diffusion boundaries from the two surfaces meet, after which the longer dimension increases more rapidly.

E. L. U.

Antagonistic influence of cations on the diffusion velocity of OH ions in gelatin jellies. V. V. EFIMOV (Kolloid-Z., 1932, 39, 279—280).—The diffusion velocity of OH' in gelatin gel is increased by Na', K', NH₄', and Li', and decreased by Mg'', Ca'', Fe'', Fe''', Al''', Co''', Ni'', Zn'', Pb'', Cu'', and Cd''. The effects of two univalent ions or two multivalent ions are additive, whilst uni- and multivalent ions are antagonistic.

E. S. H.

Dependence of osmotic pressure and micellar weight of gelatin solutions on the temperature and the previous history of the solution. J. EGGERT and H. BINGER (Biochem. Z., 1932, 247, 85).—Frankel's views (A., 1931, 1368) are criticised.

P. W. C.

Liesegang rings of silver chromate in gelatin. B. N. DESAI and G. M. NABAR (J. Indian Chem. Soc., 1932, 9, 141—143).—Increase in the acidity of the gelatin causes the rings to become spiral-shaped and is accompanied by decrease in the time of appearance of the first ring, the distance between the same successive rings, and the no. of rings obtainable. The results do not support Hatschek's statement that addition of acid increases the width of the rings.

H. B.

Physico-chemistry of lecithin. I. Y. SUYEHOSHI and K. KAWAI (J. Biochem. Japan, 1932, 15, 277—283).—The isoelectric point of lecithin, as shown by the optimum of flocculation, is p_H 4.7, but after some days the val. shifts considerably to the acid side. At p_H vals. below the isoelectric point the micelles are positively charged and hence flocculated by anions; at p_H vals. above the isoelectric point they are negatively charged and flocculated by cations. The sensitivity towards flocculation by salts decreases with the age of the solution.

F. O. H.

Isoelectric points of glycine and alanine. M. HIRAKI (J. Biochem. Japan, 1932, 15, 345—357).—Titration of dil. aq. HCl solutions of varying concn. against 0.02N-NaOH gave p_H 6.16 at 18° and 6.02 at 25° for glycine and 6.18 at 18° and 6.15 at 25° for alanine.

F. O. H.

Relations between colloidal and constitutive changes in some proteins. W. PAULI (Austral. J. Exp. Biol., 1932, 9, 23—31).—The changes which occur when hydrotropic substances [salicylates, HCO-NH₂, CO(NH₂)₂] act on coagulated protein

(electrodialysed ovalbumin, serum-albumin, pseudo-globulin) depend on the nature of the protein, on that of the hydrotropic substance, and on the means by which coagulation was effected. The first stage in the interaction is the same in all cases, but subsequent changes, such as those in the optical activity of the solutions, vary with the protein. The differences suggest the formation of additive compounds (hydrotropic substance-protein). The nitroprusside reaction does not invariably serve as a test for denaturation.

W. M.

p_H Stability region of proteins and osmotic swelling. D. J. LLOYD (Nature, 1932, 130, 24—25).—Protein structures giving evidence of a definite mol. orientation show, in contrast to gelatin, a p_H stability range with regard to osmotic swelling. For collagen fibres the range is p_H 4—5.5.

L. S. T.

X-Ray study of the coagulation of ovalbumin. W. S. MILLER, K. G. CHESLEY, H. V. ANDERSON, and E. R. THEIS (J. Amer. Leather Chem. Assoc., 1932, 27, 174—182).—The view that the coagulation of ovalbumin involves the elimination of H₂O between the free NH₂ and CO₂H groups is supported by X-ray studies. The structure developed when the coagulated albumin is re-soaked indicates that the resulting linking is too firm to permit of the re-entry of H₂O.

D. W.

Complex coacervation. X. Auto-complex coacervation of lecithin sols containing triolein, cholesterol, or oleic acid, and its biological significance. XI. Auto-complex coacervates of lecithin and their significance for the permeability problem. H. G. B. DE JONG and R. F. WESTERKAMP (Biochem. Z., 1932, 248, 309—334, 335—374).—Hydrosols of soya-bean- or egg-lecithin containing triolein, cholesterol, or oleic acid are coacervated by cations of low valency, whilst the pure lecithin sols are not. In some cases the flocculation curves show several max. Multivalent cations produce a reversal of charge, which occurs at or near one of these max.; no such reversal was noted with NaCl. The point of reversal is approx. coincident with that previously noted for aq. non-electrolytes (this vol., 693). Neutral salts (e.g., NaCl) at a concn. insufficient to cause coacervation inhibit the coacervation due to ions of higher valency (e.g., Ca''); this inhibition is the more marked the greater is the valency of the anion of the added Na or K salt, or the smaller is the cation valency of an added chloride. These phenomena, which are in general similar to those observed in systems containing sol. non-electrolytes, are discussed in terms of changes in the degree of hydration of the complexes.

XI. The coacervates of lecithin vary with the conditions of formation; they may consist of liquid droplets, of granular masses, or of weakly solvated flakes. Their morphological characteristics are described and their behaviour in an electric field has been studied. The grouping of the particles in an electric field indicates a polar nature and the morphology of the clusters bears a relation to the electric charge. Under certain conditions polyphase liquid droplets are produced. The velocity of coacervation in these systems is increased strongly by adding

capillary-active substances, thereby increasing the solvation of the auto-complex coacervate. Relations between solvation, electric charge, and permeability are discussed with special reference to processes occurring in biological media. The system lecithin-triolein (cholesterol, etc.)-H₂O is regarded as a model of the protoplasm surface, which is subject to an antagonistic action of Ca⁺⁺ and Na⁺ as shown above. Factors which lower cell permeability reduce the degree of solvation of the coacervates described, whilst those which raise the permeability of the cell increase the solvation. E. S. H.

Biophysical chemistry of colloids and protoplasm. V. COFFMAN (Chem. News, 1932, 145, 1—3).

Union of biocolloids. VI. Coagulated egg-albumin and various carbohydrates. S. J. PRZYŁECKI and M. Z. GRYNBERG (Biochem. Z., 1932, 248, 16—38).—The combination of albumin with mono-, di-, and tri-saccharides, Mg hexosediphosphate, isotrihexosan, dextrans, amylose, amylopectin, starch, and glycogen has been examined. At a p_H below its isoelectric point the protein combines with phosphorylated carbohydrates. At a p_H above this point, association results from the union of the ionised group of the protein with the positively-charged polysaccharides. The union with amylose and dextrans is probably due to subsidiary valencies and with starch is conditioned by mol. size. P. W. C.

Osmosis and diffusion of some plant colloids. (Starch substances—ligninsulphonic acid—humates.) M. SAMEC [with L. KNOP and Z. PANKOVIČ] (Kolloid-Z., 1932, 59, 266—278).—Measurements of the osmotic pressure of amylopectin, ligninsulphonic acid, humates, and hylatomelanates suggest that the ion of opposite charge to the colloid particle is osmotically inactive. In dil. amylopectin solutions there is an approx. linear relation between concn. and osmotic pressure, but the relation is complicated in more conc. solutions. Amylopectin has an abnormally high diffusion velocity, in which the H⁺ plays a large part in spite of its osmotic inactivity in the same solution. The diffusion of the org. components (erythroamyloses) is normal in comparison. E. S. H.

Colloid-chemical reactions of rivanol. A. STEIGMANN (Kolloid-Z., 1932, 59, 343—344).—Aq. alkali halide solutions ppt. rivanol in the following order: I[−] > Br[−] > Cl[−] > F[−]. With I in KI rivanol forms a dark blue coloration resembling the starch reaction. E. S. H.

Swelling of graphite. H. THIELE (Z. anorg. Chem., 1932, 206, 407—415).—Graphite which has swollen in oxidising liquids (e.g., H₂S₂O₇) exhibits a series of colours in reflected light. Incompletely swollen graphite gives blue, indigo, violet, red, orange, yellow, and grey. Swelling is a property of the graphite form of C and is exhibited by all the natural forms; the "amorphous" retort-graphite and sugar-charcoal do not swell. Liquids which do not cause swelling under ordinary conditions (e.g., H₂SO₄, HNO₃, and 30% HClO₄) cause graphite to swell when it is anodically polarised. No swelling takes place under anodic polarisation in aq. HCl, HI, HBr, KCl, or KI.

Probably the swelling in oxidising media is due to the formation of a labile oxide of graphite.

E. S. H.

Flame temperatures of mixtures of ammonia and its products of dissociation. G. W. JONES, B. LEWIS, and H. SEAMAN (J. Amer. Chem. Soc., 1932, 54, 2166—2170).—For mixtures of air, H₂, and N₂ the max. flame temp., T , is inversely proportional to the amount of N₂. For mixtures of NH₃ with its products of dissociation (3H₂+N₂), T is inversely proportional to the amount of NH₃. These data and calculation show that for NH₃-air mixtures T would be about 1700°, if a suitable burner could be developed (cf. B., 1928, 881; A., 1931, 572; this vol., 127).

B. E. A. (c)

Gas-phase equilibrium between methyl nitrite, hydrogen chloride, methyl alcohol, and nitrosyl chloride. Absorption spectrum of nitrosyl chloride. J. A. LEERMAKERS and H. C. RAMSPERGER (J. Amer. Chem. Soc., 1932, 54, 1837—1845).—The equilibrium $\text{MeONO} + \text{HCl} = \text{MeOH} + \text{NOCl}$, studied by means of the light absorption due to NOCl, is free from side reactions. The equilibrium const. is 0.521 at 298.1°, 0.753 at 323.1° abs. The calc. vals. for the free energy, the heat and the entropy of formation, and the entropy of MeONO at 25° are −100, −16,750 g.-cal., −55.9, and 64.2 entropy units.

H. F. J. (c)

Vanishing line charts for the calculation of important technical gas equilibria. E. S. VON BERGMAMPF (Z. anorg. Chem., 1932, 206, 317—327).—A method of representing schematically the dependence of four variables on one another is described, and also its application to various well-known equilibria.

M. S. B.

Water-gas equilibrium. J. R. PARTINGTON and W. G. SHILLING (J.S.C.I., 1932, 51, 32t, 222t).—The curves constructed by Bryant (A., 1931, 1233) do not support his choice of sp. heats. Attention is directed to an erroneous statement by Gordon and Barnes (this vol., 695).

Water-gas equilibrium. W. M. D. BRYANT (J.S.C.I., 1932, 51, 222t).—A reply to Partington and Shilling (see preceding abstract).

Equilibrium $\text{Fe}^{+++} + \text{I}^- \rightleftharpoons \text{Fe}^{++} + \frac{1}{2} \text{I}_2$ in aqueous solution. H. M. DAWSON and E. SPIVEY (J.C.S., 1932, 1838—1844).—The mass action coeff., K_1 , for the above reaction at 25° in the presence of KCl falls from 19.4 to 6.85 as the concn. of KCl is increased from 0.5 to 3.5M, in qual. agreement with theory. Allowance must be made for the formation of ClI_2' and I_3' , and for the salting-out effect of KCl on the solubility of I₂ (cf. A., 1926, 236, 244). For the equilibrium $\text{ClI}_2' \rightleftharpoons \text{Cl}^- + \text{I}_2$, K_2 varies from 0.629 to 0.637, rising to 0.652 in the presence of 0.1M-HCl. For $\text{I}_3' \rightleftharpoons \text{I}^- + \text{I}_2$, K_3 varies from 1.52 to 1.73×10^{-3} . The val. of K_1 given by Bronsted and Pedersen (A., 1923, ii, 61) is incorrect. D. R. D.

Perhalide equilibrium in non-aqueous solutions. E. A. DANCATER (J. Physical Chem., 1932, 36, 1712—1732).—The dissociation of Fe, Sn, and Sb perhalides in glacial AcOH has been determined by a distribution method, one solvent being air. Chloroperoxides exist mainly as trihalides in both aq.

and AcOH solution, whilst perbromides exist mainly as tribromides in aq. solution and pentabromides in AcOH. For a halide with a normal val. of the dissociation const., K , in H_2O , the val. is also normal in AcOH, and each val. is approx. const. from 15° to 40° . For Cd and Hg halides, Fe, Sn, and Sb chlorides, and Sn bromides K in either aq. or AcOH solution > the normal val., and increases with the halide concn. In AcOH solutions of these compounds the percentage of simple mols. and ions increases with the halogen concn. and halide dilution. J. H. R. (c)

Salt-forming properties of iodine. M. I. USCHAKOV (J. Gen. Chem. Russ., 1931, 1, 1258—1265).—I dissociates in EtOH to yield uni- and ter-valent ions. I is pptd. by alcoholic $AgNO_3$, leaving $I(NO_3)_3$ in solution, and this, on addition of excess of I, yields $I(NO_3)_3$. Salts of these nitrates with pyridine and quinoline are described. R. T.

Equilibrium between lactic and pyruvic acids. R. WURMSER and (MLLE.) N. MAYER (Compt. rend., 1932, 195, 81—83; cf. this vol., 813).—Previous results have been confirmed by the observation that under similar conditions at p_H 7.4 lactic acid reduces cresyl-violet and pyruvic acid oxidises phenosafranin. C. A. S.

Complex salts. V. Effect of diisopropyl substitution on the stability of the dimalonatocupriate ion. D. J. G. IVES and H. L. RILEY (J.C.S., 1932, 1766—1770).— Na and Cu^{II} diisopropylmalonates have been prepared, the latter being deep blue and readily hydrolysed. Conductivity data are recorded for the Cu salt and the free acid. The val. $K=1.7 \times 10^{-5}$ for the complex Cu-diisopropylmalonate ion shows that this is much more stable than the corresponding Pr ion. D. R. D.

Classical dissociation constant of bromocresol-green, chlorophenol-red, and methyl-red in potassium chloride solutions. E. F. CHASE and M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1932, 54, 2284—2292).—The classical dissociation consts. in KCl solutions have been determined. The salt error in the colorimetric determination of $[H^+]$ is expressed by the ratio of the classical dissociation const. of the indicator in the given solution to that in the standard solution of the same tint. R. H. C. (c)

Reversible two-step oxidation. L. MICHAELIS (J. Biol. Chem., 1932, 96, 703—715).—A mathematical development of the theory of two-step oxidation—reduction of org. dyes in which semiquinones are intermediate forms (cf. A., 1931, 1309). A. C.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XIV. Products of hydrolysis and aggregation processes in salt solutions of tervalent metals, especially in aqueous chromic salt solutions. G. JANDER and W. SCHEELE (Z. anorg. Chem., 1932, 206, 241—251).—The curve representing the variation of diffusion coeff. with p_H for Cr in aq. $Cr(H_2O)_6(NO_3)_3$ is of similar form to the corresponding curves for Fe and Al solutions (A., 1931, 1369; this vol., 124), indicating the existence of a continuous and overlapping series of sol. Cr compounds, increasingly basic and more highly aggregated as the p_H of

the solution increases. Below p_H 2, however, the unimol. ion $Cr(H_2O)_6(NO_3)_3$ exists alone, but the mol. wt. increases very rapidly with increasing p_H . When the solution contains 2.35 mol. NaOH to 1 mol. $Cr(NO_3)_3$ the polymerised products of hydrolysis contain 600—700 Cr atoms and the mean mol. wt. is 84,000. When the proportion is 1 : 1 the prevailing hydrolysed product contains 2 atoms of Cr. The unimol. normal salts of Al, Cr, and Fe^{III} show increasing readiness to hydrolyse in this order, but the more basic compounds in the order Al, Fe^{III} , and Cr. The experimental data for Cr are in general agreement with those obtained by Bjerrum. M. S. B.

Activity coefficient of benzoic acid in solutions of neutral salts and of sodium benzoate. I. M. KOLTHOFF and W. BOSCH (J. Physical Chem., 1932, 36, 1685—1694).—The solubility of BzOH in H_2O at 25° is 0.02775 ± 0.00002 mol. per litre. The activity of the undissociated acid is 0.0264. The solubility in aq. NaOBz and in aq. solutions of various alkali and alkaline-earth salts has been determined, and the influence of these salts on the activity is discussed. G. M. M. (c)

Ionisation constant of benzoic acid and activity coefficient of benzoate ion in presence of neutral salts. I. M. KOLTHOFF and W. BOSCH (J. Physical Chem., 1932, 36, 1695—1701).—The ionisation const. of BzOH at 25° is 6.7×10^{-5} . The H^+ activity of dil. solutions of BzOH and NaOBz has been determined by means of the quinhydrone and H electrodes, without correction for liquid junction potential. The activity coeff. of BzO^- in 0.01M-NaOBz containing neutral salts and saturated with BzOH has been determined. G. M. M. (c)

Mean and individual ion activity coefficients of silver benzoate in salt solutions. I. M. KOLTHOFF and W. BOSCH (J. Physical Chem., 1932, 36, 1702—1711).—The solubility of AgOBz at 25° is 0.01162 ± 0.00002 mol. per litre. The mean and individual ion activity coeffs. of AgOBz have been determined in various salt solutions. Assuming that AgOBz is incompletely ionised in its saturated solution, the calc. vals. of the activity coeff. of BzO^- agree with those obtained from H electrode measurements with solutions containing BzOH, NaOBz, and a neutral salt, uncorrected for liquid junction potential. The normal potential of the Ag electrode against quinhydrone in 0.01M-HCl and 0.09M-KCl is 0.2269 ± 0.0002 volt. The activity coeff. of Ag^+ in 0.01M- $AgNO_3$ containing neutral salts has been determined. G. M. M. (c)

Thermodynamic properties of solid solutions of lead chloride and lead bromide. A. WACHTER (J. Amer. Chem. Soc., 1932, 54, 2271—2278; cf. this vol., 700).—The electrode potentials of solid solutions in which N , the mol. fraction of $PbCl_2$, varies from 0.2 to 1.0 have been measured at 200 — 300° . If $N < 0.9$ the activity of $PbCl_2 < 0.1$. The solid solution in which $N=0.75$ is the most stable. The Br ions are regularly arranged in the $PbCl_2$ lattice. A. F. (c)

Fusion curve of the system sodium nitrite-potassium nitrite. J. ETTINGER (Rocz. Chem.,

1932, 12, 362—365).—The existence of an unbroken series of solid solutions is indicated. R. T.

M.-p. curves in the system $\text{NaNO}_2\text{--KNO}_2$. J. ETTINGER (Z. anorg. Chem., 1932, 206, 260—262).— NaNO_2 and KNO_2 form a continuous series of solid solutions with a min. m.p. of 230.5° for a mixture of 70% NaNO_2 . M. S. B.

Fusion diagrams of the systems KF--AlF_3 and LiF--AlF_3 . P. P. FEDOTEEV and K. TIMOFIEV (Z. anorg. Chem., 1932, 206, 263—266).—Compounds of the cryolite type are formed in both cases: $3\text{KF}\cdot\text{AlF}_3$, m.p. 1025° , and $3\text{LiF}\cdot\text{AlF}_3$, m.p. 790° . There is probably an unstable compound $\text{KF}\cdot\text{AlF}_3$, transition point 575° , but there is no evidence for the existence of a second compound of LiF with AlF_3 . M. S. B.

Thermal analysis of isomeric dinitrobenzenes. O. WYLER (Helv. Chim. Acta, 1932, 15, 956).—A reply to van der Linden (cf. this vol., 574). R. S. C.

Crystallisation of binary mixtures of compounds of the malic-tartaric series. J. TIMMERMANS (Rec. trav. chim., 1932, 51, 585—588).—*l*-Malic acid forms a eutectic with *l*-tartaric acid and an equimol. compound with *d*-tartaric acid. Similar behaviour is shown by the normal and acid NH_4 salts, diamides, and Et_2 esters. The term "racemoid" is proposed for compounds formed from optical antipodes of different substances. The different modes of behaviour of racemic mixtures when crystallised with an optically active third substance are classified. F. L. U.

System calcium chlorate-water. V. S. EGOROV (J. Gen. Chem. Russ., 1931, 1, 1266—1270).—The solid phases consist of $\text{Ca}(\text{ClO}_3)_2$, eutectic 76° ; dihydrate, eutectic -7.8° ; tetrahydrate, eutectic -26.8° ; and hexahydrate, eutectic -41° . R. T.

System silver nitrate-pyridine. R. MÜLLER [with G. WERSITSCH and H. BAUER] (Z. Elektrochem., 1932, 38, 449—450).—E.m.f. measurements of the element $\text{Ag}|\text{sat. solution of AgNO}_3 \text{ in } \text{C}_5\text{H}_5\text{N}$ between -20° and 85° show that four transitions occur in the solid phase; Ag begins to separate from the solution at about 50° , $\text{AgNO}_3\cdot 2\text{C}_5\text{H}_5\text{N}$ is stable between 44° and 35° , $2\text{AgNO}_3\cdot 5\text{C}_5\text{H}_5\text{N}$ between 35° and 11° , and $\text{AgNO}_3\cdot 3\text{C}_5\text{H}_5\text{N}$ between 11° and 0° ; at lower temp. the solid phase is AgNO_3 . H. F. G.

Equilibrium in binary systems under pressure. II. System $\text{K}_2\text{SO}_4\text{--H}_2\text{O}$ at 25° . L. H. ADAMS (J. Amer. Chem. Soc., 1932, 54, 2229—2243; cf. A., 1931, 1370).—Compression measurements show a decrease in the compression of H_2O and an increase in fictive vol. of K_2SO_4 , as observed for NaCl . The solubility, calc. thermodynamically, increases to a max. of 16.3% K_2SO_4 by wt. at 3800 bars. The solubility curve intersects the freezing pressure curve of ice_{VI} at 10,750 bars and 13.3% K_2SO_4 . The observed pressure at the pressure eutectic was 10,880 bars. A. F. (c)

Dissociation pressure of silver oxide below 200° . A. F. BENTON and L. C. DRAKE (J. Amer. Chem. Soc., 1932, 54, 2186—2194).—Finely divided Ag slowly takes up O_2 at $160\text{--}170^\circ$, establishing at

each addition a pressure which is independent of the amount already taken up. Decomp. pressures between 173° and 192° are about 17% lower than those obtained from other data at higher temp. These new data give -2450 g.-cal. for the free energy of formation of Ag_2O at 25° . E. J. R. (c)

Thermal dissociation of calcium carbonate in an atmosphere of carbon dioxide. II. Existence of primary and secondary dissociation points of Iceland spar. K. BITO, K. AOYAMA, and M. MATSUI (J. Soc. Chem. Ind. Japan, 1932, 35, 191—195B).—Iceland spar dissociates at 929° under a CO_2 pressure of 1 atm.; dissociation continues on cooling to 915° , but ceases at 914° . On cooling and reheating the specimen, dissociation commences at 915° . H. F. G.

Thermal change of bismuth nitrate in dry air. K. BITO, K. AOYAMA, and M. MATSUI (J. Soc. Chem. Ind. Japan, 1932, 35, 195—197B).—The behaviour of $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, dried at 150° , on heating has been examined. Decomp. (loss of NO_2) commences at 440° ; the product melts at 845° , and evaporation commences at 855° . H. F. G.

Pyrolysis of metallic arsenites. E. R. RUSHTON (J. Physical Chem., 1932, 36, 1772—1798).—The decomp. of arsenites on heating in inert atms. varies with the metal. Al , Mg , Zn , and Pb arsenites have a high dissociation pressure, p , and decompose into metal oxide and As_2O_3 only, whereas $\text{Ca}(\text{AsO}_2)_2$ and $\text{Sr}(\text{AsO}_2)_2$ also form a little As . Na , K , and Ba arsenites have low p and form largely As and arsenates. For Ag and Cu arsenites p is small, but owing to easy reducibility of their oxides the metals and As_2O_3 are the chief products. The Fe in $\text{Fe}(\text{AsO}_2)_3$ is slightly reduced. The extent of thermal dissociation increases with the As_2O_3 content, and the oxidation-reduction reaction is promoted by rapid heating to a high temp. When arsenites are heated in air, oxidation may be superposed on the other reactions. J. H. R. (c)

Equilibrium in the system bismuth-sulphur-oxygen. R. SCHENCK and F. SPECKMANN (Z. anorg. Chem., 1932, 206, 378—384).—The equilibrium $2\text{Bi}_2\text{O}_3 + \text{Bi}_2\text{S}_3 = 6\text{Bi} + 3\text{SO}_2$ has been investigated from both sides. Evolution of SO_2 begins at $150\text{--}200^\circ$ and reaches a pressure of 1 atm. at 519° . Absorption of SO_2 in the reverse reaction is measurable at 400° . E. S. H.

System $\text{KCl--PbCl}_2\text{--H}_2\text{O}$ at 25° . L. J. BURRAGE (Trans. Faraday Soc., 1932, 28, 529—531; cf. A., 1926, 908).—The system has been investigated with special reference to the conditions which obtain in the neighbourhood of the quadruple point characterised by the coexistence of the solids PbCl_2 and $\text{KCl}\cdot 2\text{PbCl}_2$. J. G. A. G.

System potassium nitrate-ammonium nitrate-water. E. JANECKE, H. HAMACHER, and E. RAHLS (Z. anorg. Chem., 1932, 206, 357—368).—The equilibrium diagram is recorded. A form of mixed crystal, not formerly described, is similar to the modification of KNO_3 produced under a pressure of 115 atm. E. S. H.

System $\text{CuSO}_4\text{--CoSO}_4\text{--H}_2\text{O}$. H. D. CROCKFORD and D. J. BRAWLEY (J. Physical Chem., 1932, 36, 1594—1596).—The 0° and 25° isotherms have been determined. At both temp. the solid phases are $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and a series of solid solutions in which Cu partly replaces Co in $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$. S. L. (c)

Compounds of lithium chloride with cobalt chloride. Water as a linking agent in polynuclear cations. H. BASSETT and (Miss) I. SANDERSON (J.C.S., 1932, 1855—1864).—The system $\text{LiCl--CoCl}_2\text{--H}_2\text{O}$ has been investigated from 0° to 80° and previous results are found untrustworthy. The solid phases are $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$; $\text{CoCl}_2\cdot 2\text{H}_2\text{O}$; $\text{LiCl}\cdot 2\text{H}_2\text{O}$; $\text{LiCl}\cdot \text{H}_2\text{O}$ (I); and the double salts $7\text{LiCl}\cdot 2\text{CoCl}_2\cdot 18\text{H}_2\text{O}$; $3\text{LiCl}\cdot 2\text{CoCl}_2\cdot 6\text{H}_2\text{O}$; and $\text{LiCl}\cdot \text{CoCl}_2\cdot 2\text{H}_2\text{O}$. In addition, (I) forms a series of solid solutions with $2\text{LiCl}\cdot \text{CoCl}_2\cdot 2\text{H}_2\text{O}$. Hence, it is supposed that (I) is $(\text{LiCl}\cdot \text{H}_2\text{O})_n$. Structural formulæ are suggested in which several Li atoms are united in the same cation by means of H_2O mols. (e.g., $[(\text{H}_2\text{O})_2\text{Li}(\text{H}_2\text{O})_2\text{Li}(\text{H}_2\text{O})_2\text{Li}(\text{H}_2\text{O})_2]^{+++}$). D. R. D.

Ternary system carbamide-water-hydrogen peroxide. E. JÄNECKE (Rec. trav. chim., 1932, 51, 579—584).—Solubilities of $\text{CO}(\text{NH}_2)_2$ in aq. H_2O_2 (3—98%) over the temp. range -10° to 40° have been determined, and the behaviour of the ternary system is shown in a triangular diagram. The only compounds formed are $\text{H}_2\text{O}_2\cdot 2\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2\cdot \text{H}_2\text{O}_2$, each of which forms a eutectic with the other and with $\text{CO}(\text{NH}_2)_2$. F. L. U.

Equilibrium $\text{Sn}+2\text{CO}_2=\text{SnO}_2+2\text{CO}$. G. MEYER and F. E. C. SCHEFFER (Rec. trav. chim., 1932, 51, 569—573).—The composition of the mixture of CO and CO_2 in equilibrium with $\text{Sn}+\text{SnO}_2$ varies from 26.4% CO at 500° to 20.2% at 800°. The equilibrium const. is given by $\log K=420/T-0.988$, and the calc. heat of the reaction $\text{Sn}+2\text{CO}_2=\text{SnO}_2+2\text{CO}$ is 3.8 kcal. F. L. U.

Equilibrium and heat-toning of the reaction $\text{NiO}+\text{H}_2=\text{Ni}+\text{H}_2\text{O}$. A. SKAPSKI and J. DABROWSKI (Z. Elektrochem., 1932, 38, 365—370).—Equilibrium pressures of H_2 and H_2O over $\text{NiO}+\text{Ni}$ have been measured over the range 450—700°. The mean heat of reaction over this interval is calc. to be 4200 g.-cal. F. L. U.

Equilibria between mixtures of carbon monoxide and carbon dioxide at various pressures in contact with steels of different carbon concentrations at temperatures ranging from 750° to 1150°. A. BRANLEY and H. D. LORD (J.C.S., 1932, 1641—1669).—The main reactions are $2\text{CO} \rightleftharpoons \text{C}+\text{CO}_2$; $3\text{Fe}+2\text{CO} \rightleftharpoons \text{Fe}_3\text{C}+\text{CO}_2$; $\text{Fe}_3\text{C} \rightleftharpoons 3\text{Fe}+\text{C}$. The equilibria have been investigated by a static method over the range 0.25 to 2.0 atm., with steels containing 0.1—2.0% C, made by the gaseous cementation of pure Fe by CO. The results show that C vapour is monat., that the concn. of free C in the vapour and solid phases follows Henry's law, and that cementite is metastable to graphite at these temp. Carpenter and Keeling's data concerning the Fe-C diagram (B., 1904, 608) have been confirmed, and the graphite solubility line has been added. The following thermochemical data were obtained:

$3\text{Fe}(\gamma)+2\text{CO}=\text{Fe}_3\text{C}$ (dissolved)+ CO_2 +29,950 g.-cal.;
 $3\text{Fe}(\gamma)+2\text{CO}=\text{Fe}_3\text{C}$ (pptd.)+ CO_2 +36,950 g.-cal.;
 $3\text{Fe}(\gamma)+\text{C}=\text{Fe}_3\text{C}$ —4750 g.-cal.; $3\text{Fe}(\alpha)+\text{C}=\text{Fe}_3\text{C}$ —6950 g.-cal.
 D. R. D.

Equilibria in reduction, oxidation, and carbonisation processes in iron. XI. R. SCHENCK, H. FRANZ, and A. LAYMANN (Z. anorg. Chem., 1932, 206, 129—151).—The effect of SiO_2 , TiO_2 , P_2O_5 , and Cr_2O_3 on the reducibility of Fe_2O_3 (cf. A., 1930, 43) has been investigated at 800—1000°. In all cases the reducibility is diminished, due to the formation of less reducible compounds with the oxides. SiO_2 forms fayalite, $2\text{FeO}\cdot\text{SiO}_2$; TiO_2 forms ilmenite, $\text{FeO}\cdot\text{TiO}_2$, and also an orthotitanate, $2\text{FeO}\cdot\text{TiO}_2$, and P_2O_5 forms FePO_4 , a compound which appears to correspond with the formula $\text{Fe}^{II}_3\text{P}_4\text{O}_{13}$ or a mixture of pyro- and meta-phosphate, $\text{Fe}^{II}(\text{PO}_3)_2+\text{Fe}^{II}_2\text{P}_2\text{O}_7$, and a complex phase $\text{Fe}^{II}_3[\text{Fe}^{III}(\text{PO}_4)_2]_2$ which, on reduction, gives $\text{Fe}_3\text{P}_4\text{O}_{13}$ and Fe. Some Fe_3P is also present. The behaviour of Cr_2O_3 is similar to that of Al_2O_3 (loc. cit.). A spinel, $\text{FeO}\cdot\text{Cr}_2\text{O}_3$, is formed, and a mixed crystal phase, $\text{Fe}_3\text{O}_4\text{--FeO}\cdot\text{Cr}_2\text{O}_3$ is produced from mixed crystals of the oxides Fe_2O_3 and Cr_2O_3 . M. S. B.

Reactions of carbon dioxide with silicates under high pressures. W. WEYL (Glastech. Ber., 1931, 9, 641—660; Chem. Zentr., 1932, i, 724).—The equilibria are displaced towards the carbonate by an increase in pressure and a fall in temp. This displacement is greater with K than with Na silicates, and in glasses of the composition $\text{K}_2\text{O}:\text{SiO}_2$ 1:3 separation of K_2CO_3 occurs. During its α - β -transition $\text{CaO}\cdot\text{SiO}_2$ does not take up CO_2 . Li silicate occupies an intermediate position between the alkali and alkaline-earth silicates, since Li_2SiO_3 can take up marked quantities of CO_2 . The gas evolution with glasses containing carbonate indicates that a diffusion process and not a mol. reaction is involved.

L. S. T.

Equilibria between metals and slags in melts. II. Dependence of equilibrium $\text{FeO}+\text{Mn MnO}+\text{Fe}$ on temperature and the influence of addenda. W. KRINGS and H. SCHACKMANN (Z. anorg. Chem., 1932, 206, 337—355; cf. this vol., 125).—The equilibrium const. is lowered by the addition of SiO_2 , increased by CaO , and increased slightly by Ca_2SiO_4 . The variations of equilibrium const. with the amounts of addenda are expressed graphically. CaSiO_3 has no influence. The const. increases with rise of temp. in accordance with the formula $\log K=-7280/T+1.503$. The calc. heat of reaction is 33.2 g.-cal. E. S. H.

Dehydration of brucite. W. BUSSEM and F. KOBERICH (Z. physikal. Chem., 1932, B, 17, 310—326).—The heat of reaction calc. from the dissociation pressure agrees closely with the val. determined calorimetrically and thus affords no evidence for the formation of a pseudo-structure in the dehydration to MgO . This is confirmed by X-ray examination, which shows the product of dehydration to have the periclase structure. The periclase crystallites are oriented in two positions in relation to the original brucite lattice, and the brucite formed on rehydration is oriented. The periclase crystallites formed at low

temp. are considerably deformed, but on ignition at 1150° the deformation disappears, and with it the optical double refraction and the last of the H₂O. Complete recrystallisation occurs at 2000°. R. C.

Representation of systems of several components. E. DENINA (Rec. trav. chim., 1932, 51, 624—626).—A discussion of general principles.

F. L. U.

History and analytical expression of first and second laws of thermodynamics, and role of differentials dW and dO . G. TUNELL (J. Physical Chem., 1932, 36, 1744—1771).—The close relation between thermodynamics and the theory of functions of a real variable is discussed.

G. M. M. (c)

Axiomatic [basis] of Nernst's theorem and the limitations of thermodynamics. P. KOHNSTAMM (Rec. trav. chim., 1932, 51, 538—542).—A general theoretical discussion.

F. L. U.

Maximum available work and entropy of formation of silver bromide from its elements. H. WOLTEK (Z. Elektrochem., 1932, 38, 359—365).—The e.m.f. of the combination $\text{Ag}|\text{AgBr}|\text{0.5N-HBr}|\text{0.5N-HBr}|\text{Br}_2|\text{Pt}$ has been measured at 0° and 25°. The max. work of the condensed reaction is at 0° 22.96 and at 25° 22.88 kg.-cal. The reaction entropy calc. from the temp. coeff. of the e.m.f. is -3.08 ± 0.29 g.-cal. per degree, a result in agreement with Nernst's heat theorem.

F. L. U.

Heat of formation of cupric oxide. H. VON WARTENBERG and H. WERTH (Z. Elektrochem., 1932, 38, 401—402).—Determination of the heat effect when H₂ is admitted to a vessel containing a pellet of CuO heated at about 400° in an atm. of CO₂ yields for the heat of formation of CuO from Cu and $\frac{1}{2}\text{O}_2$ 38.5 ± 0.2 kg.-cal.

H. F. G.

Heat of formation of hydrogen fluoride. H. VON WARTENBERG and H. SCHUTZ (Z. anorg. Chem., 1932, 206, 65—72; cf. A., 1931, 912).—Redetermination of the heat of formation of HF by direct combination gave (H, F) = 64.45 ± 0.1 kg.-cal. at 20°. The measurements were made at 100° to avoid error due to heat of polymerisation.

F. L. U.

Heat of dissolution of sodium carbonate and the twin calorimeter. M. MATSUI, S. KAMBARA, and K. MIYAMURA (J. Soc. Chem. Ind. Japan, 1932, 35, 227—232B).—Using a new form of apparatus the val. at 25° is found to be 5670.8 ± 8.1 g.-cal. per mol.

J. W. S.

Heat of combustion of organic halogen compounds. I. A. KARLUKOV and F. M. PERELMAN (J. Gen. Chem. Russ., 1931, 1, 1249—1257).—The substance is placed within the calorimeter in a sealed, thin-walled glass bulb, which is burst by the pressure of the vapour at the beginning of the combustion. In this way loss due to vaporisation is avoided. A small amount of soot remains on the glass after combustion, but the error due to this does not exceed 10—20 g.-cal. The results, whilst of a higher order of accuracy than those of Berthelot or Thomsen, include a variable error due to free halogen and H halide in the products of combustion.

R. T.

Thermochemistry of sulphides of antimony, arsenic, bismuth, cadmium, tin, and iron.

E. V. BRITZKE and A. F. KAPUSTINSKI (Tsvet. Met., 1931, 1147—1156).—Equilibrium consts. for the reduction of the sulphides with H₂ have been determined. The values of $\log P_{\text{S}_2}$ (S v.p.) are given by (FeS) $-(14,329/T) + 5.80$; (SnS) $-(15,430/T) + 8.10$; (CdS) $-(15,130/T) + 3.02$; (Bi₂S₃) $-(16,270/T) + 14.25$; (Sb₂S₃) $-(12,660/T) + 8.95$. The heats of formation (g.-cal.) from diat. S and solid metals are calc. as: 2FeS, 65,460; 2SnS, 70,520; 2CdS, 69,140; Bi₂S₃, 111,540; Sb₂S₃, 86,490; As₂S₃, 51,430. Heats of formation from rhombic S and heats of roasting reactions are also calc.

CH. ABS.

Thermochemistry of calcium orthophosphates. C. MATIGNON and M. SEON (Compt. rend., 1932, 194, 2184—2187).—The heats of formation (in solution) of $\text{CaH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $2(\text{CaHPO}_4 \cdot 2\text{H}_2\text{O})$, and $\text{Ca}_3(\text{PO}_4)_2$ from H₃PO₄ (sol.) and CaO (sol.) are respectively 53.92, 97.57, and 115.51 g.-cal.; the heats of hydration of the anhyd. salts are 4.95, 7.66, and 8.17. Addition of SiO₂ facilitates the reduction of $\text{Ca}_3(\text{PO}_4)_2$; the thermal data recorded are $\text{Ca}_3(\text{PO}_4)_2 + 5\text{C} = 5\text{CO} + \frac{1}{2}\text{P}_4$ (vap.) $+ 3\text{CaO} - 382.9$ g.-cal.; and $\text{Ca}_3(\text{PO}_4)_2 + 5\text{C} + 3\text{SiO}_2 = 5\text{CO} + \frac{1}{2}\text{P}_4$ (vap.) $+ 3\text{CaSiO}_3 - 297.9$ g.-cal.

C. A. S.

Heats of formation and combustion of cellulose nitrate. K. TOMIOKA (J. Cellulose Inst., Tokyo, 1932, 8, 88—94).—The heat of combustion and the heat of formation decrease linearly with increase in the N content of the material. The heat of formation changes by 75 g.-cal. for 1% N from 958.9 g.-cal. (7.66% N) to 568.7 g.-cal. (13.58% N), and the heat of combustion changes by 135 g.-cal. for 1% N, from 3071 g.-cal. (7.66% N) to 2286 g.-cal. (13.58% N).

B. P. R.

Absolute magnitude of the diffusion current in stirred electrolytes. A. EUCKEN (Z. Elektrochem., 1932, 38, 341—345).—The limiting current in an electrolyte maintained in steady laminar flow parallel to the surface of a polarisable electrode is obtained by calculating the concn. gradient of the depolariser at right angles to the surface, the velocity gradient being assumed proportional to the distance from the electrode. This current $= 0.807 F c h \sqrt{D \eta^2 u / a}$, in which h and y are the respective dimensions of the electrode at right angles to and parallel with the direction of streaming, c is the bulk concn. of the depolariser, D its diffusion coeff., and u the velocity of a liquid lamina at a distance a from the electrode. An experimental arrangement has been devised for testing the applicability of the above expression, which is in agreement with observations. Measurement of the limiting current at known rates of stirring enables the diffusion coeff. of a depolariser to be calc. with an accuracy of 10%.

F. L. U.

Transport number of magnesium chloride. C. DRUCKER (Rec. trav. chim., 1932, 51, 574—576).—The transport no. of the anion in aq. MgCl₂ exhibits a pronounced min. at about 0.005 mol. per litre, as with CaCl₂, BaCl₂, BaBr₂, and CdBr₂. The limiting val. is 0.605, whence it follows that the mobility of the Mg ion is < that usually assumed.

F. L. U.

Hydration of ions. J. BABOROVSKY (Arch. Hemiju, 1932, 6, 85—106).—By a modification of

Remy's method the following ionic hydration vals. have been found in M and $0.1M$ solutions, respectively: K^+ 5, 29.3; Na^+ 8—9, 44.5; Li^+ 13—14, 62; H^+ 1, 5; Cl^- 4, 26.6; Br^- 3, 29.6; I^- 2, 31.4. A membrane of parchment-paper separated the anode from the cathode solution. Electro-osmotic action was neglected. The hydration nos. of the halogen ion appear to tend towards a common limit with increasing dilution, suggesting that in the more dil. solution hydration depends on physical rather than chemical forces. The results are compared with those of other investigators. M. S. B.

Hydration of solute ions of the heavier elements. L. H. FLINT (J. Washington Acad. Sci., 1932, 22, 211—217).—Hydration vals. have been assigned to the ions of the heavier elements in accordance with the relation assumed for ions of the light elements (this vol., 467). These vals. have been tested by reference to experimental data for electrical conductivity etc., and are found to be, in general, of the right order. M. S. B.

Potential effect on conductivity of strong and weak acids. J. SCHEELE (Ann. Physik, 1932, [v], 7, 811—830).—The method of Wien and Malsch has been improved so that very small resistance changes can be measured. The effect with strong acids is small, as is to be expected from the theory. With weak acids the effect is much more marked. A. J. M.

Electrode potential of iron. E. MULLER and J. JANITZKI (Z. physikal. Chem., 1932, 160, 245—256).—The observed potential of an electrode of massive Fe in contact with an aq. solution of Fe^{II} salt is a limiting potential corresponding with equality in the rates of dissolution of Fe^{II} at active points and of diffusion of the H liberated at the remainder of the surface, which is inactive. By continual scraping of the electrode beneath the surface of a neutral solution its potential becomes less positive and approaches the reversible potential, which is not more positive than -0.512 volt (e_0) in $N-FeSO_4$. In contact with acid, gentle scraping renders the potential more positive. Experiments with Fe electrodes in aq. NaOH are described. R. C.

Electrode potential of iron. I. Measurements in a hydrogen atmosphere. K. MURATA (J. Soc. Chem. Ind. Japan, 1932, 35, 209—214B).—E.m.f. measurements have been made with the cell $Fe|FeCl_2(0.1 \text{ or } 0.01M)|sat.KCl|0.1N-KCl, Hg_2Cl_2|Hg$, special precautions being taken to avoid formation of Fe^{III} salt. The Fe electrode consisted of reduced Fe sintered on to an electrolytic Fe wire. The e.m.f. becomes const. after a few days, but a green film is gradually formed on the surface of the Fe and high readings are then obtained. The shape of the electrode, when formed of solid wire, influences the e.m.f. to the extent of about 0.04 volt. The standard electrode potential of Fe at 25° is -0.4265 volt, and the calc. free energy of formation of Fe^{II} at 25° is -19.670 g.-cal. H. F. G.

Electrochemistry of iron. S. BODFORSS (Z. physikal. Chem., 1932, 160, 141—157; cf. A., 1930, 423; 1931, 172).—The potential, E , in contact with

an aq. solution at room temp. of an Fe electrode, the surface of which is continually renewed by grinding within the solution, depends on the p_H and the anions present. In a given buffer mixture E is a linear function of the p_H . Cations, even Fe^{II} , do not affect E . In absence of grinding, E in a buffer solution is not appreciably affected by addition of $FeSO_4$. It is suggested that in these experiments the Fe is "inactive," and that none of the data so far published for the potential of Fe electrodes in solutions of Fe salts gives a real normal electrode potential. R. C.

Periodate[-iodate] potential. E. ABEL and O. SMETANA (Monatsh., 1932, 60, 181—188).—For the reduction of IO_4^- to IO_3^- the normal potentials are $e_0 = 1.175(\pm 0.005)$ and $e_0 = 1.510(\pm 0.005)$ volts; the free energy of formation of IO_3^- from I and O_2 is $-18,500$ g.-cal. (all at 25°). In the determination the platinised Pt electrodes must be free from Cl. Vals. of e_0 for a series of reactions of IO_4^- with H^+ and H_2O are tabulated. E. W. W.

Oxidation-reduction potential of system lactic acid-pyruvic acid. R. WURMSER and (ALLE.) Z. DE BOE (Compt. rend., 1932, 194, 2139—2141).—A satisfactory catalyst for the reaction $OH\cdot CHMe\cdot CO_2H(I) \rightleftharpoons AcCO_2H(II)$ is an autolysate of *B. coli* prepared by Stephenson's method (cf. A., 1928, 549). In presence of PhMe this inhibits oxidation of (II), but accelerates that of (I). Colorimetric and electrometric observations indicate -0.200 volt as the probable normal potential of the system. C. A. S.

Ammonium acetate as a neutral buffered standard. C. J. SCHOLLENBERGER (J. Amer. Chem. Soc., 1932, 54, 2568; cf. this vol., 709).—The p_H of a solution of the commercial reagent may be far from 7.0. A mixture of equal vols. of $2N-AcOH$ and $2N-aq. NH_3$ is invariably very nearly neutral. C. J. W. (c)

Potentiometric measurements with borax-sodium hydroxide and disodium hydrogen phosphate-sodium hydroxide buffer solutions. C. NÄGELI and A. TRYBBI (Helv. Chim. Acta, 1932, 15, 751—758).—The p_H vals. of buffer solutions of $Na_2B_4O_7-NaOH$ (9.94—12.39) and of Na_2HPO_4-NaOH (10.87—11.42) are recorded. The inflexion in the p_H-NaOH concn. curve for the first-named is displaced somewhat to the alkaline side of the equivalence point. H. F. G.

Precipitation indicators. C. NÄGELI and A. TRYBBI (Helv. Chim. Acta, 1932, 15, 758—792).—A comprehensive survey is given of the theory and application of colloidal indicators which at a definite p_H undergo flocculation with or without a noticeable colour change; the sharpest end-point is obtained with sparingly sol. weak acids or bases of high mol. wt. the salts of which form so-called colloidal electrolytes. The flocculation point (p_H 9—11.8) and the range of p_H over which flocculation occurs (0.1—0.3), have been determined for certain azo-compounds containing $N-OH$ and Ac groups. Details are given of the results obtained in titrating weak acids such as $BzOH$, $PhOH$, veronal, alanine, and As_2O_3 with these indicators. The results are usually repro-

ducible within close limits, although a correction factor has frequently to be applied. H. F. G.

Physico-chemical studies of complex formation involving weak acids. VI. Solutions of complex cyanides of silver, zinc, cadmium, mercury, and nickel. H. T. S. BRITTON and E. N. DODD. VII. Glass-electrode titrations of vanadic acid. H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1932, 1940—1954, 1955—1964).—The p_H of solutions obtained by adding aq. KCN to aq. metallic sulphates were determined, using a glass electrode. The conductivities of similar solutions, and of aq. KCN, were also measured, and the % hydrolysis of the Hg solutions was determined (cf. A., 1931, 1233). The concns. of simple metal cation in solutions of the cyanides in aq. KCN were determined potentiometrically, using electrodes of the respective metal or amalgam and (in most cases) a HgCl electrode. The results indicate formation of $Ag(CN)_2^-$, $M(CN)_4^{2-}$ ($M=Zn, Cd, Hg, Ni$), and probably $Cd(CN)_3^-$. The solubility product $Ag^+ \times Ag(CN)_2^-$ is 5.1×10^{-12} at 25° ; the other compounds do not give const. vals.

II. The data obtained when HCl is added to aq. Na_3VO_4 , $Na_4V_2O_7$, and $NaVO_3$ indicate the formation, slow in the cold but immediate on boiling, of Na_2HVO_4 and NaH_2VO_4 . A yellow compound, approx. $Na_2O \cdot 3.5V_2O_5$, is also formed, which is not decolorised by boiling with HCl, but is converted into NaH_2VO_4 , Na_2HVO_4 , and Na_3VO_4 on boiling in alkaline solution. p_H curves for the back-titration of the acidified solution with NaOH, aq. NH_3 , $Ca(OH)_2$, and $Ba(OH)_2$ indicate the formation of $Na_2O \cdot 2.5V_2O_5$, but not of NaH_2VO_4 , Na_2HVO_4 , or Na_3VO_4 , which are formed only on long keeping or boiling. The complex formed with excess of AcOH is approx. $Na_2O \cdot 2V_2O_5$. D. R. D.

Glass electrode. G. HAUGAARD (Z. physikal. Chem., 1932, 160, 279—289).—The double layers set up on the opposite sides of a glass membrane separating two solutions are mutually independent. It is suggested that the boundary potentials are determined not by chemical interaction of membrane and solution so much as by physical effects, the membrane acting purely as a boundary wall. In a solution of a uni-univalent salt the smaller ion will be able to approach the membrane more closely than the other, and will therefore determine the sign of the charge of the double layer nearest the wall. The magnitude of the boundary potential will increase with the difference in radii of the two ions and with the salt concn. The effect of alkali chlorides agrees qualitatively with this theory. When the ions differ in valency, the difference in dielectric const. between the two phases at the interface may be a cause of the formation of a double layer. R. C.

New use of vacuum tube in electrometric titrations. I. Polarisation of platinum electrodes in oxidation and reduction reactions. J. L. KASSNER, R. B. HUNZE, and J. N. CHATFIELD (J. Amer. Chem. Soc., 1932, 54, 2278—2284).—A positive grid bias is used, the resulting grid current polarising the Pt electrodes. The arrangement is insensitive to variations in circuit consts. up to 20%.

The equiv. point is indicated by galvanometer "kick." R. H. C. (c)

Use of thermionic valves for measurement of the potential of cells. F. MÜLLER [with G. MEYER] (Z. Elektrochem., 1932, 38, 418—428).—Thermionic valve methods are especially suitable for determination of the c.m.f. of cells which have high resistance or are easily polarised. The theory and practical details of such methods are critically reviewed. H. F. G.

Limiting current in the anodic polarisation of metals in aqueous solutions. E. MÜLLER and K. SCHWABE (Z. Elektrochem., 1932, 38, 407—418).—Current-voltage curves have been obtained for Th, Pb, Cd, Cu, and Zn anodes in saturated and unsaturated solutions of their salts. Increase of the anode potential from one const. val. to another causes always a transient rise of the current to a val. greater than its new const. val. Complete passivity is never produced. The results are discussed at length, particularly as regards the nature of the high-resistance film formed on the anode by polarisation; it is probable that friction between the ions in the solution and the walls of the pores in the film is the factor which determines the resistance. H. F. G.

Passivity of electrolytic iron in an alkaline medium. A. TRAVERS and J. AUBERT (Compt. rend., 1932, 194, 2308—2309).—The negative potential of electrolytic Fe in N -NaOH increases by 0.72 volt when O_2 is completely removed. The passivity produced by anions such as CO_3 or PO_4 disappears in absence of O_2 . The passivity produced in an alkaline medium is due to dissolved O_2 , not to OH ions, and the protection of boilers due to addition of 0.5 g. of Na_2CO_3 per litre is diminished if the H_2O is degassed. C. A. S.

Electrochemical periodicities. E. S. HEDGES (Nature, 1932, 129, 870—871).—At low c.d., the potential of a Cu cathode in 10% HNO_3 oscillated continuously in periods lasting approx. 1 sec. with an amplitude of approx. 0.1 volt (cf. this vol., 575).

L. S. T.

Peltier effect in the system $Ag-AgNO_3-H_2O$. E. LANGE and T. HESSE (Z. Elektrochem., 1932, 38, 428—442).—Thomson's equations are not directly applicable to electrolytic systems, in which transport of material takes place, and a modified equation for the rate of change of the effect with temp. is developed. Measurements with $Ag|AgNO_3$ aq., however, show that the first equation ($e=\pi/T$) is valid. The variation of π with the Ag concn. and activity is in agreement with that calc. on the basis of a simplified assumption regarding the isothermal heat of transfer. The Peltier effect at the interface between single crystals of the same metal cannot be explained unless the existence of a heat of transfer is assumed. H. F. G.

Affinity of chemical reactions. B. MACKU (Publ. Fac. Sci. Univ. Masaryk, 1932, No. 151, 15 pp.).—The van't Hoff expression is derived by two methods. H. J. E.

Difficulty of deducing the mechanism of a reaction from determination of its velocity. A.

PRINS (Rec. trav. chim., 1932, 51, 576—578; cf. A., 1930, 995).—A further example is given. F. L. U.

Mathematical representation of the course of chemical reactions. J. P. TREUB (Rec. trav. chim., 1932, 51, 543—548).—The usual velocity equations are transformed into others stated to be useful in supervising chemical processes, by taking as unit of time the time required for a given mol. species to reach a certain fraction of its initial concn. Examples are given. F. L. U.

Effect of foreign gases on unimolecular reactions. W. H. RODEBUSH and M. J. COPLEY (J. Amer. Chem. Soc., 1932, 54, 2560). C. J. W. (c)

Explosion of oxy-hydrogen mixtures in soap bubbles. A. N. MITRA, H. N. CHATTERJEE, and H. K. SEN (J. Indian Chem. Soc., 1932, 9, 163—170).—The ignition temp. of mixtures of O_2 and H_2 in soap bubbles is reproducible provided the same arrangement is used; the temp. depends on the length, shape, and surface of the Pt wire used for ignition (cf. A., 1929, 1016). The ignition temp. is lower for large than for small bubbles and becomes const. when the vol. is greater than 500 c.c. H_2O_2 and O_3 are produced in increasing quantities with 3 : 2, 2 : 1, and 1 : 1 mixtures of O_2 and H_2 , but not with 8 : 2 or 7 : 3 mixtures. H. B.

Flame speeds during the inflammation of moist carbonic oxide-oxygen mixtures. W. PAYMAN and R. V. WHEELER (J.C.S., 1932, 1835—1838).—The speed of "uniform movement," when flame travels from an open end towards a closed end of a horizontal tube, has been determined in mixtures of CO and O_2 saturated with H_2O vapour at room temp. The max. is obtained with mixtures near the composition $2CO + O_2$, thus conforming with the theoretical deduction of Payman (*ibid.*, 1920, 117, 48). E. S. H.

Taylor's theory of active centres and kinetics of heterogeneous gaseous reactions. S. HORIBA and T. RI (Rec. trav. chim., 1932, 51, 641—647; cf. A., 1928, 376).—The order of reaction in the decomp. of CO at 255° on reduced Ni is successively (1) retarded, (2) first, (3) zero, (4) fractional, (5) first. The initial retardation is caused by poisoning of the active centres by separated C. The peculiar course of the reaction can be best explained by assuming the presence of active centres of different kinds. F. L. U.

Thermal reaction between chlorine and ozone. A. HAMANN and H. J. SCHUMACHER (Z. physikal. Chem., 1932, B, 17, 293—309).—At 35—60° there is a period of induction, after which $-d[O_3]/dt = k[Cl_2]^{1/2}[O_3]^{3/2}$, where n is about 3, and k for a given Cl. concn. diminishes towards the end of the reaction. The validity of the reaction scheme previously proposed (A., 1929, 1394) seems to have depended on the ClO formed by the reaction reacting rapidly with some impurity. In the present experiments the ClO is present in higher concns., the reaction $ClO + ClO = Cl_2 + O_2$ being assumed to have a heat of activation, and by entering into side reactions complicates the course of the reaction. R. C.

Homogeneous combination of ethylene and hydrogen: second-order association reaction. R. N. PRASE (J. Amer. Chem. Soc., 1932, 54, 1876—1884).—In a pyrex vessel at 475—550° and under 1 atm. the reaction is homogeneous and bimol. A collision theory calculation indicates that 10% of the collisions between C_2H_4 and H_2 mols. possessing the activation energy of 43,150 g.-cal. per mol. result in formation of C_2H_6 . The rates of formation and dissociation of C_2H_6 give a val. for the equilibrium const. of the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ which agrees with the observed val. S. L. (c)

Reaction between oxygen and propylene: activation, oxidation, and polymerisation. S. LENIHER (J. Amer. Chem. Soc., 1932, 54, 1830—1837).—The reaction at high C_3H_6 and low O_2 concns. has been studied at 500—600°. There occur both oxidation of C_3H_6 to $MeCHO$, CH_3O , HCO_2H , CO , CO_2 , and H_2O , and its pyrolysis to higher mono-olefines, butylenes, amylenes, and hexylenes as primary, and olefines, paraffins, and H_2 as secondary products. The presence of a little O_2 lowers the temp. at which pyrolysis is appreciable greatly, and markedly accelerates the pyrolysis. A mechanism of the oxidation and pyrolysis of C_3H_6 and the mono-olefines generally based on activation of the double linking is outlined. S. L. (c)

Kinetics of thermal dissociation of gaseous ethyl bromide. E. L. VERNON and F. DANIELS (J. Amer. Chem. Soc., 1932, 54, 2563—2564).—The reaction $EtBr = C_2H_5 + HBr$ appears to be as satisfactory a unimol. reaction as any yet reported. Above 100 mm. at 390—420° the velocity coeff., k , is $3.85 \times 10^{14} e^{-54800/RT}$. Below 120 mm. k falls, and at 20 mm. has about one third of its initial val. Under these low pressures the reaction appears to be purely bimol., and addition of N_2 or H_2 reduces k . C. J. W. (c)

Chemical kinetics of high valency type electrolytes in dilute aqueous solutions. V. K. LA MER and R. W. FESSENDEN (J. Amer. Chem. Soc., 1932, 54, 2351—2366).—The thiosulphate-bromacetate reaction has been studied at 25°, at low concn., in presence of Na, K, Mg, Ca, Ba, and La ions. The kinetics agree with the Debye-Huckel limiting law in presence of univalent ions, and deviate by 40—80% with bivalent ions and by 440% with La^{+++} at $\sqrt{\mu} = 0.09$. G. M. P. (c)

Speed of decomposition of hydrogen peroxide in presence of hydrochloric acid. E. A. BUDGE (J. Amer. Chem. Soc., 1932, 54, 1769—1778).—The decomp. has been studied at 25°, 30°, and 35°. The reaction is strictly unimol., but when followed by observation of the rate of evolution of O_2 exhibits a short period of acceleration, ascribed to supersaturation. The velocity coeffs. obtained agree closely with those of Livingston and Bray (A., 1925, ii, 981). The temp. coeff. is about 3.1. H. F. J. (c)

Reaction between sodium nitrite and hydroxylamine sulphate. R. STRATTA (L'Ind. Chimica, 1932, 7, 435—438).—The evolution of N_2O in the reaction between $NaNO_2$ and $(NH_2OH)_2H_2SO_4$ is a unimol. reaction, in which the intermediate NH_2OH, HNO_2

is decomposed. The latter also decomposes to give small amounts of $\text{H}_2\text{N}_2\text{O}_2$. O. J. W.

Velocity of the reaction between sulphur trioxide and carbon tetrachloride. A. SCONZO (Gazzetta, 1932, 62, 295—299).—Errors in a previous paper (A., 1927, 432) are noted. Recalculation shows that the results do not serve to establish whether the reaction is uni- or bi-mol., and that the preliminary formation of an additive compound $2\text{SO}_3\cdot\text{CCl}_4$ is doubtful. H. F. G.

Rate of hydrolysis of pyrophosphoric acid. A. KAILAN (Z. physikal. Chem., 1932, 160, 301).—Muus' vals. for the velocity coeff. (this vol., 576) agree with Pessel's data (A., 1923, ii, 396). R. C.

Rate of decomposition of xanthic acid. C. V. KING and E. DUBLON (J. Amer. Chem. Soc., 1932, 54, 2177—2186).—The decomp. of ethyl- and methyl-xanthic acids in presence of $\text{AcOH}\cdot\text{NaOAc}$ and $\text{NH}_2\text{Ph}\cdot\text{NH}_2\cdot\text{Ph}\cdot\text{HCl}$ buffers has been followed. The primary and secondary salt effects are analysed. The temp. coeff. averages 6.75. E. J. R. (c)

Kinetics of a thermal *cis-trans* isomerisation. II. M. NELLES and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1932, 54, 2208—2215).—For the isomerisation of gaseous Me_3 maleate at 300° up to 5 atm. $k=7.7\times 10^{-4}/(1+1400/P_{\text{mm.}})$ mm.^{-1} . C_3H_8 accelerates the reaction slightly, CO_2 accelerates it markedly, with decomp. of the esters, and H_2 and N_2 have no effect. At equilibrium the amount of fumarate is $>50\%$. H. A. B. (c)

Degradation of quaternary ammonium salts. VI. Effect of substitution on velocity of intramolecular rearrangement. J. L. DUNN and T. S. STEVENS (J.C.S., 1932, 1926—1931).—The effect of substitution in the C_6 nucleus of the phenacyl radical on the velocity of the rearrangement $\text{COPh}\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\text{Ph})\text{Me}_2\text{X}$ (I) \rightarrow $\text{COPh}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{NMe}_2$ (II) has been investigated for *o*-Br, *m*-Br, *o*-NO₂, *m*-NO₂, *p*-NO₂, *p*-Cl, *p*-Br, *p*-I, *p*-OMe, and *p*-Me. The reaction velocity is diminished by introducing negative substituents, the effect showing an approx. inverse proportion to the dissociation consts. of the similarly substituted benzoic acids. This effect is $<$ and in the opposite sense to the influence of similar substitution in the CH_2Ph radical of (I). Probably the velocity of the process is determined by that of the conversion of the postulated intermediate $\text{COPh}\cdot\text{CH}^+\cdot\text{NMe}_2\cdot\text{CH}_2\text{Ph}$ into (II), which is due to the instability of the anionic C atom, and hence retarded by negative substitution near that point. E. S. H.

Velocity of evolution of hydrocarbons in the reaction between chloromagnesium phenylacetate and aliphatic magnesium compounds. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1932, [iv], 51, 619—622).—The reaction between $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{MgCl}$ and $\text{R}\cdot\text{MgX}$ follows two parallel courses. A hydrocarbon RH , together with the complex $\text{CHPh}(\text{CO}_2\text{MgCl})(\text{MgX})$ is formed in one reaction and the other leads to the formation of a *tert.* alcohol. The velocity of the first reaction may be taken as a measure of the force of attraction

between R and MgX . The attraction increases in the order given for the following R groups: Me, Bu^β , *sec.*-Bu, Pr^α , Et, Pr^β . M. S. B.

Exponential analysis applied to the asymmetric hydrolysis of some β -glucosides with emulsin. S. MITCHELL and I. MACARTHUR (J.C.S., 1932, 1669—1675).—Application of exponential analysis to the time-hydrolysis curve of *dl*-*sec.*-octyl glucoside gave 8.6 as the ratio of the reaction consts. of the two components, as compared with 8.4 obtained when the glucosides were hydrolysed separately. The β -glucoside of *dl*-*sec.*-hexyl alcohol gave the ratio 1.5; the β -glucoside of *dl*-*sec.*-butyl alcohol gave the ratio 5.5, but in this case the *l*-alkyl component was hydrolysed more rapidly than the *d*-alkyl component. E. S. H.

Kinetics of heterogeneous systems. B. TEZAK (Bull. Soc. Chim. Yougoslav., 1932, 3, 25—31).—The Cl content (*S*) of BaSO_4 suspended in boiling *N*-HCl falls with time, according to the equation $-dS/dt = KS(S-S_\infty)$, where S_∞ is the val. of *S* at $t=\infty$ and *K* is const. This effect is ascribed to dissolution of primary particles, with growth of larger crystals of BaSO_4 . R. T.

Corrosion with and without the co-operation of oxygen. U. R. EVANS and C. W. BORGMANN (Z. physikal. Chem., 1932, 160, 194—204).—The intensity and distribution of the corrosion of a vertical Fe or steel surface under 0.1*N*-KCl are quite different according as the gas above the solution is air or O_2 , or is N_2 or H_2 . The corrosion of a horizontal surface under a drop of solution is not affected by variations in the relative humidity of the surrounding air. These findings cannot be reconciled with Liebreich's results (A., 1931, 1016). R. C.

Rusting under conditions of differential aeration. G. SCHIKORR (Z. physikal. Chem., 1932, 160, 205—210).—Experiments supporting Evans' differential aeration theory of corrosion are described. It is suggested that Liebreich's results (A., 1931, 1016) are not wholly incompatible with this theory. R. C.

Theory of corrosion. E. LIEBREICH (Z. physikal. Chem., 1932, 160, 211—224).—Experiments are described which cannot be explained by Evans' theory of rusting and indicate that the distribution and intensity of corrosion produced on an Fe surface by a liquid such as aq. KCl depend on the products of corrosion, and not on the electrode potential being rendered more positive by O_2 . Criticisms (cf. preceding abstracts) are answered. R. C.

Mechanism of primary reaction between oxygen and graphite. Kinetics of combustion of carbon. L. MEYER (Z. physikal. Chem., 1932, B, 17, 385—404).—The reaction between O_2 and graphite has been investigated under such conditions that mols. leaving the C could not return to it or undergo secondary reactions in the gas phase. Below about 1200° the rate of reaction is proportional to the O_2 pressure and CO , and CO appear as primary products in the mol. ratio 1:1, which is independent of the temp. and pressure and corresponds with $4\text{C}+3\text{O}_2\rightarrow 2\text{CO}_2+2\text{CO}$. This reaction is explained by supposing

that the O_2 penetrates deeply into the graphite lattice by dissolution and at the same time passes into a reactive state and disintegrates the lattice. The basal planes are attacked preferentially. As the temp. rises above 1200° , the reaction rapidly slows down, and the ratio $CO_2:CO$ falls, and at 1600° is about 0.5, the reaction then being of zero order. This change is attributed to diminution in the solubility of O_2 in C, as a consequence of which less and less of the combustion is effected by the above process until ultimately the slower surface reaction (cf. A., 1931, 321) becomes solely responsible.

R. C.

Velocity of dissolution of aluminium in aqueous solutions of ferric salts. W. HELLER (Rocz. Chem., 1932, 12, 341–361).—The velocity of dissolution V of Al in aq. $Fe_2(SO_4)_3$ is very small, in aq. $Fe(NO_3)_3$ greater, and is still greater in aq. $FeCl_3$. V is diminished by addition of SO_4^{2-} to aq. $FeCl_3$, and increased by addition of Cl^- to aq. $Fe_2(SO_4)_3$. 90% of the H produced during the reaction is used for reduction of Fe^{3+} to Fe^{2+} , whilst the remaining 10% is liberated as H_2 . The low temp. coeff. of the reaction (1.27 for the interval $25\text{--}35^\circ$) and the dependence of V on the rate of stirring indicate that its val. depends on the velocity of diffusion. For $FeCl_3$ the velocity coeff. is const. at concns. of 0.15–0.43M. V of Mg in aq. NH_4Cl , H_3PO_4 , mandelic, fumaric, or gallic acid is a function of $[H^+]$. R. T.

Reduction of cupric oxide by carbon monoxide and hydrogen. A. JULIARD (Bull. Soc. chim. Belg., 1932, 41, 234–247; cf. this vol., 577).—The influence of temp., streaming velocity, and other factors on the reduction of CuO by H_2 at $400\text{--}900^\circ$ has been investigated. Under certain conditions CuH is formed intermediately. Photomicrographs of sections of CuO pastilles partly reduced by CO or H_2 show a sharply marked Cu/CuO boundary, indicating that the velocity of reduction is much greater than the velocity of diffusion into the interior. The grains of reduced metal are polyhedral when reduction has occurred at low temp., but this structure is lost at higher temp., whilst d is diminished simultaneously. The structure of the reduced Cu depends not only on the temp. but also on the structure of the original CuO . When CuO is reduced by H_2 at about 450° a section of the reduced pastille shows alternate bands of Cu in two different states, one of which has been produced probably by decomp. of CuH ; in such cases the time curve shows periodic fluctuations in rate of reaction. E. S. H.

Reactions between gas and solid. III. Azotization of calcium carbide and effect of pressure of nitrogen on the reaction velocity. T. AONO (Bull. Chem. Soc. Japan, 1932, 7, 143–154).—The velocity of the reaction $CaC_2 + N_2 = CaCN_2 + C$ has been studied over the range $786\text{--}1028^\circ$; $-dP/dt = KP/(1-\alpha P)$, where P =pressure, t =time, K and α are consts. depending on temp. and other conditions. The effect of coarseness and of addition of CaF_2 and $CaCl_2$ has been investigated. D. R. D.

Reaction between calcium carbonate and silica. W. MASKILL, G. H. WHITING, and W. E. S. TURNER (J. Soc. Glass Tech., 1932, 16, 94–110).—Mixtures of calcite and quartz (1:1, 1:2, and 1:3 mol.) were

heated at 700° , 750° , and 800° . 1 mol. of quartz scarcely affected the rate of decomp. of $CaCO_3$, but marked acceleration was caused by 2 and 3 mols. At 700° , 99% dissociation was reached in 170 min. with $1SiO_2$, in 160 min. with $2SiO_2$, and in 80 min. with $3SiO_2$. Similar vals. at 800° were 30, 20, and 15 min. The results could be represented (see following abstract) by: $\log \alpha = K \log t + C$. Experiments using sillimanite grains in place of SiO_2 gave a rate of decomp. greater than that for calcite alone. Au grains also promoted the rate of decomp. The equation $K = \log_e [1/(1-\alpha)]/t$ applied equally well for calcite with SiO_2 or Au. Microscopical and chemical examination for “sol. SiO_2 ” showed that reaction occurred between the SiO_2 and $CaCO_3$. Appreciable reaction was found at 610° in 5 weeks, at 700° in 3 hr., at 800° in 1 hr. The sol. SiO_2 with the equimol. mixture was after heating 1 hr. at 800° , 4–5%; at 1100° , 19%; at 1200° , 25%; at 1400° , 60%. The amount of reaction at $700\text{--}800^\circ$ was small and its effect on the rate of liberation of CO_2 slight. At 1050° calcite was found to be more reactive than lime (cf. Hedvall, A., 1917, ii, 205, 208). The decomp. of $CaCO_3$ occurring on heating with SiO_2 was mainly the result of heat alone and not of chemical reaction. M. P.

Rate of decomposition of calcium carbonate. W. MASKILL and W. E. S. TURNER (J. Soc. Glass Tech., 1932, 16, 80–93; cf. A., 1931, 800).—The rate of decomp. was increased by enlarging the reaction chamber, and was affected by the depth of the layer of carbonate when >5 mm. Heating in a current of dry CO_2 -free air (200 c.c. per min.) gave results slightly higher than those of the standard crucible method, but when the CO_2 evolved was absorbed in weighed U-tubes, good agreement was obtained. Attempts to study the effect of grain size by heating large single calcite crystals failed owing to disintegration of these even when the rate of heating was $<2^\circ$ per min.; with limestone grains ($\frac{1}{8}$ in.), in one case evidence of a lower rate of decomp. was obtained.

Discrepancies between the results and those of Whiting and Turner are attributed to different dispositions of the thermocouple. The time t and degree of decomp. α were given by $\log \alpha = K \log$ vals. of K and C being at 610° , 0.833 and -0.85 ; 700° , 0.633, 0.49; 750° , 0.75, 0.80; 800° , 0.80, 0.93, respectively. Decomp. and temp. T are related by $\log \alpha = K(10^4/T) + C$, where K has the common val. of $-8/9$. A numerically const. val. is obtained for the velocity coeff. K from the equation $K = \log_e [1/(1-\alpha)]/t$, where α is the fraction decomposed in t min. Vals. for $K \times 10^4$ are at 610° , 6.3; 700° , 81; 750° , 485; 800° , 1000, respectively, giving a val. of approx. 2 for the temp. coeff. (10°). The crit. increment, 95,000 g.-cal., compares well with 80,000 (Bruza) and 89,000 (Schaefer and Schubert). The authors consider that the process of decomp. is not so simple. M. P.

Velocity of crystallisation of supercooled liquids. W. REINDERS (Rec. trav. chim., 1932, 51, 589–592).—The flatness of the max. sometimes observed in the curve connecting rate of crystallisation with the apparent degree of supercooling is due to the actual temp. being maintained near the m.p. by the latent heat of fusion, and is not found with

substances which crystallise slowly. Regarding the velocity of crystallisation as a linear function of the difference between the free energy of the crystals and of the liquid, this velocity may be expressed by the formula $e^{B(T_0-T)}/e^{A/T}$, in which T_0 is the abs. m.p., and B and A are consts. which can be expressed in terms of the max. velocity of crystallisation, the corresponding temp., and the m.p. An example is given in which the agreement with observation is good. F. L. U.

Aldehyde hydrogen sulphite compounds. I. Rate of dissociation of benzaldehyde sodium hydrogen sulphite as measured by its first order reaction with iodine. T. D. STEWART and L. H. DONNALLY (J. Amer. Chem. Soc., 1932, 54, 2333—2340).—The rate of reaction with I depends on the velocity of the dissociation reaction yielding HSO_3^- or SO_3^{2-} , and not on the I concn. It varies with the p_H , and is a min. at 1.8. The apparent heat of activation increases from 19,000 to 24,000 g.-cal., following a sigmoid curve, from p_H 6.5 to 0.03. H. A. B. (c)

Absorption of oxygen by benzaldehyde. H. J. ALMQUIST and G. E. K. BRANCH (J. Amer. Chem. Soc., 1932, 54, 2293—2302).—If PhCHO purified by distillation until it shows no induction period, and containing 3% BzOH, is shaken with O_2 in the dark at 25° the reaction is of the first order with respect to O_2 ; in absence of BzOH it is antoinhibited. The rate of formation of peroxide and BzOH at const. O_2 pressure indicates that, with BzOH initially present, a peroxide-BzOH compound (I) is formed and reaches a const. concn. (I) readily oxidises PhCHO to BzOH and so acts as a weak inhibitor by removing active PhCHO. With no BzOH initially present, the primary peroxide changes to BzO_2H which oxidises PhCHO less rapidly than (I); the total concn. of BzO_2H thus passes through a max. In both cases, 3% of the O absorbed enters an unknown side reaction. H. A. B. (c)

Neutral salt effect in ionic reactions. V. Neutral salt effect in concentrated salt solutions. A. VON KISS [with I. BOSSANYI] (Z. physikal. Chem., 1932, 160, 290—294).—Criticisms are refuted (cf. this vol., 584). R. C.

Nature of the catalytic action of hydrochloric acid in the intramolecular change of N-chloroacetanilide. H. M. DAWSON and H. MILLET (J.C.S., 1932, 1920—1926).—The rate of transformation of N-chloroacetanilide as measured by the unimol. const. k is approx. proportional to $[\text{H}^+][\text{Cl}^-]$. For the series of solutions represented by (1) $\text{CHCl}_3 + x\text{NaNO}_3$, (2) $\text{CHCl}_3 + x\text{NaCl}$, (3) $\text{CHCl}_3 + x\text{HClO}_4$, and (4) $x\text{HCl}$ (c const., x variable) the val. of $k/[\text{H}^+][\text{Cl}^-]$ passes through a min., however, as x increases. The observed reaction velocities may be explained on the assumption that the active catalyst is the HCl mol., when due consideration is given to the change in degree of dissociation of the acid with the nature and concn. of the ions in the reaction medium. Since the ionisation const. K passes through a max. as the ionic strength μ of the solution increases, the concn. of the non-ionised acid will pass through a min. corresponding with the min. val. of $k/[\text{H}^+][\text{Cl}^-]$. The variation

of K for weaker acids is expressed by $\log K/K_0 - a\sqrt{\mu} - b\mu$ when K_0 is the const. in absence of electrolyte. The results obtained for the above series of solutions can be explained by assuming that ionisation of the strong acids varies in the same way with the environment. The results are incompatible with the hypothesis that the reaction velocity is determined by the thermodynamic activities of the reactants. E. S. H.

Catalytic decomposition of hydrogen peroxide by iodine-iodide couple at 25°. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1932, 54, 1792—1806).—The mechanism previously proposed (A., 1931, 916) has been confirmed. For vals. of $a_H < 10^{-4}M$, the rate of decomp. is accounted for by the reactions (a) $\text{I} + \text{H}_2\text{O}_2 \rightarrow \text{IO} + \text{H}_2\text{O}$ and (b) $\text{IO} + \text{H}_2\text{O}_2 \rightarrow \text{I} + \text{H}_2\text{O} + \text{O}_2$. As a_H increases the reaction (c) $\text{HIO} + \text{H}_2\text{O}_2 \rightarrow \text{H} + \text{I} + \text{H}_2\text{O} + \text{O}_2$ becomes increasingly important, but at the steady state the abs. rate of (a) is always equal to the sum of the abs. rates of (b) and (c). H. F. J. (c)

Effect of salts on the reaction of esterification. A. V. LOZOVOR (J. Gen. Chem. Russ., 1932, 2, 65—79).— NaOAc retards, AgCl , AgCNS , Li_2SO_4 , $\text{Ba}(\text{NO}_3)_2$, Na_2WO_4 , and $\text{Ti}_2(\text{SO}_4)_3$ slightly accelerate, and $\text{Sr}(\text{NO}_3)_2$, KI , Ag_2SO_4 , Na_2SO_4 , RbCl , $\text{Pb}(\text{NO}_3)_2$, HgCl_2 , NaCl , $\text{Th}(\text{SO}_4)_2$, NH_4CNS , $\text{UO}_2(\text{OAc})_2$, $\text{Ti}(\text{SO}_4)_2$, CoCl_2 , $\text{Ni}(\text{NO}_3)_2$, AgNO_3 , HgNO_3 , $\text{Ce}(\text{NO}_3)_3$ and $\text{Hg}(\text{NO}_3)_2$ considerably accelerate reaction, in the order given, to an extent increasing with their mol. concn. At certain concns. of AgNO_3 the equilibrium point is shifted from 71.6 to 73% of EtOAc . The catalytic effect of salts is ascribed to elimination of H_2O as a result of hydration of their mols., and to orientation of acid and alcohol mols. within the sphere of hydration. R. T.

Shifting of equilibria by catalysts. N. A. SCHLESINGER [with E. I. BEFORT, N. A. KUPRIANOVA, K. D. PANFEROVA, E. A. ZABUGINA, A. D. ISTIUNINA, E. I. KAMIENSKAJA, and R. G. MALKINA-ORUN] (Thesis, Saratov, 1932, 1—170).—The esterification of AcOH and EtOH has been studied in the presence of H_2SO_4 , HBr , or HCl alone, or together with the corresponding halide of K, Na, Li, Ca, Ba, Cd, or Hg. Using low concns. of acids, no shifting of equilibrium in the direction of esterification was observed, whilst with high concns. the reaction is complicated by formation of Et_2O . In the presence of salts, the equilibrium const. K varies for low concns. of salt according to the equation $K = b - aC$, where a and b are const. for a given org. acid and salt, and C is the concn. of catalyst. The action of acids and salts is not due to hydration of their ions or mols., since it varies with the org. acid taken, it is greater at higher than at lower temp., and, finally, since glucose, which is hydrated in solution, has no catalytic action. The results are interpreted on the basis of the activity theory. R. T.

Impulse phenomena on heterogeneous catalysts, and possibility of detecting chain reactions. K. BENNEWITZ and W. NEUMANN (Z. physikal. Chem., 1932, B, 17, 457—459).—Attempts to repeat Cantor's radiometer experiment (Ann. Physik, 1891, 62, 482) have failed. The theory that the hydro-

genation of C_2H_4 on Pt is a chain reaction occurring mainly in the gas phase (A., 1930, 715) must therefore be abandoned (cf. A., 1931, 1374). R. C.

Heterogeneous catalysis of binary gas reactions. II. C. KROGER (Z. anorg. Chem., 1932, 206, 289—303; cf. this vol., 579).—The following reactions are discussed with reference to the author's views of heterogeneous chemical catalysis of the first and second kinds: $2NH_3 + 3O_2 = N_2O_3 + 3H_2O$; $2HCN + 7O = H_2O + 2NO + 2CO_2$; $2CH_4 + 3O_2 = 2CO + 4H_2O$; $CH_4 + CO_2 = 2CO + 2H_2$; $P_4 + 10H_2O \rightarrow 2P_2O_5 + 10H_2$; $4HCl + O_2 = 2Cl_2 + 2H_2O$; $H_2 + Cl_2 = 2HCl$; $N_2 + 3H_2 = 2NH_3$. M. S. B.

Activation of metals by the addition of foreign substances. II. R. SCHENCK, F. KURZEN, and H. WESSELKOCK (Z. anorg. Chem., 1932, 206, 273—288).—When Fe or W is mixed with MgO the formation of carbide by CH_4 (cf. this vol., 238) takes place to a much smaller degree than with the pure metal if the carbide is one in which the at. ratio of metal to C > 1, as in Fe_3C or W_5C_2 . If the ratio is 1, as in WC, the presence of MgO has no influence. The effect is apparently steric. The inhibited tendency to form carbide, however, is probably a cause of the catalytic activity of mixtures of metals of the Fe series with MgO in the formation of CH_4 from CO and H_2 . M. S. B.

Effect of supports on the catalytic activity of nickel. C. R. GLASS and L. KAHLENBERG.—See B., 1932, 644.

Role of liquid stationary films in batch absorption of gases. III. Rates of hydrogen absorption and relative rates of catalytic hydrogenation in alcohol. H. S. DAVIS, G. THOMSON, and G. S. CRANDALL (J. Amer. Chem. Soc., 1932, 54, 2340—2350).—The rates of hydrogenation of CMe_3CHMe , Δ^2 -pentene, and CH_3CHPr^i in EtOH with Pt—Pt oxide catalysts with particles 0.1 — 0.3×10^{-4} cm. in diameter have been measured. In the hydrogenation of mixtures of olefines the order of reduction is mono-, di-, and tri-substituted. P. T. N. (c)

Decomposition of nitrous oxide on glowing platinum. II. H. CASSEL and E. GLÜCKAUF (Z. physikal. Chem., 1932, B, 17, 380—384; cf. A., 1930, 1380).—Measurements of the rate of decomp. at 900 — 1100° abs. with the partial pressure of N_2O kept const. at about 10^{-4} mm. have shown that under this pressure the retardation by O is due to the adsorption, not of O_2 , but of at. O. R. C.

Thermal combination of ethylene and bromine at glass surfaces. I. General kinetics at 16° . II. The influence of water. G. WILLIAMS (J.C.S., 1932, 1747—1758, 1758—1765).—I. The combination of C_2H_4 and Br₂ is a surface reaction in a glass vessel at room temp. The reaction is a simple addition of Br to the double linking unless Br is in excess, when some supplementary reaction is induced. The kinetics of the reaction are complex: (a) the rate of reaction decreases with rising temp.; (b) the order of reaction varies in different reaction vessels. For a given surface, lowering the temp. or raising the pressures of the reactants tends to lower the order of reaction. (c) For a given surface and

reaction order, the velocity coeff. is independent of the initial pressure of C_2H_4 , but rises with increasing initial pressure of Br. It does not seem probable that the variation of the adsorption of the reactants with temp. and pressure can account for the magnitude of the observed effects, which imply that the reaction involves more than one stage.

II. H_2O vapour accelerates the C_2H_4 -Br₂ reaction, partly by participating in some action at the glass surface. Transition from a second- to a first-order reaction is favoured by (a) a wet surface, (b) high initial proportion of Br to C_2H_4 , (c) low temp. Probably Br is hydrated at the glass surface and C_2H_4 reacts with the complex. The rate of reaction becomes independent of the bulk Br pressure when the surface concn. of hydrated Br is relatively high. Chains may start at the glass surface and spread into the gaseous phase. Introduction of $C_2H_4Br_2$ vapour before the reaction increases the rate of reaction. E. S. H.

Catalytic activity of reduced copper chromate and of vanadium oxide in reduction of nitro-compounds. H. A. DOXAL and O. W. BROWN (J. Physical Chem., 1932, 36, 1549—1561).—The Cu chromate catalysts are superior to the V oxide catalysts for the production of high-grade NH_4Ph by reduction of $PhNO_2$ with H_2 , the yield being 99% of theoretical, as against 91.8%, and less $NHPh_2$ is formed. S. L. (c)

Reactions of ethyl alcohol on nickel-chromium catalysts. E. H. BOOMER and H. E. MORRIS (Canad. J. Res., 1932, 6, 471—484).—The composition of the gaseous products of the decomp. of EtOH- H_2O mixtures at a series of catalysts containing Ni and Cr has been determined. Mixtures of hydroxides or $NiCrO_4$ are the most active catalysts, but the effect varies with the method of prep. and the temp. The dehydrating power of Cr is largely suppressed by the presence of Ni: with use, the Ni loses its activity more rapidly than the Cr and the dehydrating efficiency of the mixed catalyst may rise. Secondary reactions, producing C and complex org. liquids, usually occur, resulting in the formation of CO_2 . E. S. H.

Addition of hydrogen chloride to acetylene and to vinyl chloride in the gaseous phase under the influence of catalysts. J. P. WIBAUT and J. VAN DALFSEN (Rec. trav. chim., 1932, 51, 636—640; cf. A., 1931, 598, 1393).—HCl reacts smoothly with C_2H_2 at 25 — 195° in presence of $HgCl_2$ on SiO_2 gel (0.1 mol. per 100 g.) to form CH_3CHCl . With $BiCl_3$, $FeCl_3$, or $ZnCl_2$ the yield is poor. $ZnCl_2$ catalyses the addition of HCl to CH_2CHCl , the product being exclusively $CHMeCl_2$. F. L. U.

Mechanism of hydrogenation catalysis with sodium hydride. II. G. HUGEL and GIDALY (Bull. Soc. chim., 1932, [iv], 51, 639—644).—The catalytic activity of NaH is limited to those parts of the mol. which can take up Na. Under suitable conditions Na is then replaced by H. This conclusion has been confirmed by the hydrogenation of styrene to dibenzyl, anisylidenefluorene to 9-methylfluorene, benzylidenefluorene to fluorene and methylfluorene, owing to the removal of $PhMe$ or C_6H_6 from the

hydrogenated mol., and diphenylbutadiene to $\alpha\delta$ -diphenylbutane. M. S. B.

Transformations of cyanogen. Polymerisation and action of potassium carbonate and sodamide. A. PERRET and A. KRAWCZYNSKI (Bull. Soc. chim., 1932, [iv], 51, 622—636).—Polymerisation of $(CN)_2$ takes place very slowly at 450—500° under a pressure of approx. 1 atm., but it is catalysed by certain solid surfaces, especially salts. Powdered quartz has a slightly catalytic effect and powdered Thuringian glass a somewhat greater one. KCN has a strong catalytic activity at 440° and remains unaltered. K_2CO_3 shows a still greater activity beginning at 120°, but the salt itself is transformed into KCN to the extent of 21.6%, when heated to 370°. $NaNH_2$ catalyses without chemical change at 90—105°, but above that temp. Na_2NCN and NaCN are obtained, $NaNHCN$ being probably formed as an unstable intermediate product. Above 300° Na_2NCN is gradually changed into NaCN by the action of $(CN)_2$. HCN on $NaNH_2$ gives Na_2NCN and NaCN directly, but more slowly than $(CN)_2$. The N_2 formed in these reactions is probably due to the oxidation of $NaNH_2$ at approx. 160° by its products of decomp. in presence of air. M. S. B.

Zinc electrolytes. I. Purification from nickel. L. CAMBI and V. TOJA [with F. CREMASCOLI].—See B., 1932, 607.

Electro-deposition of alloys from metallic cyanides in cyanide solution. K. MASAKI (Bull. Chem. Soc. Japan, 1932, 7, 158—168).—The p.d. between electrodes of Cu, Cd, Ag, Ni, Co, Hg, and Zn, and solutions of their cyanides in aq. NaCN, have been determined. From the curves obtained, the best compositions for depositing Cu-Cd, Ag-Ni, Ag-Co, Cu-Ni, and Ni-Co alloys are deduced, experimental details being given for the first three. D. R. D.

Electro-deposition of platinum, palladium, and rhodium. W. KEITEL and H. E. ZSCHIEGNER.—See B., 1932, 645.

Reaction of ammonia with active nitrogen, and existence of free NH and OH radicals. J. K. DIXON and W. STEINER (Z. physikal. Chem., 1932, B, 17, 327—352).—The amount of NH_3 formed by interaction of active N and H atoms is proportional to the concn. of H atoms as long as N atoms are present in excess. NH_3 reacts very slowly with active N. Calculation from the observed rate of reaction shows that various of the exothermic exchange reactions of NH_3 with constituents of active N involve a heat of activation, and even N atoms in the metastable 2P state exhibit reaction inertia. Attempts to draw off NH from the region of discharge when a high-voltage alternating discharge is passed through NH_3 have failed. It is probable that NH is either resolved into N and H by the discharge, or is decomposed by chemical reaction in the region of discharge. It has proved impossible to draw off OH from H_2O vapour through which a discharge is passing (cf. A., 1931, 1215). R. C.

Chemical action of the electric discharge. VI. Influence of the nature of the electrodes on the fixation of nitrogen as nitric oxide, ammonia,

and hydrogen cyanide. Measurement of the power factor of the arc. E. BRINER and C. H. WAKKER. VII. Study of a 3-kw. furnace using copper electrodes containing small quantities of lithium and calcium. E. BRINER, C. H. WAKKER, and H. PAILLARD (Helv. Chim. Acta, 1932, 15, 959—969, 970—977).—VI. The increase of yield (per unit power consumption) obtained by using Cu electrodes containing alkali or alkaline-earth metals for the direct synthesis of NO has been determined; with 3% of Li the increase is 152%, and with 1% Li and 1% Ca 116%. With electrodes containing 9.6% of Ag and 3.8% of Li the increase is 120%, and the potential across the arc (10 mm. long, 140 milliamp.) is only 380 volts. The increase of yield is due not only to the lower voltage required but also to the larger quantity of NO formed. In similar experiments on the synthesis of NH_3 the formation of Li and Ca nitrides interfered. An increase of the yield of HCN, at 730 mm. pressure, of 65% has been obtained by using electrodes containing 1.7% Li. The power factor of the arc is 0.92—0.96, and is practically independent of the composition of the electrodes. The results are discussed from the viewpoint of electron emission by the electrodes.

VII. The results obtained previously with small arcs have been confirmed by using 2—4-kw. arcs 40—60 cm. long between electrodes containing Li or Li and Ca. Spectroscopical examination of the radiation emitted by the arc shows that Li (and Ca) atoms are present in certain regions, in confirmation of the view that the increase of yield is due to increased ease of ionisation. H. F. G.

Photokinetics of ozone. I. Decomposition in red light. H. J. SCHUMACHER. II. Decomposition in ultra-violet light. U. BERETTA and H. J. SCHUMACHER (Z. physikal. Chem., 1932, B, 17, 405—416, 417—428).—I. The kinetics of the decomp. in red light may be quantitatively deduced from the scheme (1) $O_3 + E = O_2 + O$, (2) $O + O_3 = 2O_2$, (3) $O + O_2 + M = O_3 + M$ ($M = O_2$ or O_3), (4) $O_2^* + O_3 = O_2 + O_2 + O$, (5) $O_2^* + O_3 = O_2 + O_3$, (6) $O_2^* + O_2 = 2O_2$. The absorption spectrum in the yellow and red shows the primary process to be decomp. into normal O_2 (3P) and normal O (3P).

II. The decomp. in light of wave-length 313 m μ follows the above scheme, the velocity coeffs. having the same vals. In the primary process excited O_2 mols. ($^1\Sigma$) or O atoms (1D) may be produced, but must react in the same way as when unexcited. The temp. coeff. of 1.25 is partly due to (2), which has a heat of activation of 4—6 kg.-cal. Reaction (3) occurs once in 10^3 — 10^5 collisions. In presence of a foreign gas (X) the reactions (7) $O + O_2 + X = O_3 + X$ and (8) $O_2^* + X = O_2 + X$ also play a part. In respect of (7) He and A have about one tenth and N_2 has about half the effect of CO_2 and O_2 in retarding the reaction, and the effects in (8) are qualitatively similar. R. C.

Photochemical dissociation of carbonyl sulphide. W. LOCHTE-HOLTGREVEN, C. E. H. BAWN, and E. EASTWOOD (Nature, 1932, 129, 869—880).—With a H discharge tube as light source, COS shows a continuous absorption spectrum from a sharp limit

at $2550 \pm 20 \text{ \AA}$. extending far towards the ultra-violet. The spectrum appears to correspond with the dissociation of the COS mol., and the observed photochemical dissociation energy of 111.1 kg.-cal. indicates a reaction $\text{COS} \rightarrow \text{CO} + \text{S} - 76 \text{ kg.-cal.}$ The difference, 35 kg.-cal., between the calc. and observed vals. corresponds with the excitation energy of the S atom. L. S. T.

Study of photochemical reactions using photo-galvanic elements. S. SCHLIVIC (Bull. Soc. Chim. Yougoslav., 1931, 2, 129—137).—A photovoltaic accumulator is prepared by immersing Pt electrodes in a solution of Na fluorescein in aq. glycerol. The fluorescein is reduced in the presence of light, and is re-oxidised in the dark. This element has a const. e.m.f. Elements containing methylene-blue in place of fluorescein give a higher e.m.f. under diminished than under atm. pressure. R. T.

Photo-reduction of metallic oxides. C. RENZ (Helv. Chim. Acta, 1932, 15, 839—842).—When in contact with a liquid possessing reducing properties, such as PhCHO, the yellow form of In_2O_3 is light-sensitive, becoming first grey and then black: the product resembles that obtained by heating In_2O_3 in H_2 , and is reconverted into the yellow oxide by air. Neither aldehydes nor light, separately, have any action on In_2O_3 . The phenomenon does not occur with Sm_2O_3 . H. F. G.

Silver nucleus theory of the latent image. I. Critical nuclear size. W. REINDERS and L. HAM-BURGER (Z. wiss. Phot., 1932, 31, 32—53).—In experiments with attenuated Ag layers formed by sublimation in high vac., the limit of physical developability is reached when the average thickness of the layer is equiv. to 0.001—0.005 atom (cf. Esterman and Stern, Z. physikal. Chem., 1926, 106, 399). Only Ag aggregates of 3—4 or more atoms are developable. Reversal may occur in layers of more than 0.01 atom equiv. thickness. The developed solarised layers have a fine-grain structure and a smoother surface than usual. Solarisation in photographic plates is ascribed to the formation of more or less complete Ag layers on the surface of the grains in the first stages of development. J. L.

Nature of the latent image for physical development. II. H. ARENS (Z. wiss. Phot., 1932, 31, 68—76; cf. A., 1929, 1382).—For artificially prepared suspensions of Ag (Ag_2S or Au) nuclei in gelatin, the amount of Ag physically developed is dependent only on the no. of grains per sq. cm. and is independent of their size or nature; for a given wt. of Ag per sq. cm., it increases with the degree of dispersion. These relations are shown to hold also for the Ag nuclei in a latent image. J. L.

Photo-electric theory of the latent image. G. SCHWARZ and F. URBACH (Z. wiss. Phot., 1932, 31, 77—79).—Experiments are briefly summarised in support of the theory that unexposed Ag halide grains possess a protective negative charge on the surface (repelling negative reducing ions) which is removed by exposure to light. Part, at least, of the electrons so displaced are taken up by Ag ions in the cryst. lattice to form Ag nuclei, which are hence

only a by-product indicative of latent image formation. The protective action of gelatin is also considered.

J. L.

Ultramicroscopic observations on light-sensitive crystals. I. K. SCHAUUM and F. KOLB (Z. wiss. Phot., 1932, 31, 2—31).—The photolysis occurring in crystals when dry, or in Canada balsam or in H_2O has been examined microscopically by direct illumination, with dark-ground illumination, and with vertical and grazing incidence illumination. The substances examined were Ag, Cu^I, Cu^{II}, Hg^I, Hg^{II}, and Tl halides, Ag oxalate, tartrate, and benzoate, and mixed crystals of Ag and Tl halides. Photographs are given. The rate of darkening, occurrence of diffraction spots, etc. have been observed. Photolysis occurs in weak points of the cryst. lattice, especially at the surface and edges. Greatest sensitivity is found in skeleton and similar shaped crystals. Foreign substances in the crystals, as is to be expected, form centres of disturbance. J. L.

Einstein relation and temperature coefficient in photobromination of cinnamic acid. W. H. BAUER and F. DANIELS (J. Amer. Chem. Soc., 1932, 54, 2564—2565).—When accompanying thermal reactions are suppressed a quantum efficiency temp. coeff. of unity may be obtained. The temp. coeff. is 1 at infinite dilution and increases to a limiting val. of 2 at higher concns. The temp. coeff. of the total reaction may vary with the enon.

C. J. W. (c)

Light and dark reactions of alcoholic crystal-violet leucocyanide solution with and without addition of potassium cyanide. E. WEYDE, W. FRANKENBURGER, and W. ZIMMERMANN (Z. physikal. Chem., 1932, B, 17, 276—284).—In the photochemical conversion of the leucocyanide into the cyanide of the dye one mol. of the latter is formed for each quantum absorbed, and the velocity between -6° and 40° is independent of the temp. The velocity of the reverse dark reaction, brought about by KCN, is proportional to the dye concn., has a temp. coeff. of 5, and is greatly diminished by the presence of a little H_2O . On prolonged irradiation of leucocyanide solutions containing KCN the leucocyanide is completely destroyed, probably by oxidation. The absorption spectra of the various reactants have been determined. R. C.

Examination with ultra-violet light. M. GUYOT (Ann. Falsif., 1932, 25, 263—267; cf. B., 1931, 765).—Fluorescence is measured photographically by comparison with light passed through ordinary coloured screens and the use of panchromatic plates. Alternatively it may be determined by means of a photo-electric cell and a mirror galvanometer.

T. McL.

Photographic action of slow electrons. R. WHIDDINGTON and J. E. TAYLOR (Proc. Roy. Soc., 1932, A, 136, 651—662).—The photographic action of slow electrons (60—300 volts) has been experimentally determined. L. L. B.

Reducing power of β -radiation. H. A. COLWELL (Lancet, 1932, 222, 932—933).— β -Radiation from radon decolorises solutions of methylene-blue, brilliant-green, acid fuchsin, and safranin; it also reduces

Fehling's solution, ammoniacal AgNO_3 , alkaline picrate, KMnO_4 , and KNO_3 (to nitrite) solutions.

L. S. T.

Combination of carbon monoxide and oxygen under the influence of radon. S. C. LIND and C. ROSENBLUM (Proc. Nat. Acad. Sci., 1932, 18, 374—386).—An investigation of the influence of CO_2 on the rate of the α -ray reaction between CO and O_2 . The recoil atom effect on the oxidation was also investigated.

A. B. D. C.

Pyrogenic decomposition of sodium sulphate. K. I. LOSEV, N. I. NIKOLSKAYA, and T. G. GUSEVA.—See B., 1932, 597.

Sodium thiocyanate. C. K. BUMP (J. Physical Chem., 1932, 36, 1851—1852).—On cooling aq. NaSCN , saturated at 60° , monoclinic needles of $\text{NaSCN} \cdot \text{H}_2\text{O}$ separate, the v.p. of a saturated solution of which is 5.2 mm. at 17° , and 7.5 mm. at 25° .

J. H. R. (c)

Solid polybromide of potassium. I. W. H. HARRIS (J.C.S., 1932, 1694—1697).—The solubility curves in the system $\text{KBr}-\text{Br}-\text{H}_2\text{O}$ have been determined at 0° for the more conc. solutions. Solid $2\text{KBr}_6 \cdot 3\text{H}_2\text{O}$, but no anhyd. polybromide, exists. The assumed presence of Br_3^- and Br_5^- in considerable proportion is doubtful. Na gives no polybromide at 0° .

E. S. H.

Topochemical transformations. V. Mechanism of formation of filiform silver on silver sulphide. H. W. KOHLSCHUTTER (Z. Elektrochem., 1932, 38, 345—353; cf. this vol., 131).—The growth of filaments of Ag during reduction of Ag_2S by H_2 has been studied in relation to the velocity of reaction and the condition of the Ag_2S . The presence of excess of S in the Ag_2S , and a moderate temp. (440°) of reduction favour the formation of long filaments. Admixture of Ag powder suppresses it completely. One or two Ag nuclei are developed on each grain of Ag_2S and subsequent growth takes place exclusively on these, the Ag required for it being conveyed from other parts of the grain, probably by reason of the higher solution pressure of sub-microscopic particles of Ag formed by reduction. Possible causes of the peculiar growth form are discussed.

F. L. U.

Composition of magnesium oxychloride. H. S. LUKENS (J. Amer. Chem. Soc., 1932, 54, 2372—2380).— MgO dissolves in aq. MgCl_2 of $d > 1.16$ and a compound $5\text{MgO} \cdot \text{MgCl}_2 \cdot x\text{H}_2\text{O}$ subsequently separates. The velocity of the reaction depends on the previous thermal history of the MgO and the temp. On continued treatment with the MgCl_2 solution the compound passes into $3\text{MgO} \cdot \text{MgCl}_2 \cdot y\text{H}_2\text{O}$. The H_2O is loosely combined.

F. D. S. (c)

Calcium aluminates. I. Synthesis. II. Micro-structure. S. KONDO and T. YAMAUCHI (J. Japan. Ceram. Assoc., 1932, 40, 81—87, 87—91).—I. Mixtures of CaCO_3 and Al_2O_3 (3:1, 5:3, 1:1, 3:5) were heated at 1200 — 1700° for 1—7 hr.; the free CaO and Al_2O_3 in the products were then determined. In Rathke's method the CaO was dissolved by heating the substance with glycerol at 75° for 25 min. with const. shaking, and then keeping at 75°

for 1 hr. Practically pure 3:1, 5:3, and 1:1 aluminates were obtained in 2 hr. at 1540° , 1450° , and 1600° , respectively. The 3:5 mixture after 2 hr. at 1700° contained 1% Al_2O_3 .

II. For $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ $n_D^{20} = 1.621$; $n_D^{25} = 1.665$, 1.660 , $n_D^{30} = 1.645$. The crystals were biaxial and optically negative.

CH. ABS.

Hydrothermal syntheses of calcium aluminates and silicates from lime and alumina or kaolin. II. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 256—260B; cf. A., 1931, 1020, 1380; this vol., 707).—On heating a CaO-kaolin mixture, reaction occurs at $< 700^\circ$, the extent of reaction increasing with rise of temp. up to 1100° . Compounds $x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{H}_2\text{O}$ can be obtained by heating CaO- Al_2O_3 or CaO- $\text{Al}_2(\text{OH})_6$ mixtures under H_2O v.p. in an autoclave. Under similar conditions CaO reacts with kaolin at 150° .

J. W. S.

Double salts of zinc iodide. E. VOYATZAKIS (Bull. Soc. chim., 1932, [iv], 51, 670—672).—The following compounds of ZnI_2 or $\text{ZnI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$ with bases have been obtained: $\text{ZnI}_2 \cdot 2\text{B}$ ($\text{B} = m\text{-C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$), white needles becoming red on exposure to air with the probable loss of 1 mol. of PhMe ; $\text{ZnI}_2 \cdot \text{KI} \cdot 2\text{B}$, white cubes which become green in the air probably losing 1 mol. of B; $\text{ZnI}_2 \cdot \text{KI} \cdot 2\text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ (o), white prisms sol. in H_2O ; $\text{ZnI}_2 \cdot 2(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, white crystals; $\text{ZnI}_2 \cdot \text{KI} \cdot 2(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, yellow crystals sol. in H_2O ; $\text{ZnI}_2 \cdot \text{KI} \cdot 2\text{C}_3\text{H}_7\text{N}$, white crystals sol. in dil. HCl.

M. S. B.

Action of mercuric oxide on zinc chloride and of zinc oxide on mercuric chloride. H. PELABON and (MLLE.) DELWAULLE (Bull. Soc. chim., 1932, [iv], 51, 650—653).—If aq. ZnCl_2 is shaken up with increasing proportions of HgO , Hg completely displaces Zn at first and the ZnO formed combines with excess of ZnCl_2 to form $\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 3\text{H}_2\text{O}$. If the mol. proportion of HgO is greater than that of ZnCl_2 the reverse reaction of ZnO on HgCl_2 becomes possible. HgCl_2 also crystallises as a new solid phase and excess of HgO combines with HgCl_2 to form a series of oxychlorides. The colour changes from white, through grey, to maroon as the proportion of Hg increases. 0.02 mol. ZnO with 0.02 mol. HgCl_2 in 20 c.c. H_2O gives the same equilibrium as the same proportions of ZnCl_2 and HgO . By reducing the quantity of ZnO in the first case the same equilibrium is still obtained. Hence ZnO forms a pure phase. The HgO formed combines with excess of HgCl_2 to give $2\text{HgCl}_2 \cdot \text{HgO}$.

M. S. B.

Mercuric chlorobromide. R. STRATTA (L'Ind. Chimica, 1932, 10, 726—727).—The Debye-Scherrer diagram of the product obtained by melting equimol. mixtures of HgCl_2 and HgBr_2 confirms the formation of the compound HgClBr which Losana (cf. A., 1926, 908) had foreseen from thermal analysis. O. F. L.

Analysis of solutions of basic aluminium chloride. W. D. TREADWELL and M. ZURCHER [with W. WEBER and J. W. HOEKSTRA-KLEIN] (Helv. Chim. Acta, 1932, 15, 980—995).—When a solution of basic AlCl_3 is titrated potentiometrically, breaks in the curve occur at p_H 3, due to neutralisation of acid, at p_H 5—6 (AlOCl), p_H 8.5 [$\text{Al}(\text{OH})_3$], and p_H 11 (aluminate). F.-p. measurements with solutions

having an Al:Cl ratio of 1 indicate the presence of AlOCl . Potentiometric titration shows that several hr. are required for complete conversion of the basic salt into normal AlCl_3 . Basic AlCl_3 solutions yield with $\text{Na}_2\text{C}_2\text{O}_4$ solution a cryst. ppt. of probable structure $(\text{HO}\cdot\text{Al}\cdot\text{O}_2\cdot\text{Al})_2\text{C}_2\text{O}_4$; the reaction will detect 5% of basic chloride in solution. When NaOH is added to a solution containing AlOCl , the AlO^+ is converted first into $\text{Al}_2\text{O}_3\cdot\text{OH}$, and then into a form of $\text{Al}(\text{OH})_3$ which is much less sol. in NaOH than is the normal form. Analysis of a basic AlCl_3 solution may be effected by adding an excess of $\text{Na}_2\text{C}_2\text{O}_4$, to remove AlO^+ , and then KI and KIO_3 , and titrating the I liberated with $\text{Na}_2\text{S}_2\text{O}_3$ solution, but electro-metric titration with NaOH is more satisfactory; for accurate determination of the basic salt content the solution should be heated for 1 hr. on the water-bath with an excess of dil. HCl , the excess of acid being titrated with NaOH . Basic Al perchlorates are formed in solution, but have little stability, probably because of the great affinity of ClO_4^- for H_2O ; conditions are similar in nitrate solutions, whilst solutions of sulphate occupy a position intermediate between those of perchlorate and chloride. H. F. G.

Preparation and properties of titanium tetrabromide and titanium tribromide hexahydrate. J. C. OLSEN and E. P. RYAN (J. Amer. Chem. Soc., 1932, 54, 2215—2218).—The solubility of $\text{TiBr}_4 \cdot 6\text{H}_2\text{O}$, 3.25, in g. per 100 c.c. at 20° is: EtOH , 287; Et_2O , 3.6. It is sol. in CCl_4 , CHCl_3 , HBr , and HCl , and decomposed by HNO_3 , H_2SO_4 , aq. NH_3 , and aq. NaOH . $\text{TiBr}_3 \cdot 6\text{H}_2\text{O}$ has m.p. 115° . F. D. S. (c)

Heteropoly-acids of germanium. III. A. BRUKL and B. HAHN (Monatsh., 1932, 60, 145—149; cf. this vol., 351).—Electrometric titration of 12-molybdogermanic acid (A., 1930, 1537; 1931, 322) shows no unsaturated complex acids; in neutral 4-basic Na, Ba, or Hg salts the complex is unstable, only acid salts being stable. E. W. W.

Lead suboxide, Pb_2O . M. LE BLANC and E. EBERIUS (Z. physikal. Chem., 1932, 160, 129—140).—The thermal decomp. of Pb_2O_3 may be represented by $2\text{Pb}_2\text{O}_3 = \text{PbO} + \text{Pb} + 3\text{CO}_2 + \text{CO}$. The proportion of CO in the gas given off diminishes as reaction proceeds, due to its reducing PbO . X-Ray and microscopic examination shows the residue to consist of Pb and PbO only. R. C.

Hydrazine tetrathionate. J. VORISEK (Chem. Listy, 1932, 26, 286—287).—In the presence of air oleic acid is reduced to stearic acid by $(\text{N}_2\text{H}_5)_2\text{S}_4$, part of which is simultaneously oxidised to N_2H_4 tetrathionate. R. T.

Reversibility of the reaction $\text{NaNO}_2 + \text{NO} = \text{NaNO}_3 + \text{NO}$. J. SZPER and K. FISZMAN (Z. anorg. Chem., 1932, 206, 257—259).—In the electrolysis of fused NaNO_2 pure NO separates at the anode in the early stages. This is due to a secondary reaction: $\text{NaNO}_2 + \text{NO} = \text{NaNO}_3 + \text{NO}$. When heated in a stream of NO , for 3—4 hr. at 315 — 450° NaNO_2 is completely oxidised to NaNO_3 . The process may be reversed, but by heating NaNO_3 in NO for 6—7 hr. at 315° only about 5% is reduced to NaNO_2 . M. S. B.

Decomposition of metallic nitrates and nitrites. III. Manganous nitrite. C. MONTEMARTINI and E. VERNAZZA (L'Ind. Chimica, 10, 577—582).—By mixing anhyd. MnSO_4 and $\text{Ba}(\text{NO}_2)_2$ in presence of abs. EtOH and rapidly evaporating the EtOH solution, minute crystals of $\text{Mn}(\text{NO}_2)_2$ were obtained. The decomp. of $\text{Mn}(\text{NO}_2)_2$ on ebullition is complex and produces NO , NO_2 , N_2 , MnO , Mn_2O_3 , and $\text{Mn}(\text{NO}_3)_2$. O. F. L.

Reaction of gases with incandescent tantalum. M. R. ANDREWS (J. Amer. Chem. Soc., 1932, 54, 1845—1854).—Ta filaments have been heated at 3400° abs. in gases under low pressure. With N_2 absorption increases with the pressure until 100 vols. are absorbed, beyond which the equilibrium pressure falls as absorption increases. Absorption continues until TaN is formed. The amount of H_2 absorbed depends on the concn. of H atoms in the gas. With O_2 absorption is followed by oxide formation. In hydrocarbons the carbides Ta_6C_5 and TaC , both of high m.p., and with the sp. resistances of 180×10^{-6} and 18×10^{-6} , respectively, are formed. S. L. (c)

Behaviour of tungstic acids towards sodium hydroxide. A. M. MORLEY (J. Physical Chem., 1932, 36, 1655—1671).— WO_3 and four standard tungstic acids (A., 1930, 1262) were digested in various concns. of NaOH at 25° for about 200 days. At intervals the amounts of W in solution were determined before and after ultrafiltration. p_{H} measurements showed that neutralisation occurs at once. The WO_4^{2-} formed reacts with the excess of acid to form negative colloids, which are dispersed by low concns. of NaOH , but coagulated by higher concns. The max. amount of acid thus peptised varies with the type of acid. Variation in results may be due to change in the dispersing medium owing to formation of intermediate tungstates, or in the solid or disperse phase, or to the hydrolytic formation of colloidal tungstic acid. J. H. R. (c)

Polyhalides containing fluorine. H. S. BOORN, C. F. SWINEHART, and W. C. MORRIS (J. Amer. Chem. Soc., 1932, 54, 2561—2562).—These compounds may be prepared by chlorinating a mixture of a saturated alkali fluoride solution with 1 equiv. of I , preferably acidified with HCl , until the colour of I disappears, by chlorinating a mixture of 1 mol. of alkali fluoride with 1 g.-atom of I to const. wt., or by treating the acidified saturated fluoride solution with a slight excess of aq. ICl_3 . The compounds CsFICl_2 , m.p. 194° , d 3.565, decomp. above 300° to give CsF , and RbFICl_3 , m.p. 172° , d 3.159, decomp. at about 300° , have been prepared. C. J. W. (c)

Reduction of permanganate by manganous sulphate. P. DUBOIS (Compt. rend., 1932, 194, 2213—2215; cf. A., 1891, 270; 1929, 1156).—The interaction of KMnO_4 and MnSO_4 has been examined by varying relative amounts, concn., temp., and p_{H} of the reactants and solutions; in no case is it represented by $2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$, but the oxide varies from $\text{MnO}_{1.65}$ to nearly MnO_2 . C. A. S.

Preparation and properties of iodine monochloride. J. CORNOC and R. A. KARGES (J. Amer.

Chem. Soc., 1932, 54, 1882—1887).—ICl, m.p. 27.19°, is prepared by adding solid I to an excess of liquid Cl₂, driving off part of the Cl₂ by warming, again adding I to make the composition correspond with ICl, and keeping above the m.p. for 24 hr. V.-p. measurements indicate that ICl is a polar liquid. At a vapour concn. of 0.00507 mol. per litre the entropy of vaporisation is 33.4 g.-cal. The liquid acts as a dissociating solvent for KCl and NH₄Cl.

H. F. J. (c)

Rhenium and its compounds. N. PUSHIN (Bull. Soc. Chim. Yougoslav., 1931, 2, 111—128).—A review of the chemistry of Re. R. T.

Dark blue nickel oxide. M. CENTNERSZWER and H. ZYSKOWICZ (Z. anorg. Chem., 1932, 206, 252—256).—NO has no action on Ni foil between 50° and 150°, but it reacts with Ni powder with the formation of a dark blue Ni oxide. The same oxide is obtained with increasing ease as the temp. rises to 290° in NO, air, or O₂, the readiness of formation increasing for the gases in the order given. Above 290° it passes into yellowish-green NiO. M. S. B.

Supposed isomerism among the pallado-diammines. H. D. K. DREW, F. W. PINKARD, G. H. PRESTON, and W. WARDLAW (J.C.S., 1932, 1895—1909).—The pink and yellow series of compounds of formula PdA₂X₂ (where A is an amine and X an acid radical) are not isomeric. The pink compounds, [PdA₄]PdX₄, are analogues of Magnus' salts. This is shown by the formation of pink compounds from the pallado-tetrammines, [PdA₄]Cl₂, and K₂PdCl₄, by the formation of [PdA₄]PtCl₄ and [PtA₄]PdCl₄, by decomp. of the pink compounds with AgNO₃ (giving [PdA₄](NO₃)₂), and by chlorination under various conditions to give the anticipated products. Similar reactions show the yellow series to consist of monomeric substances corresponding with the α-platinous diammines. Mixed α-tetrammines, [PdA₂A'₂]Cl₂, have been prepared and their decomp. with HCl has been studied. β-Diammines and β-tetrammines are absent from the Pd series. The stereochemistry of the Pd atom is compared with that of the Pt atom (cf. this vol., 562). There are no longer any chemical grounds for assuming *cis*- and *trans*-planar isomerism among Pd compounds. E. S. H.

Spark-in-flame method of spectrographic analysis, and mutual effects of elements on one another's emission. R. HULTGREN (J. Amer. Chem. Soc., 1932, 54, 2320—2328).—A new method of spectrographic analysis, utilising the spectrum of a spark discharge through a flame, overcomes the disadvantages of the low excitation of the flame, and has the advantage that the sample is introduced uniformly into the exciting spark. Elements of low resonance potential, notably Na, introduce error into the determination of other elements. A new type of step sector photometer is described. H. A. S. (c)

Disgregation of insoluble mixtures. A. SCONZO (L'Ind. Chimica, 1932, 7, 145—147).—In the analysis of mixtures of salts containing a constituent insol. in acid, only such constituent and not the whole mixture should be fused with Na₂CO₃ and K₂CO₃. Volatile compounds are liable to be lost entirely during the fusion. T. H. P.

Short method for calculating moisture percentages. N. MCKAIG, jun. (Science, 1932, 75, 612—614). L. S. T.

Photometric micro-analysis of drinking and service water. II, III. C. URBACH.—Sec B., 1932 658.

Determination of active chlorine. J. C. HARRAL and F. W. M. JAFFÉ.—See B., 1932, 641.

Determination of traces of hydrochloric acid in the presence of hydrobromic acid. G. G. LONGINESCU and T. PIRTEA (Bul. Chim. Soc. Romane Stiinte, 1930, 33, 65—67).—The mixture of chloride and bromide is pptd. completely by AgNO₃ after acidifying with HNO₃. The washed ppt. is extracted with dil. aq. NH₃. 1 c.c. of 0.1% KBr is added, the solution acidified with HNO₃ and filtered. Any chloride in the original ppt. now appears as KCl in the filtrate (AgCl + KBr = KCl + AgBr). If on the addition of AgNO₃ the ppt. formed is pure white, and therefore contains no AgBr, the original ppt. must have contained at least 1 mg. of AgCl. The operation may be repeated with successive amounts of 1 c.c. of the KBr solution until a yellow ppt. is obtained; from the amount of KBr used the Cl content of the original mixture can be calc.

A. B. M.

Colour reagents for detecting Cl', Br', and I'. C. PALMERI and G. RIZZI (L'Ind. Chimica, 1932, 7, 147—149).—The reagents recommended are: (1) microcryst. Hg₂CrO₄ mixed with pptd. CaCO₃; (2) powdered Ag₂CrO₄ mixed with pptd. CaCO₃; (3) powdered mixture of AgCNS and Fe₂(SO₄)₃·(NH₄)₂SO₄·24H₂O; (4) solution of Cl₂ in CCl₄, (1) and (2) keep indefinitely and react with halide salts, either dry or in neutral or slightly acid solution, to give sol. chromates, which form yellow solutions; 0.0005% of Cl' is detectable in solution. Reagent (3), which must be stored in a closed vessel in the dark, gives red Fe(CNS)₃ with halide salts, even in highly acid solution. Reagent (4) remains unchanged almost indefinitely. The prep. of the reagents is described. T. H. P.

Colour reaction for the identification of Cl', Br', and I'. A. SCONZO (L'Ind. Chimica, 1932, 10, 573—575).—The test proposed by Palmeri and Rizzi (preceding abstract) is not characteristic of these ions. BaCl₂, forming insol. BaCrO₄, gives no reaction, whilst HgCl₂ producing a slightly sol. chromate shows only a weak coloration. Dil. solutions of KCNS, Na₂S, KIO₃, Na₂S₂O₃, and cyanides as well as CaCO₃ in presence of NH₄ salts give a positive reaction. O. F. L.

Determination of bromides in presence of iodides and chlorides. A. G. BAITSCHIKOV (J. Chem. Ind., Russia, 1931, 8, No. 15—16, 54—58).—Conditions for oxidation with KMnO₄ of I' to IO₃', Br' to Br, and Cl' to Cl₂ are specified. Br and Cl₂ are removed with CHCl₃ and treated with NaHSO₃, giving Br and Cl'. Treatment with MnO₄' under other conditions gives Br but not Cl₂; the Br is then determined iodometrically. CH. ABS.

Analytical application of the reduction of sulphurous acid to hydrogen sulphide. E. DONATH

(Chem.-Ztg., 1932, 56, 483).— SO_2 is reduced to H_2S by SnCl_2 in hot HCl . As and Sb if present are successively pptd. as sulphides. The reaction is sensitive. H. J. E.

Analysis of nitrous oxide by solubility in water. A. L. CHANEY and C. F. LOMBARD.—See B., 1932, 598.

Rationalisation of gravimetric analysis. II. Colorimetric determination of phosphoric acid.

III. Colorimetric determination of phosphoric acid in fertilisers. N. E. PESTOV (J. Chem. Ind., Russia, 1931, 8, No. 15—16, 22—36; No. 20, 15—22).—II. Optimal conditions are specified, and a considerable increase in accuracy is recorded.

III. Details of procedure are given. CH. ABS.

Reduction of phosphomolybdic acid to "molybdenum blue," and the determination of phosphate in biological materials in presence of silicate and arsenate. ERNST TSCHOPP and EMILIO TSCHOPP (Helv. Chim. Acta, 1932, 15, 793—809).—The literature relating to the formation of molybdenum blue, especially by reduction of phosphomolybdic acid by means of phenolic and NH_2 -compounds, is reviewed. The relative reducing activities of many amines and phenols in a solution containing NaHSO_3 and Na_2SO_3 have been determined; reduction occurs in all cases, but is relatively slow for *m*- and *o*-derivatives as compared with *p*-derivatives, and is most rapid and complete with compounds containing an NH_2 group para to an OH group. *p*-Methylaminophenol sulphate in 0.2% solution is suitable for the quant. reduction of phosphomolybdate, since its action is, within wide limits, independent of the acidity of the solution, relatively high salt concns. do not interfere, the depth of colour produced is proportional to the P present, and no reduction of excess MoO_3 takes place; Fe^{2+} and (after addition of HSO_3^-) Fe^{3+} do not interfere, but oxalate, citrate, and tartrate must be absent. For determination of PO_4^{3-} in presence of SiO_3^{2-} or arsenate an excess of HSO_3^- should be added to inhibit formation of complex molybdic acids. Methods based on these considerations for the determination of PO_4^{3-} in, especially, org. materials such as urine, egg, milk, bile, etc., are given in detail. H. F. G.

Colorimetric determination of arsenic. G. E. YOUNGBURG and J. E. FARBER (J. Lab. Clin. Med., 1932, 17, 363—366).—The biological material is oxidised with H_2SO_4 , HNO_3 , and perhydrol; As is pptd. as sulphide, which is oxidised and the As determined colorimetrically after addition of Na_2MoO_4 and SnCl_2 . CH. ABS.

"Chloramine" as reagent. O. TOMÍČEK and B. SUCHARDA (Časopis Českoslov. Lek., 1931, 11, 285—289, 309, 320; Chem. Zentr., 1932, i, 1123).—0.1N-Chloramine-T, which is stable when kept in brown bottles, is applicable to the determination of As^{III} , Sb^{III} (with Me-red), As^{III} , Sb^{III} , Sn^{II} , Fe^{II} , $\text{Fe}(\text{CN})_6^{4-}$, and I^- (potentiometrically). A. A. E.

Determination of soluble silica in volcanic tuffs. A. SREPOPE (Bul. Chim. pura apl. Bukarest, 1929, 32, 37—44; Chem. Zentr., 1932, i, 710; cf. this vol., 588).—Extraction with 10% Na_2CO_3 +1% NaOH or 1% NaOH gives vals. which vary according to the

fineness of the material and the duration of treatment. Al_2O_3 and Fe_2O_3 are also dissolved. L. S. T.

Detection of traces of alkali metals. R. BOSUET (Bull. Soc. chim., 1932, [iv], 54, 681—686).—A solution of the alkali salts is absorbed on a small plate of $\text{Mg}_2\text{P}_2\text{O}_7$ obtained by calcining $\text{Mg}(\text{NH}_4)\text{PO}_4$. The $\text{Mg}_2\text{P}_2\text{O}_7$ is heated on graphite supports in the O_2 - C_2H_2 flame, when it melts to a small ball and practically disappears, the alkali salt having thus been practically all employed in colouring the flame, which is examined spectrographically. The principal spectral rays of the alkali metals are obtained without interference from other rays and the method is extremely sensitive. The following limiting wts. (mg.) were detected: Li 0.5, Na 0.03, K 0.015, Rb 0.015, and Cs 0.03. M. S. B.

Double ferrocyanides and some of their applications. T. GASPAR (Anal. Fis. Quim., 1932, 30, 398—405).—A review of the author's work on the use of double ferrocyanides for the detection and determination of the alkali metals and Tl, determination of Mg, separation of Ca and Mg from Ba and Sr and of Sn from Sb, and for determination of Co.

H. F. G.

Determination of sodium. G. B. VAN KAMPEN and L. WESTENBERG (Chem. Weekblad, 1932, 29, 385—386).—For (*e.g.*) vegetable matter, the sample (5 g.) is ignited and the ash is boiled for a few min. with HCl ; powdered CaO is added until, after boiling for 10 min., the solution is alkaline. The mixture is filtered and the filtrate evaporated to dryness with HClO_4 ; after separation of the pptd. KClO_4 , which should be washed first with 1% HClO_4 solution and then with 96% EtOH , the solution is evaporated to dryness, a small quantity of MgO being added to reduce the danger of explosion. The residue is dissolved in H_2O , the filtered solution is evaporated to about 2 c.c., and a solution of Mg U acetate, prepared by Kahane's method, is added to ppt. Na. The ppt., after drying at 105° , contains 1.5% Na. H. F. G.

Reagent for the lithium ion. Separation of lithium from magnesium. Determination of lithium. Separation of arsenite from arsenate. T. GASPAR (Anal. Fis. Quim., 1932, 30, 406).—The reagent is prepared by adding to a 5% solution of Na_2AsO_4 an excess of aq. NH_3 and then sufficient EtOH to produce turbidity; the solution is filtered, or sufficient H_2O is added to yield a clear solution. With Li the reagent gives a quant. copious faintly pink ppt., which may be dried or ignited, and weighed. If Mg is present it may first be pptd. with NaAsO_2 solution. AsO_4^{3-} may be separated from AsO_2^- by addition of an ammoniacal solution of LiCl containing EtOH . H. F. G.

Indicator for titration of silver. I. F. SIERRA and F. BURRIEL (Anal. Fis. Quim., 1932, 30, 366—371).—KI solution is added slowly to a mixture of 20 c.c. of the solution containing Ag, 1 c.c. of 5% $\text{Cu}(\text{NO}_3)_2$ solution, and a few drops of benzidine sulphate suspension or, for dil. solutions, of benzidine acetate solution; if the solution is stirred vigorously a characteristic greenish-yellow to blue coloration is produced at the end-point, owing to adsorption of Cu benzidine iodide and oxidation products of benzidine by the pptd. AgI . The method is satisfactory for

$N=0.001N$ -Ag solutions and the result is independent of the quantity of indicator present and of the acidity, within fairly wide limits. The error is $<0.5\%$.

H. F. G.

Colorimetric determination of small amounts of silver. E. E. JELLEY (J.S.C.I., 1932, 51, 191—193T).—A rapid and accurate colorimetric method of determining Ag in solutions and suspensions containing 1—20 mg. Ag per litre is based on reduction of ammoniacal Ag solutions by $Na_2S_2O_4$ in presence of gelatin to form clear yellow Ag sols of reproducible shade. The Ag content of Ag and Ag₂S deposits may be determined by adding Br-H₂O to convert the Ag into AgBr and then adding NH₃ to bring the Ag into a solution suitable for reduction by $Na_2S_2O_4$. Cu, Co, Ni, and Cd interfere, and must be separated if present. In particular, a trace of Cu in any of the reagents used gives the sols an orange instead of a yellow colour, and so vitiates the accuracy of the result. As gelatin is added to the ammoniacal Ag solution prior to reduction, any gelatin present in the material for analysis need not be removed.

Volumetric determination of magnesium in presence of free acid and alkali metals. J. CLARENS and J. LACROIX (Bull. Soc. chim., 1932, [iv], 51, 667—668).—Mg can be completely pptd. as $MgCO_3$ by just neutralising the acid solution to the yellow of Me-red with KOH, boiling for about 10 min. with Na_2CO_3 in presence of a little pptd. and dried Al_2O_3 , and titrating the excess Na_2CO_3 in the boiling solution using Me-red as indicator. If Ca is also present the total Mg and Ca must be determined as carbonate and Ca then determined in another sample as oxalate.

M. S. B.

Antimony electrode in electrometric determination of magnesium. B. B. MALVEA and J. R. WITHEROW (J. Amer. Chem. Soc., 1932, 54, 2243—2247).—An electrode of commercial stick Sb, sand-papered smooth, may satisfactorily replace the H electrode in the electrometric determination of Mg in its salts and in presence of Ca salts, if there is not less than 0.10 g. of MgO in 150 c.c. of solution. In fairly conc. solutions a large excess of Ca does not influence the result, but in dil. solutions much smaller amounts cause error. The graph of potential against vol. of alkali added exhibits a sharp inflexion corresponding with the commencement of the pptn. of Mg. A second inflexion marks the completion of pptn., but is so indefinite that the exact end-point of the titration is not readily located. The graph of $\Delta E/\Delta V$ against the vol. of alkali, however, has two well-defined maxima.

E. B. S. (c)

Quantitative spectrum analysis. III. Cadmium contained in zinc oxide. IV. Copper in lead. A. IWAMURA (Mem. Coll. Sci. Kyoto, 1931, A, 14, 327—331, 332—335; cf. A., 1931, 1143).—III. The ZnO is made into a pellet with a little HCl and the intensity of the Cd line at 2288 Å. measured. The method will detect 0.00015% Cd in ZnO.

IV. For the determination of traces of Cu, an org. compound is melted with 20 g. of Pb and the intensity of the Cu line 3274 Å. in the emission spectrum is measured. The sensitivity is 0.00035% Cu in the Pb.

A. R. P.

Traces of copper and lead in conductivity water. N. SCHOORL (Chem. Weekblad, 1932, 29, 338—343).—Methods for the determination of traces of Pb and Cu are reviewed. Removal of Pb from H₂O by shaking with pptd. $CaCO_3$, and determining the Pb colorimetrically, gives accurate results if the $CaCO_3$ is sufficiently fine; with Cu the removal is less complete. Freshly-pptd. $Mg(OH)_2$ removes the last traces of Cu, but it also readily adsorbs humus etc., which interferes with the subsequent colour reaction; Br-H₂O should therefore be added if necessary before the $Mg(OH)_2$ treatment. By this method, also, all As present is transferred to the ppt. Traces of Pb may be removed by $CaCO_3$ in presence of large quantities of Cu if KCN is first added to the slightly alkaline H₂O, and the Cu may be subsequently removed by acidifying the solution and shaking with $Mg(OH)_2$. Full practical details are given.

H. F. G.

Adsorption indicators. I. Iodometry of copper. F. SIERRA (Anal. Fis. Quim., 1932, 30, 359—365).—When a solution of a Cu salt [$CuSO_4$, or preferably $Cu(NO_3)_2$] is added drop by drop to a solution containing $Na_2S_2O_3$, an excess of KI, and 2—3 c.c. of 4% benzidine acetate solution, $Na_2Cu_2(S_2O_3)_2$ is formed under certain conditions of concn. On addition of an excess of Cu⁺⁺ beyond the quantity equiv. to the $Na_2S_2O_3$ originally present the momentary liberation of I causes the appearance of a deep blue coloration, but subsequently a Cu benzidine iodide is produced; this compound forms with the oxidation products of the benzidine present and the $Na_2Cu_2(S_2O_3)_2$ an adsorption complex, and the end-point of the reaction is rendered evident by a characteristic and sharp colour change. The result is influenced considerably by variations of the concns. of the solutions used; a suitable solution contains 20 c.c. of 0.02N- $Na_2S_2O_3$, 10—15 c.c. of 0.2N-KI, and 3 c.c. of 5% benzidine acetate solution, whilst the Cu solution should contain 0.79—7.9 g. of Cu per litre. For more dil. solutions a greater excess of KI should be used with 1 c.c. of indicator solution. Benzidine gives a sharper end-point than does starch in iodometric titrations, but a correction, dependent on the concn. of the solutions used, is usually necessary.

H. F. G.

Volumetric determination of aluminium. J. CLARENS and J. LACROIX (Bull. Soc. chim., 1932, [iv], 51, 668—670).—The free acid is first neutralised by KOH until the red colour of Me-orange added to the solution suddenly decreases in intensity. Me-red is then added and the solution boiled and titrated with KOH to a permanent yellow, the difference between the two readings giving the val. required. When the initial solution is only slightly acid it is advisable to add excess of HCl. The same method is employed if Ca or Mg is present, but in the latter case a little $Mg(OH)_2$ may also be pptd. This can be determined by back-titration with acid and a correction applied. Mg in the solution may then be determined as previously described (see above).

M. S. B.

Physical method of determining ferrous and ferric iron formed by the actions of potassium dichromate and potassium permanganate on ferrous salt. M. PRASAD and P. Y. DESHPANDE

(J. Indian Chem. Soc., 1932, 9, 133—136).—The amounts of Fe^{2+} and Fe^{3+} in solutions obtained by incomplete oxidation of Fe^{2+} with $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 are determined by measuring the absorption borders and comparing them with those of known solutions.

H. B.

Characterisation of trivalent iron with thiocyanates. C. H. LIBERALI (Rev. Soc. Brasil. Chim., 1931, 2, 485—492).—The well-known interference of certain salts etc. with the CNS test for Fe^{3+} is attributed to interaction of the coloured complex ion $[\text{Fe}(\text{CNS})_6]^{3-}$ (cf. Schlesinger and van Valkenburgh, A., 1931, 670) with Cl^- , F^- , Br^- , NO_2^- , $[\text{Fe}(\text{NO}_2)_6]^{3-}$ is probably formed), etc. in neutral media, and can be obviated in many cases by performing the test in a slightly acid solution. Contrary to the observations of Treadwell, small amounts of NO_3^- do not interfere with the test; excess of HNO_3 , as of any other mineral acid, destroys the red colour as H^+ interacts with the $[\text{Fe}(\text{CNS})_6]^{3-}$ complex, forming Fe^{3+} and HCNS . PO_4^{3-} and HPO_4^{2-} interfere in neutral or only slightly acid solutions, FePO_4 being pptd. (with H_3PO_4 , complex ferriphosphate ions may be formed), but in the presence of HCl , PO_4^{3-} , like AsO_4^{3-} , does not interfere. Cu^{2+} (cf. Ag) gives an insol. thiocyanate, and Au^{3+} an insol. complex thiocyanate of unusual type, but with excess of the reagent the colour due to Fe^{3+} appears in the filtrate.

E. L.

Separation of common elements into groups. I. Precipitation by ammonium hydroxide. E. H. SWIFT and R. C. BARTON (J. Amer. Chem. Soc., 1932, 54, 2219—2229).—The separation of Fe, Cr, and Al from Mn, Ni, Co, and Zn by adding aq. NH_3 to the dil. solution in presence of NH_4Cl is most effective when the amount of aq. NH_3 is sufficient to make the solution alkaline to methyl-red, and excess is avoided. If the solution has a vol. of only 3—5 c.c. and is saturated with NH_4Cl , addition of a large excess of aq. NH_3 causes a better separation of Fe from Mn, Ni, Co, and Zn, but 5 mg. of Al and considerably more Cr remain in solution. An excess of aq. NH_3 is essential for separating Bi from Cu, but not for separating Bi from Cd.

W. T. H. (c).

Separation of the ammonium sulphide precipitate. J. KUNZ (Helv. Chim. Acta, 1932, 15, 854—855).— CoS and NiS are separated from the group ppt. by means of dil. HCl . To the acid solution is added NaOAc , and Zn is pptd. by H_2S . The solution is then boiled and rendered strongly alkaline with NaOH , and NaOCl solution is added to ppt. Fe and Mn, Cr and Al remaining in solution as CrO_3^{2-} and aluminate, respectively. The ppt. is dissolved in HCl and basic Fe^{3+} acetate is pptd. from the neutral solution; the Mn may then be pptd. as MnS .

H. F. G.

Transformations of salts of trivalent metals in solution. II. Separation and determination of the violet and green forms of chromic sulphate and of chrome alum. C. MONTEMARTINI and E. VERNAZZA (L'Ind. Chimica, 1932, 7, 432—435).—The violet and green forms of $\text{Cr}_2(\text{SO}_4)_3$ can be separated quantitatively by pptg. the former with EtOH . If not already present in the solution an amount of

K_2SO_4 equiv. to that necessary for the formation of Cr alum should be added, and the concn. of the latter adjusted to about 4—5% before the addition of EtOH , sufficient of which should be added to make its concn. 70%.

O. J. W.

Determination of uranium in carnotite ore. W. W. SCOTT.—See B., 1932, 598.

Determination of tin in ferrotungsten and tungsten ores. K. KIEFER.—See B., 1932, 644.

Automatic micro-compensation calorimeter. L. ALGERA (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 906—917).—An automatic micro-compensation calorimeter for botanical use is described and the accuracy of measurement discussed. W. R. A.

Apparatus for optical studies at high pressure. T. C. POULTER (Physical Rev., 1932, [ii], 40, 860—871).—Selection of materials and constructional methods for high-pressure equipment up to 30,000 atm. are discussed.

N. M. B.

Lens effect of pressure windows. T. C. POULTER and C. BENZ (Physical Rev., 1932, [ii], 40, 872—876; cf. preceding abstract).—Measurements and methods of correction of the lens effect for glass or quartz windows in high-pressure optical systems are discussed.

N. M. B.

Colorimetric determinations. E. CANALS and E. CABANES (Bull. Soc. Chim. biol., 1932, 14, 238—262).—Experiments carried out with I, CuSO_4 , KMnO_4 , methylene-blue, glucose (Lewis-Benedict method), and cholesterol (Grigaut method) to compare the accuracy of colorimetric determinations using the Duboseq colorimeter, the Arsonval differential spectrometer, the Pellin spectrocolorimeter, the method of comparison with standards, and the dilution method, indicate that the first of these gives the best results. The determinations should be made in a dark room using artificial light from a source of variable intensity placed behind a ground-glass screen. The liquid column should be 5—30 mm. high. A technique for the colorimetric determination of cholesterol based on Grigaut's method (J. Pharm. Chim., 1910, 1, 138) is described.

A. L.

C.I.E. colorimetric standards and their use. T. SMITH and J. GUILD (Trans. Opt. Soc., 1932, 33, 73—134).—A discussion based on resolutions of the Commission Internationale de l'Eclairage, 1931.

C. W. G.

New type of interference refractometer. W. E. WILLIAMS (Proc. Physical Soc., 1932, 44, 451—464).—The beam from the central part of the collimator is divided into halves, which are then laterally displaced, and reunited after passing through the gas tubes. Interference patterns are formed at the focal plane of the telescope. A new method of combining it with a spectrograph for dispersion measurements is developed.

C. W. G.

Photochemical technique. I. Simple capillary mercury-vapour lamp. F. DANIELS and L. J. HEIDT. II. Construction and tests of a quartz monochromator. L. J. HEIDT and F. DANIELS (J. Amer. Chem. Soc., 1932, 54, 2381—2384, 2384—2391).—I. A cheap quartz lamp useful as an intense

source of ultra-violet for photochemical investigations and for illuminating the slit of a monochromator is described.

II. Attempts have been made to increase the radiation intensity by using a large monochromator and working under favourable optical conditions.

M. M. (c).

Preparation of dust specimens for microscopical examination. W. SCHEFFER (Angew. Chem., 1932, 45, 148).—The dust is sprinkled sparingly on a slide coated with a thin film of warm gelatin solution; alternatively, the slide may be pressed lightly on the surface from which the specimen is to be taken. Cellulose ester solution or linseed oil films should be used for dusts which may not be wetted. For fine particles which exhibit Brownian movement a 7% gelatin solution is heated for 30 min. on the water-bath with albumin and a little PhOH ; the solution, after decantation, is optically clear.

H. F. G.

Preparation of purified gold electrodes for the spectrograph. T. A. WRIGHT (Met. and Alloys, 1932, 3, 146—150).—Ag is removed as AgCl from the solution in aqua regia; Au is pptd. by SO_2 and aq. NH_3 , redissolved in aqua regia, diluted, and reprecipitated by $\text{H}_2\text{C}_2\text{O}_4$ and aq. NH_3 . The metal is spectroscopically free from Cu, Ag, Ni, Zn, and the Pt group metals. In view of its extreme softness, special precautions are required for cold-rolling or drawing.

E. S. H.

Electroanalysis with rectified alternating currents. I. A. ATANASIU and T. IONESCU (Bul. Chim. pura apl. Bukarest, 1931, 33, 69—74; Chem. Zentr., 1932, i, 707—708).—Pulsating direct current from rectified alternating current is suitable for analysis. The rectifier consists of a Ta plate, 6×1 — 1.5 cm., as anode, a Pb wire 0.9 cm. diameter as cathode, and 750 c.c. of H_2SO_4 , d 1.2, with 1% FeSO_4 , as electrolyte.

L. S. T.

Apparatus for the continuous recording of p_{H} . A. E. J. VICKERS, J. A. SUGDEN, and R. A. BELL (Chem. and Ind., 1932, 545—554, 570—574).—The construction and technique of an apparatus consisting of a glass electrode, a thermionic potentiometer, and a milliammeter or Cambridge thread recorder are described. A pair of matched valves is used as resistances in the potentiometer; the principles of design of thermionic potentiometers are discussed fully. It is claimed that the apparatus eliminates the drift of zero usually experienced with the use of the thermionic valve. Whilst designed particularly for measuring $[\text{H}^+]$ of soils, clays, coloured liquids, cloudy suspensions, and materials which are strongly reactive with dye indicators, or which may have a poisoning effect on the H or quinhydrone electrode, the apparatus is of general applicability, especially when a continuous record is required.

E. S. H.

Mercury electrodes. P. S. TUTUNDZIC (Bull. Soc. Chim. Yougoslav., 1931, 2, 163—174).—A rotating Hg electrode giving accurate results in the electro-titration of Hg and Cu is described. The results obtained for Zn are high owing to oxidation of the amalgam.

R. T.

New gravimetric microanalytical method. J. DONAU (Monatsh., 1932, 60, 129—140).—The author's filtering cup (A., 1912, ii, 199; 1913, ii, 424) has been improved.

E. W. W.

Surface-tension measurement. A. FERGUSON and S. J. KENNEDY (Proc. Physical Soc., 1932, 44, 511—520).—A capillary tube method for determining surface tension, not involving a knowledge of the d of the liquid, is developed. The surface tensions of aq. solutions containing up to 0.6% of $p\text{-C}_6\text{H}_4\text{Me-NH}_2$ have been determined.

C. W. G.

Apparatus for accurate and rapid gas analysis. E. MARTINI (Biochem. Z., 1932, 247, 86—88).—An absorption pipette is described.

P. W. C.

Distillation apparatus for the preparation of very pure water. L. RAMBERG (Svensk Kem. Tidskr., 1932, 44, 130—135).—Two forms of laboratory stills, fitted with special spray arresters and quartz condenser tubes, are described; these are utilised for redistilling ordinary distilled H_2O when a very pure product is required, as in conductivity experiments.

H. F. H.

Apparatus for continuous extraction by chloroform. H. PAGET (J.S.C.I., 1932, 51, 190r).—The apparatus depends on the principle that the vessel containing the aq. solution to be extracted is closed, so that the solvent is forced back into the reservoir.

Direct-reading γ -ray electroscope. L. G. GAMMERT (Proc. Physical Soc., 1932, 44, 445—450).—A Lindemann electrometer, a high resistance, and a special ionisation chamber are used. The γ -ray activity of 1 mg. Ra can be determined to 0.5% in 3 sec.

C. W. G.

Evaporation of Ag, Be, Cr, and Si. C. H. CARTWRIGHT (Rev. Sci. Instr., 1932, [ii], 3, 298—304).—Full experimental details for the prep. of thin films of these elements by evaporation are given.

Nomogram for determining the solubility of brushite in dilute sodium chloride solutions. J. W. H. LUGG (Austral. J. Exp. Biol., 1932, 9, 231—233; cf. A., 1931, 911).—If the p_{H} is known it is possible, with the aid of the nomogram, to calculate, from the inorg. analytical figures of solutions containing small amounts of Ca and P and a preponderance of NaCl over all other salts present, whether there is saturation, under-saturation, or supersaturation with regard to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

W. M.

Calibration of volumetric glassware and analytical weights. ANON. (Paper Trade J., 1932, 94, T.A.P.P.I. Sect., 270—271).—The T.A.P.P.I. tentative standard methods are described.

H. A. H.

Preparation and standardisation of volumetric solutions. ANON. (Paper Trade J., 1932, 94, T.A.P.P.I. Sect., 272—274).

H. A. H.

Determination of coefficients in chemical equations. C. H. LIBERALI (Rev. Soc. Brasil. Chim., 1930, 2, 256—265).—The method of working out the coeffs. for equations of oxidation-reduction reactions by equating the electric charges (valencies) of the participating elements is illustrated.

E. L.

Geochemistry.

Lysimeter investigations. II. Composition of rain water at Geneva, N.Y., for a 10-year period. R. C. COLLISON and J. E. MENSCHING (New York State Agric. Exp. Sta. Tech. Bull., 1932, No. 193, 19 pp.).—The annual average pptn. contained 9 lb. of N (>86% of this as NH_3 and remainder as NO_3), 41 lb. of S, and 16 lb. of Cl per acre. Variations in the proportion of S per annum were less than those of N. HCO_3 occurred at the rate of 12–92 lb. per acre. The mineral contents of rainfall are sufficient to necessitate their consideration in lysimeter trials.

A. G. P.

Conductivity of Belgrade drinking water. P. S. TURUNDŽIĆ (Bull. Soc. Chim. Yougoslav., 1931, 2, 77–95).—The content of dissolved substances may be deduced from the conductivity of drinking water.

R. T.

Mineral water of Rogaske Slatine. A. REZEK (Bull. Soc. Chim. Yougoslav., 1931, 2, 213–223).—The temp. and composition of the waters of two springs have not changed since 1907.

R. T.

Conductivity of Makisch and Sava River water. P. S. TURUNDŽIĆ (Bull. Soc. Chim. Yougoslav., 1932, 3, 33–42).—The conductivity method for determination of salt content gives good results for river and other natural waters.

R. T.

Salts in subterranean waters around Palmyra. V. FROLOW (Compt. rend., 1932, 194, 2153–2155).—The total salts in the waters of a spring at Palmyra, and of two wells, determined throughout a year, vary between 1.27 and 2.29; 1.27 and 3.07; and 1.61 and 6.97 g. per litre, respectively.

C. A. S.

Microbiological lime precipitation in tropical seas. W. BAVENDAMM (Arch. Mikrobiol., 1932, 3, 205–276).—The calcareous sludge from waters surrounding the Bahamas contains S bacteria, cellulose- and carbamide-decomposing organisms, SO_4 -reducing and N-fixing bacteria. Chalk pptn. is essentially a biological process, the mechanism of which is discussed.

A. G. P.

Liquid carbon dioxide in the depths of the ocean. H. WATTENBERG (Nature, 1932, 130, 26).—A crit. discussion relating to the occurrence of plankton.

L. S. T.

"Rain of ashes" at Bucharest in February, 1929. A. STROPOE (Bul. Chim. Soc. Romane Stiinte, 32, 1932, 51–54).—A yellow dust which fell together with snow in a gale of wind in various parts of Roumania consisted mainly of SiO_2 , and was in many respects similar to a volcanic tuff. The presence of humic acid, however, indicated that the dust originated from wind-swept fields bare of snow.

C. I.

Volatile constituents in magma and formation of magmatic residual solutions. P. NIGGLI (Rec. trav. chim., 1932, 51, 633–635).—A general theoretical discussion.

F. L. U.

Minerals containing calcium and antimony. G. NATTA and M. BACCAREDDA (Atti R. Accad. Lincei, 1932, [vi], 15, 389–395).—Various Sb ochres

containing Ca have been examined. Those containing less than about 4% of CaO consist essentially of partly hydrated Sb_2O_3 , but in those containing >12% of CaO the Sb is present as Sb_2O_5 ; the composition of ochres of this second group ranges from $\text{CaO}, \text{Sb}_2\text{O}_5, 3\text{H}_2\text{O}$ to $3\text{CaO}, 2\text{Sb}_2\text{O}_5, 8\text{H}_2\text{O}$. The X-ray spectra of several such ochres have been determined; the crystals are cubic, with a 10.25–10.26 Å. Vals. of $d_{\text{calc.}}$, $d_{\text{obs.}}$ after heating at 750°, and no. of mols. in the unit cell are: romelite, 4.98, 4.71–5.07, 4; atopite, 5.32, 5.03, 8; Galieia ochre, 5.00, 4.30, 4; Cordova ochre, 4.66, 4.21, 8; and China ochre, 4.28, 4.44, 2.

H. F. G.

Ferro-titaniferous mineral from Alto Egitto, in the Arabian Desert. A. STELLA (Atti R. Accad. Lincei, 1932, [vi], 15, 336–339).—A detailed description of a mineral containing about 40% of TiO_2 is given.

H. F. G.

Original materials of oolites of Lorraine and Luxemburg. J. P. AREND (Compt. rend., 1932, 195, 54–56; cf. this vol., 595).—The suggested origin of these deposits is substantiated by analyses of the dried mud deposited from the ferruginous spring at Mondorf, the accompanying marls, the dried parts of molluscs and fish, and of the "green layer."

C. A. S.

Formation of kaolin and alunite in the eastern part of the Polish Mittelgebirge. J. KUHL (Bull. Acad. Polonaise, 1931, A, 665–675).—The kaolin in the clefts in the shale and quartzite in the Mittelgebirge was probably formed by the action on the aluminosilicates of traces of H_2SO_4 , a decomp. product of the co-existing pyrites. The kaolin contains particles of Na_2SO_4 and $\text{Al}_2(\text{SO}_4)_3$, probably formed by the further action of H_2SO_4 .

J. W. S.

Origin of auriferous deposits of jacutinga. E. DE OLIVEIRA (Ann. Acad. Brasil. Sci., 1931, 3, 151–157).—The Au contained in Brazilian jacutinga deposits is of secondary origin. H_2SO_4 formed by oxidation of pyrites reacts with the NaCl and MnO_2 which are also present, and the resulting solution containing free Cl dissolves the Au from the surface deposits and carries it, as AuCl_3 , to the lower strata, where it is reduced to Au by FeSO_4 . Au is found in jacutinga only when the latter occurs below deposits of auriferous quartz pyrites.

H. F. G.

Two nepheline-sodalite-syenites from new localities in Northern Rhodesia. F. D. ADAMS and F. F. OSBORNE (Canad. J. Res., 1932, 6, 571–576).—These rocks, which are similar in chemical composition to lavas found at the north end of Lake Nyassa, are characterised by a low content of binary oxides and the presence of an aluminous ægirine.

E. S. H.

Twin structure and surface indications of rock quartz with reference to the temperature of its formation. O. MUGGE (Z. Krist., 1932, 82, 451–467).—The effect of heating at 609° on quartz of various origins is examined, and from the changes effected in the crystal form etc. a method of determin-

ing the probable conditions as to temp. etc. of the rocks in which it occurs is deduced. C. A. S.

Spinel structures, with and without variate atom equipoints. T. F. W. BARTH and E. POSNJAK (Z. Krist., 1932, 82, 325—341; cf. A., 1931, 1001).—The variate atom equipoint structure is possessed by MgFe_2O_4 (a 8.36 Å.), MgGa_2O_4 (a 8.26), MgIn_2O_4 (a 8.81), TiMg_2O_4 (a 8.41), TiFe_2O_4 (a 8.50), and SnZn_2O_4 (a 8.61): the normal spinel structure by XAl_2O_4 ($\text{X}=\text{Co, Fe, Mn, Ni, and Zn}$). MgIn_2O_4 , TiMg_2O_4 , and SnZn_2O_4 are prepared by prolonged heating of the constituent oxides in the required proportions at temp. $>1300^\circ$ for MgIn_2O_4 ; TiFe_2O_4 by heating in vac. TiO_2 , Fe_2O_3 , and Fe at 1150° . C. A. S.

Magnesium-gallium spinel. F. MACHATSKI (Z. Krist., 1932, 82, 348—354; cf. this vol., 12, and preceding abstract).—The distribution of cations in MgGa_2O_4 is different from that required by strict structure theory, Ga and Mg being largely interchangeable. This may be due to rapid cooling of the artificial crystals, or to the two cations having

nearly identical space requirements, but is certainly not uncommon in similar compounds (cf. A., 1930, 1137). C. A. S.

Spanish vanadinite. F. M. MARTIN (Anal. Fis. Quim., 1932, 30, 377—383).—A specimen of vanadinite from Albuñuelas had d_{15}^{25} 6.94 and contained Pb 71.98%, VO_3 22.33%, AsO_4 2.33%, and Cl 2.49%. The AsO_4 content is thus intermediate between the amounts found in vanadinite from Arizona (5.2%) and in that from Sierra Grande (1.6%). V should not be determined as V_2O_5 if As is present. H. F. G.

Presence of germanium in Brazilian metallic meteorites. H. E. DE ARAUJO (Rev. Soc. Brasil. Chim., 1931, 2, 365—369).—0.1% of Ge sulphide was isolated from a meteorite from Sta. Lucie de Goyaz, where it occurs in the "graphitic fraction." Ge was also found and identified spectroscopically in two other meteorites and may be of more general occurrence. E. L.

Collinsies of minerals. XXII. H. COLLINS (Chem. News, 1932, 144, 427—430).

Organic Chemistry.

Co-ordinative theory of the constitution of organic compounds. G. URBAIN (Compt. rend., 1932, 194, 1993—1997).—The electrovalency of C in org. compounds varies from +4 (as in CCl_4 , where C has lost all its peripheral electrons) to -4 (as in CH_4 , where C has 8 electrons in its second group). Various examples are discussed. H. B.

Simple organic compounds of radial structure. H. J. BACKER (Natuurwetensch. Tijds., 1932, 14, 175—177).—Radial compounds CX_4 are characterised by small mol. cohesion, stability of the cryst. phase, small temp. range of the liquid phase, simple cryst. form, inertness, and tendency to ring formation. H. F. G.

Active product of the reaction of sodium vapour with alkyl halides. M. POLANYI and D. W. G. STYLE (Naturwiss., 1932, 20, 401—402).—When the reaction products of Na vapour on MeBr or EtBr (cf. A., 1931, 174) are immediately swept into an atm. of Cl_2 or I the corresponding alkyl chloride or iodide is formed, thus affording additional evidence of the momentary existence of the free alkyl radical. A. R. P.

Thermal decomposition of isopentane in presence of silica gel. MAILHE and CREUSOT (Compt. rend., 1932, 194, 2220—2222).—Thermal decomp. of 1000 g. of isopentane in presence of silica gel at 680° /atm. pressure affords 750 litres of gas containing CH_4 , C_2H_2 , C_3H_6 , and butadiene and 245 g. of liquid, b.p. $<20^\circ$ to $>280^\circ$ (condensed by solid CO_2), rich in ethylenic and aromatic hydrocarbons. J. L. D'S.

Polymerisation of diolefines with olefines. I. Isoprene and Δ^2 -pentene. C. A. THOMAS and W. H. CARMODY (J. Amer. Chem. Soc., 1932, 54, 2480—2484).—Isoprene and Δ^2 -pentene (I) react in presence of AlCl_3 to form hydrocarbon-sol. and

-insol. polymerides. The quantity of the sol. polymeride formed is a function of the amount of (I) present, whilst its hardness is an inverse function of the quantity of (I) used. The quantity of the insol. polymeride is also an inverse function of the (I) present. The sol. resin polymeride, exposed in a thin film to air, slowly oxidises, thereby becoming harder; the I val. gradually decreases whilst the acid val. increases; O_3 is rapidly absorbed by this polymeride in CCl_4 , but the product, after absorption ceases, has an I val. as high as 140 (in some cases). The insol. polymeride, $(\text{C}_5\text{H}_8)_x$, begins to depolymerise about 116° ; it is decomposed by strong acids and gives reddish-violet colorations (with decomp.) with phenols. No insol. polymeride is formed when (I) is treated with AlCl_3 . C. J. W. (6)

Preparation of pure octene. H. I. WATERMAN and T. W. TE NUYL (Rec. trav. chim., 1932, 51, 533—537).—The preps. of octan- β -ol from castor oil and thence of octene, b.p. 121.6 — $123.6^\circ/760.2$ mm., are described. Octan- α -ol gives an octene similar in physical properties. R. S. C.

Fluorine derivatives of chloroform. H. S. BOOTH and E. M. BIXBY (Ind. Eng. Chem., 1932, 24, 637—641).— CHCl_2F , b.p. 13.5 — 15.5° , m.p. -127° , is prepared from CHCl_3 (containing a little CS_2), SbF_3 , and a little SbCl_5 at room temp., whilst *chlorodifluoromethane*, b.p. -39.8° , m.p. -147° to -146° , is formed from CHCl_3 , SbF_3 , and SbCl_5 at 100° under pressure. CHF_3 could not be obtained from CHCl_3 , SbF_3 , and SbCl_5 at 200° (bath) under pressure. The toxicity (towards guinea-pigs) of the above compounds decreases with increase in the no. of F atoms substituted for Cl. H. B.

Action of ultra-violet light on halogenated hydrocarbons. I. Action on tetrachloroethane.

E. MULLER and A. LUBER (Ber., 1932, 65, [B], 985—987).—Irradiation of $\text{CHCl}_3\text{-CHCl}_2$ through which moist air is passing results in the production of HCl , $\text{CHCl}_3\text{-CO}_2\text{H}$, and *octachlorobutane*, m.p. 81° . The hypothesis that the primary change is loss of HCl with formation of $\text{CHCl}_2\text{-CCl}$, which combines with activated O to produce $\text{CHCl}_2\text{-COCl}$, is supported by the production of $\text{CHCl}_2\text{-CO-NH}_2$ by the action of NH_3 on the solution remaining when dry air is used. $\text{H}_2\text{C}_2\text{O}_4$ is produced in small amount. $\text{C}_2\text{H}_2\text{Cl}_4$ appears stable towards O_2 at room temp. Similar irradiation of CHCl_3 produces COCl_2 and C_2Cl_6 .
H. W.

Synthesis of aliphatic alcohols by catalytic reduction of carbon monoxide. G. NATTA and R. RIGAMONTI (Giorn. Chim. Ind. Appl., 1932, 14, 217—225; cf. B., 1931, 874).—The catalytic reduction of CO by H_2 under pressure and in presence of ZnO and KOAc yields MeOH , higher aliphatic alcohols, about 0.9—1.1% of aldehydes and ketones, 0.02—0.5% of hydrocarbons, 1.4—2.4% of free acids, and 2.5—2.6% of esters. The proportion of alcohols higher than MeOH may be increased somewhat by increasing the amount of alkali metal in the catalyst, but the effect is small over the range 14—9% K_2O . The methods used for separating and identifying the different alcohols are described in detail. Besides MeOH , the following are formed: Bu^nOH , 51.3—46.6; Pr^nOH , 13.1—11.6; $\text{CHMeEt-CH}_2\text{-OH}$, 4.9—4.8; EtOH , 3.3—4.2; Pr^iOH , 2.6—3.7; $\text{CHMePr-CH}_2\text{-OH}$, 2.5; BuOH , 1.8—2.0; $n\text{-C}_5\text{H}_{11}\text{-OH}$, 0.4, and β -methylhexanol, 1.6%; γ -methylpentanol, *iso*- $\text{C}_4\text{H}_9\text{-OH}$, $\text{CHMePr}^i\text{-CH}_2\text{-OH}$, $\text{CHEtPr}^i\text{-OH}$, $\text{CHPr}^i\text{-OH}$, $\text{CHPr}^i\text{-OH}$, *tert*- BuOH , and *tert*- $\text{C}_5\text{H}_{11}\text{-OH}$, all in small proportions. The alcohols formed contain 94.7—98.4% or, excluding MeOH , 87.5—90.1% of primary alcohols. Among the normal-chain alcohols, those with odd nos. of C atoms predominate, and among the ones with branched chains, those with the Me in the β -position to the OH .
T. H. P.

Preparation of mixed ethers. R. TRUCHET and M. GRAVES (Bull. Soc. chim., 1932, [iv], 51, 686—689).—The action of alkyl arylsulphonates on Na alkoxides gives 55% yield of ethers.
A. A. L.

Ethyl ethers of α -glycols, and the ketones obtained by their dehydration. IV. D. BARDAN (Bul. Chim. Soc. Romane Stiinte, 1930, 33, 25—32; cf. this vol., 368).—*iso*-Valeryl chloride (from the acid with SOCl_2) gives the α -Br-derivative, converted into the Et ester, which gives *Et α -ethoxyisovalerate*, b.p. $73\text{--}76^\circ/31$ mm. From this the following are obtained with the appropriate Grignard reagent: γ -ethoxy- β -methyl- δ -ethylhexan- δ -ol, b.p. $74\text{--}77^\circ/19$ mm. (60%); γ -ethoxy- β -methyl- δ -propylheptan- δ -ol, b.p. $105\text{--}109^\circ/20$ mm. (70%); γ -ethoxy- β -methyl- δ -butyloctan- δ -ol, b.p. $143\text{--}145^\circ/26$ mm.; and γ -ethoxy- β -methyl- δ -diphenylbutan- δ -ol, b.p. $204\text{--}209^\circ/17$ mm. Conversion of these substances into the following ketones is best effected by treatment with P_2O_5 in anhyd. pyridine, followed by hydrolysis with 20% H_2SO_4 : β -methyl- δ -ethylhexan- γ -one, b.p. $52\text{--}54^\circ/21.5$ mm. (yield 80%); β -methyl- δ -propylheptan- γ -one, b.p. $74\text{--}78^\circ/23$ mm.; β -methyl- δ -butyloctan- γ -one,

b.p. $116\text{--}121^\circ/14$ mm.; and δ -diphenyl- β -methylbutan- γ -one, b.p. $159\text{--}165^\circ/21$ mm.
A. A. L.

Alkyl peroxides and ozonides. A. RIECHE (Angew. Chem., 1932, 45, 441—444).—A review.

Glycerophosphoric acids. G. CARRARA (Giorn. Chim. Ind. Appl., 1932, 14, 236—237).—The two free OH of the glycerol residue in α -glycerophosphates are vicinal and, like analogous glycols (Criegee, A., 1931, 461) and unlike β -glycerophosphates, these compounds are readily oxidised by Pb(OAc)_4 , which is converted into Pb(OAc)_2 . As the tetra-acetate liberates I from KI , α -glycerophosphates may be determined accurately by means of this reaction. When tested in this way, Ca glycerophosphate poly. F.U.VI (Erba) proves to be the almost pure α -compound; it is readily convertible into the Na salt (Charpentier and Bocquet, this vol., 251). The quinine α - and β -compounds show the m.p. given by King and Pyman (J.C.S., 1914, 105, 1238). During the alkaline hydrolysis of the di-esters of glycerophosphoric acid, 20—40% of a polyglycerol polyphosphate (?) is formed.
T. H. P.

Metallic compounds of the enolic forms of monocarbonyl compounds. XIV. Action of sodium alkoxide on esters, ester-condensation, and substitution reactions of metallic compounds of esters. H. SCHEIBLER (Ber., 1932, 65, [B], 994—999).—Mainly a reply to Adickes (this vol., 599) and Hückel ("Theoret. Grundlagen d. organ. Chemie," 1931, Vol. I, p. 188). The course of the reaction between BzOEt and NaOEt is represented, $\text{BzOEt} + \text{NaOEt} \rightarrow \text{NaOBz} + \text{C}_2\text{H}_5 + \text{EtOH}$. The production of the salt is not quantitatively explicable by assuming the action of "traces of H_2O ."
H. W.

Addition of alkali alkoxides to esters. VII. Kinetics and statics of the decomposition of ethyl formate by sodium ethoxide. F. ADICKES and G. SCHAFER [with, in part, W. BRUNNERT] (Ber., 1932, 65, [B], 950—955; cf. this vol., 614).—The course of the change is observed by measurement of the CO evolved during the action of alkali alkoxide on HCO_2Et in EtOH . The rate is independent of the initial concn. of ester and directly proportional to the NaOEt concn. Na^+ (HCO_2Na , NaOAc) is without catalytic action. KOEt is more powerful than NaOEt , whilst Ca(OEt)_2 is still less active and Al(OEt)_3 without action. The results do not throw light on the mechanism of the change. Solubility data of HCO_2Na in anhyd. EtOH and in NaOEt-EtOH are recorded.
H. W.

Oxidation and degradation of various sugars and their decomposition products. XIII. Conversion of acetic into succinic acid. K. BERNHAUER and W. STEIN (Biochem. Z., 1932, 249, 219—222).— AcOH (50 g.) on oxidation with $\text{K}_2\text{S}_2\text{O}_8$ gave 0.2 g. succinic acid. The smallness of the yield is due to further oxidation of succinic acid to HCO_2H , AcOH , and CO_2 .
P. W. C.

Preparation of branched-chain fatty acids of high mol. wt. H. RUPE and E. WILL (Helv. Chim. Acta, 1932, 15, 842—853).—Heptaldehyde, COMe_2 , and 3% NaOH first at 0° and then at room temp. give *Me β -hydroxyoctyl ketone* (I), b.p. $128\text{--}129^\circ/10$

mm., *di-β-hydroxyoctyl ketone* (3—5% yield), m.p. 85—86°, and Δ^7 -decen- β -one (II), b.p. 105°/10 mm. (β -semicarbazidosemicarbazone, m.p. 172°) [also formed when (I) is heated in vac. with a little I]. (II), when hydrogenated (Ni) in 75% EtOH and subsequently oxidised by Beckmann's mixture, gives *n*-decan- β -one, b.p. 92°/10 mm., m.p. 2·5° (*semicarbazone*, m.p. 126°), which with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Zn in hot, dry C_6H_6 yields *Et* β -hydroxy- β -methylundecate, b.p. 157°/10 mm., dehydrated, best by distillation at 60—70 mm. with anhyd. ZnCl_2 , to *Et* β -methyl- Δ^7 -undecenoate, b.p. 142—143°/10 mm. This was hydrogenated (Ni), best in 90% EtOH at 60—70 atm., to *Et* β -methylundecate, b.p. 134°/10 mm., hydrolysed to the corresponding acid, b.p. 165·5°/10 mm. (K, Na, and Cu salts) (together with a small amount of an acid, b.p. 185°/10 mm.), the acid chloride of which, an oil (prepared by SOCl_2), with ZnMe_2 , gives *Me* β -methyldecyl ketone, b.p. 129°/10 mm. (*semicarbazone*, m.p. 81·5°). From this by similar methods were prepared: *Et* β -hydroxy- $\beta\delta$ -dimethyltridecate, b.p. 170—175°/11 mm., *Et* $\beta\delta$ -dimethyl- Δ^7 -tridecenoate, b.p. 160°/10 mm., $\beta\delta$ -dimethyltridecoic acid, b.p. 183—184°/10 mm. (*Et* ester, b.p. 153°/10 mm.; Na salt: acid chloride, b.p. 162—163°/10 mm.), *Me* $\beta\delta$ -dimethyldodecyl ketone (III), b.p. 162°/10 mm. (*semicarbazone*, m.p. 77°), *Et* β -hydroxy- $\beta\delta\zeta$ -trimethylpentadecate (impure), b.p. 203—205°/11 mm., *Et* $\beta\delta\zeta$ -trimethyl- Δ^7 -pentadecenoate (IV), b.p. 191—192°/10 mm., $\beta\delta\zeta$ -trimethylpentadecoic acid, b.p. 209—210°/10 mm. (Na salt; *Et* ester, b.p. 189°/10 mm.). (IV) was reduced only at 50°. (III) with MgBu^nBr gives impure $\epsilon\eta$ -trimethylheptadecan- ϵ -ol, b.p. 173—175°/9 mm., yielding (probably) impure $\epsilon\eta$ -trimethyl- Δ^8 -heptadecene, b.p. 168°/10 mm. η is recorded for the new compounds, whence the average val. $+0\cdot272 \times 10^{-5}$ for log is obtained for the grouping $\cdot\text{CHMe}\cdot\text{CH}_2\cdot$ in agreement with the lit. R. S. C.

Fatty acids associated with cassava starch. L. LEHRMAN (J. Amer. Chem. Soc., 1932, 54, 2527—2530).—The fatty acids liberated during the hydrolysis of cassava starch (free from extraneous fatty materials) are palmitic, oleic, linoleic, and linolenic. The detection of small amounts of linolenic acid in presence of oleic and linoleic acids by bromination is better than oxidation. The test for phytosterol was negative. C. J. W. (b)

Unsaturated fatty acids and their derivatives.
II. Configuration of tetrabromostearic acid from linoleic acid. T. MARUYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, 8, 186—189).—The tetrabromostearic acid, m.p. 114°, from linoleic acid is treated with EtOH-KOH at 0° for 120 hr. or at 20° or 35° for 20 hr. and the Me ester of the resulting Br₂-acid (I) oxidised by Armstrong and Hilditch's method (A., 1925, i, 355); Me H sebacate and tartronic [from CHBr(CO₂H)₂] and *n*-valeric acids are thereby obtained. (I) is, therefore, 9*a*-dibromo-Δ¹⁴-octadecadienoic acid. Dehalogenation at 50° gives 6-bromo-Δ¹⁴-octadecatrienoic acid (oxidation products, H₂C₂O₄, *n*-valeric and α-hydroxysebacic acids); at 80°, Δ¹⁴-octadecatetraenoic acid (oxidised to H₂C₂O₄, suberic and *n*-valeric acids) results. Elimination of HBr occurs simultaneously with almost

equal readiness between the μ - and κ - and the μ - and ν -C atoms to give (1). Linoleic acid is considered to have the *cis-cis*-structure; the grouping, $\begin{array}{c} \text{Br Br} \quad \text{H H} \\ | \quad | \quad | \quad | \\ \cdot \text{CH}_2 \cdot \text{C} - \text{C} \cdot \text{CH}_2 \cdot \text{C} - \text{C}_{(6)} \cdot \text{C}_{(n)} \text{H}_n \cdot \end{array}$, probably occurs in the Br_4 -acid. H. B.

Action of hydrazine polysulphide on oleic acid.
J. VORIŠEK (Chem. Listy, 1932, 26, 285—286).— N_2H_4 polysulphide and oleic acid yield a mixture of the hydrazones of oleic and stearic acid. R. T.

Hydrogenation of linoleic acid. I. Ethyl linoleate. H. VAN DER VEEN (Chem. Umschau, 1932, 39, 104—109).—Et linoleate (prepared from linoleic acid tetrabromide by Rollett's method) was hydrogenated at 200° with a Ni-kieselguhr catalyst (reduced at 500°), and the reaction was followed by thiocyanometric analysis. The first stage of the reaction converting linoleic into Δ^6 -octadecenoic acid was highly selective, <9% of stearic acid (checked by the Bertram method) being formed. Under the given conditions no wandering of the double linking occurred, the octadecenoic acids produced consisting of about equal proportions of Δ^6 -oleic and elaidic acids (cf. Suzuki and Inoue, B., 1930, 956). E. L.

Odour and constitution of some alkoxy-acids and their esters. I. B. ROTHSTEIN (Bull. Soc. chim., 1932, [iv], 51, 691—696).—The action of $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ on the appropriate Na alkoxide gives the following alkoxyacetic acids: *n*-heptyl-, b.p. $157^\circ/18$ mm. (*Me* ester, b.p. $115^\circ/18$ mm.; *Et* ester, b.p. $123.5^\circ/16$ mm.) (60%); octyl-, b.p. $162^\circ/15$ mm. (*Me* ester, b.p. $119^\circ/15$ mm.; *Et* ester, b.p. $125^\circ/13$ mm.) (A., 1929, 1174); benzyl-, b.p. $180\text{--}182^\circ/15$ mm. (*Me* ester, b.p. $136.5^\circ/15$ mm.; *Et* ester, b.p. $143^\circ/15$ mm.); phenylethyl-, m.p. 46° , b.p. $183^\circ/14$ mm. (*loc. cit.*) [*Me* ester, b.p. $145^\circ/13$ mm.; *Et* ester, b.p. $153^\circ/16$ mm.] (50%); phenylpropyl-, m. p. 55° , b.p. $198^\circ/15$ mm. (*Me* ester, b.p. $157^\circ/14$ mm.; *Et* ester, b.p. $162\text{--}163^\circ/15$ mm.); rhodiny-, b.p. $180\text{--}181^\circ/16$ mm.: and geranyl-, b.p. $180^\circ/16$ mm., $143^\circ/0.86$ mm. (*Et* ester, b.p. $155\text{--}157^\circ/16$ mm.).

Electrolytic oxidation of aliphatic dicarboxylic acids. E. A. TOMMILA (Ann. Acad. Sci. Fennica, 1932, 36, 114 pp.).—The anodic oxidation products of a no. of aliphatic dicarboxylic acids have been determined, mostly in strongly alkaline solutions ($5N\text{-NaOH}$), but in some cases in presence of $2N\text{-H}_2\text{SO}_4$ or without any addition. Electrodes of polished and platinised Pt, Fe, and Ni were used in the alkaline solutions, and Pt and PbO_2 in the acid solutions. The course of the oxidation varies with the composition of the electrolyte, and with the nature and material of the anode. In general, the anodic oxidation of malic acid in alkaline solution gives relatively large yields of malonic acid (by oxidation of the univalent malate ion), MeCHO (from the bivalent malate ion), and $\text{H}_2\text{C}_2\text{O}_4$ (especially at low potentials and at anodes of Ni or Fe). Secondary changes and the mechanisms of the reactions involved are discussed. In H_2SO_4 solution the current efficiency is low, except with PbO_2 anodes, and the

products of oxidation are malonic acid, HCO_2H , AcOH , MeCHO , CO , and CO_2 , no $\text{H}_2\text{C}_2\text{O}_4$ being obtained; in this case the undissociated malic acid is the depolariser, rather than the malate ions. The anodic oxidation products of oxaloacetic acid are mainly CO_2 and MeCHO in acid solution, but in alkaline solution a yellowish-red condensation product of unknown composition is produced. Malonic acid in alkaline solution is oxidised electrolytically mainly to CO_2 , with some $\text{H}_2\text{C}_2\text{O}_4$ and HCO_2H (probably indicating tartronic acid as intermediate). No CO or hydrocarbon is formed. Alkaline mesoxalic acid gives equiv. amounts of CO_2 and $\text{H}_2\text{C}_2\text{O}_4$ in quant. yield, whilst the acid solution is oxidised to CO_2 alone. Succinic acid is oxidised with difficulty to CO_2 , accompanied by traces of org. acids. Alkaline solutions of maleic or fumaric acid are oxidised anodically with difficulty; the products are CO_2 , a little $\text{H}_2\text{C}_2\text{O}_4$ (not found with fumaric acid), and traces of MeCHO and HCO_2H . Tartaric and meso-tartaric acids give approx. equal yields of HCO_2H and CO_2 . A comparison of the c.d.-p.d. curves shows oxaloacetic and mesoxalic acids to be the best depolarisers. The following general conclusions are reached: (1) ease of electrolytic oxidation increases with the no. of O atoms in the mol.; (2) a double linking has no special influence on anodic oxidisability; (3) a CH_2 group is more easily oxidised when situated between two CO_2H groups than in any other position; (4) oxidation proceeds more readily the lower is the $[\text{H}^+]$ of the solution; (5) the products contain a smaller no. of C atoms than the original substance; (6) univalent ions having OH attached to a middle C atom produce aldehydic acids, which subsequently undergo further oxidation, but, if two OH radicals are attached, acids are produced directly; (7) bivalent ions having O attached to a middle C atom are oxidised with elimination of both CO_2H groups; (8) hydroxylation is the first process to occur when the acid does not already contain a OH radical attached to a central C atom.

E. S. H.

Chromic acid oxidation of dicarboxylic acids. L. SEMICHON and M. FLANZY (Compt. rend., 1932, 194, 2063—2065).—Oxidation of dibasic acids (oxalic—adipic) (0.05 g. in 10 g. of H_2O) with CrO_3 (0.525 g.) in 5 c.c. of H_2SO_4 (d 1.71) proceeds more slowly than with the monobasic acids (this vol., 719). Oxidation of the acids above succinic is favoured by the presence of $\mu\text{-CH}_2$ groups (adipic is oxidised more rapidly than glutaric at 100°), and succinic acid (which is oxidised slowly at 100° after 3 hr.) is the intermediate. OH-acids are oxidised to CO_2 and H_2O ; CH_2O is an intermediate.

H. B.

Action of peracetic acid on mono- and di-allyl-malonic and -acetic acid. J. BOESEKEN (Rec. trav. chim., 1932, 51, 551—556).—Mono- and di-allyl-malonic and -acetic acids are slowly oxidised by AcO_2H in AcOH . Oxidation is fastest if the unsaturated group contains a CH_2 group and is affected by the nature of the other substituents. The following are described: Et_2 β -hydroxy- γ -acetoxy- n -propylmalonate, b.p. $127\text{--}145^\circ/\text{cathode vac.}$; β -lactone of $\beta\gamma$ -dihydroxy- n -propylmalonic acid, an oil, and its γ -Ac derivative,

an oil; compound $\begin{array}{c} \text{CO}-\text{O} \\ | \quad | \\ \text{CH}_2-\text{CH}_2 \end{array} > \text{CH}-\text{CH}_2-\text{CO}_2\text{Me}$, an oil; γ -hydroxy- κ -acetoxy- n -undecenoic acid, an oil.

R. S. C.

Ether-like compounds. VI. Synthesis of ether-lactones from di-etheral acids. M. H. PALOMAA and Y. T. JARVENKYLA (Ber., 1932, 65, [B], 923—925; cf. A., 1931, 1033).—Hydroxyethoxy-acetolactone, b.p. 213° , m.p. 26.7° , is obtained in 70% yield by gradually heating β -methoxyethoxy-acetic acid with 67% HBr to 150° , distilling the residue under atm. pressure, repeated addition and expulsion of small amounts of H_2O , and final distillation; m.p., d , and n increase with age of the product. α - β -Methoxyethoxypropionic acid, b.p. $105\text{--}108^\circ/1.5$ mm., does not yield the corresponding ether-lactone when similarly treated, probably because of the secondary linking of the intermediate O atom.

H. W.

Preparation of ammonium l-tartrate. E. G. KELLETT (J.S.C.I., 1932, 51, 204T).— d -Tartaric acid is racemised by boiling with excess of NaOH , and the concn. and acidity of the resulting solution are so adjusted that Na H racemate is salted out practically pure. Cinchonine H tartrate is prepared by direct interaction of Na H racemate and cinchonine hydrochloride. A rapid method of controlling the process of resolution by observations of crystal form is described.

Sugar acids. I. Products obtained by the action of phosphorus pentachloride on mucic acid. K. BERNHAUER and A. IGLAUER. II. Preparation of d -mannonic acid. III. Preparation of gluconic acid. K. BERNHAUER and K. IRBANG (Biochem. Z., 1932, 249, 211—215, 216—218, 227—233).—I. By the action of PCl_5 on mucic acid two chlorohydroxymuconic acids are obtained (as Me esters), one, m.p. 196° , probably the precursor of Me_2 d -dichloromuconate, m.p. 156° , and the other, m.p. 110° , the precursor of Me_2 β -dichloromuconate. Hydrolysis of the first ester gives an acid which sublimes without melting above 260° .

II. The hydrolysis of ivory-nut meal and the electrolytic oxidation of the mannose syrups are described. The yield of crude Ca mannonate was 110% on the mannose oxidised.

III. The oxidation of glucose to gluconic acid by Br under various conditions is studied. P. W. C.

Selenium dioxide, a new oxidising agent. I. Its reaction with aldehydes and ketones. H. L. RILEY, J. F. MORLEY, and N. A. C. FRIEND (J.C.S., 1932, 1875—1883).— SeO_2 has a sp. oxidising action on aldehydes ($\text{CH}_2\text{R}\cdot\text{CHO}$) and ketones ($\text{CH}_2\text{R}\cdot\text{COR}'$); α -ketoaldehydes and $\alpha\beta$ -diketones are thereby produced. When the CH_2 is activated by proximity to a negative group, oxidation proceeds at moderately low temp. The reactions are sometimes carried out in presence of EtOH . The SeO_2 is recovered by ignition or oxidation of the pptd. Se with HNO_3 and sublimation. The following are prepared: $(\text{CHO})_2$ from MeCHO ; AcCHO from COMe_2 and EtCHO ; $\text{EtCO}\cdot\text{CHO}$ from COMeEt and PrCHO ; BzCHO from COPhMe and $\text{CH}_2\text{Ph}\cdot\text{CHO}$; Ac_2 from COMeEt ; AcCOEt from COEt_2 ; AcCOPh from COPhEt ;

cyclohexane-1:2-dione (I) from cyclohexanone; cyclopentane-1:2-dione from cyclopentanone; buchucamphor (diosphenol) from menthone. The enol content of freshly-distilled (I) is small; the amount increases gradually during 2 months to an equilibrium val. of about 40%. Fructose gives a red ppt. of Se when boiled with SeO_2 in acid solution; glucose, lactose, and maltose do not, whilst prolonged boiling is necessary with sucrose. H. B.

Stereoisomerism of unsaturated compounds.

I. Composition of crotonaldehyde. W. G. YOUNG (J. Amer. Chem. Soc., 1932, 54, 2498—2503).—Oxidation of commercial ("niacet") and *trans*-crotonaldehydes (prepared from the commercial material by treatment with HCl and sunlight) with O_2 below 30° and $\text{Ag}_2\text{O}-\text{H}_2\text{O}$ at $15-20^\circ$ gives *trans*-crotonic acid in each case; some *cis*-acid is produced when the temp. is not controlled. The *cis*-acid obtained by Kauffler (A., 1929, 1423) is probably formed by stereomutation of the *trans*-form during the oxidation. C. J. W. (b)

Polyen compounds. I. Condensation products of crotonaldehyde and β -methylcrotonaldehyde. K. BERNHAUER and E. WOLDAN (Biochem. Z., 1932, 249, 199—210).—The prep. of β -methylcrotonaldehyde, b.p. $24-37^\circ/12$ mm. (acetal, b.p. $55-62^\circ/12$ mm.), is described. Fractionation of its condensation products gives a fraction, b.p. $72-74^\circ/0.5$ mm., probably *dimethyloctatrienal* (*p*-nitrophenylhydrazone, m.p. 139° ; *semicarbazone*, m.p. 195° ; *azide*, m.p. 140°), and a fraction, b.p. $132-135^\circ/0.4$ mm. probably β -methylcrotonaldehyde aldol (*p*-nitrophenylhydrazone, m.p. 234° ; *semicarbazone*, m.p. 222°). P. W. C.

Glyceraldehyde- γ -phosphoric acid. II. Calcium salt. H. O. L. FISCHER and E. BAER (Ber., 1932, 65, [B], 1040—1041; cf. this vol., 364).—Ca glyceraldehyde- γ -phosphate dihydrate is obtained from the acid and $\text{Ca}(\text{OAc})_2$ in H_2O . H. W.

Mechanism of the diacetyl reaction of guanidines, their reactions and application to the colorimetric determination of creatine and arginine. K. LANG (Z. physiol. Chem., 1932, 208, 273—280).—Diketones of the type of Ac_2 combine with guanidines in alkaline solution, giving violet-coloured products. 2 mols. of AcBz unite with 3 mols. of creatine. This is the basis of a colorimetric micro-method for the determination of creatine in muscle extracts and of arginine in proteins. The error does not exceed 5%. J. H. B.

Thermal decomposition of acyloins. M. URION (Compt. rend., 1932, 194, 2145—2146; cf. A., 1930, 1160).— δ -Ketohexan- γ -ol at 320° in presence of Al_2O_3 and pumice gives EtCHO and dipropionyl. Similarly, acetal gives MeCHO and Ac_2 , and glycidic gives acetaldehyde, acetal, and the products from the latter. Pyruvic acid at 300° in presence of Cu gives mainly methylsuccinic acid, MeCHO , Ac_2 , methylglyoxal, and CO_2 . A. A. L.

Preparation of tetrathiopentone. S. A. KARASIEWICZ (J. Amer. Chem. Soc., 1932, 54, 2556—2557).—I (20 g.) in COMe_2 (60 c.c.), treated with H_2S for 7 hr., gives 20 g. of tetrathiopentone, m.p.

$170-171^\circ$; reduction with Na in liquid NH_3 gives Pr^{SH} . C. J. W. (b)

Course of the oxidation of aldose sugars by bromine water. H. S. ISHELL and C. S. HUDSON (Bur. Stand. J. Res., 1932, 8, 327—338).—When a slightly acid buffered glucose solution is oxidised by $\text{Br}-\text{H}_2\text{O}$ the rotation first rises rapidly to a point corresponding approx. with that of the δ -gluconolactone, then decreases to a min. val. at a rate corresponding with the hydrolysis of this lactone, and finally increases slowly to a point corresponding with the equilibrium rotation of gluconic acid. Mutarotation occurs in the solution if the oxidation is interrupted by removal of Br with either olive oil or $\text{Na}_2\text{S}_2\text{O}_3$. This suggests that the initial oxidation product of the glucopyranose is the δ -lactone which then becomes hydrolysed to the gluconic acid. The latter finally reaches equilibrium with the δ - and γ -lactones. This view is confirmed by similar observations with *d*-galactose, *l*-arabinose, *d*-xylose, and lactose, and in the last case, no final rise in rotation occurs owing to the impossibility of γ -lactone formation. J. W. B.

Reaction between potassium cyanide and sugars. Its relation to the forms of sugars in aqueous solution. F. LIPPON (Biochem. Z., 1932, 248, 280—308).—Hexoses (also hexosephosphates) and reducing and mutarotatory bioses combine under suitable conditions with definite amounts of HCN. Study of these amounts and of the variations which they undergo in certain circumstances (presence of alkali, acid, phosphate, proteins, NH_2 -acids, synthalin, insulin, or thyroxine) leads to conclusions concerning the various forms in which the sugars exist and the alterations which take place in equilibrium mixtures of these forms. W. M.

X-Ray evidence of structure of the furanose and pyranose forms of α -methylmannoside. E. G. COX and T. H. GOODWIN.—See this vol., 798.

Passage from the hexose to the cyclitol series. F. MICHEEL (Annalen, 1932, 496, 77—98).—Successive treatment of mannitol with CPh_3Cl and BzCl in pyridine gives 1:6-di(triphenylmethyl)mannitol 2:3:4:5-tetrabenzoate (I), m.p. 185° , $[\alpha]_D^{25} +46.9^\circ$, hydrolysed by HBr in $\text{AcOH}-\text{CHCl}_3$ at 0° to mannitol 2:3:4:5-tetrabenzoate, m. p. 155° , $[\alpha]_D^{25} \pm 0^\circ$ in CHCl_3 , which is convertible into (I) and with PCl_5 in CHCl_3 at $130-150^\circ$ (bath) affords 1:6-dichloromannitol 2:3:4:5-tetrabenzoate, m.p. $108-109^\circ$, $[\alpha]_D^{25} +20.6^\circ$ in CHCl_3 , also formed by benzoylation of the (1:6)-dichloromannitol (II) of Siwoloboff (A., 1886, 681). (II), COMe_2 , anhyd. CuSO_4 , and a little conc. H_2SO_4 give 1:6-dichloro-3:4(or 2:3)-isopropylidenemannitol, m.p. 75° , $[\alpha]_D^{25} +25.7^\circ$ in CHCl_3 (diacetate, m.p. 46° , $[\alpha]_D^{25} +21.8^\circ$ in CHCl_3), whilst saturation of a mixture of (II) (1 pt.) and 40% CH_2O (1.5 pts.) with HCl affords 1:6-dichloro-2:3:4:5-dimethylenemannitol (III), m.p. 156° , $[\alpha]_D^{25} +74.7^\circ$ in CHCl_3 , converted by NaI in COMe_2 at $110-115^\circ$ into the 1:6-di-iodo-derivative (IV), m.p. $194-195^\circ$, $[\alpha]_D^{25} +50^\circ$ in CHCl_3 . (IV) and K in xylene and N_2 give $\gamma\delta\delta$ -di(methylenedioxy)- $\Delta^{\alpha\alpha}$ -hexadiene, m.p. 81° , $[\alpha]_D^{25} +280.3^\circ$ in CHCl_3 , which consumes

approx. 20 per mol. when titrated with BzO_2H and is hydrolysed by 5% HCl to $\gamma\delta$ -dihydroxy- $\beta\epsilon$ -diketohexane, m.p. 74° . (IV) and "mol." Ag in PhMe or xylene at 165 – 170° afford 1:6-deoxy-2:3:4:5-dimethylenemannitol [$\beta\gamma\delta\epsilon$ -di(methylenedioxy)hexane], b.p. 70 – $71^\circ/0.04$ mm., m.p. 60° , $[\alpha]_D^{25} +54.8^\circ$ in CHCl_3 [also formed from (IV), H_2 , and $\text{Pd}-\text{CaCO}_3$], and the dimethylene ether, b.p. $103^\circ/0.04$ mm., m.p. 215° , $[\alpha]_D^{25} +17.03^\circ$ in CHCl_3 , of tetrahydroxymannocyclitol [1:2:3:4-tetrahydroxycyclohexane] (V), m.p. 229° , $[\alpha]_D^{25} +31.6^\circ$ in H_2O . $\alpha\zeta$ -Deoxymannitol [$\beta\gamma\delta\epsilon$ -tetrahydroxyhexane] has m.p. 148° , $[\alpha]_D^{25} -17.6^\circ$ in CHCl_3 . (V) and Zn dust at 250 – 280° give C_6H_6 , whilst oxidation with HNO_3 (d 1.4) affords succinic acid. 6-Chloro-1-deoxydimethylenemannitol [α -chloro- $\beta\gamma\delta\epsilon$ -di(methylenedioxy)hexane], b.p. $98^\circ/0.04$ mm., m.p. 81° , $[\alpha]_D^{25} +55.9^\circ$ in CHCl_3 , is the sole cryst. product isolated from (III) and "mol." Ag in xylene at 180° .
H. B.

α - and β -D-Glucose 2:3:4:6-tetra-acetate, and a source of error in the determination of m. p. in a capillary tube. A. GEORG (Helv. Chim. Acta, 1932, 15, 924–935).—The prep. of β -D-glucose tetra-acetate (I), m.p. 137.5 – 138° , $[\alpha]_D^{25} -3.0^\circ$ to $+80.25^\circ$ in 95% EtOH ($c=4$), and $[\alpha]_D^{25} +14.8^\circ$ (const.) in CHCl_3 ($c=4.116$), is modified to give a 92% yield. Acetobromoglucose with "active" AgNO_3 (prepared by pouring a 10% solution in warm MeOH into 2 vols. of Et_2O) in dry Et_2O gives tetra-acetyl- β -glucosidyl nitrate; in presence of a little H_2O , excess of AgNO_3 , and some HNO_3 (formed by hydrolysis), the β -nitrate is (a) partly inverted to the α -nitrate, which hydrolyses to yield (I), and (b) partly hydrolysed to yield by inversion α -glucose tetra-acetate, dimorphic, plates, m.p. 99 – 100° (from Et_2O -ligroin), and needles, m.p. 112.5 – 113° (from Et_2O alone), $[\alpha]_D^{25} +142^\circ$ to $+80.2^\circ$ in 3 days in 95% EtOH ($c=4$), $[\alpha]_D^{25} +135.1^\circ$ in CHCl_3 ($c=4.36$). Hudson's rule is not accurately obeyed by these substances. The m.p. of sugars containing a free α -aldehydic or -ketonic group may be depressed if the surface of the capillary tube contains free alkali. This may be obviated by heating the tube with 1:1 HCl . Traces of acid remaining after this treatment depress the m.p. of sucrose, but not of substances less sensitive to acids.
R. S. C.

Physical properties of fructose and its determination by copper reduction methods. R. F. JACKSON and J. A. MATTHEWS (Bur. Stand. J. Res., 1932, 8, 403–444).—Accurate data for the densities of 0–70% aq. solutions of cryst. fructose (d 1.598) at 20° and 25° are tabulated: $d_{20}^{25}=0.99823+0.038893p+0.0140p^2$ and $d_{25}^{25}=0.99708+0.03855p+0.0139p^2$ (0–20%) and $d_{25}^{25}=0.99936+0.037842p+0.01636p^2$ (24–70%), whence the mean expansion of such solutions between 20° and 25° is given by $\Delta D/\Delta t = -(0.03231+0.05672p-0.0224p^2)$ (0–20%) and $-(0.032145+0.05795p-0.017136p^2)$ (20–70%), respectively. The vals. of n_D^{25} for such solutions are given by similar interpolation formulæ, the vals. of the consts. being 1.33300, 0.0214159, 0.05491 (0–20%); 1.33344, 0.0213625, 0.056645 (20–63%); and 1.33377, 0.0213570, 0.06680 (63–90%), all for $t=20^\circ$; the vals. for $t=25^\circ$ are 1.33252, 0.0214059, 0.05487;

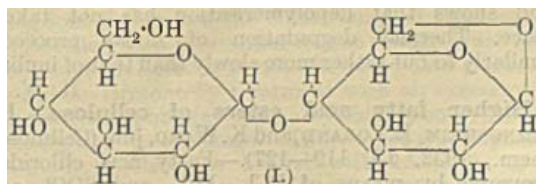
3 K

1.33312, 0.0213415, 0.056722; and 1.33345, 0.0213360, 0.056800, respectively. The saccharimetric rotations of fructose solution at 20° and 25° are submitted to similar analysis, the saccharimetric normal wt. of cryst. fructose being 18.407 at 20° and 19.003 at 25° . Between room temp. and 75° the change in rotation of 1 g. of fructose in 10 c.c. is $-0.0344^\circ S$ per 1° . The reducing powers of glucose and fructose by Munsen and Walker's method (A., 1906, ii, 634) are not const., but are a function of the sugar concn. Nyn's method (B., 1925, 21) for the selective determination of fructose is improved by effecting the reduction for 75 min. at 55° and determination of the pptd. Cu_2O by oxidation with an excess of standard $\text{K}_2\text{Cr}_2\text{O}_7$ and electrometric titration of the excess with Fe_2SO_4 . Under these conditions the fructose/Cu ratio, which varies with the concn. of the sugar, has been determined over a wide range of concn. Except in very high concn. the reducing power of glucose in mixtures containing fructose is essentially independent of the concn. of either sugar, 12.4 mg. of glucose being equiv. in reducing power to 1 mg. of fructose. In sucrose-fructose mixtures, containing S g. of sucrose, the reducing effect of the former is represented by mg. $\text{Cu}=3.32S-0.31S^2+0.27$, for quantities between 1 and 5 g. of sucrose. The above data and other analytical processes are applied to deduce methods of calculating the fructose concn. in various sugar mixtures.
J. W. B.

Sir James Irvine's view on the constitution of di- and poly-saccharides. E. L. HIRST (J. Amer. Chem. Soc., 1932, 54, 2559–2560).—Polemical with Irvine and McGlynn (this vol., 255).
C. J. W. (b)

Possible source of error in determining the constitution of di- and poly-saccharides. J. C. IRVINE (J. Amer. Chem. Soc., 1932, 54, 2567–2568).—A reply to Hirst (preceding abstract).
C. J. W. (b)

Polysaccharides. XLVI. A new maltose anhydride, α -4-glucosido- β -glucosan. P. KARRER and L. KAMIENSKI (Helv. Chim. Acta, 1932, 15, 739–745; cf. this vol., 46).— β -Octa-acetylmaltosidyl bromide (modified prep.) with 33% alcoholic NMe_3 at 70° or, better, with NHMe_3 in CHCl_3 at room temp. gives 1-dimethylaminomaltose hepta-acetate, m.p. 164° , the methiodide of which (prepared in boiling MeOH) with boiling aq. $\text{Ba}(\text{OH})_2$ yields glucosido- β -glucosan (I), + (?) H_2O (lost at 125° in a high vac.), m.p. (dried at 100° , + approx. $0.5\text{H}_2\text{O}$) 157 – 158° (Ac_3 derivative, m.p. 184°). (I) is stable to Fehling's solution, Br and I solutions, malt diastase, and emulsin, but a hepatopancreatic extract gives glucose (not isolated) and β -glucosan, identical with that obtained from starch. (I) is methylated with



difficulty by Me_2SO_4 and NaOH in $\text{COMe}_2-\text{H}_2\text{O}$, and a product containing 37.8% OMe gives, when

hydrolysed, tetramethylglucose. The constitution of (I) is thus proved. R. S. C.

Synthesis of anthocyanins. Isomeric glucosides of pelargonidin chloride. A. LÉON and others. See this vol., 859.

Chemical constituents of tobacco. II. Glucosides of tobacco leaf. I. K. YAMAFUJI.—See this vol., 888.

Crotonoside. E. CHERBULIEZ and K. BERNHARD (Helv. Chim. Acta, 1932, 15, 978—980).—The sugar from crotonoside (I) is *d*-ribose, the structure of (I) as 6-amino-2-hydroxypurine-*d*-riboside being thus confirmed. "Hydroxyadenine" (A., 1927, 584) is not identical with *isoguanine* and may, therefore, be an unknown isomeride. R. S. C.

Vanillin as a colour reagent. L. PAVOLINI (L'Ind. Chimica, 1932, 7, 149—152).—Purified starches (1—2 g.) give little colour with a few drops of 2% solution of vanillin in EtOH (95%) and 4—5 c.c. of conc. HCl, but flours yield a pink colour changing to violet with an intensity depending on the proportion of protein present; bran gives this colour, but sawdust an indistinct green. Casein, albumin, and peptone give reddish-violet colorations. Bleached cotton, artificial silk, flax, and hemp yield no colour, the first two dissolving in the reagent. Raw vegetable fibres give greenish colorations (lignin), but animal fibres show the same colour as flour, silk dissolving and wool remaining undissolved. Glucose and lactose remain colourless, but fructose and sucrose gradually yield a pink or red colour. Resin (in EtOH) turns pink or reddish-violet. T. H. P.

Glycogen. W. S. REICH (Compt. rend., 1932, 194, 2141—2143).—Repeated treatment of glycogen with 33% KOH combined with electrodialysis gives a product containing <0.002% P_2O_5 , and giving a true solution in resorcinol, in which the mol. wt. corresponds with $4C_6H_{10}O_5$. A. A. L.

Measurements by methods based on dialysis. Mol. wt. and thermal degradation of inulin and inulan in aqueous solution. H. BRINTZINGER, K. MAURER, and J. WALLACH (Ber., 1932, 65, [B], 988—994).—Application of Brintzinger's method (A., 1931, 416) shows the mol. wt. of inulin purified by the method of Irvine and Steele and of a technically pure inulin to be about 80,000 and above 100,000, respectively. Hydrolysis of inulin to fructose by hot H_2O without catalyst is complete in 30—40 hr.; uniform intermediate products of measurable life period are not produced. Investigation of inulan, prepared by heating inulin in glycerol at 90—95°/vac., discloses the presence of compounds of low mol. wt. (glycerol, EtOH; cf. Berner, A., 1931, 716, 941) and shows that depolymerisation has not taken place. Thermal degradation of inulan proceeds similarly to but rather more slowly than that of inulin. H. W.

Higher fatty acid esters of cellulose. H. PRINGSHEIM, E. LORAND, and K. WARD, jun. (Cellulosechem., 1932, 13, 119—127).—Fatty acid chlorides prepared by means of PCl_5 , PCl_3 , and $SOCl_2$ are allowed to act on cellulose in presence of pyridine and an inert solvent, e.g., C_6H_6 . In preparing insol.

esters the method of drying the cellulose is important, and the esters are weak if the treatment with acyl chloride is prolonged. These esters become sol. when heated at a high temp., e.g., 180°, with tetrahydronaphthalene, EtOAc, camphor, or $CH_2Ph\cdot OAc$, the last being the best. This is essentially a heat effect catalysed by $PhSO_3H$, etc. Such esters are somewhat coloured in solution and their films are weak. If cellulose is esterified at a high temp., e.g., in boiling xylene, sol. esters are formed directly and contain 2—2.8 acyl groups per C_6 , but their quality is inferior. A. G.

Alkali-cellulose. I. O. SCHWARZKOPF (Z. Elektrochem., 1932, 38, 353—358).—The distribution of NaOH between cellulose (ramie and Cu-silk) and an aq. solution has been studied by analysing the liquid and residue furnished by a hydraulic press at different pressures. The amount of H_2O taken up was determined by the use of an unabsorbed solute (NaCl) as reference substance. The results agree with X-ray evidence in showing that H_2O as well as NaOH is fixed by the cellulose. In the case of cellulose hydrate the process is reversible. F. L. U.

Additive compound of diethylamine and phenylboric acid. G. E. K. BRANCH and D. L. YABROFF (J. Amer. Chem. Soc., 1932, 54, 2569).— $BPh(OH)_2$ and NH_2Et_2 in Et_2O give the compound $3BPh(OH)_2\cdot NH_2Et_2$, m.p. 85°. $BPh(OH)_2$, like H_3BO_3 , can be titrated in presence of glycerol. C. J. W. (b)

Glycine anhydride. I. H. SANBORN (J. Physical Chem., 1932, 36, 1799—1830).—Glycine anhydride (I) forms an adsorption complex with HCl (the amount of which is determined volumetrically) and a series of compounds with HF [the mol. ratio depends on time of contact and concn., and is a max. at 4 mols. of HF per mol. of (I)]. A compound of 2 mols. of $HClO_4$ and 1 mol. of (I) and a disulphate of (I) are described. The formation of these compounds favours the onic structure of (I). Previous work on the structure of (I) is reviewed. R. B. (b)

Knoop's degradation of amino-acids, F. Ehrlich's alcoholic fermentation of amino-acids, and C. Neuherg's fourth fermentation form. E. BAUR (Helv. Chim. Acta, 1932, 15, 734—738).—Aminolysis of alanine in presence of C is considered to occur by the following stages: alanine $\rightarrow NH_3 + AcCHO$ (I); (I) \rightarrow lactic acid + $AcCO_2H$ (II) + glycerol (III); (II) $\rightarrow MeCHO + CO_2$; (III) $\rightarrow EtOH + HCO_2H$. However, failure to detect (I) amongst the reaction products renders this hypothesis uncertain. R. S. C.

Aminolysis of alanine. K. WUNDERLY (Helv. Chim. Acta, 1932, 15, 721—734; cf. A., 1931, 1015).—When degassed animal charcoal is used, NH_4 lactate (I) is almost the sole product of aminolysis of alanine. This is not an oxidation process, since it is unaffected by replacement of air by H_2 , N_2 , CO_2 , or H_2O vapour when the C is not degassed. The products of the reaction with ordinary C include (I), EtOH, NH_4HCO_2 , HCO_2NH_4 , $AcCO_2NH_4$ (II), and MeCHO, but AcCHO and glycerol are absent. The proportions in which the products are formed, however, vary in different

experiments. Aminolysis is brought to a premature end by lactate and pyruvate ions. NH_4^+ , pyruvate and lactate are unaffected by C at 90°. The determination of (I) and (II) is modified. R. S. C.

Configuration of natural valine. P. KARRER and F. C. VAN DER S. VEER (Helv. Chim. Acta, 1932, 15, 746—750).—Natural valine is $l(+)$, since the vals. of $[\alpha]_D$ for a no. of *N*-acylvaline esters are parallel to those for the corresponding *l*-leucine derivatives. Parallelism is not complete between derivatives of the corresponding acids owing to the free CO_2H group. The following *N*-acyl derivatives of *l*-valine are described, the rotations quoted being all $[\alpha]_D^{20}$ in EtOH: *Bz*-, m.p. 127°, $+17.18^\circ$ (*Et* ester, m.p. 82°, -3.44°); *PhSO}_2*-, m.p. 153°, $+18.35^\circ$ (*Et* ester, m.p. 56°, -1.04°); *p*-toluenesulphonyl-, m.p. 147°, $+25.0^\circ$ (*Et* ester, m.p. 59°, $+3.99^\circ$); β -naphthalenesulphonyl-, m.p. 173°, $+6.19^\circ$ (*Et* ester, m.p. 99°, -24.7°). The *Et* esters of *N*-*p*-nitrobenzoyl- $l(+)$ - and $-d(-)$ -valine have m.p. 88° and $[\alpha]_D^{20} +4.12^\circ$ and -3.5° in EtOH, respectively. *N*-*p*-Toluenesulphonyl-*l*-leucine has $[\alpha]_D^{20} -4.05^\circ$ (lit. $+4.50^\circ$). R. S. C.

Synthesis of peptide-like substances from amino-sugars and amino-acids. II. *N*-Dialanylglicosamine. A. BERTHO and J. MAIER (Annalen, 1932, 495, 113—121).—Glucosamine hydrochloride and *dl*- α -azidopropionyl chloride (I) in *N*-NaOH give *N*- α -azidopropionylglucosamine, decomp. 188°, $[\alpha]_D^{20}$ (in H_2O) $+60^\circ \rightarrow 23.3^\circ$ (24 hr.), reduced catalytically (Adams) or by Al-Hg in H_2O to impure *N*-alanylglicosamine, which when heated with a little NaOH in EtOH passes into *N*-alanyldehydroglucosamine anhydride (A., 1931, 470). Tetra-acetylglucosamine and (I) in CHCl_3 -pyridine give tetra-acetyl-*N*- α -azidopropionylglucosamine, m.p. 146° (slight decomp.), $[\alpha]_D^{20} +13.6^\circ$ in CHCl_3 , reduced catalytically (Adams) in EtOAc to tetra-acetyl-*N*-alanylglicosamine, m.p. 180° (decomp.), $[\alpha]_D^{20} +3.0^\circ$ in CHCl_3 , converted by α -bromopropionyl chloride in CHCl_3 -pyridine into tetra-acetyl-*N*-(α - α' -bromopropionamidopropionyl)glucosamine, m.p. 156—162°, $[\alpha]_D^{20} +18.7^\circ$ and $+26.4^\circ$ in CHCl_3 (according to solvent used for crystallisation). This with MeOH-NH_3 at room temp. for 4 days gives *N*-(α - α' -aminopropionamidopropionyl)glucosamine (*N*-dialanylglicosamine), decomp. about 125°. H. B.

Identification of nitriles. H. P. HOWELLS and J. G. LITTLE.—See this vol., 854.

Reducing action of the Grignard reagent. II. Comparison with the ease of removal of hydrogen bromide from alkyl bromides and with the amount of magnesium dialkyl in the Grignard reagent. C. R. NOLLER and F. B. HILMER (J. Amer. Chem. Soc., 1932, 54, 2503—2506; cf. this vol., 474).—There is no relationship between the amount of reduction of COPh_3 by Grignard reagents from 7 alkyl bromides and the relative ease of formation of alkenes from these bromides. The amount of reduction increases (not proportionally) with rise in the Mg dialkyl content of the solutions. The amount of Mg dialkyl present in Grignard solutions appears to be influenced more by the structure than by the mol. wt. of the hydrocarbon radical. The following figures give the equiv. % of Mg dialkyl and % of

benzhydrol formed, respectively: *tert*.-Bu 32, 0; Et 51, 2; Pr^i 59, 13; *sec*.-Bu 62, 40; Pr^n 71, 58; Bu 74, 59; Bu² 78, 86. C. J. W. (b)

Stereoisomeric-1:2-dimethylcyclohexanes. O. MILLER (Bull. Soc. chim. Belg., 1932, 41, 217—227).—*o*-Xylene, b.p. 143.95—144.15°, m.p. -25.0° , when hydrogenated in presence of Pt, gives *cis*-1:2-dimethylcyclohexane, b.p. 130.0°, m.p. -50.2° , mixed with 9% of the *trans*-isomeride, b.p. 123.7°, m.p. -89.6° . Reduction could not be effected using activated Ni catalysts. Physical consts. for the isomerides are recorded. R. S. C.

Slow oxidation of 1:2-dimethylcyclohexane. M. G. CHAVANNE, (MLLE.) KATZENSTEIN, and (MME.) PAHLAVOUNI (Bull. Soc. chim. Belg., 1932, 41, 209—216).—1:2-Dimethylcyclohexane (I) is more rapidly oxidised by O_3 than are the 1:3- and 1:4-isomerides. (I), when prepared from *o*-xylene by hydrogenation in presence of Pt, has b.p. 128.9—129.7°, d_4^{20} 0.7978, and is more rapidly oxidised than the product, b.p. 125.5—127.1°, d_4^{20} 0.7884, obtained by use of Ni. 2-Methylcyclohexanone gives by the Grignard reagent a product, b.p. 129—130°, d_4^{20} 0.7977. Oxidation at room temp., more rapidly in direct light, gives peroxides. At 100—110° there are formed much AcOH with some HCO_2H , *n*-hexoic acid, and δ -keto-*n*-hexoic acid, 1:2-dimethylcyclohexan-1-ol, Me *n*-hexyl ketone, β -diketohexane, and an oil, transformed by boiling HCO_2H into an unsaturated ketone, $\text{C}_8\text{H}_{14}\text{O}$ (semicarbazone, m.p. 107°). Oxidation thus starts at a $>\text{CH}$ group. R. S. C.

Mobility of groups containing a sulphur atom. D. T. GIBSON (J.C.S., 1932, 1819—1826).—*Me benzenethiolsulphonate* (I), b.p. 123°/1 mm. (from Na benzenethiolsulphonate and Me_2SO_4) (1 mol.), and benzenesulphonylacetone (II) (1 mol.) with Na_2CO_3 (1 mol.) in EtOH give α -benzenesulphonyl- α -methylthiolacetone (III), m.p. 60°, hydrolysed to benzenesulphonylmethylthiolmethane, which is oxidised by KMnO_4 to benzenesulphonylmethanesulphonylmethane (A., 1931, 1394). *Me p*-toluenethiolsulphonate (IV) (1 mol.) and (II) (5 mols.) with Na_2CO_3 also give (III), which is converted by the further action of (IV) into α -*p*-toluenesulphonyl- α -methylthiolacetone (V), m.p. 81° (cf. *loc. cit.*) [also formed from equimol. amounts of *p*-toluenesulphonylacetone and (IV)], which is reconverted into (III) by an excess of (I), and on hydrolysis and subsequent oxidation affords *p*-toluenesulphonylmethanesulphonylmethane, m.p. 158°. (III) is also obtained from *p*-toluenesulphonylacetone (1 mol.) and (I) (3 mols.). It is suggested that the interconversion of these derivatives involves the separation of PhSO_2^\ominus and its replacement by $\text{p-C}_6\text{H}_4\text{MeSO}_2^\ominus$; the excess or deficiency of the attacking ions determines the main course of the reaction. The SMe group is essential for the change, since benzenesulphonylacetone is not converted into *p*-toluenesulphonylacetone by treatment with an excess of Na *p*-toluenesulphinate. The alkylthiol groups are also susceptible to exchange. Thus, α -benzenesulphonyl- α -methylthiolacetone heated with 15 mols. of Et *p*-toluenethiolsulphonate (VI), m. p. 32°, and Na_2CO_3 (1 mol.) in EtOH is converted into α -*p*-toluenesulphonyl- α -ethylthiolacetone, m. p. 93—94°, also

prepared from *p*-toluenesulphonylacetone and (VI). The replacement of SR is not necessarily accompanied by replacement of $\text{Ar}\cdot\text{SO}_2$; thus, 2:5-dichlorophenyl 2':5'-dichlorobenzenethiolsulphonate, (V), and NaOEt give a mixture of 2:5:2':5'-tetrachlorodiphenyl disulphide, 2:5-dichlorobenzenesulphinic acid, and α -*p*-toluenesulphonyl- α -2:5-dichlorophenylthiolacetone, m.p. 111°. Exchange of groups is also observed with Et benzenesulphonylacetate (VII) and (IV) (3 mols.) (whereby impure Et α -*p*-toluenesulphonyl- α -methylthiolacetate results) and with ω -benzenesulphonylacetophenone and (IV) (5 mols.); saturation of the solution obtained in the last case with CO_2 gives the salt, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}(\text{SMe})\cdot\text{COPh}\cdot\text{Na}_2\text{CO}_3$, hydrolysed to *p*-toluenesulphonylmethylthiolmethane. Et α -benzenesulphonyl- α -methylthiolacetate, m.p. 84°, is obtained from equimol. amounts of (I), (VII), and Na_2CO_3 . Equimol. amounts of (II) and diphenyl disulphide with NaOEt give α -benzenesulphonyl- α -phenylthiolacetone, m.p. 69–70°, whilst di-*p*-tolyl disulphide and *p*-toluenesulphonylacetone afford α -*p*-toluenesulphonyl- α -*p*-tolylthiolacetone, m.p. 98°. Exchange of $\text{Ar}\cdot\text{SO}_2$ occurs very slowly (if at all) with purely aromatic disulphides; thus, *p*-toluenesulphonylacetone and diphenyl disulphide (5 mols.) give α -*p*-toluenesulphonyl- α -phenylthiolacetone, m.p. 83°, whilst (II) and di-*p*-tolyl disulphide (4 mols.) afford α -benzenesulphonyl- α -*p*-tolylthiolacetone. *p*-Chlorobenzenesulphonylacetone, m.p. 79° (from Na *p*-chlorobenzenesulphonate and $\text{Ac}\cdot\text{CH}_2\text{Cl}$), reacts with (IV) (5 mols.) in $\text{EtOH}\text{-Na}_2\text{CO}_3$ forming (V) and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{H}$; with a deficiency of (IV), there results (after hydrolysis) *p*-chlorobenzenesulphonylmethylthiolmethane, m.p. 93°, also formed from (V), $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{Na}$, and a little Na_2CO_3 in EtOH .

No indication of exchange of $\text{R}\cdot\text{SO}_2$ is observed with $\text{CH}_2(\text{SO}_2\text{R})_2$ and an excess of alkyl thiolsulphonate. Thus, benzenesulphonyldi(methanesulphonyl)methane, m.p. 225°, is formed from benzenesulphonylmethanesulphonylmethane (VIII) and (IV) (with subsequent oxidation) and from $\text{CH}_2(\text{SO}_2\text{Me})_2$ and diphenyl disulphide. *p*-Toluenesulphonyldi(methanesulphonyl)methane, m.p. 185°, is prepared similarly. Di-*p*-tolyl disulphide, (VIII), and NaOEt give a little benzenesulphonylmethanesulphonyl-*p*-tolylthiolmethane and not the expected trisulphide, whilst (VIII), $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Me}$, and NaOEt afford α -benzenesulphonyl- α -methanesulphonylethane.

The sulphones obtained by Posner (A., 1903, i, 279; 1908, i, 21) from PhSH and acrylic and cinnamic acids are probably mixtures resulting by (partial) migration of the sulphonyl group. H. B.

Quantitative nitration of *p*-chloro- and *p*-bromo-toluene. (Miss) F. R. SHAW and E. E. TURNER (J.C.S., 1932, 1884–1888).— $p\text{-C}_6\text{H}_4\text{MeCl}$ and HNO_3 (d 1.5) at 0° and –15° give 38 and 35.6±0.2%, respectively, of 3- NO_2 -derivative; the amounts are determined by the piperidine method (this vol., 259). $p\text{-C}_6\text{H}_4\text{MeBr}$ gives 38.1 and 36.3±0.7% at 0° and –15°, respectively. The ratio of 3:2-nitration increases more rapidly with rise of temp. for $p\text{-C}_6\text{H}_4\text{MeCl}$ than for $p\text{-C}_6\text{H}_4\text{MeBr}$. H. B.

Substitution in compounds containing two or more phenyl groups. I. Nitration of 4-methyl-

diphenyl. W. S. M. GRIEVE and D. H. HEY (J.C.S., 1932, 1888–1894).—Nitration of 4-methyldiphenyl [with HNO_3 (d 1.42) in AcOH] gives rise to both homo- and hetero-nuclear substitution; substitution is primarily controlled by the strongly *op*-directing Ph and *p*-tolyl groups. 4-Nitro-4'-methyl- (I), m.p. 140° (40–45%), 2-nitro-4'-methyl-, and 2-nitro-4-methyl-diphenyls are formed. The oil remaining after separation of (I) from the nitration product is oxidised by KMnO_4 to 2-nitrodiphenyl-4'-carboxylic acid (II), m.p. 250° (nitrated further to 2:2'-dinitrodiphenyl-4-carboxylic acid); oxidation with $\text{CrO}_3\text{-AcOH}$ gives also some 2-nitrodiphenyl-4-carboxylic acid. Reduction of the oil with SnCl_4 and EtOH -conc. HCl and subsequent acetylation affords 2-acetamido-4-methyldiphenyl, m.p. 145°, oxidised by neutral KMnO_4 to 2-acetamidodiphenyl-4-carboxylic acid, m.p. 222°, also prepared by acetylation of the reduction product of 2-nitrodiphenyl-4-carboxylic acid, m.p. 191° (formed together with 2:2'-dinitrodiphenyl-4:4'-dicarboxylic acid by hydrolysis of the reaction product from PhI , Et 4-bromo-3-nitrobenzoate, and Cu -bronze). 2-Benzamido-4-methyldiphenyl has m.p. 221°. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{Cl}$, PhNO_2 , and 40% NaOH below 5° give 2- and 4-nitro-4'-methyldiphenyl; the former is reduced to 2-amino-4'-methyldiphenyl (Acderivative, m.p. 103°) and oxidised (CrO_3) to (II). 3-Acetamido-4-methyldiphenyl, m.p. 150°, is prepared similarly by way of 2-nitro-*p*-toluenediazonium chloride and C_6H_5 . (I) is nitrated further to 2(or 3):4'-dinitro-4-methyldiphenyl, m.p. 178°, and oxidised by $\text{CrO}_3\text{-AcOH}$ to 4-nitrodiphenyl-4'-carboxylic acid, m.p. 340° [the acid thus described by Kühling (A., 1895, i, 290; 1896, i, 236) is the 2'-carboxylic acid], which is nitrated to 2:4'-dinitrodiphenyl-4-carboxylic acid. H. B.

Benzhydryl rule and the constitution of alkali triphenylethides which are stable in liquid ammonia. C. B. WOOSTER and J. F. RYAN (J. Amer. Chem. Soc., 1932, 54, 2419–2424).—Reaction between NaNH_2 or KNH_2 and phenylated paraffins in liquid NH_3 at its b.p. occurs only when the CHPh_2 group is present in the hydrocarbon; this generalisation is termed the "benzhydryl rule." $\text{CPh}_2\text{:CHPh}$ and Na in liquid NH_3 give $\text{CNaPh}_2\text{:CHNaPh}$, which is then ammonolysed to $\text{CNaPh}_2\text{:CH}_2\text{Ph}$, which with EtBr gives $\alpha\beta\beta$ -triphenylbutane, m.p. 79–79.5°, also synthesised from $\text{CPh}_2\text{:CHMe}$ and K in liquid NH_3 followed by CH_2PhCl . In one experiment in which NH_3 was condensed on $\text{CPh}_2\text{:CHMe}$ and then K slowly added until present in slight excess, reaction with CH_2PhCl gave $\alpha\alpha\delta$ -triphenyl- Δ^2 -butene (?), m.p. 122–124°. $\text{CHPh}_2\text{:CH}_2\text{Ph}$ and KNH_2 in liquid NH_3 with CH_2PhCl give $\alpha\beta\beta\gamma$ -tetraphenylpropane (?), m.p. 125–127°, also obtained from $\text{CPh}_2\text{:CHPh}$ and Na in liquid NH_3 with CH_2PhCl , but not from CPh_2Cl_2 and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$. $\text{CPh}_2\text{:CH}_2\text{Cl}$ and Na give the compound, $\text{C}_{20}\text{H}_{15}\text{Na}$, which with NH_4Cl gives $\text{CHPh}_2\text{:CH}_2\text{Ph}$ (showing that mol. rearrangement occurs) and with EtBr affords $\text{CH}_2\text{Ph}\cdot\text{CPh}_2\text{Et}$; the initial reaction gives $\text{CPh}_2\text{:CH}_2\text{Na}$, which rearranges to $\text{CNaPh}_2\text{:CH}_2\text{Ph}$. C. J. W. (b)

Photosynthesis of *cis*- and *trans*-isomerides of organic halogen compounds. S. KATO (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 765–768).

Bromination of CPh:CHPh in CCl_4 affords the *cis*- Br_2 -derivative (30% yield), whilst bromination of CHPh:CHPh in MeOH gives a 90% yield of the *trans*- Br_2 -derivative, these solvents having approx. the same fundamental mol. frequencies as those calc., respectively, for the two reactions. J. W. B.

1-Vinylnaphthalene and polyvinylnaphthalene resins. L. PALFRAY, S. SABETAY, and (Mlle.) D. SONTAG (Compt. rend., 1932, 194, 2065–2068).— β -1-Naphthylethyl alcohol heated with KOH under 30–40 mm. gives 1-vinylnaphthalene, b.p. 126–128°/15 mm. (with appreciable resinification) [*picrate*, m.p. (Maquenne block) 101–102°; *styphnate*], which is readily polymerised (by heat) to a resin, sol. in CHCl_3 , C_6H_6 , and PhMe , which does not decolorise Br .

Benzylmethylcarbinol and $\alpha\beta$ -diphenylethyl alcohol are partly dehydrated by KOH to propenylbenzene and stilbene, respectively; benzylidimethylcarbinol is largely decomposed to PhMe and COMe_2 . The ease of dehydration of the alcohols, $\text{CH}_2\text{Ph}\cdot\text{CR}_2\cdot\text{OH}$, decreases in the order $\cdot\text{CR}_2\cdot\text{OH}$ = primary, *sec.*, and *tert.*

H. B.

Syntheses of 2:6- and 2:7-dibenzyl-naphthalene and of ketone derivatives of the $\beta\beta$ -naphthalene series. K. DZIEWONSKI and S. WODELSKI (Rocz. Chem., 1932, 12, 366–377).— CH_2PhCl reacts with C_{10}H_8 at 170° in the presence of AlCl_3 to yield 2-benzyl-naphthalene, 2:7-, m.p. 91°, and 2:6-dibenzyl-naphthalene, m.p. 123° (NO_2 -derivative, m.p. 133°), which on oxidation gives 2:6-dibenzoyl-naphthalene (*diphenylhydrazone*, m.p. 235°; *dioxime*, m.p. 281°). 2:6-Dibenzamidonaphthalene, m.p. 306°, is prepared by applying the Beckmann change to the *dioxime*, and also by benzoylation of 2:6-diaminonaphthalene. 2:7-Dibenzyl-naphthalene yields on oxidation 2:7-dibenzoyl-naphthalene (*dioxime*, m.p. 176°). 2-Benzyl-naphthalene yields 6-benzoyl-2-benzyl-naphthalene, m.p. 126–127°, with BzCl in the presence of ZnCl_2 , and 6-acetyl-2-benzyl-naphthalene (I), m.p. 96° (*oxime*, m.p. 127°), with AcCl in presence of AlCl_3 . The *oxime* is converted into 6-acetamido-2-benzyl-naphthalene, m.p. 189°, which on hydrolysis yields 6-amino-2-benzyl-naphthalene, m.p. 95°. 2-Benzoyl-6-naphthoic acid, m.p. 98°, is obtained by the oxidation of (I). R. T.

Acenaphthenesulphonic acids. II. Derivatives of acenaphthene- α -sulphonic acid. K. DZIEWONSKI, (Mlle.) J. KRASOWSKA, and (Mlle.) J. SCHOENOWNA (Bull. Acad. Polonaise, 1931, A, 400–405).—Na acenaphthene-5-sulphonate with PCl_5 gives the *chloride* (I), m.p. 109–111° (*anilide*, m.p. 177–178°), reduced by Zn and dil. H_2SO_4 to 5-thiol-acenaphthene (II), m.p. 51–52° (*Pb* and *Hg* salts; *picrate*, m.p. 133–134°), oxidised by air in NH_3 - EtOH to diacenaphthyl 5:5'-disulphide, m.p. 168–169°, which is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ and AcOH to anhydride-(1:8-dicarboxynaphthyl) 5:5'-disulphide, decomp. 300–310°. With 35% NaOH and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ at 40–50° (II) affords 5-acenaphthylthiolacetic acid, m.p. 150–151° (*Na* salt). Oxidation of the amide of (I) with $\text{Na}_2\text{Cr}_2\text{O}_7$ and AcOH gives the *anhydride*, m.p. 249–250° (decomp.), of 5-sulphonamidonaphthalene-1:8-dicarboxylic acid. J. W. B.

Syntheses of alkylphenanthrenes. II. Pimanthrene, 1:4:7-trimethylphenanthrene, retene, and 1:4-dimethyl-7-isopropylphenanthrene. R. D. HAWORTH, B. M. LETSKY, and C. R. MAVIN (J.C.S., 1932, 1784–1792; cf. this vol., 608).—Succinic anhydride, $2\cdot\text{C}_{10}\text{H}_7\text{Me}$, and AlCl_3 in cold PhNO_2 give β -(6-methyl-2-naphthoyl)propionic acid (I), m.p. 162° [*Me* ester (II), b.p. 210–212°/12 mm., m.p. 82–83°], reduced (Clemmensen) to γ -(6-methyl-2-naphthyl)-butyric acid, m.p. 111–112°, and cyclised by warm H_2SO_4 to 4-keto-7-methyl-1:2:3:4-tetrahydrophenanthrene, m.p. 62–63°, which when reduced (Clemmensen) and then dehydrogenated (Se) affords 2-methylphenanthrene. (I) is oxidised by alkaline $\text{K}_2\text{Fe}(\text{CN})_6$ to 6-methyl-2-naphthoic acid, m.p. 225–227° (*Me* ester, m.p. 116–117°), also obtained by hydrolysis of 2-cyano-6-methylnaphthalene [prepared in small yield by distillation of Na 6-methylnaphthalene-2-sulphonate and $\text{K}_4\text{Fe}(\text{CN})_6$], which is oxidised further to 2:6- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$. MgMeI and (II) in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ give γ -(6-methyl-2-naphthyl)- Δ^8 -pentenoic acid, m.p. 143–144°, which when reduced with red P and HI (*d* 1.7) and then treated with H_2SO_4 affords 4-keto-1:7-dimethyl-1:2:3:4-tetrahydrophenanthrene (III), b.p. 190–192°/0.4 mm. (*semicarbazone*, m.p. 206–208°). Reduction (Clemmensen) of (III) and subsequent dehydrogenation with Se at 300–340° furnishes 1:7-dimethylphenanthrene (pimanthrene). The product from MgMeI and (III) is similarly dehydrogenated to 1:4:7-trimethylphenanthrene, m.p. 72–73° (*picrate*, m.p. 141–142°; *styphnate*, m.p. 129–130°; *quinone*, m.p. 170–171°; *quinoxaline*, m.p. 140–141°), which differs from the methylpimanthrenes obtained from *d*-pimaric acid (Ruzicka and Balas, A., 1924, i, 1311) and *isoagathidicarbonylic* acid (Ruzicka and Hosking, A., 1931, 359).

Succinic anhydride and $2\cdot\text{C}_{10}\text{H}_7\text{Pr}^i$ (by reduction of 2-isopropenylnaphthalene or from C_{10}H_8 , Pr^iBr , and AlCl_3) give (as above) β -(6-isopropyl-2-naphthoyl)-propionic acid, m.p. 159° [*Me* ester (IV), m.p. 81–82°], oxidised to 6-isopropyl-2-naphthoic acid, amorphous (*Me* ester, m.p. 109–110°), and thence to 2:6- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$. MgMeI and (IV) give γ -(6-isopropyl-2-naphthyl)- Δ^8 -pentenoic acid, m.p. 144°, convertible into 4-keto-1-methyl-7-isopropyl-1:2:3:4-tetrahydrophenanthrene (V), b.p. 180–185°/0.5 mm., m.p. 71–72°, and thence (by reduction and dehydrogenation) into retene. (V) is converted [as (III)] into 1:4-dimethyl-7-isopropylphenanthrene, m.p. 61–62° (*picrate*, m.p. 115°; *styphnate*, m.p. 142–143°), which is not identical with the methylretene obtained by Ruzicka and Meyer (A., 1922, i, 829) from abietic acid.

The hydrocarbon obtained from C_{10}H_8 , PrBr , and AlCl_3 probably contains a large amount of $2\cdot\text{C}_{10}\text{H}_7\text{Pr}$; condensation with succinic anhydride gives (probably) β -(6-propyl-2-naphthoyl)propionic acid, m.p. 147–148°. H. B.

Constitution of rubicene. R. SCHOLL and K. H. MEYER (Ber., 1932, 65, [B], 926–927).—The formation of 9:10-diphenylanthracene and rubicene when 9:10-dihydroxy-9:10-diphenyldihydroanthracene-1:5-dicarboxylactone is heated with Zn dust in CO_2 at 500° confirms the constitution assigned to rubicene by Schlenk and Karplus (A., 1928, 1235). H. W.

Condensation of formaldehyde with arylamines. N. S. DROSDOV (J. Gen. Chem. Russ., 1931, 1, 1170—1176).— CH_2O condenses with NH_2Ph and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ to compounds of the type $\text{CH}_2\cdot\text{NAr}$ (I) and $\text{CH}_2(\text{NHAr})_2$ (II); the type of product formed depends, not on the proportions of the reactants, but on the p_H of the solution, compounds of type (II) being unstable in an acid medium. They are formed almost exclusively at p_H 8 and compounds of type (I) at p_H 7. (I) ($\text{Ar}=p\text{-C}_6\text{H}_4\text{Me}$) passes into (II) on keeping with H_2O at p_H 4. G. A. R. K.

Interaction between thionyl chloride and substances containing the reactive methylene group. K. G. NAIK and V. B. THOSAR (J. Indian Chem. Soc., 1932, 9, 127—132).—Thionylacetacetarilamides, $\text{NHR}\cdot\text{CO}\cdot\text{CAcSO}$, and thionylacetonedicarboxylaryl amides, $\text{NHR}\cdot\text{CO}\cdot\text{CH}(\text{SO}_2\text{CO})\cdot\text{CH}\cdot\text{CO}\cdot\text{NHR}$, are prepared from acetoacet- and acetonedicarboxyl-aryl amides and SOCl_2 in C_6H_6 . The following are described: *thionylacetacet-anilide*, m.p. (all with decomp.) 90° (shrinks at 69°), *-o-toluidide*, m.p. 110° (shrinks at 87°), *-m-toluidide*, m.p. $93\text{—}94^\circ$ (shrinks at 78°), *-p-toluidide*, m.p. $92\text{—}93^\circ$ (shrinks at 87°), *-α-naphthylamide*, m.p. 112° (shrinks at 92°), *-β-naphthylamide*, m.p. 107° (shrinks at 82°), *-1:3:4-xylidide*, m.p. 102° (shrinks at 90°), and *-1:4:5-xylidide*, m.p. 114° (shrinks at 97°); *thionylacetonedicarboxyl-anilide*, m.p. 170° (shrinks at 140°), *-o-toluidide*, m.p. 174° (shrinks at $155\text{—}156^\circ$), *-p-toluidide*, m.p. $208\text{—}210^\circ$ (shrinks at 185°), *-α-naphthylamide*, m.p. 155° (shrinks at 137°), and *-β-naphthylamide*, m.p. 207° (shrinks at 185°). These sulphoxides are more stable to moisture than the thionylmalonarylamides (A., 1930, 764) and unlike the latter, are not converted into sulphides by SOCl_2 , HCl , or I . The prep. of *acetoacet-α-*, m.p. $108\text{—}109^\circ$, and *-β-*, m.p. $103\text{—}104^\circ$, *-naphthylamides* and *-1:3:4-*, m.p. 92° , and *-1:4:5-*, m.p. 96° , *-xylidides*, and *acetonedicarboxyl-α-*, m.p. 165° , and *-β-*, m.p. 207° , *-naphthylamides* is described. H. B.

Stereochemistry of carbodi-imides. XXII. L. J. ROLL and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 2494—2498; cf. this vol., 739).—The structural relationship of allenes and diarylcarbodi-imides is pointed out and a method for proving the asymmetry of the carbodi-imide is proposed. If during the conversion of $\text{CS}(\text{NHPh})_2$ into $\text{NPh}\cdot\text{C}\cdot\text{NPh}$, the reaction temp. is much above 80° , NH_2Ph and PhNCS are also formed; NH_2Ph then reacts with $\text{NPh}\cdot\text{C}\cdot\text{NPh}$ forming triphenylguanidine. Menthyl *p*-aminobenzoate and PhNCS in C_6H_6 give *p-carbo-1-menthoxythiocarbonyl-anilide*, m.p. $124\text{—}125^\circ$, converted by HgO and CaCl_2 in C_6H_6 into *p-carbo-1-menthoxydiphenylcarbodi-imide*. *pp'*-Dicarbethoxydiphenylcarbodi-imide, m.p. $78\text{—}90^\circ$, and *s-tri-(p-carbethoxyphenyl)guanidine*, m.p. $170\text{—}171^\circ$, are prepared from *pp'*-dicarbethoxydiphenylthiocarbamide. *pp'*-Dibromodiphenylcarbodi-imide has b.p. $208\text{—}212^\circ/4\text{ mm}$. C. J. W. (b)

Formation of diarylthiocarbamides from arylamines and trithiocarbonates. N. S. DROSDOV (J. Gen. Chem. Russ., 1931, 1, 1168—1170).—An aq. suspension of ZnCS_3 or NiCS_3 (prepared by treating aq. NaCS_3 with the metal sulphate) gives with primary arylamines the corresponding diarylthiocarbamides;

the yield from NH_2Ph is 80%. Complex trithiocarbonates of NH_4 and heavy metals can also be used.

G. A. R. K.

Synthesis of 3-iodo-β-naphthylamine. H. GOLDSTEIN and E. CORNARIUS (Helv. Chim. Acta, 1932, 15, 935—939).—3-Iodo-β-naphthoyl chloride (I) and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ give 3-iodo-β-naphthoylhydrazine, m.p. about 250° (decomp.), and $\text{NN}'\text{-di-(3-iodo-β-naphthoyl)-hydrazine}$, m.p. 318° [sole product if excess of (I) is used]. The former with HNO_2 yields the azide, deflagrates at $60\text{—}65^\circ$, transformed by boiling EtOH into the urethane, m.p. 109° (which could not be hydrolysed), and by 90% H_2SO_4 at 0° into 3-iodo-β-naphthylamine, m.p. 137° (Ac derivative, m.p. 198°). The amine with HNO_2 gives 3-iodo-β-naphthol, m.p. 104° . 3-Acetamido-β-naphthoic acid and SOCl_2 give the acid chloride, which with conc. aq. NH_3 affords 3-acetamido-β-naphthamide, m.p. 237° ; this could not be degraded by Hofmann's method. R. S. C.

Trypanocidal activity. II. Derivatives of β-naphthylamine-4:6:8-trisulphonic acid. G. T. MORGAN and J. G. MITCHELL (J.C.S., 1932, 1910—1912).—Interaction of β-naphthylamine-4:6:8-trisulphonic acid (I) (prep. of Na_3 salt described) with 2-nitro-*p*-toluoyl chloride and 3-nitrobenzoyl chloride in alkaline solution affords the Na_3 salts of 3-nitro-4-methylbenzoyl- (II) and 3-nitrobenzoyl-β-naphthylamine-4:6:8-trisulphonic acid, respectively. Reduction of (II) with Fe and HCl , followed by interaction with 3-nitrobenzoyl chloride and 2-nitro-*p*-toluoyl chloride in alkaline solution, affords the Na_3 salts of 3'-nitrobenzoyl- (III) and 3'-nitro-4'-methylbenzoyl-3-amino-4-methylbenzoyl-β-naphthylamine-4:6:8-trisulphonic acid (IV). Reduction of the 3-nitrotoluoyl derivative of (I) with Fe and HCl and further reaction with 2-nitro-*p*-toluoyl chloride affords the Na_3 salt of 3'-nitro-4'-methylbenzoyl-3-aminobenzoyl-β-naphthylamine-4:6:8-trisulphonic acid (V). (III), (IV), and (V) with COCl_2 in alkali (after reduction with Fe and HCl) afford the Na salts of ureido-3'-aminobenzoyl-3-amino-4-methylbenzoyl-, ureido-3'-amino-4'-methylbenzoyl-3-amino-4-methylbenzoyl-, and ureido-3'-amino-4'-methylbenzoyl-3-aminobenzoyl-β-naphthylamine-4:6:8-trisulphonic acid. The therapeutic action of these substances against trypanosomiasis was investigated. J. L. D.

2:4-Diamino-1-methylnaphthalene. H. W. THOMPSON (J.C.S., 1932, 1830—1832).—Interaction of $\text{CHPhMe}\cdot\text{CN}$ with Et sodiocyanoacetate in boiling EtOH during 15 hr. affords *Et α-cyano-β-imino-γ-phenylvalerate*, m.p. 107° (I), different from the product of methylation of $\text{Et α-cyano-β-imino-γ-phenylbutyrate}$ (*ibid.*, 1906, 89, 1906). (I) with H_2SO_4 at 0° affords *Et 2:4-diamino-1-methylnaphthalene-3-carboxylate*, m.p. 115° (lit., 74°). Removal of the CO_2Et group followed by acetylation affords 2:4-diacetamido-1-methylnaphthalene, m.p. 303° , identical with the Ac derivative of the amine, m.p. 93° (lit., 65°), obtained by reducing 2:4-dinitro-1-methylnaphthalene with H_2O and Pt during 1 hr. at 100° . J. L. D.

Complex compounds of cobalt with *s*-diphenylethylenediamine. J. V. DUBSKY and A. LANGER (Coll. Czech. Chem. Comm., 1932, 4, 193—199).—A repetition of the work of Gapon (A., 1930, 765) has

not yielded the substances described. The products are mixtures of *s*-diphenylethylenediamine hydrochloride with CoCl_2 or with the double salt formed by these.
E. S. H.

Chromability of azo-dyes from hydroxyquinolines. C. COURTOT and H. HARTMAN (Compt. rend., 1932, 194, 1949—1952).—The coupling of all possible hydroxyquinolines with diazotised sulphanilic, metanilic, naphthionic, α -naphthylamine-5- and -8-sulphonic, amino-G and -R, and anthranilic acids has been investigated. Only the 5-, 6-, 7-, 8- (*i.e.*, all positions in the Ph nucleus) and 3-OH-derivatives couple, the bathochromic effect of the OH group being greater the closer is its proximity to the N atom, the 8-OH group having the biggest effect. Chromability is generally observed only with dyes from 5- and 8-hydroxyquinoline, but all the hydroxyquinolines give chromable dyes with diazotised anthranilic acid.
J. W. B.

Diazo-resins. I. Z. JOLLES [with W. CAMIGLIERI] (Atti R. Accad. Lincei, 1932, [vi], 15, 292—297).—Diazo-resins have been obtained in 70—93% yield in alkaline medium from the normal diazo-compounds from the following amines: NH_2Ph , *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, *o*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, *o*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, *o*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and α - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$. Small proportions of the corresponding aromatic hydrocarbons are usually formed in the reaction. In most cases the N content of the products agrees well with the equation (for NH_2Ph) $4\text{Ph}\cdot\text{N}_2\cdot\text{OH} = \text{C}_{24}\text{H}_{18}\text{ON}_2 + \text{H}_2\text{O} + 3\text{N}_2$. The resinification seems to be due to internal oxidation of the diazonium hydroxides.
T. H. P.

Stability of solutions of diazo-compounds. I, II. P. P. VIKTOROV (J. Appl. Chem., Russia, 1931, 4, 777—791, 792—805).—Reducing substances retard the decomp. of solutions of diazo-compounds during the first few hr.; $\text{Na}_2\text{S}_2\text{O}_5$ or NaHSO_3 is satisfactory, but not $\text{Na}_2\text{S}_2\text{O}_4$. The effect of NO_3^- is catalytic. The rate and degree of decomp. of *p*-nitrodiazobenzene depend on the $[\text{OH}^-]$ of the neutralising agent. When salts of the same cations are used for neutralisation the decomp. is greatest with the salt having the smallest dissociation const., whilst with salts containing the same anions the decomp. is greatest with the salt which has the most basic cation. HCO_2Na and CaCO_3 are exceptions. If $\text{Al}(\text{OH})_3$ is used, the quantity taken should be double the calc. amount.
CH. ABS.

Thermal behaviour of phenols at high pressures. A. HAGEMANN and M. NEUHAUS (Braunkohle, 1931, 20, 949—953, 976—981; Chem. Zentr., 1932, i, 1028—1029).—The tendency of the phenols of tar to produce coke, with elimination of H_2O , CO_2 , and CO, increases with increasing mol. wt. The velocity of polymerisation or condensation can be depressed by addition of solvents (*e.g.*, 2.86 mols. of C_6H_6 per mol. of phenol at 410—415°). Solvents which permit dissociation of phenols (*e.g.*, H_2O) or salt formation (*e.g.*, NaOH) considerably increase the reaction velocity. Only by the use of solvents is the catalytic hydrogenation of phenols of high b.p. possible.
A. A. E.

Effect of heating of alkali phenoxide solutions under pressure. F. HOFMANN, L. BOENTE, W. STRICK, and J. AMENDE (Naturwiss., 1932, 20, 403—404).—The reaction products obtained by heating under pressure solutions of PhOH, resorcinol, and α - and β -naphthol in 30—50% aq. NaOH or KOH have been examined. Reaction commences at 415°, 320°, and 390—400°, respectively, the nature of the alkali having no effect; 40—50% of the PhOH, 60% of the resorcinol, and about 20% of the naphthol are converted into CO_2 and H_2O and in all cases H_2 , CH_4 , and other paraffins are formed. PhOH also yields C_6H_6 , PhMe, xanthen, Ph_2O , and coumaran; from the complex reaction products of resorcinol have been isolated 2:7-dimethylnaphthalene, COMePr, and higher ketones. α - and β -Naphthol both yield C_6H_6 , MePh, *o*-xylene, *o*-ethyltoluene, C_{10}H_8 , 2-methylnaphthalene, and di-indene; in addition, α -naphthol affords $\beta\beta$ -dinaphthyl and β -naphthol 1:2-benzanthracene. AcOH is produced in all cases, salicylic acid from PhOH, *o*-toluic acid from the naphthols, and β -*o*-tolylpropionic acid from β -naphthol. The mechanism of the formation of the various products from naphthol is briefly discussed; the alkali acts as an oxidising agent, removes CO_2H groups, promotes condensation, and, when H_2 is evolved in the early stages, causes hydrogenation of part of the naphthol to C_{10}H_8 . β -*o*-Tolylacrylic acid is probably an intermediate product from β -naphthol.
A. R. P.

Molecular organic compounds. IV. Molecular organic compounds of phenol, their parachors and refractivities. C. A. BUEHLER, J. H. WOOD, D. C. HULL, and E. C. ERWIN (J. Amer. Chem. Soc., 1932, 54, 2398—2405; cf. this vol., 153).—Mol. compounds (some of which are new) of PhOH and the following substances are isolated; the mol. ratio and m.p. (corr.) are quoted after the second component: NH_2Ph , 1:1, 32.6°; *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, 1:1, 35.6°; *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, 1:1, -7°; *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, 1:1, 33°; *m*-4-xylydine, 1:1, 16°; α - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, 1:1, 29.1°; β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, 1:1, 84.4°; benzidine, 1:1, 128.4°; *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, 1:1, 44.2°; *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, 4:1, 29.7°; *m*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, 3:2, 58°; *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, 1:1, 98.6°; *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, 2:1, 106.5°; $\text{CO}(\text{NH}_2)_2$, 2:1, 61.5°; NH_2Ac , 2:1, 42.9°; $\text{NH}_2\text{Ac}\cdot\text{H}_2\text{O}$, 2:1:1, 42.1°; NH_2Bz , 2:1, 31°; NH_2Et , 1:1, 12°; pyridine, 1:1, -19°; pyridine, 2:1, 4°. Vals. of *d*, γ , and *P* (parachor) are given for PhOH, NH_2Ph , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, and *m*-4-xylydine at 25—150°; the observed *P* are lower than the calc. vals. and increase gradually with rise in temp. (as with alcohols and fatty acids). Vals. are also given for the mol. compounds of PhOH with NH_2Ph , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, and *m*-4-xylydine at 25—150°; the same relationship exists in these cases, but the temp. coeffs. and the differences between the observed and calc. vals. are greater; it is probable that in both cases association occurs, the amount of which becomes smaller with rise in temp. Vals. of *n* at 45° for the *D*, α , and β lines are given for PhOH, NH_2Ph , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, and *m*-4-xylydine, and for their mol. compounds, and vals. of MR_D and EMR_D [MR_D (obs.)— MR_D^0 (calc.)] are given for the same series of compounds at 20° (calc.), 45°, 60°, and 80°. A

comparison of these vals. indicates that the linking between the components in the mol. compounds has a negative val. C. J. W. (b)

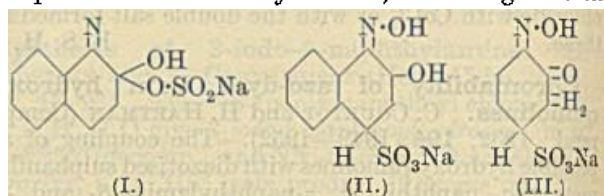
Catalytic decomposition of phenol silver salts.
VI. Synthesis of 4'-chloro-3:5-dibromo-2':6'-di-iodo-4-hydroxydiphenyl ether and the decomposition of its metallic salts. W. H. HUNTER and M. A. DAHLEN (J. Amer. Chem. Soc., 1932, 54, 2456—2463; cf. A., 1921, i, 239).—4'-Chloro-2':6'-di-iodo-4-methoxydiphenyl ether (I), m.p. 101—102°, is prepared by the usual method from the 4'-NH₂ derivative; the 4'-bromo-2':6'-di-iodo-, b.p. 209—219°/2 mm., m.p. 123—123.5°, and 2':4':6'-tri-iodo-, b.p. 220—230°/1—2 mm., m.p. 132—133°, analogues are obtained similarly. (I), HI, red P, and AcOH give 82% of 4'-chloro-2':6'-di-iodo-4-hydroxydiphenyl ether (II), m.p. 154.5°, brominated in AcOH at 75°—b.p. to 4'-chloro-3:5-dibromo-2':6'-di-iodo-4-hydroxydiphenyl ether, m.p. 194.5°, the K salt of which decomposes in aq. solution containing a trace of Br, to the amorphous oxide, (C₁₂H₄O₂ClBrI₂)_x (also formed by the action of I in KI). The Ag salt is decomposed by EtI, I, or by heat to the same oxide. The K and Ag salts of (II) are not decomposed to an amorphous oxide. These results confirm the mechanism previously suggested for the catalytic decomp. of metal salts of halogenophenols. 4-Bromo-2':6'-di-iodo-4-hydroxydiphenyl ether has m.p. 162—163°. C. J. W. (b)

Nitrous acid as a nitrating agent. II. Nitration of dimethyl-p-anisidine. H. H. HODGSON and J. H. CROOK (J.C.S., 1932, 1812—1815; cf. A., 1930, 460).—Dimethyl-p-anisidine (I) (prep. described) (picrate, m.p. 139°) affords with HNO₂ mainly 3-nitrodimehyl-p-anisidine, m.p. 14° (hydrochloride, m.p. 95°; picrate, m.p. 143°), also obtained when 4-chloro-3-nitroanisole, m.p. 45° (prep. from acet-p-anisidine), is heated in EtOH with NHMe₂, and <1% of nitro-monomethyl-p-anisidine, m.p. 47°. Nitration of (I) with conc. HNO₃ in H₂SO₄ at 0° affords 2-nitrodimehyl-p-anisidine, m.p. 44° (picrate, m.p. 175°). These results are discussed in the light of current electronic theory. J. L. D.

Structure of acetone-cresol condensation products. J. B. NIEDERL (Monatsh., 1932, 60, 150—158).—Crit. comparison of analytical results and chemical properties favours the formula C₂₃H₂₈O₂ for these products (cf. A., 1929, 551). E. W. W.

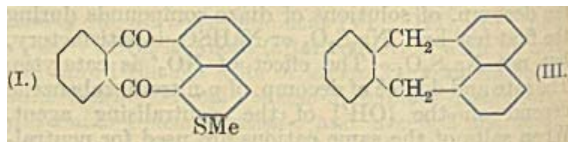
Structure of hydrogen sulphite compound of nitroso-β-naphthol (Bucherer's reaction). S. V. BOGDANOV (J. Gen. Chem. Russ., 1932, 2, 9—22).—It is contended that in the reaction between salts of H₂SO₃ and naphthol derivatives, with the formation of a H sulphite compound, the naphthol does not react in the keto-form. This view is corroborated by the stability of the H sulphite compounds towards acids, whereas the corresponding compounds of aldehydes and ketones are rapidly destroyed. By boiling nitroso-β-naphthol with NaHSO₃ 1-amino-β-naphthol-7-sulphonic acid is slowly formed. If the conventional formula (I) is assumed for the H sulphite compound, this reaction can be explained only by the sulphonating action of the excess of NaHSO₃. By treating the pure H sulphite compound, however,

with Zn dust and NH₄Cl or SnCl₂ and HCl, the same sulphonic acid is readily formed, indicating that the



sulphonating agent is the O-SO₂Na group. The constitution (II) is suggested for the H sulphite compound, and its reduction to 1-amino-β-naphthol-4-sulphonic acid follows. The possibility of its reacting in the tautomeric keto-form (III) was investigated by treating it with NH₂OH.HCl in HCl solution, in the hope of obtaining (III) with 'O replaced by 'N-OH (IV). Instead of the latter, NH₂ 2-nitroso-α-naphthol-4-sulphonate (V) was obtained. It is suggested that (IV) is formed as an intermediate stage in the reaction. In the presence of HCl the α-NOH group is hydrolysed and the NH₂OH formed reacts with the sulphonic group to give (V). This reaction gives further proof that the SO₃H of the H sulphite compound is in the 4-position. The bearing of the above conclusions on the structure and reactions of the H sulphite compounds of other naphthol derivatives is discussed. M. Z.

Action of o-phthaloyl chloride on the methyl ethers of β-naphthol and of β-thionaphthol. W. KNAPP (Monatsh., 1932, 60, 189—204; cf. A., 1929, 186; 1930, 1183, 1296).—The action of o-phthaloyl chloride and AlCl₃ on β-naphthyl Me sulphide in CS₂ gives, not thionaphtholphthalic Me₂ ether, but o-2-methylthiol-α-naphthoylbenzoic acid, m.p. 178—179°; in s-C₆H₅Cl₄ the product is 2-methylthiol-1:8-phthalalynaphthalene, (I), m.p. 195°, which is oxidised



by KMnO₄ to unsatisfactory products. Similarly, β-naphthyl Me ether gives in CS₂ o-2-methoxy-α-naphthoylbenzoic acid, m.p. 195—196° (severely degraded by HBr in AcOH), and, in s-C₆H₅Cl₄, 1:8-phthalyl-β-naphthol, (II) (cf. A., 1931, 1060), m.p. 199—200°. Oxidation of the Me ether, m.p. 206—208°, of (II) by KMnO₄ gives an ill-defined product, m.p. 210—215°; reduction of (II) by Zn in H₂ gives o-xyllylene-1:8-naphthalene (III), m.p. 113—115° (+H₂O). Again, 4-bromo-α-naphthyl Me sulphide, b.p. 200°/13 mm., obtained by the action of Me₂SO₄ on 4-bromo-α-thionaphthol (from 1-bromo-naphthalene-4-sulphonyl chloride, reduced by Sn and HCl), gives, in CS₂, o-4-bromo-1-methylthiol-α-naphthoylbenzoic acid, m.p. 185—186°, whilst 4-bromo-α-naphthyl Me ether gives, in CS₂, o-4-bromo-1-hydroxy-β-naphthoylbenzoic acid. E. W. W.

Preparation of a new ethylnaphthol. G. LÉVY (Compt. rend., 1932, 194, 1952—1954).—α-Benzyl-n-butyl acid (amyl ester, b.p. 154°/15 mm.) is converted by Braun's synthesis (A., 1927, 258) into

1-keto-3-ethyltetrahydronaphthalene, dehydrogenated by Se (this vol., 266) directly to 3-ethyl- α -naphthol, m.p. 50.5—51° [*picrate*, m.p. 145° (corr.)].

J. W. B.

Preparation of unsymmetrical diphenyl derivatives. I. R. SHERWOOD, W. F. SHORT, and R. STANSFIELD (J.C.S., 1932, 1832—1835).—An improved method of synthesising unsymmetrical Ph_2 derivatives is described. *cyclo*Hexanones or *cyclo*hexenones and MgAr halides afford *tert*-alcohols which are dehydrogenated by S (theoretical amount during 3.5—5 hr. at 180—250°), either directly or after dehydration by cone. HCO_2H , to give Ph_2 derivatives. Many arylidiphenyls are prepared in good yield. *cyclo*Hexanone in boiling Et_2O affords with Mg and 3-bromo-*p*-tolyl Me ether during 0.5 hr. 1-(4'-methoxy-*m*-tolyl)*cyclo*hexanol, m.p. 77°, dehydrogenated to 2-methoxy-5-methyldiphenyl, b.p. 170—175°/20 mm., which with HI and red P at 150° for 8 hr. affords 2-hydroxy-5-methyldiphenyl, m.p. 68°. J. L. D.

Preparation of β -arylethylamines from α -cyano- β -arylacrylic acids. J. A. McRAE and W. H. VINING (Canad. J. Res., 1932, 6, 409—416).— α -Cyano- β -arylacrylic acids (J.C.S., 1922, 121, 1699) are reduced by Na-Hg to α -cyano- β -arylpropionic acids, which when heated with Cu powder or (preferably) quinoline give β -arylpropionitriles. These are hydrolysed by cold fuming HCl to β -arylpropionamides, converted by alkaline NaOBr into β -arylethylamines. β -Piperonyl-, β -anisyl-, β -veratryl-, and β -phenyl-ethylamines are prepared. α -Cyano- β -4-hydroxy-3-methoxyphenylpropionic acid, m.p. 80°; β -4-hydroxy-3-methoxyphenylpropionitrile, b.p. 189—192°/11 mm., m.p. 58°; 3:4-methylenedioxy-cinnamionitrile, m.p. 92°, and 4-hydroxy-3-methoxycinnamionitrile, m.p. 112°, are incidentally described. α -3:4-Methylenedioxyphenylsuccinimide, m.p. 169° (from the corresponding NH_4 salt at 150—160°), is hydrolysed to the succinic acid by alkaline NaOBr; the NH_2 -acid is not produced.

H. B.

Synthesis of pharmacologically important amines. IV. Syntheses of tyramine and epinine. V. Syntheses of hydrastinine, cotarnine, and lodal. K. KINDLER and W. PESCHKE (Arch. Pharm., 1932, 270, 340—353, 353—362; cf. this vol., 54).—IV. Catalytic reduction (Pd-black) in AcOH of Me *p*-methoxycinnamate, b.p. 182°/13 mm. [prepared in 92% yield from vanillin (I), MeOAc , and Na], gives Me β -*p*-methoxyphenylpropionate, b.p. 284°, m.p. 38°, transformed by 25% aq. NH_3 at room temp. into the amide (II), which yields β -*p*-methoxyphenylethylamine; this with 37% HCl at 150—160° gives tyramine. The yields in the above reactions are nearly quant. *p*-Methoxypropionophenone, NHMe_2 , and S in C_6H_6 at 130° give β -*p*-methoxyphenylthiopropiondimethylamide, m.p. 70°, hydrolysed by hot aq.-alcoholic KOH to β -*p*-methoxyphenylpropionic acid, which with dry NH_3 at 210° gives a 90% yield of

mm. [*picrate*, m.p. 170° (lit. 162—163°)], demethylated to epinine by 37% HCl at 150—155°. By the methods used with (I) methylvanillin affords Me 3:4-dimethoxycinnamate, Me β -3:4-dimethoxyphenylpropionate (IV), b.p. 181°/13 mm., m.p. 37—38°, β -3:4-dimethoxyphenylpropionamide, and β -3:4-dimethoxyphenylethylamine (homoveratrylamine) (Bz derivative, m.p. 90—91°; *picrate*, m.p. 165°). The last amine and PhCHO give an oily CHPh compound, which with Me_2SO_4 in dry C_6H_6 at 90° yields an additive compound, transformed by further heating into (III). Veratrole, EtCOCl , and AlCl_3 in CS_2 give 3:4-dimethoxypropionophenone, which with NHMe_2 and S in C_6H_6 at 130° gives β -3:4-dimethoxyphenylthiopropiondimethylamide, m.p. 94°, transformed by hydrolysis and subsequent esterification into (IV).

V. Benzylidenhomopiperonylamine and Me_2SO_4 in C_6H_6 at 85—90° give an additive compound, which, when further heated in EtOH, yields *N*-methylhomopiperonylamine (I); the formyl derivative of this (prepared by HCO_2H at 210°) with SOCl_2 in dry C_6H_6 at 90° gives hydrastinine hydrochloride. β -3:4-Methylenedioxy-5-methoxyphenylethylamine (homomyristicylamine) gives similarly the *N*-Me derivative (II), b.p. 173°/13 mm. (*picrate*, m.p. 194°; *hydrochloride*, m.p. 171°), the formyl derivative of which affords cotarnine hydrochloride.

[With R. SCHAEFFER and H. CHRISTLIEB.] Myristicin, KMnO_4 , Na_2SO_4 , and MgCO_3 in cold EtOH give myristic and homomyristic acid, m.p. 127°; the latter with dry NH_2Me at 210° gives the methylamide, m.p. 134°, transformed by K_2S and P_2S_5 in xylene at 150° into the methylthioamide, m.p. 152°, which, when reduced electrolytically, gives (II). The formyl derivative of *N*-methylhomoveratrylamine with SOCl_2 in hot C_6H_6 gives lodal. The yields in the above syntheses are very good.

R. S. C.

Action of halogens and of alkyl halides on the salts of tribromothiophenol. W. H. HUNTER and A. H. KOHLHASE (J. Amer. Chem. Soc., 1932, 54, 2425—2432).—2:4:6-Tribromothiophenol and its salts react normally with halogens and alkyl halides to give the disulphide or thio-ethers in nearly quant. yield. Products analogous to the amorphous polydihalogenophenylene oxides (obtained from the trihalogenophenols and phenoxides) are not formed. The first stage in the reaction of both phenoxides and thiophenoxides is probably the formation of metal halide and an unstable product containing halogen directly attached to O or S. Details are given for the prep. of 2:4:6-tribromophenyl ethylxanthate [obtained together with a small amount of di(tribromophenyl) dithiolcarbonate], hydrolysed by MeOH-KOH to 2:4:6-tribromothiophenol (I), m.p. 115.5—115.9° (corr.) [*acetate*, m.p. 102.1—102.7° (corr.)]. Di-2:4:6-tribromophenyl dithiolcarbonate, m.p. 194.2—194.7° (corr.), is also hydrolysed to (I). The Ag salt of (I) and I in C_6H_6 give 92% of 2:4:6:2':4':6'-hexabromodiphenyl disulphide (II), m.p. 221.8—222.7° (corr.), reduced by Na and C_6H_6 -EtOH to (I). (II) is readily prepared by atm. oxidation of the NH_4 or Na salt of (I), by the action of halogen on (I) (or its salts), and by the reduction of tribromobenzenesulphonic acid with PBr_5 . The Ag salt and

3:4-Dimethoxyacetophenone and NH_2Me at -15° give a product, which, when heated with S, affords 3:4-dimethoxyphenylthioacetmethylamide, m.p. 130°. This, when reduced electrolytically, affords *N*-methyl- β -3:4-dimethoxyphenylethylamine (III), b.p. 159°/11

EtI give tribromophenyl *Et* sulphide, an oil; with MeI, the *Me* sulphide (2:4:6-tribromothioanisole), m.p. 59.6—60.5°, results. The Na salt of (I) and Br in aq. KBr give about 45% of (II) and about 50% of 2:4:6-tribromophenylsulphonyl bromide, m.p. 74.5—75.7°. The Na salt and liquid Br give as the only definite product (II), also formed from (I) and Br in C_6H_6 . PhSH and Br in AcOH afford 4:4'-dibromodiphenyl disulphide. C. J. W. (b)

Germicidal activity of aromatic sulphides. E. MONESS, W. BRAKER, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1932, 21, 557—569).—By a modified Hinsberg reaction were prepared 4-hydroxy- (I), b.p. 162—164°/3—4 mm., 4-hydroxy-3-methyl- (II), m.p. 72°, b.p. 185—190°/4 mm., -2-methyl- (III), b.p. 192—197°/5 mm., -3-carboxy- (IV), b.p. 162—167°/3—4 mm., cryst., and -3-ethyl- (V) (from *o*-ethylphenol)-diphenyl sulphide. *p*-Bromophenotole, NaOEt, and Cu powder at 280° give the *Et* ether (VI) of (I) in poor yield. (I), NaOEt, and β -diethylaminoethyl bromide in hot EtOH give the β -diethylaminoethyl ether (VII) (hydrochloride) of (I); the corresponding ether (VIII) of 4-hydroxy-3-methyl-diphenyl sulphide was similarly prepared. *o*-Hydroxy-diphenyl and SCl_2 in cold CS_2 give 6:6'-dihydroxy-3:3'-didiphenyl sulphide (IX), an oil, and PhOH gives similarly 4:4'-dihydroxydiphenyl sulphide (X). *p*-Methoxythiophenol, NaOEt, and *n*-amyl bromide in hot EtOH give *p*-anisyl *n*-amyl sulphide, an oil, hydrolysed (Ac_2O-HBr) to the *p*-OH-compound, b.p. 123—130°. The following were the sole products of the appropriate Hinsberg reaction: 4-hydroxy-3-nitro- (XI), b.p. 175—181°/5 mm., -3-bromo- (XII), b.p. 173—179°/3—4 mm., and -3-phenyl-diphenyl disulphide. The toxicity to typhoid bacillus is in the order (I) > (V) and (VIII) > (VII) > (IX) > (X) > (III), (VI), (XI), and (XII) > (II) and (IV), and to staphylococcus (V) > (II) > (III) > (I) > (IX) > (VI), (XI), and (XII) > (IV) > (VII) and (VIII) > (X). Numerous *OAc.Hg* compounds were prepared, but did not show increased toxicity. R. S. C.

2-Aminocyclopentanol and its resolution. M. GODCHOT and M. MOUSSERON (Compt. rend., 1932, 194, 2061—2063).—cyclopentene oxide and conc. aq. NH_3 at 110° give (trans)-dl-2-aminocyclopentanol (I), b.p. 114—115°/13 mm., 205—206°/760 mm. (hydrochloride, m.p. 192—193°; chloroplatinate; mercurichloride; *Ac*, b.p. 194—195°/15 mm., and *p*-toluenesulphonyl, m.p. 142—143°, derivatives; *H* d-tartrate, m.p. 69—70°; *H* l-tartrate, m.p. 69—70°), converted by PCl_5 in $CHCl_3$ at 0° into 2-chlorocyclopentylamine, b.p. 63—64°/12 mm. (hydrochloride, m.p. 169—170°). (I) is resolved by *d*- and *l*-tartaric acids into (+)-, $\alpha_D + 38.25^\circ$ (hydrochloride, m.p. 155—156°, $\alpha_D + 29.3^\circ$; d-tartrate, m.p. 77—78°, $\alpha_D + 29.55^\circ$), and (—)-forms, $\alpha_D - 38.25^\circ$ (hydrochloride, m.p. 155—156°, $\alpha_D - 29.3^\circ$; l-tartrate, m.p. 77—78°, $\alpha_D - 29.5^\circ$). The former and PCl_3 in $CHCl_3$ give (—)-2-chlorocyclopentylamine, b.p. 61—62°/12 mm., $\alpha_D - 44.9^\circ$, converted by $AgNO_3-Na_2CO_3$ into the latter. H. B.

cis-trans-Isomerism and steric hindrance. XIII. 2-Methylcyclohexanols. G. VAVON, (MILL.) A. PERLIN, and A. HOREAU (Bull. Soc. chim., 1932,

[iv], 51, 644—650).—Pure *trans*- (*H* succinate, m.p. 43—44°; 3:5-dinitrobenzoate, m.p. 115°) and *cis*-2-methylcyclohexanol (*H* succinate, m.p. 44—44.5°; 3:5-dinitrobenzoate, m.p. 99—100°; *H* phthalate, m.p. 104—105°) have been obtained by various methods (cf. this vol., 157). Conditions for the conversion of the *trans*- into the *cis*-alcohol with *p*-toluenesulphonyl chloride are given. The *trans*-*H* phthalate and succinate are hydrolysed more quickly than the *cis*-, whilst the *cis*-alcohol is more quickly oxidised by CrO_3 , and dehydrated by H_2SO_4 .

A. A. L.
 Δ^1 -cyclopentenylalkylcarbinols. URION (Compt. rend., 1932, 194, 2311—2313).— Δ^1 -cyclopentenyl-methyl-, b.p. 165—166°/749 mm., -ethyl-, b.p. 179—180°/749 mm., and -*n*-propyl-, b.p. 197—198°/760 mm., -carbinols, prepared from Δ^1 -cyclopentene-l-aldehyde (A., 1930, 1039) and the requisite Mg alkyl bromide, are dehydrated by Al_2O_3 at about 320° to α - Δ^1 -cyclopentenyl-ethylene, b.p. 114—115°/704 mm., - Δ^2 -propene, b.p. 142—144°/754 mm., and - Δ^2 -butene, b.p. 59—62°/14 mm., respectively.

H. B.
Colour reaction of the sterols. E. MONTIGNIE (Bull. Soc. chim., 1932, [iv], 51, 690).—Cholesterol, phytosterols, stigmasterol, and ergosterol on evaporation with silicotungstic acid in EtOH give a reddish-brown coloration, α - and β -cholesterylene and cholestenone give a reddish-yellow, turpentine, eucalyptus oil, terpene, camphor, and borneol give an orange-yellow, whilst menthol, lemon oil, abietic acid, and aromatic hydrocarbons give negative results. The colour with the sterols may be due to the presence of an indene grouping, since this substance gives a red coloration with the above test. A. A. L.

β -Cholesterol. T. WAGNER-JAUREGG and L. WERNER (Z. physiol. Chem., 1932, 208, 72—76).— β -Cholesterol, obtained as a by-product in the reduction of cholestenone with Na and EtOH (or preferably MeOH), is a mol. compound of cholesterol and dihydrocholesterol. J. H. B.

Colloidal condition of cholesterol, cholesteryl ester, and lethicin. VII. Tautomerism of cholesterol. I. REMESOV (Biochem. Z., 1932, 248, 256—263; cf. this vol., 632).—The catalytic action of cholesterol is strengthened by ultra-violet radiations and to a much slighter extent by filtered ultra-violet radiations (λ 400—300 m μ). The portion of the irradiated material which is pptd. by digitonin lacks catalytic activity almost entirely, whilst the non-pptd. material is catalytically active, especially if irradiation takes place in an atm. of N_2 . Over-irradiated cholesterol (oxycholesterol) is without catalytic properties. It is concluded that ordinary cholesterol is an equilibrium mixture of a catalytically inactive enol form and a keto-form (the "peroxide form") which is produced by the ultra-violet irradiation and is responsible for the catalytic property.

W. M.
Number of carbon atoms in the mol. of sitosterol and other sterols. A. WINDAUS, F. VON WERDER, and B. GSCHAUER (Ber., 1932, 65, [v], 1006—1009).—Elementary analysis of esters and determination of *Ac* in acetates establishes the fol-

lowing formulæ: cholesterol, $C_{27}H_{46}O$; sitosterol, $C_{29}H_{50}O$; stigmasterol, $C_{29}H_{48}O$; agnosterol, $C_{30}H_{48}O$; lanosterol, $C_{30}H_{50}O$. For ergosterol the data lie between C_{28} and C_{29} , but exclude C_{27} . The following esters of sitosterol are described: 3:5-dinitrobenzoate, m.p. 203°, $[\alpha]_D^{25} -10.6^\circ$; 2-chloro-3:5-dinitrobenzoate, m.p. 174—175°, $[\alpha]_D^{25} -7^\circ$; 3:5-dinitro-p-toluatoate, m.p. 189°, $[\alpha]_D^{25} -6.4^\circ$; 4-bromo-3-nitrobenzoate, m.p. 169°, $[\alpha]_D^{25} +0^\circ$; bromoacetate, m.p. 174—175°, $[\alpha]_D^{25} +0.31^\circ$ in $CHCl_3$. Ergosteryl 3:5-dinitro-p-toluatoate, m.p. 213—214°, $[\alpha]_D^{25} -49^\circ$ in $CHCl_3$, and 2-chloro-3:5-dinitrobenzoate, m.p. 203—204°, $[\alpha]_D^{25} -38^\circ$ in $CHCl_3$, and vitamin-D₂ 3:5-dinitro-p-toluatoate, m.p. 115—116°, $[\alpha]_D^{25} +91^\circ$ in $COMe_2$, and 2-chloro-3:5-dinitrobenzoate, m.p. 132°, $[\alpha]_D^{25} +60^\circ$ in $COMe_2$, are described. H. W.

Sterol group. XII. Oxidation of α -ergosterol and derivatives. I. M. HEILBRON, J. C. E. SIMPSON, and D. G. WILKINSON. XIII. Hydrocarbons of ergosterol series. I. M. HEILBRON, F. S. SPRING, and E. T. WEBSTER. XIV. β -Ergosterol and derivatives. I. M. HEILBRON and D. G. WILKINSON. XV. Relationship between α - and β -ergosterol and derived hydrocarbons. A. L. MORRISON and J. C. E. SIMPSON (J.C.S., 1932, 1699—1705, 1705—1707, 1708—1710, 1710—1714).—XII. Oxidation of α -ergosterol (I) with CrO_3 -AcOH at 67—70° gives only a little α -ergosterone (II) (cf. Reindel, A., 1929, 61); the main product is a yellow neutral compound (III), $C_{27}H_{44}O_2$, m.p. 185° (hydroxylamine, m.p. 196—198°, and semicarbazide, m.p. 275°, derivatives), and is accompanied by a minute amount of a crystalline acid (IV), $C_{27}H_{44}O_4$, m.p. 214—216° (?) (isolated as Me ester, m.p. 211—213°). Reduction of (III) by Clemmensen's method gives a hydrocarbon, $C_{27}H_{44}$, m.p. 85—86°. Catalytic dehydrogenation of (I) with Cu-bronze at its b.p./0.1 mm. gives (II) in about 60% yield; (II) and (IV) are also formed by oxidation of (I) with the Beckmann reagent. Oxidation of α -ergosterol acetate with CrO_3 -AcOH at 60° gives α -ergosteronol acetate (V), m.p. 170—171° (semicarbazone, m.p. 199—200°), two substances, $C_{27}H_{44}O_4$, m.p. 134—135°, and 214—215°, and a volatile liquid, $C_9H_{18}O$ (semicarbazone, m.p. 156—158°) (a dihydrothujaketone; cf. this vol., 611). Hydrolysis of (V) with NaOH in MeOH gives α -ergosteronol, $C_{27}H_{44}O_2$, m.p. 155—156°, further oxidised by CrO_3 to α -ergostadiene, m.p. 183°.

XIII. α -Ergostadienyl chloride, m.p. 137°, prepared by interaction of α -dihydroergosterol with $POCl_3$, is reduced by Na and amyl alcohol to α -ergostadiene, $C_{27}H_{44}$, m.p. 124—125°, also obtained by reduction of α -ergostadienone by Clemmensen's method. This is converted by HCl in $CHCl_3$ into β -ergostadiene, m.p. 66—67°, also prepared by reduction of β -ergostadienyl chloride. α -Ergosterol chloride, m.p. 109—110°, gives on reduction α -ergosterone, m.p. 77—78°, more readily obtained by reduction of α -ergosterone. Ergostatrienone-D (A., 1929, 1065), m.p. 204—205°, is obtained in good yield by dehydrogenation of α -ergostadienone with $Hg(OAc)_2$ in AcOH-EtOH at the b.p., and is reduced by Clemmensen's method to ergostatriene-D, m.p. 134—135°, also obtained from α -ergostadiene by the action of $Hg(OAc)_2$.

XIV. β -Ergosterol benzoate, m.p. 158—160°, is prepared from the α -isomeride by the action of HCl in $CHCl_3$, and is hydrolysed by KOH in EtOH to β -ergosterol (VI), m.p. 141—142° (acetate, m.p. 111—112°), which with H_2 -Pd gives ergosterol (allo- α -ergosterol; cf. A., 1928, 295). Distillation of (VI) at 0.5 mm. with Cu-bronze gives β -ergosterone (oxime, m.p. 220°) (cf. A., 1929, 61); this is reduced by Clemmensen's method to β -ergosterene, m.p. 87—88°, also obtained by reduction of (crude) β -ergosterol chloride with Na and amyl alcohol.

XV. Oxidation of α - and β -ergosterol with BzO_2H in $CHCl_3$ at 0° gives α -, m.p. 114—116° (clear at 122°), and β -ergosterol oxide, $C_{27}H_{44}O_2$, m.p. 152—153°, respectively; these with aq. H_2SO_4 in EtOH at its b.p. give dehydroergosterol, also formed by the action of Br (1 mol.) on (VI) (cf. A., 1930, 1178). Both the β -oxide and dehydroergosterol give (I) with H_2 and PtO_2 in AcOH; β -ergosterene under the same conditions gives ergostane. α -, m.p. 118—119°, and β -ergosterene oxide, $C_{27}H_{44}O$, m.p. 122—123°, are similarly prepared, and with H_2SO_4 in EtOH give dehydroergosterene, $C_{27}H_{44}$, m.p. 71—72°, converted by H_2 - PtO_2 into α -ergosterene. The similarity of these reactions to those of apocholic and dihydroxycholeonic acids (cf. A., 1931, 841, 957) is pointed out, and a similarity of nuclear structure in the two series is suggested. H. A. P.

Esters of dialkylaminomethyl alcohols. E. V. LYNN and F. L. LOFGREN (J. Amer. Pharm. Assoc., 1932, 21, 541—548).—The following esters were prepared by condensation of the appropriate sec. amine with CH_2O , acylation (Schotten-Baumann), and, when a nitro-acid was used, reduction: diethylaminomethyl benzoate, b.p. 157—158°/16 mm., cinnamate, m.p. 66—67°, b.p. 190°/17 mm. (sulphate, m.p. 121—122°), m- and p-nitrobenzoate, m.p. 70—72° and 62—63°, b.p. 200—207°/11 mm. and 200—211°/10 mm., respectively; m- and p-aminobenzoate, m.p. 75—76° and 121—122°, b.p. 200—208°/11 mm. and 200—215°/vac. (hydrochlorides, m.p. 184—185° and 189—190°), respectively; di-n-propylaminomethyl benzoate, b.p. 168—171°/17 mm., cinnamate, m.p. 54°, b.p. 200—215°/16 mm. (sulphate, m.p. 113—114°); m- and p-nitrobenzoate, b.p. 213—218°/11 mm., and m.p. 37—39°, b.p. 210—233°/17 mm., respectively; m- and p-aminobenzoate, b.p. 205—210°/9 mm., and m.p. 75—76°, b.p. 215—220°/9 mm. (hydrochlorides, m.p. 141—142° and 152—153°), respectively; di-n-butylaminomethyl benzoate, b.p. 187—188°/17 mm., cinnamate, b.p. 226—227°/14 mm., m- and p-nitrobenzoate, b.p. 227—228°/11 mm. and 230—234°/11 mm., respectively; m- and p-aminobenzoate, b.p. 215—220°/10 mm. and 210—228°/9 mm. (hydrochlorides, m.p. 150—160° and 136—137°), respectively; diisopropylaminomethyl benzoate, b.p. 193—194°/16 mm., cinnamate, b.p. 227—229°/11 mm., m- and p-nitrobenzoate, b.p. 230—233°/11 mm., and m.p. 52—54°, b.p. 232—233°/8 mm., respectively; m- and p-aminobenzoate, b.p. 220—233°/10 mm. and 220—235°/10 mm. (hydrochlorides, m.p. 178—180° and cryst.), respectively. Some of these compounds have local anæsthetic action, but are irritant. R. S. C.

Natural classification of amines related to adrenaline. RAYMOND-HANET (Compt. rend., 1932,

194, 1982—1984).—Adrenaline-like bases are classified as "adrenalinomimetic" or "nicotinic," according as to whether they are vaso-contracting or -dilating in high concn. Bases containing the adrenaline skeleton belong to the first type if (a) there are phenolic OH groups in positions 3 and 4, irrespective of the presence of a side-chain OH group [e.g., β -(3:4-dihydroxyphenyl)ethylmethanamine, adrenalone, or adrenaline], or (b) there is a OH group on the α -C atom of the side-chain and also in the *p*-position [e.g., (β -hydroxy- β -*p*-hydroxyphenyl)ethylmethanamine but not tyramine]. J. W. B.

Enzymic formation and hydrolysis of esters. P. RONA, E. CHAIN, and R. AMMON.—See this vol., 776.

Manufacture of β -amino- α -phenyl alcohols containing hydroxyl in the phenyl residue. I. G. FARBININD. A. G.—See B., 1932, 636.

Action of lithium hydride on benzoyl chloride. A. HODAGHAN and R. LEVAILLANT (Compt. rend., 1932, 194, 2059—2060).—LiH and BzCl in petroleum (b.p. 110—130°/15 mm.) and N₂ at 150—210° give benzyl benzoate (I) in 65% yield: $2\text{BzCl} + 2\text{LiH} \rightarrow 2\text{LiCl} + \text{I}$; LiOBz is a by-product. (I) arises from the intermediate PhCHO under the action of LiH.

H. B.

Dynamic isomerism involving mobile hydrocarbon radicals. IV. Rearrangement of 3:5-dichloro-substituted triphenylbenzamides. A. W. CHAPMAN and C. H. PERROTT (J.C.S., 1932, 1770—1775).—Extension of the previous investigation (A., 1931, 87) to the cases where R=Ph and R'=C₆H₄Cl₂ (3:5-), and conversely, gave the expected results. The following were prepared by methods previously described (cf. A., 1929, 1294): benz-3:5-dichloroanilide, m.p. 147° (iminochloride, m.p. 41°, b.p. 231—232°/16—20 mm.); N-3:5-dichlorophenylbenzimidophenyl ether, m.p. 69—70°; 3:5-dichlorodiphenylamine, m.p. 41—42°, b.p. 222—224°/25 mm. (Bz derivative, m.p. 107—109°); N-3:5-dichlorobenzimidophenyl ether, m.p. 71°; 3:5:3':5'-tetra-chlorodiphenylamine, m.p. 160—161° (Bz derivative, m.p. 135—136°); NN'-diphenyl-N-3:5-dichlorophenyl, m.p. 112°; N-diphenyl-N'-3:5-dichlorophenyl, m.p. 94—95°; N-phenyl-NN'-bis-3:5-dichlorophenyl, m.p. 95—97°, and N'-phenyl-N-bis-3:5-dichlorophenylbenzamide, m.p. 131—132°.

H. A. P.

Ring-closure in triarylamidine series. Source of disecundary o-diamines. A. W. CHAPMAN and C. H. PERROTT (J.C.S., 1932, 1775—1778).—NN'-Diphenyl-N-o-chlorophenylbenzamide, m.p. 171°, gives when heated at 267—269° for 30 min. a water-soluble product, probably 1:2:3-triphenylbenzimidazolium chloride (I), hydrolysed by cold aq. NaOH to benzoyl-s-diphenyl-o-phenylenediamine, m.p. 152° (identified by hydrolysis). Similarly, NN'-di-o-chlorophenyl-N-phenylbenzamide, m.p. 142°, gives benzoyl-N-phenyl-N'-o-chlorophenyl-o-phenylenediamine (position of Bz group not determined), m.p. 124—126°, and N-diphenyl-N'-o-chlorophenylbenzamide, m.p. 94°, gives (I) in poor yield at 330°. N-o-Chlorophenylbenzimidino-o-chlorophenyl ether, m.p. 75—76°, and benzoyl-2:2'-dichlorodiphenylamine, m.p. 149°, are described.

H. A. P.

Alkamine esters of aromatic acids. Novocaine analogues. II. H. C. BRILL (J. Amer. Chem. Soc., 1932, 54, 2484—2487; cf. A., 1925, i, 833).—The following b.p. are reported: NHMeEt, 36—37°; NHMePr^s, 76°; NHMeBu, 108—109°; NPhMeEt, 202°; NPhMePr^s, 211°; NPhMeBu, 247°; γ -(methyl-ethylamino)propanol, 170°; γ -(ethylisopropylamino)propanol, 188°; β -(phenylethylamino)ethanol, 268°; β -(ethylisopropylamino)ethanol, 175°; β -(ethylbutylamino)ethanol, 195°. The following alkamine ester hydrochlorides are prepared: γ -(methylethylamino)propyl benzoate, m.p. 123°; β -(phenylethylamino)ethyl propionate, m.p. 171°; β -(ethylisopropylamino)ethyl benzoate, m.p. 96°; γ -(ethylisopropylamino)propyl benzoate, m.p. 105°; β -(ethylbutylamino)ethyl cinnamate, m.p. 151°; γ -diethylaminopropyl *p*-methoxycinnamate, m.p. 142°; γ -piperidylpropyl *p*-nitrobenzoate, m.p. 205°, and *p*-aminobenzoate, m.p. 213°. All these compounds (except the *p*-NO₂-derivative) possess anaesthetic properties.

C. J. W. (b)

Preparation and properties of *tert*-butyl phenylacetate. D. L. YABROFF and C. W. PORTER (J. Amer. Chem. Soc., 1932, 54, 2453—2455).—CMe₃OH (40 g.) in Et₂O (50 c.c.), slowly added to approx. 0.5 mol. of MgEtBr in Et₂O (300 c.c.), gives CMe₃O-MgBr, which (after refluxing for 15 min.) is then treated with CH₂Ph·COCl (46.1 g.) in Et₂O (50 c.c.) and the mixture boiled for 1 hr. *tert*-Bu phenylacetate, b.p. 110°/15 mm. (b.p. curve given from about 5 to 30 mm.), m.p. -23° to -21°, is thereby obtained in 65% yield. A prep. of this ester which boils at the same temp. after repeated distillation may show a const. but erroneous val. of *n*.

C. J. W. (b)

Nitration of the methyl, ethyl, and *tert*-butyl esters of phenylacetic acid. D. L. YABROFF and C. W. PORTER (J. Amer. Chem. Soc., 1932, 54, 2507—2510; cf. this vol., 511).—Nitration of the Me, Et, and *tert*-Bu esters of CH₂Ph·CO₂H gives 12.1, 10.3, and 5.6%, respectively, of the *m*-NO₂-derivative. The effective residual charge in these esters must be slightly more negative than in the free acid, since less of the *m*-derivative is formed.

C. J. W. (b)

Phenyl-substituted aliphatic acids. J. HARMON and C. S. MARVEL (J. Amer. Chem. Soc., 1932, 54, 2515—2526).—Ph-substituted fatty acids are prepared by thermal decomp. of the corresponding malonic acids. The following compounds are described: phenyloctyl-, b.p. 124—129°/3 mm., and phenylnonyl-, b.p. 121—124°/0.2 mm., -carbinols; Et α -phenylamyl-, b.p. 143.5—147°/3.3 mm., α -phenyl-nonyl-, b.p. 186—191°/4 mm., α -phenyldecyl-, b.p. 163—166°/0.3 mm., δ -phenyloctyl-, b.p. 176—182°/3 mm., ζ -phenyldecyl-, b.p. 185—190°/3 mm., θ -phenyl-dodecyl-, b.p. 180—188°/0.13 mm., δ -phenyltridecyl-, b.p. 187—194°/0.13 mm., ζ -phenyltetradecyl-, b.p. 205—211°/0.25 mm., η -phenylhexadecyl-, b.p. 220—225°/0.2 mm., and θ -phenylhexadecyl-, b.p. 217—224°/0.15 mm., -malonates; δ -phenyltridecan- α -ol, b.p. 158—160°/0.14 mm., formed with a high-boiling acetal from Mg γ -phenyldodecyl bromide and CH₂O; δ -phenyl-octan- α -ol, b.p. 125—130°/3 mm., obtained together with an acetal and γ -phenylheptane, b.p. 68—71°/3

mm., from Mg γ -phenylheptyl bromide; ϵ -phenyl-nonan- α -ol, b.p. 137—144°/0.94 mm., from Mg γ -phenylheptyl bromide and $(\text{CH}_2)_8\text{O}$; ζ -phenyl-decan- α -ol, b.p. 140—144°/3 mm.; α -bromo- γ -phenyl-heptane, b.p. 118—121°/3 mm. (from the alcohol, HBr, and H_2SO_4); α -bromo- δ -phenyloctane, b.p. 124—126°/3 mm.; α -bromo- ϵ -phenylnonane, b.p. 125—127°/2 mm.; α -bromo- ζ -phenyldecane, b.p. 135—139°/3 mm.; α -bromo- γ -phenylundecane, b.p. 147—150°/3 mm.; α -bromo- γ -phenyldodecane, b.p. 141—147°/0.13 mm.; α -bromo- δ -phenyltridecane, b.p. 150—155°/0.12 mm.; α -bromo- θ -phenylhexadecane, b.p. 169—172°/0.1 mm.; α -chloro- θ -phenyldodecane, b.p. 129—136°/0.1 mm.; α -chloro- ζ -phenyltetradecane, b.p. 166—173°/3 mm.; α -chloro- η -phenylhexadecane, b.p. 160—165°/0.1 mm.; β -phenylheptoic acid, b.p. 144—149°/3 mm. (Et, b.p. 117—120°/3 mm., and p-bromophenacyl, m.p. 47.4—48.2°, esters); ϵ -phenyldecoic acid, b.p. 176—180°/3 mm. (p-bromophenacyl ester, m.p. 55.5—56°); β -phenylundecoic acid, b.p. 167—172°/2.5 mm. (Et, b.p. 154—159°/4 mm., and p-bromophenacyl, m.p. 65.5°, esters); β -phenyldodecoic acid, b.p. 165—171°/0.3 mm. (Et, b.p. 142—148°/0.2 mm., and p-bromophenacyl, m.p. 74.5—75.5°, esters); γ -phenyldodecoic acid, b.p. 184—187°/3 mm. (p-bromophenacyl ester, m.p. 89—90°); ι -phenyltetradecoic acid, b.p. 178—183°/0.1 mm. (p-bromophenacyl ester, m.p. 79—80°); ϵ -phenylpentadecoic acid, b.p. 182—185°/0.1 mm. (p-bromophenacyl ester, m.p. 73.5—74.5°); η -phenyl-hexadecoic acid, b.p. 190—195°/0.12 mm. (Et, b.p. 174—180°/0.13 mm., and p-bromophenacyl, m.p. 77—78°, esters); θ -phenylhexadecoic acid, b.p. 200—204°/0.09 mm., m.p. 36.5—38° (p-bromophenacyl ester, m.p. 83.5—94.5°); ι -phenyloctadecoic acid, b.p. 199—205°/0.09 mm., m.p. 40—41.5° (p-bromophenacyl ester, m.p. 71—72°). γ -Phenylheptan- α -ol, b.p. 116—120°/3 mm., γ -phenylundecan- α -ol, b.p. 139—145°/2.5 mm., γ -phenyldodecan- α -ol, b.p. 140—142°/0.2 mm., and θ -phenylhexadecan- α -ol, b.p. 168—174°/0.1 mm., are prepared by reduction of the above Et esters. The phenylstearic acid prepared from oleic acid, C_8H_8 , and AlCl_3 contains approx. equal amounts of θ - and ι -phenyloctadecoic acids. C. J. W. (b)

α -Naphthoylhydrazine and 3-hydrazino- β -naphthoic acid. H. GOLDSTEIN and E. CORNAMUSAZ (Helv. Chim. Acta, 1932, 15, 939—943).—Et 3-iodo- β -naphthoate and boiling $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (I) give β -naphthoylhydrazine (II), m.p. 147.5° (Ac derivative, m.p. 138°), also obtained from Me β -naphthoate (modified prep.) and (I) at 100° and, with NN'' -di- β -naphthoylhydrazine (III), m.p. 241°, from β -naphthoyl chloride and (I). The product, m.p. 186°, previously (A., 1897, i, 638) described as (II), must have a different constitution. (III) is also formed from (II) and I in boiling EtOH. Diazotised 3-amino- β -naphthoic acid and SnCl_2 afford 3-hydrazino- β -naphthoic acid, m.p. indef. (Ac derivative, m.p. 233°; benzylidene derivative, m.p. 241°), changed by heating in vac., finally to 300°, to $\beta\beta'$ -naphthopyrazolone, m.p. about 275—280°. R. S. C.

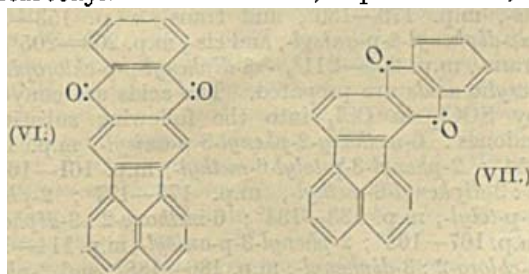
Fluoranthene and its derivatives. IV. J. VON BRAUN and G. MANZ (Annalen, 1932, 496, 170—196; cf. A., 1931, 1044).—Acylation (Friedel-Crafts) of fluoranthene, unlike nitration, bromination, and

sulphonation (*loc. cit.*), gives mainly the 12-derivative; the 4-isomeride is a by-product.

[With B. KRATZ.] Fluoranthene, $(\text{COCl})_2$, and AlCl_3 in CS_2 at 0° give a mixture of mono- (7 pts.) and di- (3 pts.) -carboxylic acids. The former are separated by esterification (EtOH-HCl) and fractionation; Et fluoranthene-12-carboxylate (I) (A, R=OEt), m.p. 90—91°, is separated and the residual ester shown to contain Et fluoranthene-4-carboxylate by



conversion into 4-aminofluoranthene by way of the hydrazide, azide, and urethane. Fluoranthene-12-carboxylic acid (II), m.p. 283—285° (chloride, m.p. 100—103°; amide, m.p. 233°; anilide, m.p. 233°), is converted through the hydrazide, m.p. 213°, azide, decomp. 110°, and urethane, m.p. 140—142°, into 12-aminofluoranthene (III), m.p. 168—169° (hydrochloride, decomp. 270—280°; Ac derivative, m.p. 191°), which is reduced (Na-Hg) to an oily H_2 -derivative (diazotisable), the Ac derivative, m.p. 179—180°, of which on oxidation (*cf. loc. cit.*) and hydrolysis, gives an amino-keto-acid, $\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}$, decomp. from 190°. Oxidation of (II) with CrO_3 -AcOH gives fluorenone-1:6- and -1:7-dicarboxylic acids, whilst reduction (Na-Hg) affords 5:6:7:8-tetrahydrofluoranthene-12-carboxylic acid, m.p. 237—239°, oxidised to fluorenone-1-carboxylic-6-propionic acid, m.p. 300—305° (Me, ester, m.p. 120°), and thence to fluorenone-1:6-dicarboxylic acid, m.p. 320—325° (decomp.) (Me ester, m.p. 163—165°). Fluoranthene, BzCl , and AlCl_3 in CS_2 give (mainly) 12-benzoylfluoranthene (A, R=Ph), m.p. 111—112°, purified through its oxime, m.p. 212—213°; rearrangement of the oxime with PhSO_2Cl and pyridine, followed by hydrolysis, affords (III) and BzOH . 4-Benzoylfluoranthene is also produced, since the crude oxime is similarly converted into a little 4-aminofluoranthene. Fluoranthene, $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, and AlCl_3 in CS_2 give 12-o-carboxybenzoylfluoranthene [A, R= $o\text{-C}_6\text{H}_4\text{-CO}_2\text{H}(o)$], m.p. 212° [chloride (IV), m.p. 163—165°; Me ester, m.p. 180—181°; oxime, m.p. 224—225°, rearranged (as above) to (III)], and some 4-o-carboxybenzoylfluoranthene (V), m.p. 230° (oxime, m.p. 207—209°, convertible into 4-aminofluoranthene). When (IV) is heated in $\text{C}_6\text{H}_5\text{Cl}$, the quinones (VI), red (violet vat), m.p. 228°, and (VII), yellow (blue vat), m.p. 332—333°, are produced. Distillation of (VII) with Zn dust gives the corresponding hydrocarbon, $\text{C}_{24}\text{H}_{14}$, m.p. 290—291°, whilst oxidation (CrO_3 , AcOH) affords a mixture, m.p. 345—347° (decomp.), of phthaloylfluorenonecarboxylic acids, decarboxylated to a mixture, m.p. 326—337°, of the



anthraquinonefluorenone of Schaarschmidt and Herzenberger (A., 1919, i, 26) and an isomeride. Similar

oxidation of (VI) gives an acid, $C_{21}H_{16}O_6$, m.p. 290—295° (decomp.), decarboxylated to the anthraquinone-fluorenone of Ullmann and Dasgupta (A., 1914, i, 413). (V) is cyclised and sulphonated by H_2SO_4 at 95°; subsequent hydrolysis with $HCl-BaCl_2$ at 200° gives a quinone, $C_{21}H_{12}O_6$, m.p. 328—331°.

5:6:7:8-Tetrahydrofluoranthene (VIII) and $ClSO_3H$ in $CHCl_3$ give, after treatment with $NaCl$ and $POCl_3$, the 4-sulphonyl chloride, m.p. 118°; the 4-sulphonethylamide, m.p. 156—157°, is dehydrogenated by S at 180—210° to fluoranthene-4-sulphonethylamide (*loc. cit.*). (VIII) and Br (1 mol.) in $AcOH$ give the 4-Br-derivative, m.p. 135°, reduced ($Na-Hg$) to (VIII) and oxidised by $Na_2Cr_2O_7$ in $AcOH$ to 4-bromofluoranthene and 2-bromofluorenone-1-propionic acid, m.p. 233°, the chloride of which is not cyclised by $AlCl_3$ in CS_2 . Fluorenone-1-propionyl chloride is cyclised by this treatment to the fluorenone-hydrindone (IX), m.p. 236°. (VIII), $o-C_6H_4(CO)_2O$, and $AlCl_3$ in CS_2 give the 4-o-carboxybenzoyl derivative, m.p. 220°, since rearrangement of its oxime, m.p. 212°, and subsequent hydrolysis affords 4-amino-5:6:7:8-tetrahydrofluoranthene (*loc. cit.*). The formation of small amounts of 12-Br- and 12- NO_2 -derivatives during the bromination and nitration of fluoranthene is demonstrated. 4-Bromo- and 4-nitro-fluoranthenes are oxidised by CrO_3-AcOH to 2-bromo-, m.p. 252°, and 2-nitro-, decomp. 233—235°, fluorenone-1-carboxylic acids; fluoranthene-4-carboxylic acid gives fluorenone-1:2-dicarboxylic acid [anhydride (X), m.p. 318—320°] [also formed by oxidation of (IX) with 20% HNO_3] and a product which is esterified to a *Me* ester, $C_{17}H_{12}O_4$, m.p. 199°, and a *Me H* ester, $C_{16}H_{10}O_4$, m.p. 230—233° (decomp.), re-solidifying at 240°, and thereby passing into (X). H. B.

Syntheses with magnesium triarylvinyl bromides. Triarylacrylic acids and the indones derived from them. C. F. KOELSCH (J. Amer. Chem. Soc., 1932, 54, 2487—2493).—The following triarylvinyl bromides are prepared by bromination of triaryl-ethylenes or -ethyl alcohols in $AcOH$: α -phenyl- $\beta\beta$ -di-p-tolyl, m.p. 132—133°; α -phenyl- $\beta\beta$ -di-p-anisyl, m.p. 109—111°; $\alpha\beta$ -diphenyl- β -p-tolyl, m.p. 114—116°; $\alpha\beta$ -diphenyl- β -p-anisyl, m.p. 118—120°; cis-, m.p. 156—158°, and trans-, m.p. 103—105°, $\alpha\beta$ -diphenyl- β -p-chlorophenylvinyl bromides, separable by crystallisation from C_6H_6-MeOH . The Grignard reagents from these bromides are converted by CO_2 into triarylacrylic acids: α -phenyl- $\beta\beta$ -di-p-tolyl, m.p. 205—206°; α -phenyl- $\beta\beta$ -di-p-anisyl, m.p. 169—170°; cis- $\alpha\beta$ -diphenyl- β -p-tolyl, m.p. 185—195°; cis-, m.p. 179—180°, and trans-, m.p. 153—155°, $\alpha\beta$ -diphenyl- β -p-anisyl, and cis-, m.p. 203—205°, and trans-, m.p. 205—211°, $\alpha\beta$ -diphenyl- β -p-chlorophenylacrylic acids are prepared. The acids are converted by $SOCl_2$ in CCl_4 into the following substituted indones: 6-methoxy-2-phenyl-3-p-anisyl, m.p. 153—154°; 2-phenyl-3-p-tolyl-6-methyl, m.p. 161—161.5°; 2:3-diphenyl-6-methyl, m.p. 175—177°; 2-phenyl-3-p-tolyl, m.p. 133—134°; 6-methoxy-2:3-diphenyl, m.p. 167—168°; 2-phenyl-3-p-anisyl, m.p. 114—115°; 6-chloro-2:3-diphenyl, m.p. 186—188°, and 2-phenyl-3-p-chlorophenyl, m.p. 162—164°, indone.

$\alpha\beta$ -Diphenyl- α -p-tolylethyl alcohol, m.p. 89°, is pre-

pared from $CO(C_6H_4Me-p)_2$ and $CH_3Ph-MgCl$ (the intermediate must be decomposed with aq. NH_4Cl); $\alpha\beta$ -diphenyl- α -p-chlorophenylethyl alcohol has m.p. 83°. β -Phenyl- α -di-p-tolylethylene, b.p. 258—259°/24 mm., and $\alpha\beta$ -diphenyl- α -p-tolylethylene, b.p. 245—250°/27 mm., are obtained by distilling the corresponding alcohol with a trace of H_2SO_4 in vac.

C. J. W. (b).

Decalin series. I. Preparation of 9-substituted decalins. G. R. CLEMO and J. ORMSTON (J.C.S., 1932, 1778—1783).—9-Aminodecalin (prep. described) [NO -derivative, m.p. 243° (decomp.)] is converted into $\Delta^9:10$ -octalin (A., 1929, 921). This with HBr at 0° affords 9-bromodecalin, m.p. 29—30°, which regenerates the octalin with Et sodio-(or potassio)-malonate, and does not afford a Grignard reagent. $Et Na$ malonate does not react with $\Delta^9:10$ -octalin oxide, and with $\Delta^9:10$ -octalin dibromide affords octalin and Et ethanetetra-carboxylate. *cyclo*Hexene oxide with CH_3Br-CO_2Et and Zn in boiling C_6H_6 during 4 hr. affords *Et* 2-hydroxycyclohexylacetate, b.p. 114°/13 mm. (probably the *trans*-form) [hydrazide, m.p. 154°, not identical with the hydrazide of *Et* 2-hydroxycyclohexylacetate described previously (A., 1923, i, 696)]. Similarly, *cyclo*hexanone affords *Et* 1-hydroxycyclohexylacetate (hydrazide, m.p. 103°) and $\Delta^9:10$ -octalin oxide during 6—7 hr. affords 2-keto-cyclohexanospirocyclopentane (I) (A., 1899, i, 742) and an ester (II), b.p. 125°/0.1 mm., giving a hydrazide, $C_{12}H_{20}O_2N_2$, m.p. 122°. It is probably *Et* 9-hydroxy-decalin-10-acetate. It is not 2-hydroxycyclohexanospirocyclopentane-2-acetate, since the latter [from (I) and CH_3Br-CO_2Et with Zn in C_6H_6] gives a non-crystallising hydrazide of low m.p. Prolonged dehydrogenation of (II) with Se at a high temp. affords $C_{10}H_8$ and a compound, $C_{16}H_{12}$, m.p. 142—143°.

J. L. D.

Manufacture of [alkoxy- and alkylthiol] derivatives of 2:3-hydroxynaphthoic acid. A. CARPMAEL. From I. G. FARBERIND. A.-G.—See B., 1932, 494.

Differing solubilities of optical antipodes in active solvents. E. SCHROER (Ber., 1932, 65, [B], 966—974).—A solution of *r*-mandelic acid in *d*-carvone is fractionally extracted with H_2O . The successive extracts are diminishingly levorotatory, then inactive and increasingly dextrorotatory. The activities are not very marked. Similar results are obtained when *l*-carvone is employed, but the sequence of activity is reversed.

H. W.

Condensation of butylchloral with gallic acid and the three cresotic acids. (Miss) B. N. KATRAN and A. N. MELDRUM (J. Indian Chem. Soc., 1932, 9, 121—125).—Gallic acid (1 mol.) and butylchloral hydrate (I) (1 mol.) in 95% H_2SO_4 give (after 24 hr.) 3:4:5-trihydroxy-2- $\alpha\beta$ -trichloropropylphthalide, m.p. 260° (triacetate, m.p. 161—162°, reduced by Zn dust and $AcOH$ to 3:4:5-triacetoxy-2- α -chloropropenylphthalide, m.p. 145°); with 2 mols. of (I), a compound, $C_{23}H_{20}O_6Cl_{12}$ (structure suggested), m.p. 281—282°, also results. Gallic acid Me_3 ether and (I) in 80% H_2SO_4 afford (after 10 days) 3:4:5-trimethoxy-2- $\alpha\beta$ -trichloropropylphthalide, m.p. 90—91°, reduced by Zn dust and $AcOH$ to 3:4:5-trimethoxy-2- α -

chloropropenylphthalide, m.p. 110—111°, whilst 4-hydroxy-3:5-dimethoxy-2- $\alpha\beta$ -trichloropropylphthalide, m.p. 154—155° (acetate, m.p. 169—170°), is obtained from syringic acid, (I), and 95% H_2SO_4 . *o*-Cresotic acid, (I), and H_2SO_4 give $\beta\beta$ -trichloro- $\alpha\alpha$ -di-(4-hydroxy-5-carboxy-3-methylphenyl)butane, m.p. 289°; similar compounds, m.p. 277° and 298°, are obtained from *p*- and *m*-cresotic acids, respectively. *m*-Cresotic acid, (I), and a little NaCl in 95% H_2SO_4 afford 3-hydroxy-6- $\alpha\beta\beta$ -tetrachlorobutyl-*p*-toluic acid, m.p. 210°; corresponding acids, m.p. 211—212° and 204—205°, are prepared from *p*- and *o*-cresotic acids, respectively. Similarly, *o*-cresotic acid and $\text{CCl}_3\text{CH}(\text{OH})_2$ give 2-hydroxy-5- $\alpha\beta\beta\beta$ -tetrachloroethyl-*m*-toluic acid, m.p. 184—185°. H. B.

Stereoisomerism of 2:2'-disubstituted derivatives of diphenyl. A. CORBELLINI and C. PIZZI [Atti R. Accad. Lincei, 1932, [vi], 15, 287—291; cf. this vol., 56].—Crystallisation of the brucine salt of 2-(hydroxydiphenylmethyl)diphenyl-2'-carboxylic acid from EtOH yields (1) about 70% of a fraction, m.p. 200°, $[\alpha]_D^{25} +41.15^\circ$, the rotation of which approaches that of the racemic salt, viz., -14.86° , after a few days, and (2) a residue, m.p. 182°, $[\alpha]_D^{25} -7.48^\circ$. T. H. P.

Action of hydrogen selenide on acid chlorides. II. *o*-Phthalyl chloride. L. SZFERL and J. BOHM [Rocz. Chem., 1932, 12, 378—380].—*o*-Phthalyl monoselenide, m.p. 126—127°, obtained from *o*-phthalyl chloride and H_2Se at room temp. in the presence of AlCl_3 , decomposes readily with liberation of Se in the presence of H_2O , acids, and alkalis. R. T.

Electrolytic reduction of alkylphthalimides. IV. Complete reduction. B. SAKURAI (Bull. Chem. Soc. Japan, 1932, 7, 155—157).—When acid solutions of phthalimide and its *N*-Me and -Et derivatives are electrolysed at 80—90° and 30—60 amp./100 sq. cm., both CO groups are reduced at the cathode with formation of the corresponding dihydroisindole. Phenylphthalimide yielded phthalic acid and NH_4Ph . (NH_4)₂ phthalate yielded phthalide. D. R. D.

Sulphamide. M. BATTEGAY and L. DENIVELLE (Compt. rend., 1932, 194, 2216—2218).—*N*-Chlorosulphonylphthalimide (cf. this vol., 153) in dry C_6H_6 treated with dry NH_3 gives a ppt. which dissolves in H_2O . The solution, freed from NH_3 , rapidly deposits phthalimide. The filtrate is evaporated in vac. at 25°, and the sulphamide extracted by EtOAc in 92% yield. The *N*-aminosulphonylphthalimide first formed probably decomposes to phthalimide and trisulphimide, which then hydrolyses: $(\text{SO}_2\text{NH})_3 + 3\text{H}_2\text{O} = \text{SO}_2(\text{NH}_2)_2 + \text{NH}_2\text{SO}_3\text{H} - \text{H}_2\text{SO}_4$, an explanation rendered probable by the fact that if NH_3 is replaced by NHPMe there is formed cryst. $\text{C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{SO}_2\text{NPhMe}$, m.p. 160°. C. A. S.

Ketens from acylphthalimides and other substituted amides. C. D. HUND and M. F. DULL (J. Amer. Chem. Soc., 1932, 54, 2432—2440).—Both acetylphthalimide and *N*-acetylcarbazole undergo decomp. at refluxing temp. into cyclobutane-1:3-dione (dimeric keten), in yields of 30—38 and 20—

37%, respectively; with the former, careful removal of H_2O increases the yield to 53—75%. NACPh_2 is unchanged after 24 hr. at 290° or after passage through tubes at 500—600°. NHAc_2 gives good yields of AcOH and MeCN when passed rapidly through a tube at 635°, but evidence for the formation of keten or its dimeride was not obtained. *Propionylphthalimide*, m.p. 143—144°, begins to decompose at 220° and when heated at 322° for 3 hr. gives 38—47% of COEt_2 and 25—29% of $(\text{EtCO})_2\text{O}$; the latter is determined by heating with $\text{H}_2\text{C}_2\text{O}_4$ in pyridine, whereby 100% of CO and CO_2 are formed. The gaseous products consist of 81.9% CO_2 and 6.7% CO , with some N_2 . *Propionylcarbazole* gives the same two products. *Butyrylphthalimide*, softens at 70—72° but does not melt until the m.p. of $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$ is reached, decomposes on keeping for a few hr.; pyrolysis gives $(\text{PrCO})_2\text{O}$, COPr_2 , and CO_2 . *Hexoylphthalimide*, m.p. 98.5—99.5°, is pyrolysed to hexoic acid and trimeric butylketen, b.p. 213—216°/5 mm.; 12% of the original material is recoverable after 20 min. at 145—150°. *isoButyrylphthalimide*, m.p. 96—98°, gives a considerable amount of free dimethylketen when heated to 225°. *Diphenylacetylphthalimide*, m.p. 170—171°, is pyrolysed to $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$ and diphenylketen. These methods are suitable for the prep. of dimeric keten, and dimethyl- and diphenyl-ketens. C. J. W. (b)

Bile acids. XXXV. M. SCHENCK (Z. physiol. Chem., 1932, 208, 120—124; cf. this vol., 614).—A discussion of the constitution of cholic acid. The formula with CHMe between C_{11} and C_{12} of ring III is preferred. J. H. B.

Structure of apocholic acid and the carbon skeleton of the sterols and bile acids. A. R. TODD (Chem. and Ind., 1932, 509—570).—The bridged-ring structure of Borsche and Todd (A., 1931, 841) for apocholic acid affords a more satisfactory explanation of its reactions than does that of Rosenheim and King (this vol., 736). The chrysene structure of the latter authors for cholanolic acid is at variance with several of the established facts. H. B.

Quinic acid. II. Constitution and configuration of quinic acid. H. O. L. FISCHER and G. DANGSCHAT [with C. TAUBE, F. RADT, and H. STETTENE] (Ber., 1932, 65, [B], 1009—1031; cf. A., 1921, i, 419).—Since the diisopropylidenequinamide, m.p. 155°, $[\alpha]_D^{25} -25.1^\circ$ in EtOH , of Karrer and others (A., 1925, i, 673) does not evolve NH_3 when heated with NaOH and yields diacetyl-diisopropylidenequinamide, m.p. 73—75°, -62.2° in CHCl_3 , instead of a nitrile, when heated with Ac_2O , it cannot contain the $\text{CO}\cdot\text{NH}_2$ group. The presence of a free OH group is established by the production of 3-*p*-toluenesulphonyl-diisopropylidenequinamide, m.p. 103°, $[\alpha]_D^{25} -92.2^\circ$ in anhyd. MeOH (converted by hot 80% AcOH into 3-*p*-toluenesulphonylisopropylidenequinamide, m.p. 181° (decomp.), $[\alpha]_D^{25} -31.8^\circ$ in MeOH), 3-acetyl-diisopropylidenequinamide, m.p. 157°, $[\alpha]_D^{25} -73.7^\circ$ in CHCl_3 (hydrolysed to 3-acetylisopropylidenequinamide, m.p. 162°), and dimethoxydiisopropylidenequinamide, b.p. 128—129°/1.5 mm. (hydrolysed by 2.5*N*- HCl to

3-methoxyquinic acid, from which by means of boiling AcOH, 1 : 4 : 5-triacetyl-3-methoxyquinic acid, m.p. 168—169°, is derived: mixed anhydride of acid and AcOH, m.p. 118—120°. The structure (I) is therefore ascribed to diisopropylidenequinamide. (I) is transformed by hot 80% AcOH into isopropylidenequinamide, m.p. 176—178° after slight softening, $[\alpha]_D^{25} -25.0^\circ$ in H_2O (Ac_4 derivative, m.p. 163°, $[\alpha]_D^{25} -63.1^\circ$ in $CHCl_3$),

converted by Ag_2O and MeI followed by hydrolysis into 3 : 4 : 5-trimethoxyquinic acid, identified as the chloralide, $C_{12}H_{17}O_6Cl_3$, m.p. 104—106°, $[\alpha]_D^{25} -54.2^\circ$ in anhyd. MeOH. Quinamide, Ac_2O , and pyridine at room temp. afford tetra-acetylquinamide, m.p. 186—187° (decomp.), $[\alpha]_D^{25} -28.6^\circ$ in $CHCl_3 \cdot CHCl_3$, transformed by boiling Ac_2O into tetra-acetylquinonitrile, m.p. 161—162°, $[\alpha]_D^{25} -29.9^\circ$ in $CHCl_3$. 1 : 3-Diacetyl-4 : 5-isopropylidenequinonitrile, m.p. 113° after softening, 1-methoxy-4 : 5-isopropylidenequinamide, m.p. 158—159°, 1-methoxy-3-acetyl-4 : 5-isopropylidenequinamide, m.p. 148—149° (corresponding nitrile, m.p. 107°), 4 : 5-isopropylidenequinamide, m.p. 120° (decomp.), anilide, m.p. 148—149°, $[\alpha]_D^{25} -16.4^\circ$ in $CHCl_3$, and methylamide, m.p. 108—110°, $[\alpha]_D^{25} -48.7^\circ$, are described.

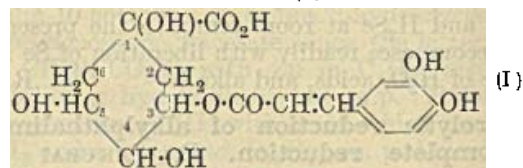
4 : 5-isoPropylidenequinide (II) is transformed by $N_2H_4 \cdot H_2O$ into 4 : 5-isopropylidenequinhydrazide, m.p. 150—151° (decomp.), $[\alpha]_D^{25} -54.0^\circ$ in H_2O , converted through the corresponding azide into 3-hydroxy-4 : 5-isopropylidenedioxy-cyclohexanone (III), m.p. 79°, $[\alpha]_D^{25} +147^\circ$ in EtOH. In aq. solution it shows strong mutarotation, from $[\alpha]_D^{25} +126^\circ$ to -146° in 20 hr. The ketone is preferably obtained by transforming (II) by a large excess of $MgMeI$ into 1 : 3 : 4 : 5-tetrahydroxy-4 : 5-isopropylidene-cyclohexylidimethylcarbinol (IV), m.p. 151—152°, which is treated with $Pb(OAc)_4$ in C_6H_6 at 40—50°. Treatment of (IV) with AcOH removes $COMe_2$, leaving a compound, $C_9H_{15}O_5$, m.p. 115°, which affords an isomeric isopropylidene derivative, $C_{12}H_{22}O_5$, m.p. 163°, also derived by treating the Grignard product with $COMe_2$ + 1% HCl. The formation of the isopropylidene ketone establishes the presence of a free OH in the α -position to CO_2H in (II). Since (III) affords a phenylhydrazone, $C_{15}H_{20}O_3N_2$, m.p. 150—152° (decomp.), $[\alpha]_D^{25} +42.7^\circ$ in MeOH, under conditions which lead to phenylsazones with cyclohexanolones, it follows that the OH groups are in positions 1, 3, 4, 5 in quinic acid. (III) is characterised by an Ac derivative, m.p. 68—69°, not affected by $CH(OEt)_3$ and NH_4Cl , a semicarbazone, m.p. 171—172°, $[\alpha]_D^{25} +65.2^\circ$ in H_2O [transformed by $C_6H_5MgSO_2Cl$ and pyridine into a compound, $C_{10}H_{15}O_3N_3$, m.p. about 200° (decomp.), and by $COMe_2$ + HCl into a substance, $C_{10}H_{15}O_3N_3$, m.p. 196° (decomp.)], and by conversion by $MgMeI$ into 1 : 3-dihydroxy-4 : 5-isopropylidenedioxy-1-methylcyclohexane, b.p. 122°/0.2 mm., $[\alpha]_D^{25} -35.2^\circ$ in EtOH [monohydrate, m.p. (indef.) 80—83°, $[\alpha]_D^{25} -31.12^\circ$]. The crystalline ketone (III) probably exists in the oxycycloform, since it is inactive towards $CH(OEt)_3$ and cannot be reduced catalytically. Removal of the isopropylidene residue causes the ring system to become aromatic.

Methylisopropylidenequinide and $N_2H_4 \cdot H_2O$ give 1-methoxy-4 : 5-isopropylidenequinhydrazide, m.p. 142—143° (decomp.), $[\alpha]_D^{25} -45.6^\circ$ in H_2O , converted through the azide into the cyclic urethane (V), m.p. 144—145°, $[\alpha]_D^{25} +73.8^\circ$ in $CHCl_3$, also obtained by the Hofmann degradation of 1-methoxy-4 : 5-isopropylidenequinamide; hydrolysis with AcOH produces $COMe_2$ and the substance $C_9H_{15}O_5N$, m.p. 214—215° (decomp.) (obtained also by the degradation of 1-methoxyquinamide), which is transformed by Br in $CHCl_3$ into a mixture of bromomethoxy- and bromo-quinol.

Quinide is transformed by MeI and Ag_2O in boiling dioxan into 1 : 4 : 5-trimethoxyquinolactone, converted by $NH_3 \cdot MeOH$ into 1 : 4 : 5-trimethoxyquinamide, m.p. 128° after softening, $[\alpha]_D^{25} -85.4^\circ$ in H_2O , which does not yield an isopropylidene derivative. With Br and H_2O the lactone yields isovanillic acid. 3-p-Toluenesulphonyl-1-methoxy-4 : 5-isopropylidenequinamide, m.p. 145°, and 3-p-toluenesulphonyl-1-methoxyquinamide, m.p. about 108°, have been prepared.

H. W.

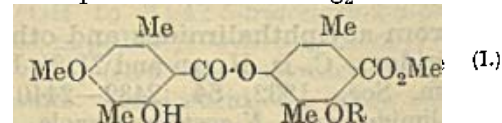
Quinic acid and its derivatives. III. Constitution of chlorogenic acid. H. O. L. FISCHER and G. DANGSCHAT (Ber., 1932, 65, [B], 1037—1040).—Since chlorogenic acid is not converted by Ac_2O into a lactone it is probable that the 3-OH group is substituted. The constitution (I) is established, since



it is transformed by $COMe_2$ and $ZnCl_2$ into diisopropylidenechlorogenic acid, m.p. 196—197°, insol. in K_2CO_3 , reaction occurring with OH groups at positions 4 and 5, and OH and CO_2H groups at position 1. Treatment with diazomethane methylates the phenolic OH and CO_2H groups and subsequent treatment with Ag_2O and MeI leads to Me pentamethylchlorogenate, b.p. 225—232°/0.1 mm., hydrolysed by $NaOH \cdot MeOH$ to 3 : 4-dimethoxycinnamic acid and 1 : 4 : 5-trimethylquinide.

H. W.

Lichen acids. III. Constitution of barbatic acid and syntheses of isorhizonic acid and methyl barbatate. A. ROBERTSON and R. J. STEPHENSON (J.C.S., 1932, 1675—1681; cf. A., 1930, 472).—Me, m.p. 170° (I; R=H) and Et barbatate, m.p. 189°, are prepared from the acid (extraction from *Usnea barbata* improved) and the diazoalkane in Et_2O ; excess of CH_3N_2 gives Me O-methylbarbatate (I; R=Me), m.p. 123°. The Et ester, m.p. 132°, of Hesse (A., 1898, 1, 378) and Zopf (A., 1899, i, 716) is probably a degradation product. MeI and Ag_2O in boiling CO_2Me



give an amorphous product. The structure (I; R=Me) is determined by its synthesis from O-acetyl-

rhizonoyl chloride, (II), m.p. 84° [from the acid (*loc. cit.*) and PCl_5 in CHCl_3] (anilide, m.p. 179°), and Me isorhizonate (III) by interaction in pyridine. Similarly, (I; R=H) was synthesised from (II) and Me β -oreinocarboxylate. isorhizonic acid (*cf.* this vol., 396) was synthesised from the Ac derivative, m.p. 67°, of isorhizonaldehyde (A., 1930, 472) by oxidation with neutral aq. KMnO_4 and deacetylation of the resulting acetylisorhizonic acid, m.p. 160°. H. A. P.

Syntheses of aromatic acetyl-carboxylic and polycarboxylic acids. F. FEIST (Annalen, 1932, 496, 99—122).—Benzenepolycarboxylic acids are prepared by chlorinating acetylpolymethylbenzenes at high temp. and subsequently hydrolysing the trichloroacetyl poly(trichloromethyl)benzenes produced; the Ac group facilitates chlorination of the Me groups. Thus, 4-acetyl-*m*-xylene is chlorinated at 120—130° under intensive irradiation to 2:4-di(trichloromethyl)phenyl trichloromethyl ketone, m.p. 94°, hydrolysed by aq. EtOH - NaOH to trimellitic acid (I) (*Et* ester, b.p. 230°/28 mm.), and converted by boiling MeOH or EtOH into *Me*, b.p. 218°/12 mm., m.p. 129°, or *Et* (II), m.p. 130—131°, 2-trichloroacetyl-5-trichloromethylbenzoates. Hydrolysis of (II) with 21% H_2SO_4 at 140° gives 4-trichloroacetylsophthalic acid, m.p. 242° (decomp.) (*Et* H ester, m.p. 252—253°, formed as a by-product), converted readily by aq. NaOH into (I) and CHCl_3 , and reduced (H_2 , Pd- CaCO_3 , 50% EtOH) to 4-acetylsophthalic acid, m.p. 162° (decomp.). Acetyl-*p*-xylene is similarly chlorinated to 2:5-di(trichloromethyl)phenyl trichloromethyl ketone, m.p. 144°, convertible by the above methods into *Me*, m.p. 95—96°, and *Et*, m.p. 122—123°, 2-trichloroacetyl-4-trichloromethylbenzoates (?), trichloroacetyl-, m.p. 228° (decomp.), and acetyl-, decomp. about 345°, -terephthalic acids, and (I). 2:4-Diacetyl-*m*-xylene is chlorinated at 210° to a Cl_2 -derivative, b.p. 240—242°/15 mm., m.p. 225—226°, hydrolysed by 50% NaOH at 190°/16 atm. to pyromellitic acid (III). Acetyl-*p*-cumene is chlorinated at 160° to a mixture (A) of a compound, $\text{C}_{11}\text{H}_9\text{OCl}_{11}$, m.p. 210°, and a substance, m.p. 200—210°, separable through their differing solubilities in AcOH ; A is hydrolysed by KOH and a little H_2O at 170° to (probably) a keto-acid, $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_3\cdot\text{CO}\cdot\text{CO}_2\text{H}\cdot 2\text{H}_2\text{O}$, m.p. 249° (decomp.), m.p. (anhyd.) 270°, whilst hydrolysis with aq. KOH and subsequent treatment of the hydrolysate with Cl_2 gives (III). Diacetylmesitylene is chlorinated to (mainly) 2:6-di(trichloroacetyl)-3:5-di(trichloromethyl)toluene, m.p. 182°, hydrolysed by conc. H_2SO_4 or by aq. NaOH at 189°/14 atm. (and subsequent treatment with Cl_2) to methylpyromellitic acid (+3 H_2O), m.p. 233° (decomp.), m.p. (anhyd.) 243° (decomp.) (Ag salt; *Me* ester, m.p. 103—104°); the latter method of hydrolysis gives also a little $\text{C}_6\text{H}(\text{CO}_2\text{H})_5$.

Aromatic carboxylic acids cannot be acetylated by the Friedel-Crafts reaction. The following are prepared from the requisite bromoaryl Me ketone by Rosenmund and Struck's method (A., 1920, i, 44): acetophenone-4-carboxylic acid; acetophenone-3:5-dicarboxylic (5-acetylsophthalic) acid, m.p. 228° [Ag salt; phenylhydrazone, m.p. 274° (decomp.); semicarbazone, decomp. 305°]; 2:1-acetylnaphthoic acid, m.p. 140° (sinters at 95°) (*Me* ester, m.p. 89°; phenyl-

hydrazone, m.p. 165°; semicarbazone, m.p. 150°); 2(or 7)-acetylnaphthalene-1:5-dicarboxylic acid (?), m.p. 115°, prepared from 1:5-dibromo-2(or 7)-acetylnaphthalene (?), m.p. 149°, which is formed from 2- $\text{C}_{10}\text{H}_7\text{Ac}$, Br, and Fe powder or from a mixture of 1:4- and 1:5- $\text{C}_{10}\text{H}_8\text{Br}_2$, AcCl , and AlCl_3 in CS_2 . Bromination of 2- $\text{C}_{10}\text{H}_7\text{Ac}$ in CCl_4 gives a Br-derivative, m.p. 82°; a Br_4 -derivative, m.p. 120—122°, is also described. H. B.

Lichen substances. XIV. Synthesis of gyrophoric acid. Y. ASAHINA and F. FUJIKAWA (Ber., 1932, 65, [B], 983—984).—Orsellinic acid *Me* ether is converted by SOCl_2 into the corresponding chloride, which is condensed in $\text{COMe}_2\text{-C}_6\text{H}_4\text{N}$ with *Me* lecanorate, m.p. 146°. The neutral product of the reaction when treated with diazomethane in Et_2O affords *Me* gyrophorate *Me* ether, m.p. 196—197°, thus confirming the constitution assigned to gyrophoric acid (A., 1931, 221). H. W.

Trinitrobenzaldehyde and its derivatives. A new and convenient method for the preparation of *s*-trinitrobenzene. S. SECAREANU (Bull. Soc. chim., 1932, [iv], 51, 591—596; *cf.* A., 1931, 730).—2:4-Dinitro-6-anilinobenzylideneaniline and its $\text{C}_6\text{H}_4(\text{NO}_2)_2$ additive compound give 2:4-dinitro-6-anilinobenzaldehydephenylhydrazone, m.p. 227°, with $\text{NHPh}\cdot\text{NH}_2$. $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{CHO}$ reacts with amines in cold AcOH to give 2:4:6-trinitrobenzylidene- β -naphthylamine, m.p. 206—207° (explodes), -*m*-nitroaniline, m.p. 161—162°, -*p*-bromoaniline, m.p. 184°, -*p*-toluidine, m.p. 177—178°, and -2-bromo-*p*-toluidine, m.p. 209°. 2:4-Dinitrobenzylideneaniline, m.p. 133°, is similarly obtained. 2:4:6- $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{CHO}$ with alkalis (preferably NH_3) in EtOH gives *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$. A. A. L.

α -Keto-aldehydes. W. MADELUNG and M. E. OBERWEGNER (Ber., 1932, 65, [B], 931—941).— COPhMe in AcOH is converted by Br into ω -bromoacetophenone, which, when shaken with KOAc in MeOH , affords benzoylcarbonyl acetate in 95% yield. The product is transformed by Br in CS_2 into the unstable benzoylbromocarbonyl acetate (I), which decomposes when distilled under diminished pressure into AcBr and crude phenylglyoxal, purified by dissolution in MeOH and agitation with BaCO_3 , followed by distillation; b.p. 108—110°/15 mm. (yield 82%). The hydrate (II) (yield 75%) is prepared by crystallising the crude aldehyde from H_2O or by repeated extraction of the Br-compound with boiling H_2O or 5% H_2SO_4 . A compound, $\text{C}_{24}\text{H}_{18}\text{O}_4$, m.p. 197—198° (decomp.) (*Ac* derivative, m.p. 169—170°), is obtained as by-product. Phenylglyoxal dimethylacetal (III), b.p. 133—134°/16 mm., from (I) and boiling MeOH in 78—80% yield, is converted by Ac_2O containing a trace of conc. H_2SO_4 into ω -acetoxy- ω -methoxyacetophenone, b.p. 160—162°/14 mm., readily hydrolysed to (II). Treatment of phenylglyoxal with MgPhBr in Et_2O yields $\alpha\beta$ -triphenylethane- $\alpha\beta$ -diol, m.p. 164°, converted by conc. H_2SO_4 into triphenylvinyl alcohol, m.p. 135°, whereas (III) gives hydroxydiphenylacetaldehyde, b.p. 180—194°/17 mm. (semicarbazone, m.p. 238—5°), oxidised by conc. HNO_3 to benzoic acid. (I) and NPhMe_2 afford benzoyltetramethyldiaminodiphenylmethane, m.p. 164°, ob-

tained also from phenylglyoxal or $\text{COPh}\cdot\text{CHBr}_2$ and NPhMe_2 , and converted by MgPhBr into α -diphenyl- β -tetramethyldiaminodiphenylethyl alcohol, m.p. 215° , dehydrated by boiling conc. HCl to α -diphenyl- β -tetramethyldiaminodiphenylethylene, m.p. 212° . β -Naphthyl Me ketone yields the Br-derivative, m.p. $82\text{--}5^\circ$, and thence 2-naphthylcarbinyl acetate (IV), m.p. 80° , hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to 2-naphthylcarbinol, m.p. 114° (hydrate, m.p. 96°). Bromo-2-naphthylcarbinyl acetate, m.p. 73° , is transformed into 2-naphthylglyoxal hydrate, m.p. 98° , from which are derived 2-naphthylglyoxal (V) b.p. $183^\circ/20$ mm. (partial decomp.), its dimethylacetal, b.p. $194^\circ/16$ mm., and Ac_2 derivative, m.p. 150° ; evidence of the existence of an isomeric Ac_2 compound is obtained. Protracted warming of (IV) or (V) with dil. H_2SO_4 gives a compound, m.p. 260° (decomp.) (Na salt; Ac derivative, m.p. 205°). Acetol acetate, prepared from chloroacetone and KOAc in $\text{MeOH}\text{--}\text{COMe}_2$ (evidence of existence of a tautomeric form is obtained), is converted by successive treatment with Br in CS_2 and MeOH into methylglyoxal dimethylacetal, b.p. $56\text{--}58^\circ/16$ mm.

H. W.

Hydroxy-carbonyl compounds. VIII. Derivatives of 2:6-dihydroxytoluene. E. T. JONES and A. ROBERTSON (J.C.S., 1932, 1689—1693).—6-Nitro-*o*-tolyl *p*-toluenesulphonate, m.p. 94° (from the nitro-cresol and *p*-toluenesulphonyl chloride in pyridine), is reduced by $\text{SnCl}_2\text{--HCl}$ in AcOH to the NH_2 -compound, m.p. 108° , which on diazotisation, decomp., and hydrolysis of the product gives 2:6-dihydroxytoluene (I). This is also obtained from 6-methoxy-*o*-cresol (II) or from 2-hydroxy-6-methoxy-*m*-toluic acid by action of aq. HI (d 1.7) at its b.p., and gives 2:6-dihydroxy-*m*-tolualdehyde (III), m.p. 147° , by the Gattermann reaction [$\text{Zn}(\text{CN})_2$ as condensing agent]. 2-Hydroxy-6-methoxy-*m*-tolualdehyde, m.p. 64° , is obtained from (II) by the Gattermann reaction or by partial methylation of (III) (MeI and K_2CO_3 in COMe_2); its structure is confirmed by its condensation with *p*-methoxyacetophenone and HCl in EtOAc to 7:4'-dimethoxy-8-methylflavylum chloride (ferrichloride, m.p. $177\text{--}178^\circ$); therefore the acid derived by oxidation with KMnO_4 in aq. COMe_2 , which is identical with *C*-methylated β -resorcylic acid (J.C.S., 1895, 67, 990), is 2-hydroxy-6-methoxy-*m*-toluic acid.

Condensation of (I) with MeCN in Et_2O in presence of HCl and ZnCl_2 gives 2-hydroxy-4-methoxy-3-methylacetophenone, m.p. 83° (*C*-methylpæanol; cf. A., 1894, i, 521; 1895, i, 43; J.C.S., 1918, 113, 868), the orientation of which follows from its conversion into 2-hydroxy-4-methoxy-3-methylbenzoylacetone, m.p. 118° , by interaction with Na and EtOAc , and thence into 7-methoxy-2:8-dimethyl-1:4-benzopyrone ($+\text{xH}_2\text{O}$), m.p. 142° , by AcOH containing a little HCl at its b.p.

2-Hydroxy-4-methoxy-3-methylbenzophenone, m.p. 125° , was not obtained by decarboxylation of its carboxylic acid (A., 1930, 1167), but results from partial methylation (MeI and K_2CO_3 in COMe_2) of the corresponding (OH)₂-compound, m.p. 177° , which is prepared by condensation of (I) with PhCN in Et_2O by $\text{ZnCl}_2\text{--HCl}$, or from (II) by the action of BzCl and AlCl_3 in CS_2 . It does not undergo ring-closure with Ac_2O and NaOAc .

H. A. P.

Formula of fir lignin. P. KLASON (Svensk Pappers-Tidn., 1931, 34, 543—548, 578—581; Chem. Zentr., 1931, ii, 3458—3459).—Concn. of β -lignosulphonic acid must be effected at room temp. or in vac. to avoid the development of a deep brown colour. The brown substance is a polymericide of β -lignosulphonic acid in which the CHO and SO_3H groups are unaffected. The lignin of this compound is named "melanolignin," and the sulphonic acid "melanoligninhydrosulphonic acid." β -Lignin has the formula $2(\text{C}_9\text{H}_9\text{O}_3\cdot\text{OH})\cdot\text{C}_{10}\text{H}_{10}\text{O}_3$. Oxidation of β -lignosulphonic acid with H_2O_2 and pptn. with $\text{C}_{10}\text{H}_7\text{NH}_2\cdot\text{HCl}$ produces the salt $\text{C}_{10}\text{H}_{10}\text{O}_3\cdot\text{C}_9\text{H}_8\text{O}_3\cdot\text{H}_2\text{SO}_3\cdot\text{C}_{10}\text{H}_9\text{N}\cdot\text{H}_2\text{O}$; the α -acid is fairly stable towards H_2O_2 at room temp. On the assumption that lignin consists of 2 mols. of α - and 1 mol. of β -lignin, lignin has the formula $\text{C}_{32}\text{H}_{38}\text{O}_{38}$; M 1820. Sulphuric acid-lignin is $6\text{C}_{10}\text{H}_{10}\text{O}_3\cdot 2\text{C}_9\text{H}_{10}\text{O}_4\cdot\text{C}_{10}\text{H}_{12}\text{O}_4$. α -Lignosulphonic acid is much less sensitive to acid than the β -acid; the former does not pass into the latter during boiling with sulphite.

A. A. E.

Chemistry of conifers. P. KLASON (Cellulose-chem., 1932, 13, 113—119).—Lignin, which comprises 31.8% of wood, is extracted from it with H_2SO_4 in the form of $\frac{2}{3}$ α - and $\frac{1}{3}$ β -lignin-sulphonic acids. α -Lignin-sulphonic acid is a trimeric form of coniferylaldehydehydrosulphonic acid in which the 3 mols. of coniferylaldehyde are linked through the CHO and OH groups. In β -ligninsulphonic acid two of the OMe groups are replaced by OAc . In wood the two forms of lignin appear to be combined with each other and with cellulose. In untreated lignin the side-chains are aldols, $\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHO}$, and the sulphonic acids are formed by the displacement of OH by SO_3H . When treated with 66% H_2SO_4 lignin loses its aldol water and also acetic acid from β -lignin. Lignin is simply related to the pentoses, thus $2\text{C}_5\text{H}_{10}\text{O}_5 \rightarrow \text{C}_6\text{H}_5(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} + \text{CO}_2 + 4\text{H}_2\text{O}$, the alcohol being then oxidised to the aldehyde and methylated by CH_2O .

A. G.

Compounds containing the carbon-ring of β - or α -ionone and several ethylenic linkings. P. KARRER, H. SALOMON, R. MORF, and O. WALKER (Helv. Chim. Acta, 1932, 15, 878—889).—Most of the following products were mixtures, probably of stereoisomerides. β -Ionone, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn in hot C_6H_6 give *Et* δ -(1:1:3-trimethyl-2- Δ -cyclohexenyl)- β -methylbutadiene- α -carboxylate,

$\text{CH}_2\text{--}\text{CH}(\text{CMe}_2)\text{--}\text{CH}(\text{CMe}_2)\text{--}\text{CH}(\text{CMe}_2)\text{--}\text{CH}(\text{CO}_2\text{Et})$ (I), b.p. $165\text{--}168^\circ/7$ mm., hydrolysed by cold 10% $\text{KOH}\text{--EtOH}$ to (?) a mixture of stereoisomerides of the corresponding acid, b.p. $150^\circ/0\text{--}25$ mm., separable into crystals, m.p. 125° , and much oil. By a similar reaction tetrahydroionone gives *Et* β -hydroxy- δ -(1:1:3-trimethyl-2-cyclohexenyl)- β -methylvalerate, b.p. $178\text{--}184^\circ/10$ mm. (Ac derivative, b.p. $182\text{--}184^\circ/10$ mm.), transformed (not smoothly) by P_2O_5 in hot PhMe into the unsaturated ester. The formation of a OH - or unsaturated ester by the Reformatsky reaction thus depends on the degree of reduction of the ionone ring. *Et* δ -(1:1:3-trimethyl-2-cyclohexenyl)- β -methylvalerate [prepared by hydrogenation (PtO_2) of (I) in AcOH], b.p. $160^\circ/8$ mm. (corresponding acid, b.p.

mostly 155—162°/0.2 mm.), with Na and hot EtOH gives α -(1:1:3-trimethyl-2-cyclohexyl)- γ -methyl-n-amyl alcohol, b.p. mostly 150—156°/7 mm., whence the bromide (II), b.p. mostly 156—160°/8 mm., was best prepared by HBr under certain conditions. The Grignard reagent from (II) with chloromethyl ether gives a mixture containing Me ζ -(1:1:3-trimethyl-2-cyclohexyl)- δ -methylhexyl ether (not isolated pure), b.p. 157°/9 mm., and α -di-(1:1:3-trimethyl-2-cyclohexyl)- γ -dimethyl-n-decane, b.p. 166—168°/0.025 mm. α -Ionone and Mg allyl bromide give γ -hydroxy- α -(1:1:3-trimethyl-2- Δ^3 -cyclohexenyl)- γ -methyl- $\Delta^{\alpha\alpha}$ -hexadien- γ -ol, b.p. 137—140°/9 mm., yielding with hot PhNCO much CO(NHPh)₂, a cryst. substance, and some α -(1:1:3-trimethyl-2- Δ^3 -cyclohexenyl)- γ -methyl- $\Delta^{\alpha\alpha}$ -hexatriene (III), b.p. 127—130°/10 mm. The constitution of (III) is proved by oxidation by O₃ to isogeronic acid, by CrO₃ to 2 mols. of AcOH, and by KMnO₄ to 1 mol. of AcOH. In contrast, Mg allyl bromide adds on to the ethylenic linking of β -ionone. The absorption spectrum of (I) and colours given by several of the above compounds with SbCl₅ are recorded.

R. S. C.

Benzylideneacetone, cinnamic acid, and bromostyrene. P. P. SCHORIGIN, V. I. ISSAGULANTZ, and A. R. GUSSEVA (J. Gen. Chem., Russia, 1931, 1, 506—510).—A modification of Claisen's method for the manufacture of CHPh:CH:COMe (81% yield), an adaptation of Messinger's method for the iodometric determination of this in the crude product, and processes for the prep. of cinnamic acid (71% yield), Me cinnamate (80% yield), and CHPh:CHBr are described.

CH. ABS.

Electrochemical chlorination of some ketones. J. SZPER (Bull. Soc. chim., 1932, [iv], 51, 653—656).—Monochloro-derivatives are obtained in good yield by electrolysis of solutions of COMe₂, COPh₂, COPhMe, COPhPr² (two products, b.p. 215°, and 225°/760 mm.), and cyclohexanone in HCl or HCl-AcOH. No chloroacetic acid is obtained from the latter mixture.

A. A. L.

Preparation of ketochloroimines by the action of chlorine on compounds of the type CR'R''N·MgX. C. R. HAUSER, H. A. HUMBLE, and G. J. HAUS (J. Amer. Chem. Soc., 1932, 54, 2476—2480).—CPh₂N·MgBr, treated with an equiv. of Cl or *tert*-alkyl hypochlorite, develops an orange-red colour and gives a red product which apparently contains about 60% of benzophenonechloroimine (as calc. from its active Cl content); the crude product and dry HCl in Et₂O or C₆H₆ afford CPh₂NH₂·HCl. The N·Mg compound from MgPhBr and *p*-C₆H₄Cl·CN is converted by Cl into *p*-chlorobenzophenonechloroimine, m.p. 104° (32% yield); a stereoisomeride is not isolated. Similarly, the compound from *p*-C₆H₄Cl·MgBr and *p*-C₆H₄Cl·CN affords 35—40% of 4:4'-dichlorobenzophenonechloroimine, m.p. 74°.

C. J. W. (b)

Ketone hydrolysis and affinity capacity (electron attraction) of radicals. P. DE CEUSTER (Natuurwetensch. Tijds., 1932, 14, 188—202).—The decomp. of asymmetric ketones by NaNH₂ and NaOH has been studied with the object of comparing the relative affinities of different radicals. β -Naphthyl *p*-

diphenyl ketone, from naphthoyl chloride and Ph₂, has m.p. 132—132.5° (corr.), b.p. 497° without decomp.; its oxime has m.p. 170—178°. *p*-Anisyl *p*-diphenyl ketone has m.p. 167°, and its oxime m.p. 192°. *p*-Chlorophenyl *p*-diphenyl ketone has m.p. 172°; its oxime could be obtained only as a tautomeric mixture of indefinite m.p. *p*-Tolyl *p*-diphenyl ketoxime has m.p. 198—200°, and α -naphthyl *p*-diphenyl ketoxime m.p. 187—188°. The proportions of the principal products of hydrolysis of these and certain other ketones (12 in all) are in agreement with the theory of the relative affinity capacity of the radicals in only 4 cases; in 5 cases the results are opposed to the theory, and in 3 no definite conclusion could be obtained. Examination of 57 examples of ketone hydrolysis in the lit. shows that 14 accord with the theory, 34 contradict it, and 9 lead to no conclusion.

H. F. G.

Distribution of partial valencies of methyl- and methoxy-*p*-benzoquinones. H. ERDTMAN (Svensk kem. Tidskr., 1932, 44, 135—148).—Whilst *p*-benzoquinone possesses equiv. cationoid reaction centres at C atoms 2, 3, 5, and 6, the mono-methoxy- and -methyl derivatives show activity at C₅ owing to one of the conjugated systems (-CH:CH:C:O) being neutralised. Thus, methoxy-*p*-benzoquinone (I) is converted by Ac₂O and a little conc. H₂SO₄ into 2:4:6-triacetoxyanisole, m.p. 142°, by dil. H₂SO₄ in AcOH into 2:5-dihydroxy-4:4'-dimethoxydiphenyl-2':5'-quinone (II), decomp. from 210° [also formed by successive treatment of vanillin with alkaline H₂O₂, dil. HCl, and aq. FeCl₃, and when the quinhydrone from equimol. amounts of (I) and methoxyquinol is heated at 95—100°, whereby (I) and (II) result], and by alkali into methoxyquinol and polymeric material. *p*-Toluquinone behaves similarly but is less reactive than (I); the polymeric toluquinone of Spica (A., 1882, 1065) is now formulated as 2:5-dihydroxy-4:4'-dimethyldiphenyl-2':5'-quinone. Oxidation of (II) with K₂Cr₂O₇ and dil. H₂SO₄ gives the 2:5:2':5'-diquinone (III), decomp. 212—214° (slow), 220—230° (rapid heating), which passes when heated into 5-hydroxy-4:4'-dimethoxy-2:2'-diphenylene oxide-3':6'-quinone, m.p. 242—245°, and is converted by dry HCl in CHCl₃-AcOH in absence of air into (probably) 2:2'-dichloro-3:6:3':6'-tetrahydroxy-4:4'-dimethoxydiphenyl, acetylated by cold Ac₂O-H₂SO₄ to the 3:3'(?)-diacetate, m.p. 232°, and converted by hot Ac₂O into (mainly) (III) and (probably) 6:6'(?)-dichloro-5:5'-diacetoxy-4:4'-dimethoxy-2:2'-diphenylene oxide, m.p. 253°.

The nuclear activity of 2:6- and (especially) 2:5-dimethoxy-*p*-benzoquinones is very small owing to neutralisation of both conjugated systems. The former is affected only by long treatment with alkali (whereby polymerisation occurs), whilst the latter is only hydrolysed by alkali to 2:5-dihydroxy-*p*-benzoquinone. 2:6-Dimethyl-*p*-benzoquinone possesses some nuclear activity owing to the smaller neutralising power of Me (as against OMe); it is slowly converted by Ac₂O-H₂SO₄ into 2:4:6-triacetoxy-*m*-xylene, m.p. 103—104° (lit. 99°). 3:5:3':5'-Tetramethyldiphenquinone reacts readily with Ac₂O-H₂SO₄ forming 2:4:4'-triacetoxy-

3:5:3':5'-tetramethyldiphenyl, m.p. 141—142°, whilst 4:4'-dimethyldiphenyl-2:5:2':5'-diquinone similarly gives (slowly) 2:5:1:2':5':1'-hexa-acetoxy-4:4'-dimethyldiphenyl, m.p. 202—203°. H. B.

Identification of nitriles. Preparation of 2:4:6-trihydroxyphenyl alkyl ketones by the Hoesch synthesis on a semi-micro-scale. H. P. HOWELLS and J. G. LITTLE (J. Amer. Chem. Soc., 1932, 54, 2451—2453).—2:4:6-Trihydroxyphenyl Butanone (+H₂O), m.p. 87—88° (corr.), m.p. (anhyd.) 149° (corr.), is obtained in 84.7% yield when dry HCl (nearly saturated with Et₂O) is passed through a mixture of s-C₆H₃(OH)₃ (0.006 mol.), BuCN (0.01 mol.), and ZnCl₂ (0.4 g.) in Et₂O (25 c.c.). The method is applicable to MeCN, EtCN, PrCN, and *n*- and isohexonitriles; the yields of phlorophenones are 37—93%. C. J. W. (b)

Degradation of quaternary ammonium salts.
VII. Radical migration. T. THOMSON and T. S. STEVENS (J.C.S., 1932, 1932—1940).—The migration of phenacyl groups from N to C is studied. Diphenacyldimethylammonium bromide affords with NaOH ω-dimethylamino-ω-phenacylacetophenone (*picrate*, m.p. 128—130°), the methosulphate of which with Zn and H₂SO₄ affords diphenacyl. *p*-Bromophenacyl bromide and NHMe₂ in EtOH afford *di-p-bromophenacyldimethylammonium bromide*, m.p. 215° (decomp.). Diacetyldimethylammonium chloride [*picrate*, m.p. 198—199° (decomp.)] and *di-p-bromobenzoyldimethylammonium bromide*, m.p. 193—195° (softening at 170°), are similarly prepared, and with NaOH or MeOH-NaOMe afford only decomp. products. α-Dimethylaminopropiophenone and CH₂PhCl afford an oil, convertible into α-methylphenacylbenzoyldimethylammonium iodide, m.p. 160—161° (decomp.), which is isomerised by hot NaOH to α-dimethylamino-α-benzylpropionophenone (*picrate*, m.p. 161—162°), converted into α-benzylidenepropionophenone by boiling the methosulphate with NaOH. The corresponding α-Ph and α-Me₂ compounds could not be prepared. The ease of formation of quaternary salts of the above type is investigated. Bromopropiophenone and excess NHMe₂ in EtOH at 100—110° during 2 hr. afford α-dimethylaminopropiophenone (*picrate*, m.p. 128—130°), whilst chlorodeoxybenzoin affords α-dimethylaminodeoxybenzoin, m.p. 59—61° [*hydrochloride*, m.p. 222—225° (decomp.)], which does not react further with CH₂PhCl. α-Bromoisobutyrophenone and NHMe₂ in EtOH at 140—160° during 6 hr. give only traces of α-dimethylaminoisobutyrophenone (*picrate*, m.p. 153—155°). Benzoyldimethylamine and CH₂PhCl in cold C₆H₆ afford *di-benzoyldimethylammonium chloride*, m.p. 93—95° (*iodide*, m.p. 192°), unchanged by boiling MeOH-NaOMe, but at 120—140° during 2 hr. decomposed to NMe₂·CH₂Ph and CH₂Ph·OMe. Solid NaOMe at 140° affords some products of decomp. as before, together with αβ-diphenylethyl-dimethylamine, converted into stilbene by boiling the methosulphate with NaOH. When the N atom has an aryl group attached to it, isomerisation with alkali is accompanied by decomp. NHMe·CH₂Ph and ω-bromoacetophenone afford *phenyldibenzylmethylammonium bromide*, m.p. 144—146°. The iodide is decomposed by boiling MeOH-NaOMe to CH₂Ph·OMe

and benzylmethylaniline (*picrate*, m.p. 105—107°) and rearranged by NaNH₂ at 160—170° to αβ-diphenylethylmethylaniline, m.p. 92—93° (*hydrochloride*, m.p. 230—232°), converted into stilbene by the action of MeOH-NaOH on the methosulphate. The aryl radical attached to N favours the decomp. reaction. Allyl bromide and NMe₂·CH₂Ph in cold C₆H₆ afford *benzoyldimethylallylammonium bromide*, m.p. 98—100° (*picrate*, m.p. 108—110°), rearranged by NaNH₂ at 80° to β-dimethylamino-α-phenyl-*isobutylene* (*picrate*, m.p. 147—149°), reduced by H₂-Pd in AcOH to β-dimethylamino-α-phenylbutane [*hydrobromide*, m.p. 161—163°; *p-bromophenacylobromide*, m.p. 188—190° (decomp.)]. For comparison, α-dimethylamino-α-phenylbutane [*picrate*, m.p. 139—140°; *hydrobromide*, m.p. 162—163°; *p-bromophenacylobromide*, m.p. 208—210° (decomp.)] is prepared. CH₂Ph·MgCl and αγ-bisdimethylaminobutyronitrile afford βδ-bisdimethylamino-α-phenylbutane [*picrate*, m.p. 193—195° (decomp.)]. J. L. D.

Two isomeric (4:5- and 2:7-)diacetylacenaphthenes. K. DZIEWONSKI and J. SPIRER (Bull. Acad. Polonaise, 1931, A, 232—241).—Heated with AlCl₃ at 115—120°, α-acetoacenaphthene (I) affords mainly 4:5-diacetylacenaphthene (II), m.p. 149°, identical with the product obtained by the action of AcCl or Ac₂O on acenaphthene in presence of AlCl₃ at 120°. Its *dioxime*, m.p. 196—197°, is converted by the Beckmann change (dry HCl into its solution in Ac₂O) into the *Ac*₂ derivative, m.p. 227—228°, of 4:5-diaminoacenaphthene (A., 1931, 82), which is obtained by hydrolysis with 6% HCl. Oxidation of (II) with Na₂Cr₂O₇ in AcOH affords the *anhydride*, m.p. 202—203°, of 4:5-diacetylnaphthalic acid (*imide*, m.p. 284°) and 4:5:4':5'-tetra-acetobiadione ($\text{C}_{10}\text{H}_4\text{Ac}_4 > \text{C}$) not melting at 430°. With excess of AlCl₃ at 140°, (I) gives mainly 2:7-diacetylacenaphthene (III), m.p. 195° (*diphenylhydrazone*, m.p. 214°), the *dioxime*, m.p. 223—224°, of which is similarly converted into 2:7-diaminoacenaphthene (*loc. cit.*) (*Ac*₂ derivative, m.p. 329°). Oxidation of (III) with 3% NaOCl gives *acenaphthene-2:7-dicarboxylic acid*, m.p. 355° (decomp.). J. W. B.

Pinacol-pinacolin rearrangement. o-Substituted benzpinacols. C. H. BEALE and H. H. HATT (J. Amer. Chem. Soc., 1932, 54, 2405—2412; cf. A., 1929, 1175).—Contrary to Bailar (A., 1930, 1438), s-2:2'-dimethoxybenzpinacol is rearranged by I-AcOH (not successfully with AcCl) to a mixture, m.p. 161°, of two pinacolins [at a faster rate than s-2:2'-dimethylbenzpinacol (cf. *loc. cit.*)]; the OMe groups are attacked by I in boiling AcOH. The migratory power of the o-anisyl group is 0.3 and is greater than that of m-anisyl (0.2). Benzpinacol is oxidised by O₂ in AcOH or AcOH-NaOAc, or, better, with I in AcOH-NaOAc, to COPh₂. C. J. W. (b)

Aurin dimethyl ether and related compounds. A. BISTRZYCKI and S. VON JABLOŃSKI (Helv. Chim. Acta, 1932, 15, 890—906).—Previous work (A., 1908, i, 880) on aurin Me₂ ether is extended and partly corrected, and the prep. of the o-, m-, and p-cresol analogues is investigated. The α- and β-forms of p-hydroxytriphenylcarbinol are named the ψ- and

normal carbinol, respectively, and similar names are applied to the analogues. Anisilic acid (I), PhOH, and a little conc. H_2SO_4 in AcOH at room temp. give *p*-hydroxyphenyl-di-*p*-anisylacetic acid, m.p. indef., 195—211° (decomp.) after softening (*Ag* and *Na* salts; *Ac* derivative, m.p. 172.5—175.5°; gives with MeI-KOH-McOH at 100° *Me tri-p-anisylacetate*, m.p. 136—137°), which with cold, conc. H_2SO_4 gives CO and amorphous, orange ψ -*p*-hydroxyphenyl-di-*p*-anisylcarbinol (II), which could not be purified. (II) dissolves in warm *N*-KOH and is pptd. in the colourless normal form, m.p. 58—62° [best obtained pure by prolonged washing of the chloride, m.p. about 93° (decomp.) after softening from 78°] [nitrate, m.p. 117.5°; sulphate; perchlorate; *Ac* derivative, m.p. 104.5—106°, insol. in cold, dil. KOH, unchanged by hot EtOH (cf. lit.)], previously considered to be aurin Me_2 ether (III). (II) at 120—150° loses H_2O and gives (III), m.p. 186.5—187°, sol. in *N*-KOH only when boiled. The normal form rapidly passes into (II) when kept. Evaporation of a solution of (II) in Et_2O gives the normal form (25%), PhOH, and *pp'*-dimethoxybenzophenone. With Zn and boiling AcOH (II) yields *p*-hydroxyphenyl-di-*p*-anisylmethane, m.p. 70.5—73.5° after softening at 52°. (I), *o*-cresol, and H_2SO_4 in cold AcOH give a little anisic acid and 4-hydroxy-3-methylphenyl-di-*p*-anisylacetic acid, m.p. 211° after sintering from 160° (*Ag* salt; *Ac* derivative, m.p. 201.5—203.5°; *Me* ester of *Me* ether, m.p. 134—136°), which in conc. H_2SO_4 gives CO and ψ -4-hydroxy-3-methylphenyl-di-*p*-anisylcarbinol, reddish-orange, m.p. 138—140° after softening at about 125° (chloride, decomp. 164° after sintering at 155°; nitrate; perchlorate; *Ac* derivative, m.p. 86—89°), changed by passing CO_2 into its solution in 5% KOH into the unstable normal form, colourless; this gives on evaporation of its solution in Et_2O *pp'*-dimethoxybenzophenone and a little anisic acid, yields at 180° di-*p*-anisyl-3-methyl-1:4-quinomethane, $(\text{MeO}-\text{C}_6\text{H}_4)_2\text{C}(\text{C}_6\text{H}_3\text{Me})_2\text{O}$, m.p. 122—124°, insol. in 5—10% KOH, and is reduced by Zn and boiling AcOH to 4-hydroxy-3-methylphenyl-di-*p*-anisylmethane, m.p. 89—91°. (I) and *m*-cresol give similarly the lactone of 2-hydroxy-4-methylphenyl-di-*p*-anisylacetic acid, m.p. 98.5—100.5°, and 4-hydroxy-2-methylphenyl-di-*p*-anisylacetic acid, decomp. 222—223° after sintering at 219° (*Na* and *Ag* salts; *Ac* derivative, m.p. 199.5—202°; *Me* ester of *Me* ether, m.p. 154°); the latter with cold, conc. H_2SO_4 gives *m*-cresol, (I), and a little ψ -4-hydroxy-2-methylphenyl-di-*p*-anisylcarbinol (*Ac* derivative, m.p. 143.5° after sintering at 139.5°). (I) and *p*-cresol give the lactone of 6-hydroxy-3-methylphenyl-di-*p*-anisylacetic acid, m.p. 113—115° after sintering at 112°.

R. S. C.

Phenanthrene series. XXXVII. 3-Bromo- and 3:6(?) dibromo-phenanthraquinones. J. SCHMIDT and M. EITEL (J. pr. Chem., 1932, [ii], 134, 167—176).—Bromination of phenanthraquinone in PhNO_2 gives 3-bromo- [monosemicarbazone, m.p. 226—228° (decomp.); phenazine, m.p. 249°; monoxime, dimorphous, m.p. 179—181°; $(\text{NO}_2)_2$ -derivative, m.p. 295—296° (monoxime, m.p. 199—200° [decomp.]) and 3:6(?) dibromophenanthraquinone, dimorphous, yellow, m.p. 283—285°, and orange, m.p. 286—287°

[monosemicarbazone, m.p. 276° (decomp.); phenazine, m.p. 333—334°; monoxime, yellow form, m.p. 210—211° (*Cd* salt), green form (nitrosophenanthrol?), m.p. 242°; $(\text{NO}_2)_2$ -derivative, m.p. 322°]. The 3:6-structure is assigned to the Br_2 -compound on grounds of symmetry and on account of its formation from the 3- Br -compound; it gives on oxidation with CrO_3 - H_2SO_4 5:5'-dibromodiphenic acid, m.p. 303—304°.

H. A. P.

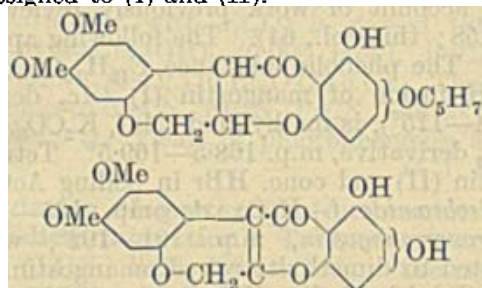
Constitution of mangostin. M. MURAKAMI (Annalen, 1932, 496, 122—151).—Mainly a more detailed account of work previously reviewed (A., 1931, 1158; this vol., 64). The following appears to be new. The phenolic substance, $\text{C}_{19}\text{H}_{18}\text{O}_6$, obtained by KOH fusion of mangostin (I) (*Ac* derivative, m.p. 114—115°), is methylated (MeI, K_2CO_3 , COMe_2) to a *Me* derivative, m.p. 168.5—169.5°. Tetrahydromangostin (II) and conc. HBr in boiling AcOH give the hydrobromide ($+\text{H}_2\text{O}$), decomp. 135—138°, of tetrahydronormangostin, m.p. 191—192°, which is methylated to dimethyltetrahydromangostin. Oxidation of (I) with alkaline KMnO_4 gives COMe_2 , AcOH, and α -hydroxyisobutyric acid; (II) similarly affords isohexanoic acid. Dimethylmangostin and KMnO_4 in COMe_2 give $\text{H}_2\text{C}_2\text{O}_4$, an acid, $\text{C}_{15}\text{H}_{18}\text{O}_7$, m.p. 226—228°, and a neutral compound (III), $\text{C}_{25}\text{H}_{30}\text{O}_{10}$, m.p. 225°; (III) is converted by SOCl_2 into a compound, $\text{C}_{25}\text{H}_{28}\text{O}_{10}\text{S}$, m.p. 204° (decomp.), and is oxidised by HNO_3 (d 1.34) to an acid, $\text{C}_{10}\text{H}_9\text{ON}$, m.p. 268°, and a neutral substance, $\text{C}_{12}\text{H}_8\text{O}_9\text{N}_2$, m.p. 231°. Trimethylmangostin is oxidised (KMnO_4 - COMe_2) to an acid, $\text{C}_{23}\text{H}_{26}\text{O}_{10}$, m.p. 240° (*Ba* salt), and a neutral substance, $\text{C}_{22}\text{H}_{18}\text{O}_6(\text{OMe})_4$, m.p. 192° (unstable oxime, decomp. 100°), whilst acetyldimethylmangostin similarly gives an acid, $\text{C}_{22}\text{H}_{28}\text{O}_{11}$, m.p. 122—123° (lactone, m.p. 197—199°), and the *Ac* derivative, m.p. 200—201°, of (III). Structural formulæ are suggested for several of the above compounds.

o-Vanillin is nitrated to 5-nitro-*o*-vanillin, m.p. 138.5—140°, which with Me_2SO_4 and MeOH-KOH gives the dimethylacetal, m.p. 96—97°, of 5-nitro-2:3-dimethoxybenzaldehyde, m.p. 116—117°. 5-Nitro-2:3-dimethoxybenzoic acid, m.p. 176°, is reduced to the 5- NH_2 -acid, m.p. 150° [the acid, m.p. 250°, thus described by Rubenstein (A., 1926, 518), is probably 5-amino-2-hydroxy-3-methoxybenzoic acid], converted through the 5-OH-acid into 2:3:5-trimethoxybenzoic acid. The *p*-iododiphenylurethanes of methylheptenol and methylheptanol have m.p. 124—125.5° and 140°, respectively.

H. B.

Toxicarol. IV. Structure of toxicarol. E. P. CLARK (J. Amer. Chem. Soc., 1932, 54, 2537—2548; cf. this vol., 619).—Toxicarol (I), heated with 5% EtOH-KOH for 3 hr., loses the elements C_8H_6 , giving apotoxicarol (II), $\text{C}_{16}\text{H}_{16}\text{O}_7$, m.p. 246—247° (*Ac* derivative, m.p. 206°; *Me* ether, m.p. 236—237°), which gives a deep reddish-violet colour with FeCl_3 , and is oxidised by I in hot EtOH-KOAc to dehydroapotoxicarol, m.p. 298° (after dehalogenation with Zn and AcOH). (I) does not give a *Me* ether, but is oxidised by alkaline H_2O_2 to hydroxynetric acid (III), $\text{C}_{12}\text{H}_{14}\text{O}_6$, m.p. 189°, or dehydronetric acid (IV), $\text{C}_{12}\text{H}_{12}\text{O}_5$, m.p. 212° (decomp.), according to the concn. of KOH used. (III) and Ac_2O give (IV), reduced to netric

acid. Dehydrodihydrotoxicarol (Ac derivative, m.p. 238°), heated with Zn and EtOH-KOH for 30 min., gives *dihydrotoxicarolic acid*, $C_{22}H_{26}O_9$, m.p. 129° (decomp.) [Me ester, m.p. 174° (Ac derivative, m.p. 143—144°)], oxidised by alkaline H_2O_2 to *dehydrotoxicarolmonocarboxylic acid*, m.p. 230° (decomp.) (Ac derivative, m.p. 163°), oxidised further to *risic acid* and reduced (catalytically) to its *dihydro-derivative*, m.p. 211° (decomp.). The following structures are assigned to (I) and (II).



C. J. W. (b)

Ouabain or g-strophanthin. W. A. JACOBS and N. M. BIGELOW (J. Biol. Chem., 1932, 96, 647—658).—Ouabain (*g-strophanthin*) (I), $C_{29}H_{44}O_{12}$ (lit. $C_{30}H_{46}O_{12}$), is a rhamnoside of a hexahydroxytetracyclic Δ^{27} -unsaturated lactone, $C_{23}H_{34}O_{18}$. Hepta-acetylanhydro-ouabain (II), m.p. 283—285°, $[\alpha]_D^{25} -59.1^\circ$ in pyridine, -51.7° in 85% EtOH, when reduced catalytically (PtO₂), best in EtOH, gives *hepta-acetyldihydrodeoxyouabain*, m.p. 273—275°, $[\alpha]_D^{25} -63.8^\circ$ in pyridine, yielding with 3% HCl in hot AcOH under certain conditions CH_2O and an *acetyl-trianhydro-lactone* (III), $C_{24}H_{30}O_4$, m.p. 172—173°, dimorphic, $[\alpha]_D^{25} -108.4^\circ$ in pyridine, which with hot aq. EtOH-NaOH gives the *hydroxytrianhydro-lactone*, $C_{22}H_{28}O_3$, m.p. 198—199°, $[\alpha]_D^{25} -41.5^\circ$ in pyridine. Catalytic reduction (PtO₂) of (III) affords α - and β -forms of an *acetylhexahydro-lactone*, $C_{24}H_{36}O_4$, m.p. 203—204°, $[\alpha]_D^{25} -22.2^\circ$ in pyridine, and m.p. 167—169°, $[\alpha]_D^{25} -21.5^\circ$ in pyridine, respectively, hydrolysis of which affords α - and β -*hydroxyhexahydro-lactones*, $C_{22}H_{34}O_3$, m.p. 94—96°, $[\alpha]_D^{25} -8.9^\circ$ in EtOH, and m.p. 164—166°, $[\alpha]_D^{25} +11.2^\circ$ in EtOH. These are *sec.* alcohols, since the α -isomeride with Kiliani's reagent gives the α -*hexahydroketolactone*, $C_{22}H_{32}O_3$, m.p. 188—191°. Hydrolysis of (I) and (II) under normal conditions gives resins. The loss of a C atom during formation of (III) is considered to be due to hydrolytic fission of a $\begin{smallmatrix} C \\ \diagup \end{smallmatrix} C:CH_2$ group. It is concluded that the rhamnose is attached to the *sec.* OH group, that the four OH groups which are acetylated are *tert.*, and that the OH group removed in formation of (II) corresponds with the *tert.* OH of the strophanthin aglucones. The presence of the last group is confirmed by isomerisation of (I) by KOH-MeOH to *isouabain*, $C_{29}H_{44}O_{12} + (?)H_2O$, m.p. 213—215° (decomp.) after softening at 200°, $[\alpha]_D^{25} -45.7^\circ$ in H_2O , which does not give the Legal reaction.

R. S. C.

Amyrilenes. K. H. BAUER and H. J. STARCKE (Arch. Pharm., 1932, 270, 334—338).—With a 0.25N-solution of BzO_2H in $CHCl_3$ α -amyrilene gives a

monoxide-A (I), m.p. 172°, and a monoxide-B, m.p. 136—137° (cf. this vol., 517), and with 0.5N-solutions gives (I) and a *dioxide*, m.p. 189—190°. β -Amyrilene gives with both solutions a *monoxide*, m.p. 169—170°, and a *dioxide*, m.p. 210—211°. Attempts to prepare derivatives of the oxides failed.

R. S. C.

Saponin group. X. Monohydroxytriterpene acids. A. WINTERSTEIN and G. STEIN (Z. physiol. Chem., 1932, 208, 9—25; cf. this vol., 61).—From *Olibanum* (frankincense), "acetyl-boswellic acid" (I) was isolated by way of the Ba salt. On acid hydrolysis and fractionation this gave two isomerides: α -boswellic acid (II), m.p. 289°, $[\alpha]_D^{25} +115^\circ$ [mixed anhydride with AcOH, m.p. 229—232°, resolidifies, decomp. 269—270°; Ac derivative (III), m.p. 241—243°, $[\alpha]_D^{25} +65^\circ$; Me ester, m.p. 214—215°, $[\alpha]_D^{25} +115^\circ$; Me ester of (III), m.p. 229—230°, $[\alpha]_D^{25} +68^\circ$; formyl derivative, m.p. 254—257°, $[\alpha]_D^{25} +65.5^\circ$; β -boswellic acid (IV), m.p. 238—240°, $[\alpha]_D^{25} +118^\circ$ [mixed anhydride with AcOH, m.p. 226—228°, decomp. 277—280°; Ac derivative (V), m.p. 271—273°, $[\alpha]_D^{25} +69^\circ$; Me ester, m.p. 189—190°, $[\alpha]_D^{25} +116^\circ$; Me ester of (V), m.p. 197.5—198.5°, $[\alpha]_D^{25} +74^\circ$; formyl derivative, m.p. 272—275° (decomp.), $[\alpha]_D^{25} +92^\circ$]. High vac. distillations of different fractions of the mixture (I) gave *hydrocarbons*, $C_{20}H_{46}$, m.p. 127°, 125°, and 119—121°, $[\alpha]_D^{25} +185^\circ$, $+253^\circ$, and $+320^\circ$, respectively. (III) and (V) gave *hydrocarbons*, m.p. 153—154°, 140—141.5°, $[\alpha]_D^{25} +132^\circ$, $+132^\circ$, respectively. All m.p. are corr., all rotations in $CHCl_3$. From equiv. wt. determinations, (II), (IV), oleanolic, ursolic, and clemolic acids have the composition $C_{30}H_{48}O_3$.

J. H. B.

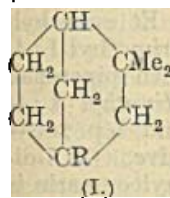
Determination of saponins. O. DE A. COSTA (Rev. Soc. Brasil. Chim., 1931, 2, 476—484).—Tests for the detection and determination of saponins are reviewed. The de Campos method (Rev. Chim. e Phys. pur. applic., 1915, No. 3) has been discarded in favour of that of Rosenthaler and Schiller (A., 1913, ii, 354), which can be applied to beers. E. L.

Syntheses of terpenes from isoprene. T. WAGNER-JAUREGG (Amal., 1932, 496, 52—77).—Isoprene (450 g.), AcOH (1500 c.c.), and conc. H_2SO_4 (5 g.) at room temp. for 3 days give a little caoutchouc and (after hydrolysis) 101 g. of a mixture, b.p. 72—160°/12 mm., of (a) primary alcohols [separated by $o-C_6H_4(CO)_2O$ in C_6H_6], (b) *tert.*-alcohols (removed as borates), and (c) hydrocarbons, containing (a) geraniol, cyclogeraniol, and sesquiterpene alcohols, b.p. (mainly) 114—126°/0.7 mm., of the composition $C_{15}H_{26}O$ and containing three double linkings, (b) *dl*-linalool, *dl*- α -terpineol, and sesquiterpene alcohols, b.p. 108—122°/0.43 mm., composition $C_{15}H_{26}O$, and (c) a monocyclic hydrocarbon, b.p. 120—125°/12 mm., containing three double linkings, converted by boiling 98% HCO_2H into a bicyclic hydrocarbon of the caryophyllene group. Geranyl acetate and AcOH-conc. H_2SO_4 under the above conditions give hydrocarbons and (after hydrolysis) some cyclogeraniol [naphthylurethane, m.p. 90—91° (corr.)]. Isoprene shaken with dil. H_2SO_4 in CO_2 for about 5 days gives a mixture of hydrocarbons, alcohols, and ethers (oxides); the last-named are formed by dehydration of polyhydric alcohols. A fraction, b.p. 55—90°/14 mm.,

is freed from alcohols (as borates), the residue reduced (H_2 , PtO_2 , $AcOH$), and the ethers removed as additive compounds with $H_4Fe(CN)_6$. Fractionation of the ethers gives a product, b.p. $170-172^\circ$, which with $HBr-AcOH$ affords terpinene dihydrobromide (thus proving the presence of 1:4-cineole), and with tetraiodopyrrole gives a little of its additive (1:1) compound, decomp. 112° , with 1:8-cineole. Isoprene is polymerised by $TiCl_4$ in $CHCl_3$ to an amorphous compound, M 2830, decomp. 190° (softens at 130°). The polymeric obtained using $SnCl_4$ is dehydrogenated by Sc at $280-340^\circ$ to 1:2:5-trimethylnaphthalene.

The possible mechanisms of formation of some of the above compounds are discussed. H. B.

Hydrocarbons corresponding with particular camphor-like substances. I. Fenchane, *apocamphane*, β -*apofenchane*, and *santenane*. G. KOMPPA and T. HASSELSTROM (Annalen, 1932, 496, 164-170).—dl-iso*Fenchonchydrazone*, m.p. $111-112^\circ$ (*Ac* derivative, m.p. $193-194^\circ$), and $EtOH-NaOEt$



at 180° give fenchane (I, $R=Me$), b.p. $151-152^\circ/765$ mm. The following are similarly prepared: *apocamphane* (α -fenchocamphorane), b.p. $148^\circ/755$ mm., from *dl*- α -fenchocamphoronehydrazide, b.p. $120^\circ/11$ mm. (*Ac* derivative, m.p. $145-146^\circ$); β -*apofenchane* (β -fenchocamphorane) (I, $R=H$), b.p. 143.5° , m.p. $17-17.5^\circ$, from *dl*- β -fenchocamphoronehydrazide, b.p. $135-138^\circ/14$ mm. (*Ac* derivative, m.p. $134-135^\circ$), identical with camphenilane, b.p. 142° , m.p. 17° (Nametkin and Chuchrikovaia, A., 1915, i, 701), from camphenilonehydrazide (*Ac* derivative, m.p. $148.5-149.5^\circ$); *santenane*, b.p. $146-148^\circ$, m.p. $66-67^\circ$, from *santenonehydrazide* (*Ac* derivative, m.p. $152-153^\circ$). H. B.

Dependence of optical rotatory power on chemical constitution. XIV. Stereoisomeric aminomethylenecamphors, iminomethylenecamphors, and their derivatives. B. K. SINGH and B. BHADURI (J. Indian Chem. Soc., 1932, 9, 109-119).—The rotatory powers of *d*- and *l*-amino- (I), -imino- (II), and -benzylamino- (III) -methylenecamphors have been measured in various solvents for different wave-lengths at 35° ; these decrease in the order $EtOH > MeOH > pyridine > COMe_2 > CHCl_3 > C_6H_6$ for (I) and (II), and in the order $MeOH > EtOH > COMe_2 > pyridine > CHCl_3 > C_6H_6$ for (III). The sp. rotatory power of (II) is nearly twice that of (I); the increase is ascribed to the conjugated system in (II). (I) and (II) obey the one-term simple dispersion formula of Drude.

d-Aminomethylenecamphor (IV), prepared by the method of Bishop *et al.* (A., 1895, i, 62), has m.p. 157° ; *l*-, m.p. 157° (V), and *dl*-, m.p. $163-164^\circ$, -aminomethylenecamphors are prepared similarly. *d*-Iminomethylenecamphor, m.p. $216-218^\circ$ (lit. $221-222^\circ$), is best obtained from (IV) and *d*-oxymethylenecamphor in $MeOH-AcOH$; *l*-, m.p. $216-218^\circ$, *dl*-, m.p. $216-218^\circ$, and *meso*-, m.p. $217-218^\circ$ [from (IV) and *l*-oxymethylenecamphor or from (V) and *d*-oxymethylenecamphor], -iminomethylenecamphors are described. *d*-Oxymethylenecamphor,

$CH_2Ph-NH_2.HCl$, and $NaOAc$ give *d*-benzylamino-methylenecamphor, m.p. $89-91^\circ$; the *l*- and *dl*-forms have m.p. $89-91^\circ$ and $84-85^\circ$, respectively.

H. B.

Isomerisation of linalolene to dihydromyrcene.

V. LONGUNOV and (MME.) R. KHASANOVA (Bull. Soc. chim., 1932, [iv], 51, 636-639; cf. A., 1929, 538).— β -Linalolene, b.p. $158-160^\circ/761$ mm., with aq. HBr at 100° gives a dibromide, b.p. $125-129^\circ/9$ mm., converted by suitable treatment with NMe_3 into β -dihydromyrcene, b.p. $168-170^\circ/760$ mm. A. A. L.

Furan reactions. I. Pyrolysis of furan. C. D. HURD and A. R. GOLDSBY. II. Furan from furfuraldehyde. C. D. HURD, A. R. GOLDSBY, and E. N. OSBORNE. III. Absorption of furan vapours. C. D. HURD and A. R. GOLDSBY (J. Amer. Chem. Soc., 1932, 54, 2530-2531, 2532-2536, 2558).

—I. Furan decomposes at $670-740^\circ$ in a quartz tube (but at 360° in presence of catalytic Ni); at 670° the gaseous products are approx. 75% of CO , 12% of saturated hydrocarbons and H_2 , and the remainder unsaturated hydrocarbons, whilst at 740° less CO and more saturated hydrocarbons and H_2 result. The 11% unsaturated hydrocarbons in the off-gas at 740° and 2.59 sec. consists of 3.1% acetylenes, 5.5% C_2H_4 , and 2.4% C_3H_6 , with undetermined amounts of allene, cyclopropene, and butadiene; the acetylenes consist largely of $CH-CMe$. C_6H_6 was definitely identified, but no difuryl was observed.

II. Furfuraldehyde decomposes above 550° into furan and its decomp. products; butadiene, C_6H_6 , $PhMe$, $PhOH$, and a xyleneol are also identified. Excellent yields of furan are obtained when furfuraldehyde (vapour) is passed through soda-lime at 350° or through fused $NaOH$; H_2 and CO_2 are produced. The hot alkali converts a small portion of the furan into gaseous products.

III. Furan (gaseous) is absorbed quantitatively by 82.5% H_2SO_4 . A mixture of furan and C_2H_4 can thus be analysed, since C_2H_4 is absorbed only by oleum. This method is not applicable to the quant. analysis of furan admixed with other unsaturated, gaseous hydrocarbons; liquefaction and distillation are necessary for exact analysis. C. J. W. (b)

Labile isomeride of 2-methylfuran. N. KJØRNER (J. Gen. Chem. Russ., 1931, i, 1212-1228).—The decomp. of furfuraldehydehydrazide with alkali under drastic conditions yields an isomeride (I) of 2-methylfuran, b.p. $78-78.5^\circ$, d_4^{20} 0.9406, n_D^{20} 1.457, which is probably 2-methylene- Δ^3 - or Δ^4 -dihydrofuran or a mixture of the two, possibly an equilibrium mixture. It gives characteristic colour reactions with *p*-diazobenzenesulphonic acid, is readily oxidised by O_2 to furancarboxylic acid, and is hydrated by dil. aq. acids to levulaldehyde and an unsaturated keto-alcohol $CHAc:CH-CH_2OH$, isolated as the semicarbazidosemicarbazone, m.p. $187-188^\circ$ (decomp.) on slow heating (acetate, m.p. $120-125^\circ$). (I) is isomerised to 2-methylfuran by alkalis, $N_2H_4.H_2O$, and especially acids. With 10% H_2SO_4 a polymeric $C_{15}H_{18}O_3$ is also formed (semicarbazone, m.p. $159-160^\circ$); this has one furan ring because it condenses with maleic anhydride to a compound, $C_{19}H_{20}O_6$, m.p. $89-90^\circ$. (I) reacts exothermically with maleic

anhydride giving a compound $C_9H_8O_4$, m.p. 71—72°, which is also formed from 2-methylfuran, probably owing to isomerisation of (I) by maleic anhydride; $C_9H_8O_4$ is decomposed by hot H_2O or $NaOH$ into methylfuran.
G. A. R. K.

Rearrangement of the α -furfuryl group. II. 5-Methylfurfuryl chloride and 5-methylfurylacetic acid. E. W. SCOTT and J. R. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 2549—2556; cf. A., 1930, 783).—Chlorination of Et 2-methyl-3-furoate at 145° and subsequent hydrolysis gives 5-chloro-2-methyl-3-furoic acid, m.p. 122—123°, in 35—50% yields (Cl is not removed by EtOH-NaOH), which with Cu-bronze in coal-tar bases (b.p. 150—200°/16 mm.) at 260—270° affords 50% of 2-chloro-5-methylfuran, b.p. 48—49°/70—75 mm., 108—110°/740 mm. This is more stable than furfuryl chloride, has no lachrymatory action, and does not undergo rapid spontaneous decomp. on keeping. Details are given for the prep. of 5-methylfurfuraldehyde, its oxime, and 5-methylfuronitrile (by dehydration of the oxime). The nitrile prepared (from furfuryl chloride and aq. NaCN) by Kirner and Richter (A., 1929, 1458) is a mixture of approx. 85% of 5-methylfuronitrile and 15% of furylacetonitrile. 5-Methylfurfuryl alcohol, b.p. 194—196° (slight decomp.)/744 mm., 70—73°/6 mm. (diphenylurethane, m.p. 52—53°), gives an unstable chloride, which with aq. NaCN affords 5-methylfurfuryl cyanide (11% yield), hydrolysed to 5-methyl-2-furylacetic acid, m.p. 57—58°, also prepared from 5-methylfurfuraldehyde. 2:5-Dimethylfuroic acid (Et ester, b.p. 83—85°/6 mm., 99—101°/14 mm.) has m.p. 134°. It is suggested that the mechanism of the rearrangement reaction involves 1:4-addition of HCN to the furan ring.

C. J. W. (b)

Coumarins and hydroxycoumarins. T. PAVOLINI (Riv. Ital. Ess. Prof., 1931, 8, 327—330; Chem. Zentr., 1932, i, 1126).—The origin of coumarin and its derivatives in plants is discussed. Coumarin is detected by boiling with resorcinol (orceinol, or orcein) in 80% H_2SO_4 , rendering alkaline, and diluting; a blue (violet) fluorescence, due to the formation of 4-hydroxycoumarin, is obtained. The reaction is not sp. in presence of β -OH- and β -keto-acids.

A. A. E.

1:2:3:4-Tetrahydroxybenzene derivatives. Synthesis of 6:7:8-trihydroxycoumarin and of dimethylfraxetin. F. WESSELY and F. LECHNER (Monatsh., 1932, 60, 159—164).—1:2:3:4- $C_6H_4(OH)_4$ (A., 1904, i, 240: improved yield by heating 4-aminopyrogallol hydrochloride with air-free H_2O in sealed tube) (Me₄ ether, new m.p. 87.5°) gives (NaOAc and Ac₂O) a Ac_4 derivative, m.p. 160°. This by $Zn(CN)_2$ and HCl yields 2:3:4:5-tetrahydroxybenzaldehyde (decomp. from 170°; sublimes at 160—170° in high vac.) (Ac_4 derivative, m.p. 143°), which by Perkin's synthesis gives 6:7:8-triacetoxycoumarin, m.p. 142.5—145.5° (also obtained from fraxetin and HBr). This with MeOH and HCl gives 6:7:8-trihydroxycoumarin, m.p. 272° (decomp.), subliming at 220°/0.02 mm., of which the 6-methylated derivative (diazomethane) is identical with fraxetin Me₂ ether.

E. W. W.

Hydroxy-carbonyl compounds. VII. Coumarins and 1:4-benzopyrones derived from *m*-cresol. A. ROBERTSON, T. B. WATERS, and (in part) E. T. JONES (J.C.S., 1932, 1681—1688).—*m*-Cresol and Et acetoacetate give 4:7-dimethylcoumarin, which is also obtained directly from *m*-tolyl Me ether, Et acetoacetate, and 86% H_2SO_4 ; this does not exclude the intermediate formation of a cinnamic acid (cf. this vol., 620), since 2-methoxy- β :4-dimethylcinnamic acid, m.p. 140—141° [oxidised to 2-methoxy-4-methylacetophenone (semicarbazone, m.p. 200—201°)], and 86% H_2SO_4 afford the same coumarin. 2-Hydroxy-4-methylpropiofenone, Ac_2O , and NaOAc yield 2:3:7-trimethyl-, m.p. 86°, which condenses with piperonal to 2-(3':4'-methylenedioxy-styryl)-3:7-dimethyl-1:4-benzopyrone, m.p. 191°. 2-Methoxy-6-methylpropiofenone, b.p. 137°/16 mm. (semicarbazone, m.p. 145°), prepared from 3-methoxy-*o*-toluonitrile and $MgEtI$, forms, after hydrolysis with Ac_2O and NaOAc, 2:3:5-trimethyl-1:4-benzopyrone, m.p. 96°. Condensation of *m*-cresol with Et α -methyl- and α -ethyl-acetoacetate in the Simonis reaction gives pairs of isomeric 1:4-pyrones. With Et α -methyl-acetoacetate, a mixture of 2:3:5-trimethyl-1:4-benzopyrone [condensation product with piperonal, 2-(3':4'-methylenedioxy-styryl)-3:5-dimethyl-1:4-benzopyrone, m.p. 166—167°] and a liquid, b.p. 200—220°/15 mm. [corresponding derivative, -3:7-dimethyl-], is obtained. 3:4:7-Trimethylcoumarin is converted into 2-methoxy- α : β :4-trimethylcinnamic acid, m.p. 159°. 2-Hydroxy-4-methyl-*n*-butyrophenone, Ac_2O , and NaOAc give mainly 2:7-dimethyl-3-ethyl-, since condensation of this with piperonal affords 2-(3':4'-dimethylenedioxy-styryl)-7-methyl-3-ethyl-1:4-benzopyrone, m.p. 160°. Similarly, Et α -ethylacetoacetate and *m*-cresol form a mixture of 2:5-dimethyl-3-ethyl-1:4-benzopyrone, m.p. 86° [piperonal condensation, 2-(3':4'-methylenedioxy-styryl)-5-methyl-3-ethyl-1:4-benzopyrone, m.p. 180°], and an oil, b.p. 180—190°/20 mm., consisting mainly of 2:7-dimethyl-3-ethyl-1:4-benzopyrone.

2-Methoxy- β :4-dimethyl- α -ethylcinnamic acid, from 4:7-dimethyl-3-ethylcoumarin, has m.p. 123°. 7-Methylflavone, m.p. 120°, is obtained from 2-hydroxy-4-methylacetophenone, Bz_2O , and NaOBz. *m*-Cresol and Et benzoylacetate with P_2O_5 give 5-methylflavone, m.p. 129—130°, and with H_2SO_4 yield 4-phenyl-7-methylcoumarin, m.p. 96°, which cannot be prepared by ring-closure of 2-hydroxy-4-methylbenzophenone (phenylhydrazone, m.p. 137—138°), the acetate, m.p. 97°, being formed. Condensation of resorcinol Me₂ ether with Et acetoacetate gives 7-methoxy-4-methylcoumarin and with Et α -methylacetoacetate, 7-methoxy-3:4-dimethylcoumarin.
F. R. S.

Coumarins and chromones from β -naphthol. B. B. DEY and A. K. LAKSHMINARAYANAN (J. Indian Chem. Soc., 1932, 9, 149—155).— β - $C_{10}H_7OH$ and CH_3CO_2Et in cold conc. H_2SO_4 give a mixture of 4-methyl- β -naphthacoumarin (4-methyl-1:2- β -naphthapyrone) (I), m.p. 179°, and 2-methyl-1:4- β -naphthapyrone (II), m.p. 168° (formed when P_2O_5 is the condensing agent), since treatment of the mixture with PhCHO and EtOH-NaOEt affords

some 2-styryl-1:4- β -naphthopyrone, m.p. 198° (dibromide, m.p. 175°) [also prepared similarly from (II)]. (I) does not form a condensation product with PhCHO.

H. B.

Preparation of dinaphtho- γ -pyrone (1:2:7:8-dibenzoxanthone). K. DZIEWOŃSKI and S. PIŻOŃ (Bull. Acad. Polonaise, 1931, A, 406—410).— β -Naphthol heated with CO(NHPh)₂ or CS(NHPh)₂ at 250—265° gives the *anil*, m.p. 263—266°, of 1:2:7:8-dibenzoxanthone (I), which is readily obtained by hydrolysis with AcOH and conc. HCl. A mechanism involving the intermediate formation of β -naphthylurethane is suggested. Fusion of (I) with KOH at 230—260° gives 2:2'-dihydroxy-1:1'-dinaphthyl ketone, m.p. 177° (decomp.) (Ac₂ derivative, m.p. 196°), which is reconverted into (I) at 180°.

J. W. B.

Synthesis of anthocyanins. The four isomeric glucosides of pelargonidin chloride. A. LEÓN, A. ROBERTSON, R. ROBINSON, and T. R. SESHADRI (Anal. Fis. Quím., 1932, 30, 267—301).—Methods similar to that used for the synthesis of 3- β -glucosidyl-pelargonidin chloride (A., 1928, 895) have now been used for the 4', 7-, and 5-glucosides. The last-named is pelargonidin chloride, and pelargonin is probably the 3:5-diglucoside. This assumption is in accord with the work of Karrer *et al.* (A., 1927, 1197; 1928, 1255).

4:6-Dihydroxy-*o*-tolualdehyde and ω -hydroxy-*p*-acetoxyacetophenone condense in EtOAc in presence of dry HCl to give 3:7:4'-trihydroxy-5-methylflavylium chloride (+H₂O). 2:6-Dihydroxy-*p*-tolualdehyde yields similarly the 7-methyl compound (+2H₂O). 4:6-Dihydroxy-2-methoxybenzaldehyde with BzCl and K₂CO₃ yields the 4-benzoyloxy-compound, m.p. 101—102°, which condenses with ω -hydroxy-*p*-acetoxyacetophenone. The Bz derivative obtained yields 3:7:4'-trihydroxy-5-methoxyflavylium chloride. 6-Hydroxy-2-benzoyloxy-4-methoxybenzaldehyde yields similarly 3:5:4'-trihydroxy-7-methoxyflavylium chloride (purified as the picrate).

ω -4-Dihydroxyacetophenone [*K* salt (+H₂O); Ag salt; osazone, m.p. 212—214°, with NHPh·NH₂] condenses with 2-*O*-benzoylphloroglucinaldehyde to give 5-*O*-benzoylpelargonidin chloride (A., 1928, 894). ω -Hydroxy-4-tetra-acetyl- β -glucosidylacetophenone, m.p. 149—150°, and 2-*O*-benzoylphloroglucinaldehyde give 5-*O*-benzoyl-4'-tetra-acetyl- β -glucosidylpelargonidin chloride (darkens 182°, softens 193°, decomp. 198°), hydrolysed to 4'- β -glucosidylpelargonidin chloride (+2.75H₂O), decomp. 184° (picrate, +3H₂O, decomp. 146—148°).

2-*O*-Benzoylphloroglucinaldehyde (*K* salt, decomp. 70°), with a little of the 2:4-OO'-Bz₂ derivative, m.p. 139—140°, is prepared by adding BzCl to the aldehyde in ice-cold aq. KOH and pptn. by NaHCO₃. The Ag salt with α -acetobromoglucose in C₆H₆ yields 4-tetra-acetyl- β -glucosidyl-2-*O*-benzoylphloroglucinaldehyde (I), m.p. 144—145°, also obtained from the phenol with α -acetobromoglucose in aq. COMe₂. The constitution of (I) is shown by methylation to the 6-*O*-Me derivative, m.p. 95—120°, hydrolysed by acid or alkali to 4- β -glucosidyl-2-*O*-methylphloroglucinaldehyde, m.p. 237—239°, which is synthesised by the condensation of 2-*O*-benzoylphloroglucinaldehyde and α -acetobromoglucose, followed by hydrolysis of the 4-tetra-

acetyl- β -glucosidyl derivative, m.p. 149—150°. ω -4-Dihydroxyacetophenone condenses with (I) to give 3:4'-dihydroxy-5-benzoyloxy-7-tetra-acetyl- β -glucosidylflavylium chloride (+0.5H₂O), m.p. 184—186° (softens 177°), hydrolysed to 7- β -glucosidylpelargonidin chloride (+3H₂O) [isolated first as the picrate (+1.5H₂O), m.p. 180° (decomp.; softens 120°)].

2:4-OO'-Dibenzoylphloroglucinaldehyde (II) is best prepared by the use of BzCl in C₆H₅N. The 2:4:6-OO'-Bz₃ derivative, m.p. 121—122° (+0.5MeOH, m.p. 80°), is obtained similarly. Methylation of (II) yields the 6-*O*-Me derivative, m.p. 133—134°, hydrolysed to 6-*O*-methylphloroglucinaldehyde. Treatment of (II) with α -acetobromoglucose and Ag₂CO₃ in C₆H₆ gave a substance, C₂₇H₂₁O₁₁, m.p. 110—145° (softens 85°). Treatment of (II) with α -acetobromoglucose and KOH in aq. COMe₂ yielded (?) 6-tetra-acetyl- β -glucosidyl-2:4-OO'-dibenzoylphloroglucinaldehyde (+3.5H₂O ?), m.p. 144—145°. This substance was also obtained by interaction of (II) with α -acetobromoglucose and Ag₂O in quinoline, accompanied by a substance, m.p. 223—224°. The crude material was hydrolysed by KOH-EtOH and condensed with ω -4-dihydroxyacetophenone in alc. HCl, giving 5- β -glucosidylpelargonidin chloride in very small yield.

The colour reactions of the 3-, 4', 7-, and 5-glucosides of pelargonidin and the 5- and 7-Me and -MeO analogues in buffer solutions at various values of *p*_H are recorded (cf. A., 1929, 477).

R. K. C.

Synthetical experiments in the isoflavone group. VI. Reactions of some keto-ethylene oxides. W. BAKER and R. ROBINSON (J.C.S., 1932, 1798—1806).—The oxide of 2:4-dimethoxyphenyl styryl ketone (I), obtained by oxidising the ketone with H₂O₂, gives with H₂SO₄ and MeOH, 2:4-dimethoxyphenyl α -hydroxy- β -methoxy- β -phenylethyl ketone, m.p. 133° (from EtOH corresponding β -ethoxy-compound, m.p. 98°), which forms with AcOH and NaOAc or with aq. EtOH-NaOH, 2:4-dimethoxyphenyl benzyl ketone (II) (α -form, m.p. 71°; β -form, more stable, m.p. 86°). *o*-C₆H₄(NH₂)₂ and (II) afford 2-(2':4'-dimethoxyphenyl)-3-benzylquinoxaline, m.p. 108—109°. (I) and HCl in AcOH yield 2:4-dimethoxyphenyl β -chloro- α -hydroxy- β -phenylethyl ketone, m.p. 131°, and (I) with EtOH-NaOH forms 2:4-dimethoxyphenylbenzylglycollic acid, m.p. 176° (efferv.), which is also similarly obtained from (II), and is oxidised to 2:4-dimethoxyphenyl CH₂Ph ketone. With HCO₂H alone, (I) gives 2:4-dimethoxyphenyl α -hydroxy- β -formoxy- β -phenylethyl ketone, m.p. 154°, but in presence of H₂SO₄, $\alpha\beta$ -diformoxy-, m.p. 141°, is formed, and when AcOH is used instead of HCO₂H, the α -hydroxy- β -acetoxy-, m.p. 136°, results; each of the three derivatives yields (II) (β -form) with AcOH and NaOAc.

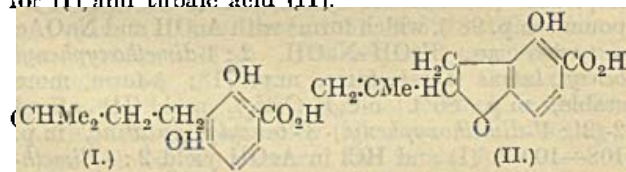
The oxide of 2:4-dimethoxyphenyl *p*-methoxystyryl ketone, m.p. 108°, similarly forms 2:4-dimethoxyphenyl α -hydroxy- β -methoxy- β -*p*-methoxyphenylethyl ketone, m.p. 143—144°, which when boiled with NaOH gives a mixture of the (A), m.p. 102°, and (B) forms, m.p. 115°, of 2:4-dimethoxyphenyl *p*-methoxybenzyl ketone, each transformed by *o*-phenylenediamine into 2-(2':4'-dimethoxyphenyl)-3-*p*-methoxybenzylquinoxaline, m.p. 76—79° (these forms are possibly *cis*- and *trans*-

isomerides of the enol form of the diketone). 2:4-Dimethoxyphenyl-*p*-methoxybenzylglycollic acid, m.p. 177° (efferv.), is oxidised to 2:4-dimethoxyphenyl-*p*-methoxybenzyl ketone, m.p. 84°. F. R. S.

Methoxy-derivatives of xanthone and thioxanthone. K. C. ROBERTS, L. A. WILES, and B. A. S. Kent (J.C.S., 1932, 1792—1798).—2-Nitro-, m.p. 180° (cf. A., 1917, i, 336), prepared from the corresponding toluene, is reduced to 2-amino-6-methoxybenzoic acid, m.p. 87°, which after diazotisation gives the thiocyanate, hydrolysed to 6-methoxy-2-dithiobenzoic acid (I), m.p. 187°. (I) and quinol Me₂ ether form 1:4:8-trimethoxythioxanthone, m.p. 208—209° (di- and mono-chlorostannate, and diperchlorate, in which the O is probably present as O^{IV}), which is hydrolysed to 1:8-dihydroxy-4-methoxythioxanthone (diacetoborate). PhOMe and (I) yield 1:7-dimethoxy-, m.p. 131—132° (monoperchlorate; trihydrochloride; chlorostannate, indicating basic character and a monochelate structure), hydrolysed to 7-hydroxy-1-methoxythioxanthone, m.p. 246° (decomp.) (dihydrochloride). 1-Hydroxy-7-methoxyxanthone forms a chlorostannate and a diacetoborate. A comparison of the relative effects of oxide O and sulphide S on the basic property has been made by comparing 1:7-disubstituted thioxanthones with the Me ethers of euxanthones.

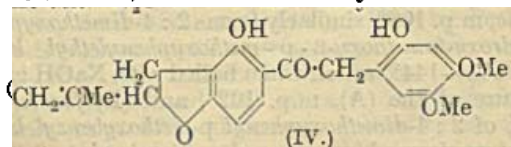
F. R. S.

Rotenone, the active constituent of the *Derris* root. IX. Constitution of tetrahydrotubaic acid and rotenone. Synthesis of some products of the degradation of rotenone. S. TAKEI, S. MIYAJIMA, and M. ONO (Ber., 1932, 65, [B], 1041—1049; cf. this vol., 400).—The recognition of isohexic acid (*p*-iodophenacyl ester, m.p. 85°) as product of the oxidation of tetrahydrotubaic acid (I) and of 2- γ -ethyl-*n*-butylresorcinol, m.p. 85°, as product of its decarboxylation necessitates amended constitutions for (I) and tubaia acid (II).



4-Hydroxyveratrole is converted by CO₂ and KHCO₃ in glycerol at 160—165° into 2-hydroxy-4:5-dimethoxybenzoic acid (III), m.p. 202° (Me ester, m.p. 93°), identical with the acid derived from dehydro-rotenone. (III) is transformed by successive treatment with NaOH and CH₂Cl·CO₂Et followed by hydrolysis into 4:5-dimethoxy-2-carboxymethoxybenzoic acid, m.p. 255° (Me₂ ester, m.p. 86°), identical with rissic acid.

Derritol (amended constitution IV), when successively treated with NaOH, CH₂Cl·CO₂Et, and hydrolysed, affords derric acid, m.p. 154°, converted by NaOAc and Ac₂O at 150° into dehydrorotenone.



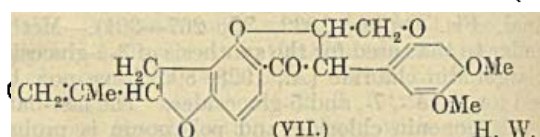
The azlactone of asaraldehyde is converted by H₂O₂ and KOH into 2:4:5-trimethoxyphenylacetic

acid, m.p. 87°, identical with homoasaronic acid and converted by tetrahydrotubanol and ZnCl₂ at 130° into tetrahydromethyliderritol, m.p. 150—160°.

Rotenonone, m.p. 298°, prepared by drastic oxidation of rotenone or dehydrorotenone, is C₂₃H₁₈O₇, and is hydrolysed by 5% KOH to rotenonic acid, C₂₃H₂₀O₈. Both compounds are converted by 20% KOH into derritol and H₂C₂O₄. Rotenonone is obtained in 65% yield from derritol, NaOAc, and Me₂C₂O₄ or Et₂C₂O₄ at 160—170°.

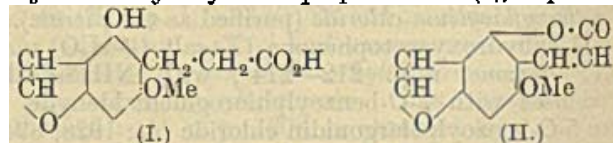
Abutic acid (V) (Me₂ ester, m.p. 156°), obtained with tubaia acid by action of H₂O₂ on rotenonic acid (VI), is dibasic, has 2 OMe groups, and hence is assigned the constitution (V). (VI) in dil. acid solution affords β -rotenonone, m.p. 275—276° [re-converted into (VI) by 5% KOH-EtOH], whereas with dil. aq. alkali it yields rotenonone.

Rotenone receives the amended constitution (VII).



isopropylidene compound of pyrocatechol. J. BOESEKEN and G. SLOOFF (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 170—172).—Pyrocatechol and COMe₂ at room temp. in presence of P₂O₅ and quartz-sand give *o*-isopropylidenedioxybenzene, b.p. 184°/765 mm., *d*₄²⁵ 1.063, 1.5060. E. W. W.

Constituents of root of *Pimpinella saxifraga*. II. F. WESSELY and (FRL.) E. NADLER (Monatsh., 1932, 60, 141—144).—The third constituent of this root (cf. this vol., 662), *isobergaptin*, m.p. 222°, a stable lactone, is oxidised by alkaline H₂O₂ to furan-2:3-dicarboxylic acid, and reduced by Na-Hg to 3-hydroxy-5-methoxybenzofuran-4-propionic acid (I), m.p. 147°



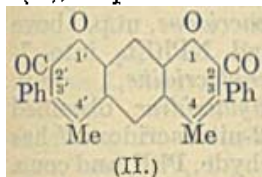
(decomp.). This distilled at 0.05 mm. and melted gives *dihydroisobergaptin* (hydrogenated in the coumarin ring); with diazomethane the acid gives the (OMe)₂ compound, new m.p. 132°, also obtainable from bergaptin (A., 1892, 71). *isobergaptin* is therefore (II). E. W. W.

Derivatives of benzodifuran. J. ALGAR, V. C. BARRY, and T. F. TWOMEY (Proc. Roy. Irish Acad., 1932, 41, B, 8—14).—4:6-Diacetoresorcinol, CH₂Br·CO₂Et, and K₂CO₃ in COMe₂ give the *Et*₂ ester, m.p. 130—131°, of 4:6-diacetyl-*m*-phenylenediglycollic acid (I), m.p. 246—266° (decomp.). (I), NaOAc, and Ac₂O at 150° afford 3:3'-dimethylbenzodifuran (II), m.p. 107—108°. The (4:6)-*dianisylidene*, m.p. 247—248° (decomp.), and *dipiperonylidene*, m.p. 210—211° (decomp.) (softens at 206°), derivatives of (I) are similarly converted into 3:3'-*di-p*-methoxystyryl-, m.p. 213—214°, and 3:3'

di-(3 : 4-methylenedioxyethyl)-, m.p. 199—200°, -benzo-difurans, respectively.

H. B.

Derivatives of dicoumarin. J. ALGAR, A. E. O'REILLY, and M. JOY (Proc. Roy. Irish Acad., 1932, 41, B, 1—7).—4 : 6-Diacetoresorcinol (I), $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, NaOAc , and Ac_2O at 140—150° give 7-acetoxy-6-acetyl-3-phenyl-4-methylcoumarin, m.p. 185—187°, whilst (I), $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$, and Ac_2O at 150° afford 3 : 3'-diphenyl-4 : 4'-dimethyldicoumarin (II), m.p. 276—277° (slight decomp.).

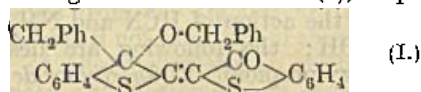


3 : 3'-Di-p-nitrophenyl-, not melted at 330°; dianisyl-, m.p. 263—264°, demethylated to the -di-p-hydroxyphenyl-, not melted at 310°; -di-(3 : 4-methylenedioxyphenyl)-, m.p. 297°, and -di-(3 : 4-dimethoxyphenyl)-, m.p. 218—219°.

4 : 4'-dimethyldicoumarin are similarly prepared from (I) and the requisite $\text{CH}_2\text{Ar}\cdot\text{CO}_2\text{Na}$.

H. B.

Indigoid dyes. Ethers of leuco-thioindigotin. M. M. TSCHILIKIN and A. F. KARPOVA (J. Gen. Chem. Russ., 1931, 1, 1158—1161).—Leuco-thioindigotin with CH_2PhCl gives the substance (I), m.p. 213—



214°, hydrolysed by H_2SO_4 to 2-benzylidene-1-ketodihydrothionaphthen, m.p. 129—130°, 1 mol. of $\text{CH}_2\text{Ph}\cdot\text{OH}$ being eliminated and the thioindigotin mol. at the same time split in two. Madelung's assumption of the wandering of the CH_2Ph group is unnecessary.

G. A. R. K.

Syntheses of 2-substituted pyrroles. H. FISCHER and M. NEBER (Annalen, 1932, 496, 1—26).—Et 2-formyl-3 : 5-dimethylpyrrole-4-carboxylate and $\text{CH}_2(\text{CN})_2$ in $\text{EtOH}\cdot\text{NH}_4\text{Et}_2$ give Et 3 : 5-dimethyl-2-β-dicyanovinylpyrrole-4-carboxylate, m.p. 170° (all m.p. are corr.). 3 : 5-Dimethyl-4-ethyl-2-β-dicyanovinylpyrrole, m.p. 191.5°, prepared similarly, is hydrolysed by 20% $\text{MeOH}\cdot\text{KOH}$ to the 2-β-cyano-β-carboxyvinyl derivative, m.p. 191°, whilst β-3 : 5-dimethyl-2-(β-dicyanovinyl)-4-pyrrolylpropionic acid, m.p. 235°, is hydrolysed by 10% NaOH to the 2-β-cyano-β-carboxyvinyl derivative, m.p. 199°; more energetic hydrolysis regenerates the original aldehydes. 2-Formyl-3 : 5-dimethyl-4-ethylpyrrole and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in $\text{EtOH}\cdot\text{NH}_4\text{Et}_2$ give 3 : 5-dimethyl-4-ethyl-2-β-cyano-β-carbomethoxyvinylpyrrole, m.p. 121°; 3 : 5-dimethyl-2-(β-cyano-β-carbomethoxyvinyl)-4-pyrrolylpropionic acid, m.p. 183°, is similarly prepared. The K salt from Et 2-formyl-4-methylpyrrole-3 : 5-dicarbonylate, MeNO_2 , and 25% $\text{MeOH}\cdot\text{KOH}$ in EtOH is decomposed by dil. HCl to the 2-β-nitro-α-hydroxyethyl derivative, m.p. 157°, and by 50% H_2SO_4 to Et 4-methyl-2-β-nitrovinylpyrrole-3 : 5-dicarboxylate, m.p. 184.5°, which is reduced by $\text{Al}\cdot\text{Hg}$ in moist Et_2O to 3 : 5-dicarbomethoxy-4-methyl-2-pyrrolylacetaldoxime, m.p. 183°. 5-Carbomethoxy-2 : 4-dimethyl-3-pyrrolylacetaldoxime, m.p. 176° (from the 3-β-nitrovinyl derivative), and $\text{Ac}_2\text{O}\cdot\text{KOAc}$ afford 5-carbomethoxy-2 : 4-dimethyl-3-pyrrolylacetone, m.p. 163°, hydrolysed by 10—15% $\text{MeOH}\cdot\text{KOH}$ to the 5-carboxynitrile, m.p. 178°

(decomp.). 5-Carbomethoxy-4-methyl-3-β-carboxyethyl-2-pyrrolylacetone (from the 2- CH_2Br compound and aq. KCN in Et_2O) is hydrolysed by conc. $\text{HCl}\cdot\text{AcOH}$ to the 2-pyrrolylacetic acid, m.p. 215° (decomp.). Et 4-methyl-2-bromomethylpyrrole-3 : 5-dicarbonylate (I) and aq. $\text{EtOH}\cdot\text{KCN}$ give 3 : 5-dicarbomethoxy-4-methyl-2-pyrrolylacetone, m.p. 165°; with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ in COMe_2 , Et 4-methyl-2-β-cyano-β-carbomethoxyethylpyrrole-3 : 5-dicarboxylate, m.p. 118°, results. Et 4-methyl-3-β-carboxyethyl-2-β-cyano-β-carbomethoxyethylpyrrole-5-carboxylate, m.p. 178.5°, is similarly prepared. (I) and $\text{CHNa}(\text{CO}_2\text{Et})_2$ in COMe_2 afford Et 4-methyl-2-β-dicarbomethoxyethylpyrrole-3 : 5-dicarboxylate (II), m.p. 95°, hydrolysed by 30% KOH in EtOH to the tetracarboxylic acid, m.p. 233°, which is rather stable and is brominated to two Br-compounds, yellow and colourless, both not melted at 280°. Hydrolysis of (II) with 20% $\text{MeOH}\cdot\text{KOH}$ gives Et 4-methyl-2-β-dicarbomethoxyethylpyrrole-3 : 5-dicarboxylate, m.p. 179° (decomp.), decarboxylated to the 2-β-carboxyethyl derivative (A., 1931, 101), which is hydrolysed further by 25% $\text{MeOH}\cdot\text{KOH}$ to Et 5-carboxy-4-methyl-2-β-carboxyethylpyrrole-3-carboxylate (III), m.p. 203°. Decarboxylation of this affords Et 4-methyl-2-β-carboxyethylpyrrole-3-carboxylate (IV), m.p. 150° (Et_2 ester, m.p. 60°; lactam, m.p. 110°). Et 5-formyl-4-methyl-2-β-carboxyethylpyrrole-3-carboxylate, m.p. 165° (oxime, m.p. 196°) [from (IV), HCN , and HCl in $\text{Et}_2\text{O}\cdot\text{CHCl}_3$], with cryptopyrrole and $\text{EtOH}\cdot\text{conc. HBr}$ gives an unidentified methene hydrobromide, m.p. 201°, whilst with opsopyrrole, 4-carbomethoxy-3 : 3'-dimethyl-4'-ethyl-5-β-carboxyethylpyrromethene hydrobromide, m.p. 184° (Br-derivative, darkens at 210°, not melted at 280°), results. (III) or (IV) with conc. HBr in HCO_2H affords 4 : 4'-dicarbomethoxy-3 : 3'-dimethyl-5 : 5'-di-β-carboxyethylpyrromethene hydrobromide, m.p. 219° (darkens at 210—215°). Et 4-methyl-2-bromomethyl-3-β-carboxyethylpyrrole-5-carboxylate [compound (1 : 1) with pyridine, m.p. 197°] and $\text{CHNa}(\text{CO}_2\text{Et})_2$ in pyridine give Et 4-methyl-3-β-carboxyethyl-2-β-dicarbomethoxyethylpyrrole-5-carboxylate, m.p. 111°, hydrolysed by 25% $\text{MeOH}\cdot\text{KOH}$ to the 2-β-dicarbomethoxyethyl derivative, m.p. 184°, which is decarboxylated to Et 4-methyl-2 : 3-di-β-carboxyethylpyrrole-5-carboxylate, m.p. 190° (slight previous sintering). This with conc. HBr and AcOH (HCO_2H) affords the hydrobromide, m.p. 229°, of 3 : 3'-dimethyl-4 : 5 : 4' : 5'-tetra-β-carboxyethylpyrromethene, m.p. 180°.

Et 4-methyl-3-ethyl-2-β-β-dicarbomethoxyvinylpyrrole-5-carboxylate, m.p. 222° (decomp.) [from the 2-CHO compound and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{EtOH}\cdot\text{NH}_2\text{Ph}$], is reduced ($\text{Na}\cdot\text{Hg}$) to the 2-β-β-dicarbomethoxyethyl derivative, m.p. 178°, which is decarboxylated to Et 4-methyl-3-ethyl-2-β-carboxyethylpyrrole-5-carboxylate, m.p. 169°. Et 4-methyl-3-ethyl-2-bromomethylpyrrole-5-carboxylate and KCNS in aq. COMe_2 give the 2-thiocyanomethyl derivative, m.p. 127—128°; the thiocyanomethyl derivative, m.p. 171°, from (I) is oxidised by 30% HNO_3 to Et 2-formyl-4-methylpyrrole-3 : 5-dicarboxylate. 3 : 5-Diacetyl-2 : 4-dimethylpyrrole [reduced (Wolff-Kishner) to 2 : 4-dimethyl-3 : 5-diethylpyrrole] and Br in AcOH give the 2-bromomethyl derivative, m.p. 149°, m.p. (+ $\text{C}_5\text{H}_5\text{N}$) 286°. β-5-Formyl-2 : 4-dimethyl-3-pyrrolylpropionic acid and

SO_2Cl_2 afford a compound, $\text{C}_9\text{H}_{10}\text{O}_4\text{NCl}_3$, m.p. 191° . *o*-Formyl-4-methyl-3-propyl-2-bromomethylpyrrole has m.p. 175° . H. B.

Interaction of magnesium phenyl bromide with 1-chloropiperidine and other *N*-chloro-compounds. R. J. W. LE FEVRE (J.C.S., 1932, 1745—1747).— MgPhBr gives with 1-chloropiperidine, C_6H_5 , PhCl , and $\text{C}_6\text{H}_{11}\text{N}$; PhCl is isolated from the reaction with NMe_3Cl , NEt_3Cl , chloramine-*T*, dichloramine-*T*, NCl_3 , and NH_4Cl (cf. Coleman and Hauser, A., 1928, 622). F. R. S.

Allyl ethers of heterocyclic enols. B. MANDER-JONES and V. M. TRIKOUJS (J. Amer. Chem. Soc., 1932, 54, 2570).—Migration of the allyl group can occur from O to the adjacent β -unsaturated C atom; thus, 4-allyloxy-2-methylquinoline heated at 200° for a short time give 4-hydroxy-2-methyl 3-allylquinoline. C. J. W. (b)

6-Hydroxyquinoline-5-aldehyde and derived 5:6-disubstituted quinolines. B. BOBRANSKI (J. pr. Chem., 1932, [ii], 134, 141—152).—Condensation of 6-hydroxyquinoline with excess of CHCl_3 and NaOH (not KOH) gives the Na salt of 6-hydroxyquinoline-*o*-aldehyde, m.p. 138.5° [NH_4 salt; phenylhydrazone, m.p. 232 — 234° (decomp.) [hydrochloride, m.p. 221 — 226° (decomp.), $+1\text{H}_2\text{O}$]; azine, m.p. 351° ; anil, m.p. 102°]. Its oxime, m.p. 235° (rapid heating), is dehydrated by heat or Ac_2O to 6-hydroxy-5-cyanoquinoline, m.p. 293° (Na salt, m.p. $>300^\circ$, $+1\text{H}_2\text{O}$); this is hydrolysed only with difficulty, and with conc. H_2SO_4 at 100° gives the amide, m.p. 227.5° , not hydrolysed by 20% H_2SO_4 or 25% KOH , but converted by HNO_3 into 6-hydroxyquinoline-5-carboxylic acid, decarboxylated $>170^\circ$ without melting (slow heating). The last-named is also obtained from 6-hydroxyquinoline by the Kolbe synthesis and gives *o*-nitro-6-hydroxyquinoline with HNO_3 or HNO_2 in H_2SO_4 (cf. A., 1888, 67). H. A. P.

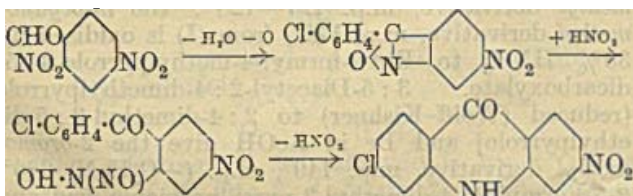
Reaction between quinolinic anhydride and phenylhydrazine. P. R. SEN-GUPTA and A. C. SIRCAR (J. Indian Chem. Soc., 1932, 9, 145—148).—Quinolinic anhydride (I) and $\text{NHPh}\cdot\text{NH}_2$ (II) in cold C_6H_6 for 2 days give quinolin-2-phenylhydrazinic acid, m.p. 146° (decomp.). Quinolinphenylhydrazide, m.p. 201° , is obtained from equimol. amounts of (I) and (II) at 120 — 130° ; with an excess of (II) at 200 — 230° , nicotinphenylhydrazide, m.p. 185° , results. *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and $\text{NPhMe}\cdot\text{NH}_2$ at 130° give *N*-methylanilinophthalimide, m.p. 124° ; *N*-methylanilinoquinolinimide, m.p. 155° , and -naphthalimide, m.p. 210° , are similarly prepared. H. B.

Acridine. X. Course of the synthesis of 3-nitroacridones according to I. Tanasescu. K. LEHMSTEDT (Ber., 1932, 65, [B], 999—1005).—The course of the synthesis is represented by: $\text{PhCl}+$

(cf. A., 1927, 574; this vol., 169). This view is supported by the observation that HNO_3 is formed by the action of conc. H_2SO_4 on 2:4-dinitro- or 4-chloro-2-nitro-benzaldehyde at room temp. 2-Nitroacridone, NPhMe_2 , and PCl_5 afford 2-nitro-5-*p*-dimethylaminophenylacridine, m.p. 255° . 6-Chloro-4-nitrobenzoic acid, *p*-chloroaniline, Na_2CO_3 , and Cu powder in boiling amyl alcohol yield 4'-chloro-5-nitrodiphenylamine-2-carboxylic acid, m.p. 242° , which is not greatly affected by conc. H_2SO_4 at 100° , but is converted by successive treatment with PCl_5 and AlCl_3 in C_6H_6 into 7-chloro-2-nitroacridone, m.p. above 380° , transformed by POCl_3 and NPhEt_2 into 7-chloro-2-nitro-5-*p*-diethylaminophenylacridine, m.p. 254° . The 5-*p*-diethylaminophenylacridine obtained from Tanasescu's "8(?)-chloro-2-nitroacridone" has m.p. 236° . 2:4-Dinitrobenzaldehyde, PhF , and conc. H_2SO_4 give 7-fluoro-2-nitroacridone, m.p. above 380° , accompanied by HF . H. W.

Hydantoins. L. Synthesis of hydantoins possessing the properties of hypnotics. R. M. HERBST and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 2463—2470; cf. A., 1930, 1446).—Amino-acid nitriles (isolated as the hydrochlorides) are prepared by the action of HCN and NH_3 on ketones in abs. EtOH ; the following are described: α -amino- α -benzylpropionitrile [hydrochloride, m.p. 148 — 150° (corr.); Ac derivative, m.p. 142 — 143°]; α -amino- α -benzylbutyronitrile [hydrochloride, m.p. 135 — 140° ; Ac derivative, m.p. 86 — 87°]; α -amino- γ -phenyl- α -methylbutyronitrile [hydrochloride, m.p. 140 — 141° (corr.)]; α -amino- γ -phenyl- α -ethylbutyronitrile (hydrochloride, m.p. 84° ; Ac derivative, m.p. 116 — 118°); 1-amino-1-cyanocyclohexane [hydrochloride, m.p. 202 — 204° (corr.)]. α -Carbamido nitriles are prepared from the above hydrochlorides and KCNO in 50% AcOH : α -carbamido- α -benzylpropionitrile, m.p. 170 — 171° ; α -carbamido- α -benzylbutyronitrile, m.p. 124 — 126° ; α -carbamido- γ -phenyl- α -methylbutyronitrile, m.p. 138 — 142° ; α -carbamido- γ -phenyl- α -ethylbutyronitrile, m.p. 139° , and 1-carbamido-1-cyanocyclohexane, m.p. 180 — 181° , are described. These are converted by warm 20% HCl into 5-benzyl-5-methyl-, m.p. 227 — 228° (corr.); 5-benzyl-5-ethyl-, m.p. 217 — 218° (corr.); 5- β -phenylethyl-5-methyl-, m.p. 179 — 180° (corr.); 5- β -phenylethyl-5-ethyl-, m.p. 198 — 199° (corr.), and 5:5-cyclopentamethylene-, m.p. 217 — 218° (corr.), hydantoins, respectively. α -Amino- α -phenylbutyric acid, m.p. 275° (corr.) [hydrochloride, m.p. 271° (corr.)]; α -phenyl-carbamido- α -phenylbutyric acid, m.p. 190 — 190.5° (corr.); and α -amino- β -phenyl- α -methylpropionic acid, m.p. 293 — 294° (corr.) [hydrochloride, m.p. 244 — 246° (corr.)]; α -phenylcarbamido-derivative, m.p. 187° (corr.), are described. 5- β -Phenylethyl-5-methyl- and -5-ethyl-hydantoins have marked hypnotic properties. C. J. W. (b)

Synthesis of pyrazolinecarboxylic esters. K. VON AUWERS and F. KÖNIG (Annalen, 1932, 496, 27—51; cf. A., 1929, 1080).—Diazo-methane (or -ethane) adds (usually readily) to various unsaturated esters to give Δ^1 -pyrazoline-5-carboxylates,



$\text{CH}_2\text{CH}_2\text{N}=\text{N} > \text{CH}\cdot\text{CO}_2\text{R}$, characterised by their in-

difference towards PhNCO, spectrochemically, and by their rearrangement with HCl (1:1) to Δ^2 -pyrazoline-5-carboxylates, $\begin{matrix} \text{CH} & \text{CH} \\ | & | \\ \text{N} & \text{NH} \end{matrix} > \text{CH} \cdot \text{CO}_2\text{R}$, which

react with PhNCO and show higher vals. of d and n . Thus, Et α -methylacrylate (I) and diazomethane in Et₂O give Et 5-methyl- Δ^1 -pyrazoline-5-carboxylate, b.p. 99–100°/11 mm., isomerised to Et 5-methyl- Δ -pyrazoline-5-carboxylate, b.p. 106–107°/15 mm. (1-phenylcarbonyl derivative, m.p. 68–69°). Similarly, Et tiglate affords Et 4:5-dimethyl- Δ^1 -, b.p. 110°/12 mm. (Me ester, b.p. 80–82°/2 mm., from Me tiglate), and Δ^2 -, b.p. 117–118°/16 mm. (1-phenylcarbonyl derivative, m.p. 91°), -pyrazoline-5-carboxylates, whilst Et Δ -propene- α -dicarboxylate furnishes Et 4-methyl- Δ^1 -, decomp. about 60°/high vac., and Δ^2 -, b.p. 152°/12 mm., m.p. 32.5–33.5°, -pyrazoline-5:5-dicarboxylates. Diazoethane and (I) give Et 3:5-dimethyl- Δ^1 -, b.p. 86–88°/2 mm., and Δ^2 -, b.p. 106–108°/11 mm., -pyrazoline-5-carboxylates, whilst Me tiglate similarly affords Me 3:4:5-trimethyl- Δ^1 -, b.p. 88°/3 mm., and Δ^2 -, b.p. 81°/2 mm. (1-phenylcarbonyl, m.p. 97°, and Ac, b.p. 146–149°/11.5 mm., derivatives), -pyrazoline-5-carboxylates. The pyrazolines from the tiglates are considered to be homogeneous and not mixtures of stereoisomerides; cis-addition of the diazomethane probably occurs. Me mesaconate and diazomethane give a little Me 4-methylpyrazoline-3:4-dicarboxylate (*loc. cit.*) and (mainly) Me trans-5-methyl- Δ^1 -pyrazoline-4:5-dicarboxylate, b.p. 120–122°/2–2.5 mm., isomerised (as above) to the Δ^2 -ester, b.p. 150°/12 mm. (corresponding Et ester, b.p. 162°/13 mm.), whilst Me dimethylfumarate similarly affords Me trans-4:5-dimethyl- Δ^1 -pyrazoline-4:5-dicarboxylate, b.p. 150°/11 mm., isomerised to the Δ^2 -ester, b.p. 158°/13 mm., m.p. 58.5–60.5. The last-named esters differ from those obtained from Me dimethylmaleate (*loc. cit.*).

Reaction between Et α -chlorocrotonate and diazomethane in Et₂O is accelerated by moisture; the resulting product is decomposed by HCl or PhNCO and eliminates HCl on distillation, giving Et 4-methylpyrazole-3(5)-carboxylate. Et γ -trichlorocrotonate affords Et 4-trichloromethylpyrazoline-3-carboxylate, m.p. 109° (phenylcarbonyl derivative, m.p. 138–139°), but Et β -chloro-, -methyl-, and -ethoxy-crotonates do not react. Me fumarate or maleate and diazomethane give Me pyrazoline-3:4-dicarboxylate, m.p. 98° [described by von Pechmann (A., 1894, i, 438) as the 4:5-derivative] (N-carbomethoxy-, m.p. 108–109°, N-benzenesulphonyl, m.p. 105°, and N-p-toluenesulphonyl, m.p. 106–107°, derivatives); the oily products obtained using CHN₂-CO₂Me, give Me N-carbomethoxypyrazoline-3:4:5-tricarboxylate, m.p. 144–145°, when treated with ClCO₂Me. The relationship between the isomeric Me tricarbomethoxypyrazolinylacetates, m.p. 104° and 153°, of Buchner and Witter (A., 1894, i, 346) could not be ascertained; the former does not give N-derivatives and is converted into the latter by ClCO₂Et (amyl) or MeI, but not by HCl. Spectrochemical data are given for most of the above and some of the previously described (*loc. cit.*) compounds.

H. B.

Some derivatives of anserine, carnosine, and histidine. W. KELL (Z. physiol. Chem., 1932, 208, 67–71).—Anserine and carnosine with Me₂SO₄ and NaOH add on 4 and 5 Me groups, respectively, the products being identical (chloroaurate, m.p. 92–96°). Histidine, when heated with phthalic anhydride, forms α -phthalylhistidine (I), m.p. 188° [picrate, m.p. 251°; Me ester hydrochloride (II), m.p. 238–240°; Me ester, m.p. 187°; Et ester, m.p. 195°]. With BzCl, (II) yields γ -dibenzamido- α -phthalimido- Δ -pentenoic acid, m.p. 194°. Distillation of (I) with soda-lime gives glyoxaline; on methylation (I) gives β -methyliminazotyl- α -phthalimidopropionate, β -1:4-methyliminazotyl- α -phthalyliminopropionic acid, and β -1:5-methyliminazotyl- α -phthalimidopropionic acid, isolated as the chloroaurates. J. H. B.

Dihydronaphthopyrazole. I. K. VON AUWERS and C. WIEGAND (J. pr. Chem., 1932, [ii], 134, 82–96).— α -Tetralone, Et formate, and Na give 1-keto-2-hydroxymethylenetetrahydronaphthalene (I), b.p. 153.5–154°/10 mm., of which the following derivatives have been prepared: Et ether, b.p. 170–170.5°/10 mm.; Ac, m.p. 124°; CO₂Et, m.p. 81.5–82.5°; Bz, m.p. 112–113°; anilide, m.p. 115–116°; methylamylide, m.p. 90–91°; monosemicarbazone (II), m.p. 200°; benzoylhydrazone, m.p. 154–155°; *o*-nitrobenzoylhydrazone, m.p. 196°; and 2-phenylhydrazone of 1:2-diketotetrahydronaphthalene, m.p. 83°. Attempts to prepare hydrazones from the free ketone derivatives result in the formation of isooxazoles. When (II) is heated with H₂SO₄, dihydronaphthopyrazole [dihydro- α -naphthisoindazole] (III), m.p. 123° (picrate, m.p. 192–193°), is obtained. (II) and NHMe·NH₂·H₂SO₄ afford 1-methyldihydro- α -naphthisoindazole, b.p. 175–175.5°/11 mm. (picrate, m.p. 187–188°), and methylation of (III) with MeI and Na gives a mixture of 1- and 2-Me derivatives (picrate, m.p. 166–167°). (I) and NHPh·NH₂ form a mixture of 5 parts of 1-phenyl-, m.p. 127–128° (picrate, m.p. 141–142°), and 1 part of 2-phenyl-dihydro- α -naphthisoindazole, m.p. 104–105° (picrate, m.p. 123°). (III) yields the following derivatives: 1-CO₂Me, m.p. 116–116.5°; 1-CO₂Et, m.p. 63–64°; 1-Ac, m.p. 82.5–83.5°; 1-Bz m.p. 141°; 1-(*o*-nitrobenzoyl), m.p. 157–158°. The results of substitution differ from those obtained with other similar compounds (cf. A., 1925, i, 585; 1927, 1088) and the significance of this is discussed. F. R. S.

Determination of structure of dihydronaphthopyrazole [dihydro- α -naphthisoindazole] derivatives. II. K. VON AUWERS and F. ENBERGS (J. pr. Chem., 1932, [ii], 134, 97–106).—Condensation of Et 1-ketotetrahydronaphthalene-2-glyoxylate (I) with N₂H₄·H₂O in EtOH gives Et dihydro- α -naphthisoindazole-3-carboxylate (II), m.p. 152° [free acid, m.p. 267° (alkaline KOH)]; this with Na and MeI gives (after hydrolysis) 1- (III), m.p. 258°, and 2-Me (IV), m.p. 244°, derivatives of the acid, which are separated by heating with 3% alcoholic HCl (which esterifies the 1-derivatives only), and identified by decarboxylation to known methylpyrazoles. Interaction of (I) with NHMe·NH₂·H₂SO₄ in H₂O in presence or absence of NaOAc gives mainly (III) and a little (IV).

Ethylation of (II) gives 1-, m.p. 231—232°, and 2-ethylidihydro- α -naphthisoindazole-3-carboxylic acid, m.p. 211°. Interaction of (I) with $\text{NH}_2\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ gives only the 1- CH_2Ph , m.p. 155—156° (free acid, m.p. 217—218°), and with $\text{NHPh}\cdot\text{NH}_2$ the 1- Ph , m.p. 155° (free acid, m.p. 248°), derivatives of (II) only. The free acid of (II) [but not (II) itself] gives an *Ac* derivative, m.p. 158—159°, with formation of a diketopiperazine derivative, with AcCl ; both (II) and the free acid give 1- CO_2Et derivatives, m.p. 70—71°, and 139—140°, respectively, with ClCO_2Et , the former of which is also formed by esterification of the latter. The benzoylhydrazone, m.p. 131—133°, of (I) is unaffected by boiling glacial AcOH or HCO_2H . Interaction of (II) with BzCl gives the diketopiperazine, $\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_4$. H. A. P.

Condensation product of *o*-phenylenediamine with quinolinic acid. A. LECCO and V. IVKOVIC (Glasn. hemisk. drus. Kralj. Jugoslav., 1930, 1, 7 pp.; Chem. Zentr., 1932, i, 1100).—Alkaline fission of the condensation product of quinolinic acid and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ affords a product which, when heated at 260°, loses CO_2 and gives 2-2-pyridylbenzimidazole; hence the condensation product is $\alpha\beta$ -nicotinoylene-2:1-benzimidazole. A. A. E.

General method for the preparation of 1-substituted glyoxalines from acetalylthiocarbimide and primary amines. A. P. T. EASSON and F. L. PYMAN (J.C.S., 1932, 1806—1812).—Acetalylthiocarbimide (I), b.p. 133°/40 mm., prepared from CS_2 and aminoacetal, combines with aliphatic, aromatic, and heterocyclic primary amines, yielding thiocarbamides, $\text{Q}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$. (I) and NH_2Ph give phenyl- and 2-amino-quinoline gives 2-quinolyl-acetalylthiocarbimide, m.p. 139—140°, which is hydrolysed to 2-(2'-thiolglyoxalyl-1')-quinoline, m.p. 263—264° (decomp.), oxidised by HNO_3 to 2-(glyoxalyl-1')-quinoline, m.p. 120—121° (monohydrochloride, m.p. 217—218°; picrate, m.p. 206°). 8-Aminoquinoline similarly affords 8-(2'-thiolglyoxalyl-1')-, m.p. 304° (decomp.) (hydrochloride), and 8-(glyoxalyl-1')-quinoline, m.p. 124—125° (monohydrochloride, m.p. 247—248°; picrate, m.p. 197—198°); 8-amino-6-methoxyquinoline yields 8-(thiolglyoxalyl-1')-, m.p. 297° (decomp.), and 8-(glyoxalyl-1')-6-methoxyquinoline, m.p. 139—140° (monohydrochloride, m.p. 243—244°; picrate, m.p. 219—220°); NH_2Me forms 2-thiol-1-methylglyoxaline, m.p. 143—144° (lit. 141—142°); $\text{NH}_2\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ gives, after hydrolysis, 2-thiol-1- β -hydroxy-, m.p. 151—152°, oxidised to 1- β -hydroxy-ethylglyoxaline, b.p. 202—206°/20 mm., m.p. 36—40° (picrate, m.p. 142—143°); and Et glycine similarly yields 2-thiolglyoxaline-, m.p. 205—206°, and glyoxaline-1-acetic acid, m.p. 268—269° (decomp.) (*Et* glyoxaline-1-acetate picrate, m.p. 124—125°). Some of these compounds were tested for antimalarial activity and found to be inactive. F. R. S.

Oxidation of uric acid in alkaline solution. W. SCHULER and W. REINDEL (Z. physiol. Chem., 1932, 208, 248—257).—The intermediate product formed by oxidation of uric acid with alkaline KMnO_4 was pptd. as the Ag salt and identified as hydroxy-acetylenediureincarboxylic acid (Ag_3 , Ag_2 salts):

$\text{CO}\langle\begin{smallmatrix}\text{NH}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{NH} \\ \text{NH}\cdot\text{C}(\text{OH})\cdot\text{NH}\end{smallmatrix}\rangle\text{CO}$. Allantoin and uroxic acid were obtained from the Ag_3 salt. J. H. B.

Porphyryn syntheses. XLIV. Synthesis of 2:3:6:7-tetramethyl-1:4:5:8-tetraethyl-malonic acid porphyrin. H. FISCHER and H. J. RIEDL (Z. physiol. Chem., 1932, 207, 193—201; cf. this vol., 173).—Condensation of 5-carbethoxy-2-methyl-4-ethylpyrrole with Et methoxymethylmalonate in presence of EtOH and HCl gives 5-carbethoxy-2-methyl-4-ethyl-3-($\beta\beta$ -dicarbethoxy)ethylpyrrole (I), m.p. 75°. Br in Et_2O converts (I) into the 2-bromomethyl derivative (II), m.p. 86°. On boiling with H_2O , (II) gives 5:5'-dicarbethoxy-4:4'-diethyl-3:3'-di-($\beta\beta$ -dicarbethoxy)ethyl-2:2'-pyrromethane (III), m.p. 106°. Hydrolysis with NaOH in aq. EtOH affords the Na_6 salt. When heated with HCO_2H and subsequently esterified (III) gives the Me_6 ester of 1:4:5:8-tetraethyl-2:3:6:7-tetra-($\beta\beta$ -dicarbethoxy)ethylporphyrin, m.p. 229° [Cu , m.p. 248° (uncorr.), Fe , m.p. 174° (uncorr.) and Zn , m.p. 264—265° (uncorr.), salts]. The Cu , Fe , and Zn salts are spectroscopically identical with the corresponding complex salts from the Me_6 ester of isuroporphyrin I.

Bromination of 5-carbethoxy-4:3':5'-trimethyl-3:4'-diethyl-2:2'-pyrromethane with 1 mol. of Br gives 5-carbethoxy-4:3':5'-trimethyl-3:4'-diethyl-2:2'-pyrromethene hydrobromide, m.p. 169° (decomp.), and with 2 mols. the corresponding 5- CH_2Br derivative, m.p. 142° (decomp.). Et methoxymethylmalonate with 5-carbethoxy-4:3':5'-trimethyl-3-ethyl-2:2'-pyrromethane gives 5:5'-dicarbethoxy-4:4'-dimethyl-3:3'-diethylpyrromethane, and with 5-carbethoxy-4:3':5'-trimethyl-3-($\beta\beta$ -dicarbethoxy)ethyl-2:2'-pyrromethane, 5:5'-dicarbethoxy-4:4'-dimethyl-3:3'-di-($\beta\beta$ -dicarbethoxy)ethylpyrromethane. J. H. B.

Stereobilin, copromesobiliviolin, and copronigrin. C. J. WATSON (Z. physiol. Chem., 1932, 208, 101—119).—Cryst. stercobilin, $\text{C}_{33}\text{H}_{44}\text{O}_8\text{N}_4$, m.p. 137—140°, was obtained from the pure hydrochloride. Reduction gave a colourless solution which could not be crystallised and HNO_3 oxidation did not yield methylethylmaleimide as with bilirubin. By CrO_3 - AcOH oxidation a product resembling hamatinic acid was obtained. An attempt to obtain aetioporphyryn by way of opsopyrrole failed. The absorption and fluorescence of the Zn salt were measured.

Copromesobiliviolin, m.p. 164—172° (Cu compound, m.p. 182—190°), is very similar to mesobiliviolin and closely related to stercobilin, and gives the hydrochloride of the latter on treatment with $\text{FeCl}_3\cdot\text{HCl}$.

Copronigrin, $\text{C}_{42}\text{H}_{55}\text{O}_{14}\text{N}_3$ (Zn compound), can be separated into an acid and a basic fraction. Faces from a case of pernicious anaemia contained deuteroporphyryn Me_2 ester. J. H. B.

Treatment of the amides of α -hydroxy- or *o*-phenolcarboxylic acids with acetone. H. O. L. FISCHER, G. DANGSCHAT, and H. STETTNER (Ber., 1932, 65, [B], 1032—1037).—Amides of α -OH-acids are converted into derivatives of tetrahydro-oxazole by COMe_2 in presence of HCl but not of ZnCl_2 . Reaction does not occur if a H atom of the NH_2

group is substituted or if the α -OH-group is protected. The following compounds are described: 4-keto-5-phenyl-2:2-dimethyltetrahydro-oxazole ("mandelamide-acetone"), m.p. 127°, converted by Ag_2O and MeI into 4-methoxy-5-phenyl-2:2-dimethyl-2:5-dihydro-oxazole, b.p. 126—127°/13 mm., m.p. 49—50°, and by boiling Ac_2O into 4-acetoxy-5-phenyl-2:2-dimethyl-2:5-dihydro-oxazole, m.p. 42°; 4-keto-2:2-dimethyltetrahydro-oxazole ("glycollamide-acetone"), m.p. 104—105°, 4-methoxy-2:2-dimethyl-2:5-dihydro-oxazole, b.p. 31—32°/13 mm., and 4-acetoxy-2:2-dimethyl-2:5-dihydro-oxazole, b.p. 79—80°/12 mm.; 4-keto-2:2:5-trimethyl-3:5-dihydro-oxazole ("lactamide-acetone"), m.p. 103—104°, 4-methoxy-2:2:5-trimethyl-3:5-dihydro-oxazole, b.p. 33°/12 mm., and 4-acetoxy-2:2:5-trimethyl-3:5-dihydro-oxazole, b.p. 83—84°/12 mm.; 4-keto-2:2-dimethyl-3:4-dihydro-1:3-benzometoxazine ("salicylamide-acetone"), m.p. 137°, 4-methoxy-2:2-dimethyl-1:3-benzometoxazine, b.p. 108—110°/13 mm., and 4-acetoxy-2:2-dimethyl-1:3-benzometoxazine, m.p. 30—32°; compound $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}$, m.p. 162—163°, from cyclohexanolicarboxylamide, COMe , and HCl . H. W.

***ψ*-1:8-isonaphthoxazone.** B. BOBRANSKI (J. pr. Chem., 1932, [ii], 134, 153—157).—The product of condensation of 6-hydroxyquinoline with malic acid in conc. H₂SO₄ is identical with "coumaroquinoline" (A., 1924, i, 87; prep. repeated) and with *ψ*-1:8-isonaphthoxazone (J.C.S., 1919, 115, 536). The constitution previously assigned (*loc. cit.*) is confirmed by its synthesis from 6-hydroxyquinoline-5-aldehyde by the Perkin condensation. H. A. P.

Chemical investigation of *Rauwolfia caffra*.
I. Rauwolfine. J. B. KOEPFLI (J. Amer. Chem. Soc., 1932, 54, 2412—2418).—Details are given for the separation of *rauwolfine* (I), $C_{20}H_{26}O_3N_2 \cdot 2.5H_2O$, decomp. 235—238° [*chloride*, $C_{20}H_{25}O_2N_2Cl$, m.p. 300—303° (decomp.), $[\alpha]_D^{20} + 29^\circ$ in H_2O , m.p. (+ H_2O) 297—300°; *bromide* (+ H_2O), m.p. 250—253° (decomp.); *iodide* (+ H_2O), m.p. 220—225° (decomp.)], from the bark of *R. caffra*, Sonder. Two other cryst. bases (*A*, m.p. 294—295°, and *B*) are also isolated. The pharmacological action of (I) is described.

C. J. W. (b)

Configuration of optically active coniine and α -pipecoline. W. LEITHE (Ber., 1932, 65, [B] 927—931).—*dl*-Pipecolic acid is resolved by *d*-tartaric acid in EtOH yielding (+)-pipecolic acid, m.p. 266° (decomp.), $[\alpha]_D^{25} +56.2^\circ$ in H_2O ($c=2.93$) [*H* *d*-tartrate, m.p. 192° (decomp.), $[\alpha]_D^{25} +29.6^\circ$ in H_2O ; corresponding *hydantoin*, $C_7H_{10}O_2N_2$, m.p. 137—139°, $[\alpha]_D^{25} +91.8^\circ$ in H_2O]. The mode of dependence of $[\alpha]$ of the acid on c and solvent shows the (+)-form to belong to the *d*-series. Since the steric relationship of (+)-conhydrin to (−)-coniine is established (Löffler and Friedrich, A., 1909, i, 180) and (+)-conhydrin

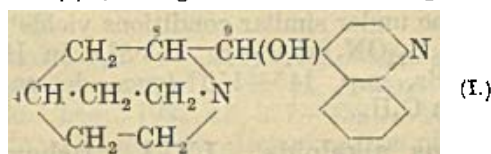
Pr can be oxidised to (-)-pipecolic
 $\text{H}_2\text{C}-\text{NH}-\text{CH}_2$ acid, the configuration of
 $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$ is expressed by (I)
 (+)-Conune, (+)- α -pipecoline, and
 (+)- α -cyclohexylethylamine have
 similar configuration. H. W.

Alkaloids of *Heliotropium lasiocarpum*. I. G. MENSCHIKOV (Ber., 1932, 65, [B], 974—977).—The

dried plant is percolated with 95% EtOH containing 1% of NH_3 and the residue after removal of solvent is treated with HCl. The acid solution is made alkaline with NH_3 and the mixed alkaloids are removed by CHCl_3 . Crystallisation from C_6H_6 -light petroleum (1:1) affords *heliotrine* (I), $\text{C}_{16}\text{H}_{27}\text{O}_8\text{N}$, m.p. 125–126°, $[\alpha]_D -75^\circ$ in CHCl_3 (*methiodide*, m.p. 108–111°), which contains two OH and one OMe and a *tert.*N atom. The residue from (I) when dissolved in HCl and fractionally pptd. with NaOH yields *lasiocarpine*, $\text{C}_{21}\text{H}_{33}\text{O}_7\text{N}$, m.p. 94–95·5°, $[\alpha]_D -4^\circ$ in EtOH, which is unsaturated towards KMnO_4 and gives the pine-shaving reaction when heated with Zn dust. (I) is hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to the saturated, aliphatic *heliotric acid*, $\text{OH}\cdot\text{C}_6\text{H}_{11}(\text{OMe})\cdot\text{CO}_2\text{H}$, m.p. 92·5–94·5°, $[\alpha]_D -12^\circ$ in H_2O , and *heliotridine*, $\text{C}_8\text{H}_{13}\text{O}_2\text{N}$, m.p. 116·5–118°, $[\alpha]_D +31^\circ$ in MeOH (*hydrochloride*, m.p. 122–124°).

H. W.

Cinchona alkaloids. XXVII. Stereochemical investigations. III. (+)- and (-)-Rubans, the parent substances of the *Cinchona* alkaloids. P. RABE and S. RIZA (Annalen, 1932, 496, 151—163). —Rubatoxanone, m.p. about 30° [*dibenzoyl-d-tartrate*, m.p. 202—203° (decomp.) (all m.p. are corr.)], is converted as previously described (A., 1922, i, 361) into 9-rubanone, m.p. 85—86° [*dibenzoyl-d-tartrate*, m.p. 173—174.5° (decomp.)], which undergoes fission (cf. A., 1909, i, 407; 1910, i, 417) to cinchonic acid and *oximinoquinuclidine*, m.p. 187—188° (decomp.), is reduced (Wolff-Kishner) to a mixture of (+)- and (-)-ruban, and is reduced (H₂, Pd-black, dil. HCl) to a mixture of the following four stereoisomeric 9-rubanolis (I) (the signs denote the configurations of



C_8 and C_9 , respectively): $(++)$ -, m.p. 229.5—230° (decomp.), $[\alpha]_D^{25} +132.5^\circ$ (all rotations are in EtOH) [*H* 1-tartrate, m.p. 186—187° (decomp.); chloride, m.p. 135—137.5°, $[\alpha]_D^{25} +4.9^\circ$]; $(+-)$ -, m.p. 118—119°, $[\alpha]_D^{25} +14.3^\circ$ [*dibenzoyl-d-tartrate*, m.p. 189—191° (decomp.); chloride, m.p. 140—142°, $[\alpha]_D^{25} +96.3^\circ$]; $(-+)$ -, m.p. 117—118°, $[\alpha]_D^{25} -14.9^\circ$ [*dibenzoyl-l-tartrate*, m.p. 189—191° (decomp.); chloride, m.p. 141—142°, $[\alpha]_D^{25} -96.8^\circ$]; and $(--)$ -, m.p. 228.5—230.5° (decomp.), $[\alpha]_D^{25} -131.8^\circ$ [*H* d-tartrate, m.p. 186—188° (decomp.); chloride, m.p. 136—138°, $[\alpha]_D^{25} -4.9^\circ$]. The $(++)$ - and $(+-)$ -chlorides are reduced [H_2 , Pd—CaCO₃, EtOH—KOH] to $(+)$ -ruban (I, $CH_2OH=CH_2$), oil, $[\alpha]_D^{25} +80.5^\circ$, whilst the $(-+)$ - and $(--)$ -chlorides similarly give $(-)$ -ruban, an oil, $[\alpha]_D^{25} -78.4^\circ$. *Dibenzoyl-l-tartaric acid hydrate* has m.p. 85°, $[\alpha]_D^{25} +103.7^\circ$.

Comparison of the sp. rotations of the rubanols with those of the 3-ethylrubanols (the isomeric hydrocinchonines and -cinchonidines) (this vol., 289) and those of the rubans with those of deoxyhydrocinchonine and -cinchonidine (*loc. cit.*) indicates that the asymmetric C₃ and C₄ atoms (of the *Cinchona* alkaloids) cause dextrorotation. H. B.

Oxidation of strychnine. B. ALESSANDRO (Nature, 1932, 129, 905).—Oxidation of strychnine with H_2CrO_4 in a carrier acidified with AcOH gives a compound $\text{C}_{21}\text{H}_{20}\text{O}_4\text{N}_2$ or $\text{C}_{12}\text{H}_{12}\text{O}_8\text{N}_4$, m.p. 309–310°, neutral to litmus, and giving colour reactions with strychnine. L. S. T.

Strychnos alkaloids. LXV. Oxidation of diketonucidine with bromine. Reaction of this base, of brucine, and of strychnidine with cyanogen bromide. H. LEUCHS and H. S. OVERBERG (Ber., 1932, 65, [B], 961–966; cf. A., 1930, 936).—Improved technique in the oxidation of diketonucidine with Br leads to the isolation of the homogeneous aldehyde, $\text{C}_{17}\text{H}_{22}\text{O}_6\text{N}_2$, as hydrobromide, $[\alpha]_D^{25} +100.8^\circ/\text{d}$, or perchlorate, $[\alpha]_D^{25} +145^\circ/\text{d}$. The perchlorate of the dioxime of the anhydride form is described. The hydrobromide is readily oxidised by yellow HgO to 2:3-diketonic acid hydrate, $\text{C}_{17}\text{H}_{20}\text{O}_8\text{N}_2$, darkening above 260°, $[\alpha]_D^{25} -166^\circ/\text{d}$ [semicarbazone perchlorate (derived from anhydride form)]. Electrolytic reduction of diketonucidine affords ketohydroxynucidine. Treatment of 2:3-diketonic acid with CNBr in C_6H_6 affords a non-decomposable quaternary bromide, $\text{C}_{35}\text{H}_{40}\text{O}_6\text{N}_5\text{Br}$, $[\alpha]_D^{25} +117.6^\circ/\text{d}$ in H_2O , and two isomeric substances, $\text{C}_{18}\text{H}_{20}\text{O}_3\text{N}_3\text{Br}$, prisms, $[\alpha]_D^{25} -205.8^\circ/\text{d}$ in AcOH , and needles, $[\alpha]_D^{25} +28.8^\circ/\text{d}$ in AcOH . Hydrolysis and reduction of the prisms leads to a compound, $\text{C}_{24}\text{H}_{26}\text{O}_4\text{N}_2$, m.p. 280–281° (vac.), $[\alpha]_D^{25} +69.4^\circ/\text{d}$ in MeOH . Brucine and CNBr in boiling C_6H_6 yield the quaternary bromide, $\text{C}_{47}\text{H}_{52}\text{O}_8\text{N}_5\text{Br}$, m.p. 209–211° (decomp.), $[\alpha]_D^{25} -24.5^\circ/\text{d}$ in AcOH , a substance, $\text{C}_{24}\text{H}_{26}\text{O}_4\text{N}_2\text{Br}$, softening and decomp. at 158–163°, $[\alpha]_D^{25} +70^\circ/\text{d}$ in C_6H_6 , and non-homogeneous material. Strychnidine under similar conditions yields the compounds $(\text{C}_{22}\text{H}_{24}\text{ON}_2\text{Br})_2$, $[\alpha]_D^{25} +43.8^\circ/\text{d}$ in H_2O , and $\text{C}_{22}\text{H}_{24}\text{ON}_2\text{Br}$, m.p. 145–150° (vac., decomp.), $[\alpha]_D^{25} -57.0^\circ/\text{d}$ in C_6H_6 . H. W.

Strychnos alkaloids. LXVI. Behaviour of brucinonic acid towards barium peroxide. H. LEUCHS and F. KROHNKE (Ber., 1932, 65, [B], 980–983).—Brucinonic acid is oxidised by H_2O_2 and Ba(OH)_2 to glycollic acid and an NH_2 -acid, $\text{C}_{20}\text{H}_{26}\text{O}_6\text{N}_2$, m.p. 254–255° (decomp.), $[\alpha]_D^{25} -15^\circ/\text{d}$ in H_2O (perchlorate, $[\alpha]_D^{25} -25.4^\circ/\text{d}$; hydrochloride, $[\alpha]_D^{25} -33.3^\circ/\text{d}$; K salt). The compound is obtained similarly from brucinonic acid hydrate b, which evolves CO , when boiled with NH_4Ph . H. W.

Narceine: new reactions and interpretation of Wangerin's reaction. J. A. SANCHEZ (Anal. farm. bioquim., 1931, 2, 68–74).—The presence of the CH_2O_2 group in narceine and narcotine may be shown (1) by heating 0.05 g. with H_2SO_4 (10 drops); the gas collected in H_2O gives a deep red coloration with Schryver's reagent (1% $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$, 1 c.c.; 5% $\text{K}_2\text{Fe(CN)}_6$, 2 drops; conc. HCl , 1–2 c.c.), (2) by gently heating a few mg. with about 0.01 g. of carbazole and 10 drops of conc. H_2SO_4 , when a deep violet-blue colour gradually develops. The emerald-green colour obtained with tannin and H_2SO_4 is also due to the CH_2O_2 group. CH. ABS.

Organic compounds of germanium. H. BAUER and K. BÜRSCHIES (Ber., 1932, 65, [B], 956–960).—

Hg di-1-naphthyl and GeCl_4 in $\text{C}_6\text{H}_5\text{Me}_2$ at 180° afford *Ge* 1-naphthyl trichloride, hydrolysed by 2*N*- NaOH to di-1-naphthylgermanic anhydride, $\text{C}^{10}\text{H}^7\cdot\text{GeO}>\text{O}$. The sole product of the interaction of GeCl_4 with Mg cyclohexyl bromide in Et_2O appears to be *Ge* tricyclohexyl bromide, m.p. 110°, converted by AgNO_3 in boiling EtOH or boiling H_2O or alkali into *Ge* tricyclohexyl hydroxide, m.p. 176–177°, whence the corresponding fluoride, m.p. 92°, chloride, m.p. 102°, and iodide, m.p. 99–100°, are derived by means of the requisite halogen acid. Successive treatment of GeCl_4 with NHPhMe at 100° and NaOH affords di-*p*-methylanilinogermanic anhydride, $(\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{GeO})_2\text{O}$; di-*p*-diethylanilinogermanic anhydride is similarly prepared. The action of H_2S on the requisite substituted germanic anhydride in dil. AcOH leads to the isolation of the following *Ge* sesquisulphides, $(\text{GeRS})_2\text{S}$: diphenyl; di-*p*-tolyl; di-*p*-diethylanilino-; di-*p*-dimethylanilino-; di-1-naphthyl. All are colourless powders without definite m.p., very sparingly sol. in H_2O , and slowly evolving H_2S when exposed to moist air: *Ge* is determined by heating the compounds with conc. H_2SO_4 at 100°, removing the acid, and repeated evaporation of the residue with conc. H_2SO_4 and fuming HNO_3 (1:3). H. W.

Halogenomercuribenzoic acids. A. N. NESMEJANOV and L. G. MAKAROVA (J. Gen. Chem. Russ., 1931, 1, 1162–1163).—The m.p. of acids of the type $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{HgHal}$ are: *o*-Cl, 253°, *o*-Br, 249°, *o*-I, stable up to 230°, *m*-Cl, 264°, *m*-Br, 250°, *m*-I, 181–185°, *p*-Cl, 273°, *p*-Br and *p*-I, above 300°. The m.p. of the *o*-Cl-compound (151°; A., 1931, 244) must be due to a misprint. The Me ester of the *o*-Br-acid has m.p. 195°, not 175° (cf. this vol., 70). G. A. R. K.

Organic antimonial compounds. III. (MISS M. E. BRENNAN, W. J. C. DYKE, W. H. JONES, and W. J. JONES (J.C.S., 1932, 1815–1819).—By using the appropriate Grignard reagents the following have been prepared: ethyldi-*n*-butylstibine, b.p. 147°/43 mm., -*n*-amyl-, b.p. 167°/51 mm., -cyclohexyl-, b.p. 122–126°/15 mm., -*o*-, b.p. 196–201°/10 mm., m.p. 102°, -*m*-, b.p. 211–216°/15 mm., and -*p*-tolylethylstibine, b.p. 226°/5 mm., m.p. 114°. The compounds of trisobutylstibine are described: double oxide; oxide; dichloride, m.p. 91°; dibromide, m.p. 88°; di-iodide, m.p. 70°; methiodide, m.p. above 155°; methylmercuri-iodide, m.p. 119°; methylmercuri-chloride, m.p. 117°; methylchloroplatinate, m.p. 158°. β -Naphthylstibinic acid is obtained from β -naphthylamine with intermediate formation of NH_4 β -naphthylchloroantimonate, and is converted into stibinous oxide, decomp. 160°. Tetraethyl- and tetra-*n*-propylphosphonium; dimethyldi-*n*-propyl-, methyltriethyl-, tetraethyl-, methyltri-*n*-propyl-, and methyltri-*n*-amylarsonium; and methyltri-*n*-propylstibonium antimonoyl d-tartrates are described. F. R. S.

Aryl di- and poly-stibinic acids, distibinous oxides, and di-stibino-compounds. S. M. MISTRY and P. C. GUHA (J. Indian Inst. Sci., 1932, 15A, 23–39).—The following have been prepared from the corresponding amines: *m*- and *p*-phenylene- and 1:4-naphthylene-distibinic acid: diphenylene-pp- (pp-distibinotetraphenylene), 3:3-dimethyldiphenylene-

4:4', 3:3-dimethoxydiphenylene-4:4', and diphenylmethane-pp-distibinous oxide; benzophenone-pp-distibinic acid; diphenyl-m-tolyl-methylcarbinol-ppp-tristibinic acid and -methane-ppp-tristibinous oxide; stilbene-4:4'-distibinic acid and -distibinous oxide; $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}\cdot\text{SbCl}_2\cdot\text{HCl})_2$ gives a secondary monostibinic acid, also obtained from *p*-aminodiphenylcarbamide; 4:4'-diacetamidodiphenylmethylenediamine, m.p. 220°, and -ethylenediamine, m.p. 284°; methylene- and ethylene-diaminophenylene-4:4'-distibinous oxide; bis-*p*-aminophenylazomethine, m.p. 258° (decomp.) [Ac_2 derivative, m.p. 279° (decomp.)]; bisphenylazomethine-pp'-distibinous oxide; *s*-oxal-, malon-, and succinamido-, *s*-carbohydrazino-diphenylene-pp-distibinic acid; *s*-pp'-diaminodiphenylhydrazo-, m.p. above 370°, and *s*-pp'-diacetamidodiphenylazo-dicarbonamide, m.p. above 370°; hydrazodicarbonaminodiphenylene-pp-distibinic acid; hydrazobenzene- and benzanilide-pp'-distibinous oxide; *p*-nitrobenzoyl-*p*'-acetamidoanilide, m.p. 293° (decomp.); triphenyl-phosphine-, -arsine-, and -stibine-mmm-tristibinic acid. F. R. S.

Derivatives of cyclo-2:5-dithia-3:4-dimethylenestibine. R. E. D. CLARK (J.C.S., 1932, 1826—1830).— $(\cdot\text{CH}_2\cdot\text{SH})_2$ and SbCl_3 give 1-chlorocyclo-2:5-dithia-3:4-dimethylenestibine (1), m.p. 124° [oxychloride (H_2O)], which heated with thiolacetic acid and $\text{C}_6\text{H}_5\text{N}$ affords pyridine cyclo-2:5-dithia-3:4-dimethylenestibine-1-thiolacetate, m.p. 101°. *m*-Thiolbenzoic acid condenses with (1) to give 1-*m*-carboxyphenylthiocyclo-2:5-dithia-3:4-dimethylenestibine (product obtained once only). *p*-Tolylchlorostibine and $(\cdot\text{CH}_2\cdot\text{SH})_2$ yield 1-*p*-tolylcyclo-2:5-dithia-3:4-dimethylenestibine, m.p. 90° (dimorphous). *p*-Carboxy- (or carbomethoxy-)phenyl-di-iodostibine, m.p. 120—132°, obtained from the stibinic acid, condenses with $(\cdot\text{CH}_2\cdot\text{SH})_2$ to give an acid, m.p. 199°, and a substance, m.p. 138°. F. R. S.

Cystine. M. OGAWA (Bull. Sci. Fak. Terkult., 1932, 5, 90—102).—The determination of cystine in gelatin by the application of the I method to the acid hydrolysate yields low results when fats, lipins, inorg. salts, or particularly when carbohydrates are present. Hence for the determination of cystine in natural substances a preliminary separation of the proteins is necessary, sulphosalicylic acid, which does not interfere with the I method, being used. HCl and H_2SO_4 are equally suitable for hydrolysis. The solubilities, isoelectric points, and properties of active and inactive cystine are given and the prep. of cystine from hair, depending on crystallisation at the isoelectric point, is described. F. O. H.

Synthesis and degradation of proteins. M. BERGMANN (Naturwiss., 1932, 20, 420—422).—The benzylurethane of an NH_2 -acid is converted through the acid chloride into a dipeptide-urethane, which is reduced catalytically, giving PbMe , CO_2 , and a dipeptide. In this way seryl-glycine, *d*- α -glutamyl-*d*-glutamic acid, and glycyl-*d*-glucosamine have been obtained. The action of dehydrodipeptidase (cf. this vol., 427) is sp. for dipeptides in which the CO_2H group of the unsaturated NH_2 -acid is free. A. C.

3 M

Constitution of the keratin molecule. J. B. SPEAKMAN and M. C. HIRST (Nature, 1932, 129, 938—939).—A reply to criticism (this vol., 529).

L. S. T.

Rapid determination of carbon and hydrogen in organic compounds. III. E. BERL and A. SCHMIDT (Ber., 1932, 65, [B], 978—980; cf. A., 1926, 749; 1928, 312).—Improvements recommended include a new type of flask for preservation and manipulation of PbCrO_4 , modified H_2SO_4 tube for absorption of H_2O , and modified CO_2 absorption tubes. H. W.

Determination of halogens in organic substances. D. BUTTESCU (Bul. Chim. pura apl. Bukarest, 1931, 33, 83—92; Chem. Zentr., 1932, i, 710).—Julkowski's method (Monatsh., 1885, 6, 447) is the best for determining halogens. The substance is burnt in O_2 (Pt-quartz catalyst) and the gaseous products are passed through aq. Na_2SO_3 - Na_2CO_3 .

L. S. T.

Organic analysis. Determination of sulphur. D. BUTTESCU (Bul. Chem. pura apl. Bukarest, 1929, 32, 79—87; Chem. Zentr., 1932, i, 710).—The S oxides after combustion are collected in 2 or 5% aq. H_2O_2 . When C and H are to be determined, they are retained by MnO_2 at 150—180°. The MnO_2 is extracted with hot H_2O and the SO_4^{2-} determined gravimetrically. L. S. T.

The Vieböck and Schwappach method for the determination of methoxyl and ethoxyl groups. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1932, 15, 136—140).—A modification of the method (H. Meyer, "Analyse und Konstitutionsermittlung," 5 Aufl., p. 487) applicable to about 0.005 g. of substance is described. W. J. B.

Determination of reducing sugars (copper-colorimetric method). E. M. EMMERT (J. Assoc. Off. Agric. Chem., 1932, 15, 327—329).—The excess of Cu remaining in solution after reduction of Bertrand's reagent is determined colorimetrically. H. R. J.

Microchemical reactions of saccharin. M. WAGENAAR (Pharm. Weekblad, 1932, 69, 614—618).—Methods of obtaining characteristic cryst. deposits by sublimation, by pptn., and by reaction with AgNO_3 , Cd salts, $\text{C}_6\text{H}_5\text{N}$ -Cu salts, HgCl_2 , and I in KI are described. The most suitable reagents are HgCl_2 and I in KI, by means of either of which 0.02 mg. at a dilution of 1 in 300 may be detected. S. I. L.

Isolation of guanidine. J. A. SAUNDERS.—See this vol., 890.

Determination of aldehydes based on the reactions of Cannizzaro and Claisen. L. PALFRAY, S. SABETAY, and (Mlle.) D. SOUTAG (Compt. rend., 1932, 194, 1502—1505).—Aromatic aldehydes are determined by heating under a reflux condenser with 0.5N- CH_3Ph -OK in CH_3Ph -OH for 2.5 hr., diluting with H_2O , and titrating the excess of alkali in presence of phenolphthalein. J. L. D'S.

Thionylaniline, a reagent for characterising acids as anilides. P. CARRÉ and D. LIBERMANN (Compt. rend., 1932, 194, 2218—2220).— $\text{PhN}\cdot\text{SO}$, unlike PhNCO , does not add on to alcohols, being without action on boiling EtOH or PhOH at 185°, but with

boiling Bu^oOH affords butylene. In general, aliphatic acids when warmed with PhN₂SO afford anilides. The malonic acids and some unsaturated acids, especially those with a double linking near the CO₂H group, react abnormally. Aromatic acids give principally coloured compounds containing S, but phthalic acid gives the anil.

J. L. D'S.

Benzylideneacetone, cinnamic acid, and bromostyrene. N. KISLIANSKIA (J. Gen. Chem. Russ., 1932, 2, 103).—In the iodometric determination of benzylideneacetone, Schorigin, Issagulantz, and Gusseva (this vol., 853) use MeOH as solvent. Since MeOH, even when free from COMe₂, reacts with I under the conditions used, it is recommended to use AcOH.

M. Z.

Colour reaction of pyrrole and indole derivatives. E. MONTIGNIE (Bull. Soc. chim., 1932, [iv], 51, 689—690).—Pyrrole (min., 0.04 mg.) when boiled with 10% H₂SeO₃ and conc. HNO₃ gives a deep violet

coloration (reddish-violet when dil.). CHCl₃ extracts a blue substance leaving a red solution. Similar treatment of indole (min., 0.05 mg.) gives a violet, tryptophan gives the yellow colour produced by HNO₃ alone, whilst skatole with H₂SeO₃ alone gives a violet changed to red by HNO₃.

A. A. L.

Microchemical reactions of atropine. Z. F. KLAN (Časopis Českoslov. Lék., 1931, 11, 289—295; Chem. Zentr., 1932, i, 1126).—Identification is best effected with 0.1N-I, 10% AgNO₃, or saturated aq. picrolonic acid solution.

A. A. E.

Colorimetric determination of eserine. M. S. MOKRAGNATZ (Bull. Soc. Chim. Yougoslav., 1931, 2, 175—183).—A solution of 1 g. of benzidine in 30 c.c. of H₂O and 10 c.c. of Ac₂O when diluted to 50 c.c. gives a violet coloration with eserine in the presence of H₂O₂, which can be applied to the colorimetric determination of eserine.

R. T.

Biochemistry.

Leucopoietic value of sulphur. T. D. POWER (Lancet, 1932, 222, 338—340).—Injections of a 1% S-oil suspension increase the no. of leucocytes in rabbit blood.

L. S. T.

Factors in food influencing hæmoglobin regeneration. I. Whole wheat flour, white flour, prepared bran, and oatmeal. M. S. ROSE and E. M. VAHLTEICH (J. Biol. Chem., 1932, 96, 593—608).—The feeding of whole wheat, oatmeal, or prepared bran to rats in which anæmia has been induced by a milk diet results in a regeneration of hæmoglobin approx. proportional to the amount of Fe present in the cereal. Regeneration due to feeding white wheat is less than that due to the same wt. of whole wheat even when the former is supplemented with Cu or Fe or their mixtures. The effect of whole wheat is always superior to that when part is replaced by Cu or Fe, but with oatmeal one half may be replaced by a mixture of Cu and Fe. Also administration of an aq. HCl solution of the ash of whole wheat or of bran does not produce regeneration equal to that shown by the original food material. Hence factors other than Cu and Fe which influence hæmoglobin regeneration are present in greater amounts in oatmeal than in white flour.

F. O. H.

Hæmoglobin content of the blood of the hen. H. H. DUKES, L. H. SCHWARTZ, and A. E. BRANDT (Science, 1932, 75, 25—26).—The influence of breed and age on hæmoglobin content are discussed, together with the correlation between season, age at maturity and egg production, and hæmoglobin content.

L. S. T.

Micro-methods for determining serum-protein fractions. B. GOZSY (Magyar orvos Archív., 1931, 32, 369—378; Chem. Zentr., 1932, i, 712).—The Berger-Petschacher-Schretter standard method is compared with that of Daranyi which yields satisfactory results and enables several fractions to be determined simultaneously.

L. S. T.

Optical density and viscosity of therapeutic sera. C. ACHARD, A. BOUTARIC, and M. GANTROT (Compt. rend., 1932, 194, 2249—2253).—The viscosity at 26° of 7 therapeutic sera heated at 55° and 62° for 1 hr. and unheated, varies considerably according to the nature of the serum, but is greater than that of normal horse serum, the effect of heating being to increase the viscosity. There is little difference between the optical density of therapeutic and normal horse serum.

A. L.

Effect of sera on the flocculation of colloidal ferric hydroxide. C. ACHARD, A. BOUTARIC, and F. MORIZOT (Compt. rend., 1932, 195, 9—11).—The time of flocculation of colloidal Fe(OH)₃ with KNO₃ is considerably shortened by addition of very dil. serum; this accelerating effect is diminished by heating the serum at 55°. Proteins separated by the COMe₂ method produce the same effect as the original serum. The sera of syphilitic subjects produce less effect than those of normal or carcinomatous subjects.

P. G. M.

Serum-bilirubin. I. Diazo-reaction as quantitative procedure. F. D. WHITE (Brit. J. Exp. Path., 1932, 13, 76—85).—When the diazo-reagent reacts with bilirubin dissolved in blood-serum, the colour produced is proportional to the amount of bilirubin; the bilirubin content of icteric sera can be determined. Van den Bergh's method gives low results, probably owing to adsorption on the proteins pptd. by EtOH. A standard solution is prepared from anhyd. CoSO₄ (1.3 g.) in H₂O (50 c.c.), treated gradually, with shaking and cooling, with HCl (d 1.19, 40 c.c.) and diluted to 100 c.c. The solution should be prepared 24 hr. before use and kept well stoppered in the dark.

CH. ABS.

Blood-cholesterol. Determination and normal values. J. CASTELLANO and I. TORRES (Anal. Fis. Quím., 1932, 30, 384—387).—The methods of Grigaut and of Autenrieth give low vals. owing to incomplete

extraction. Correct vals are obtained by the Myers-Wardell method (A., 1918, ii, 461) with slight modifications. Normal vals. are between 140 and 200 mg., mean 175 mg., per 100 c.c. Very high vals. are found in nephritis with cedema. R. K. C.

Antigenic properties of cholesterol, cholesterol derivatives, and synthetic lecithin. A. J. WEIL and F. BESSER (Klin. Woch., 1931, 10, 1941—1944; Chem. Zentr., 1932, i, 700).—Pure cholesterol, dihydrocholesterol, and synthetic distearyl-lecithin show antigenic properties of the haptene type. L. S. T.

Blood-sugar and blood-sodium curves. J. PUYAL and I. TORRES (Anal. Fis. Quím., 1932, 30, 388—393).—The rise and fall of blood-sugar following oral administration of glucose are accompanied by a small increase and decrease, respectively, of blood-Na. Na and Cl (this vol., 764), as electrolytes of small mol. wt., are eliminated in order to preserve osmotic equilibrium.

A mean val. of 294 mg. blood-Na per 100 c.c. was found in 10 patients by a slight modification of Kahane's method (A., 1930, 726, 880). R. K. C.

Turbidity micro-method for blood-sugar. A. R. ROSE, F. SCHATZNER, and W. G. EXTON (XL Ann. Mtg. Assoc. Life Insur. Med. Dir. Amer., 1929, 24—25).—The protein is pptd. with $H_2Fe(CN)_6$; the filtrate is rendered alkaline and boiled. The $Fe(CN)_6^{4-}$ is pptd. by addition of ammoniacal Ag solution and the turbidity is measured in a scopometer. The results are lower than those obtained by Folin's method. CH. ABS.

Influence of glutathione on reduction and rotation of blood-filtrates. J. GROEN and J. W. MEYER (Biochem. J., 1932, 26, 624—632).—In Folin and Wu filtrates of normal human blood the difference between reduction as determined by the Shaffer-Hartmann-Somogyi method and the rotation amounts on the average to 32 mg. per 100 c.c. expressed as glucose. There is no such difference in plasma filtrates and in filtrates of blood prepared by Herbert and Bourn's technique. The reduced glutathione present in the blood is the main cause of the differences between the results of the reduction and rotation methods. The blood of diabetic patients behaves similarly in this respect. S. S. Z.

Isolation of ergothioneine from blood. S. W. WILLIAMSON and N. U. MELDRUM (Biochem. J., 1932, 26, 815—816).—The blood is extracted with dil. H_2SO_4 , conc. in a vac., and the concentrate aerated. Ergothioneine is then pptd. from it as the Cu compound and decomposed with H_2S . S. S. Z.

Ammonia formation in the blood of the tortoise. W. MOZOLOVSKI and T. MANN (Biochem. Z., 1932, 249, 161—175).—The NH_3 formation after hæmolysis of tortoise blood amounts in 24 hr. to > 10 mg. NH_3 -N per 100 c.c. of blood, the NH_3 formation in this case not being inhibited by adjustment with borate to 9.2. For NH_3 formation it is necessary to combine the plasma with either the hæmoglobin solution or the separated stroma and erythrocyte nuclei. On hæmolysis, the urea, uric acid, and amide-N are unchanged. The

decomp. of aminopurines explains the formation of only a small portion of the NH_3 . P. W. C.

Determination of inorganic sulphate in blood-serum. M. H. POWER (Proc. Staff. Meetings Mayo Clinic, 1931, 6, 401—402).—An adaptation of Hubbard and Wakefield's method is described; benzidine sulphate is oxidised with $K_2Cr_2O_7$, the excess being determined iodometrically. 95—100% of 3—5 mg. per 100 c.c. is recoverable. The method has been modified for application to urinary sulphates. CH. ABS.

Influence of liver damage on the serum-lipase. T. KAMEO (J. Biochem. Japan, 1932, 15, 229—256).—A saline extract of rabbit's liver is injected into dogs. Injection into rabbits of the anti-serum thus obtained produces a decrease followed by an increase in the serum-lipase, whilst in the urine the carbamide decreases and the NH_3 increases. Following exposure of the liver to hard X-rays the serum-lipase in the rabbit falls to a min. in 24 hr. and then exhibits a rapid but partial recovery, completely returning to the normal in 15 days. Direct irradiation of the blood or serum has no influence on the lipase val. The variation of serum-lipase with disease in man is investigated. F. O. H.

Parenteral denaturation of foreign proteins. VI. Depolymerisation, homologisation, and re-tention. H. C. SOX, J. L. AZEVEDO, and W. H. MANWARING (J. Immunol., 1931, 21, 409—415).

Parenteral denaturation of foreign proteins. VII. Test-tube synthesis of "hybrid" specificities. H. C. SOX and W. H. MANWARING (J. Immunol., 1932, 22, 237—243).—Horse serum incubated with dog serum (10—1000 vols.) shows a rapid and consistent destruction, or total denaturation, of proteins of full horse serum specificity, accompanied by an initial increase and subsequent decrease in proteins intermediary in specificity between horse and dog. CH. ABS.

Precipitinogenic action of minute quantities of ovalbumin. L. HEKTOEN and A. G. COLE (J. Infect. Dis., 1932, 50, 171—176).—The sera of rabbits immunised by intravenous injection of approx. 0.00029 and 0.0017 g., respectively, of ovalbumin gave sp. ppts. with the homologous antigen at a dilution of 1 in 10^5 . CH. ABS.

Inception of blood-clotting. E. ARMITAGE, J. W. PICKERING, and S. N. MATHUR (Biochem. J., 1932, 26, 853—864).—The disintegration of leucocytes is not an essential occurrence in the inception of blood-clotting. The complete disintegration of blood platelets neither produces intravenous clotting nor hastens the coagulation of normal blood which has been shed in paraffined vessels. The lysis of blood platelets hastens the clotting of blood shed on to glass and also hastens the coagulation of blood shed into paraffined vessels when the blood is contaminated with tissue juices. Fresh blood-serum promptly clots both pure blood and pure blood-plasma which have been shed into paraffined vessels, but the rapid intravascular injection of amounts of fresh sera sufficient to produce extravascular clotting does not produce intravascular coagulation in non-pregnant

cats if the amount administered is not lethal. The addition of very small amounts of the fresh juices of testis, muscle, and kidney to blood shed into paraffined vessels rapidly produces complete coagulation, but the rapid intravascular or the rapid intracardiac injection after the isolation of the heart from the general circulation of these juices does not produce clotting *in vivo* in non-pregnant cats. The intravenous injection of the fresh juices of kidney and muscle into pregnant cats produces intravascular clotting.

S. S. Z.

Blood-clotting. S. PRAKASH (Biochem. Z., 1932, 249, 39—47).—The clotting of blood is analogous to gel formation, blood containing a negatively-charged fibrin sol (=fibrinogen) which coagulates as fibrin and shows a strong tendency to absorb similarly charged ions, thus being stabilised in presence of salts and alkaline solutions. The assumption of thrombin and related substances is unnecessary to explain clotting. Spontaneous blood-clotting can be imitated with sufficiently dialysed inorg. sols of FePO_4 , $\text{Fe}_3(\text{WO}_4)_2$, Sn and Ce borates, Ce molybdate, the gels in all cases showing a similar syneresis.

P. W. C.

Avitaminosis and blood-clotting function. I. N. KUGELMASS and E. L. SAMUEL (Amer. J. Dis. Children, 1932, 43, 53—57).—Withdrawal of vitamin-A or -B from the diet of rats decreases the blood-fibrinogen. Deficiency of vitamin-D may reduce the prothrombin and fibrinogen, but that of -C has no effect on the clotting components.

CH. ABS.

Corpuscular volume of blood. I. Prevention of coagulation without effecting change in corpuscular volume. II. Haematocrit method. M. HIRAKI (J. Biochem. Japan, 1932, 15, 331—337, 339—344).—I. The addition of 2.3% aq. $\text{K}_2\text{C}_2\text{O}_4$ or of 3.6% Na citrate solution to blood in the proportion 1:9 effectively prevents coagulation without influencing the corpuscular vol. especially when $\Delta = -0.560^\circ$ for the blood sample.

II. A method employing a haematocrit tube of 2.0 c.c. capacity is described. The blood (0.20 c.c.) is diluted with a 9:1 mixture of isotonic saline and 3.6% aq. Na citrate.

F. O. H.

Action of heparin on protein. A. FISCHER and A. SCHMITZ (Naturwiss., 1932, 20, 471—472).—In its action on serum-albumin, heparin shows analogy with the nucleic acids, but the latter have no anticoagulant action. Comparison of the results of electrometric titration of protein and heparin-protein lends support to the view that the combination leads to the formation of complex mol. compounds. Whilst the addition of heparin to blood-serum causes no change in the relative amounts of globulin and albumin as measured by $(\text{NH}_4)_2\text{SO}_4$ pptn., a change occurs when the blood plasma is used.

A. L.

Human skin. I. Skin of the cadaver. A. NADEL (Biochem. Z., 1932, 249, 83—94).—The accuracy of known methods for determination of H_2O , fat, fat-free dry substance, Cl, total N, and residual N when applied to skin after death is determined and tables summarise the results.

P. W. C.

Behaviour of native skin against pancreatin. M. BERGMANN and G. POJARLIEFF (Biochem. Z., 1932,

249, 1—6).—The kneading of skin collagen results in increased digestibility by pancreatin only when the piece of collagen is digested together with the fibres separated in the mechanical treatment. Pancreatic digestion of collagen at 40° in absence of large amounts of salts does not show during 3 days any considerable inhibition by the products of digestion. P. W. C.

Phosphatase and pyrophosphatase of bones and cartilage. T. YAMANE (Arb. Anat. Inst. Kais. Univ. Kyoto, 1931, III, C, No. 2, 49—61, 84—99).—The optimal for rabbit's bone phosphatase is 8.9—9.6 and for bone pyrophosphatase is 8.6—9.3. The phosphatolytic effect is parallel with the ossification mechanism. The phosphatase and pyrophosphatase of the bone tissue is intimately connected with the calcification process of bone tissue. The bone tissue of the adult rabbit contains less phosphatase than does that of the young animal. Cartilages in which no calcification occurs contain no phosphatase, and those which calcify later contain but little.

CH. ABS.

Phosphatase in the young rabbit and in the foetus. I. HORII, M. MORII, and E. NORIOKA (Arb. Anat. Inst. Kais. Univ. Kyoto, 1931, III, C, No. 2, 37—40).—Organs of newly born rabbits and foeti contain little phosphatase.

CH. ABS.

Cystine content of human hair. II. T. TADOKORO and H. UGAMI (J. Biochem. Japan, 1932, 15, 257—260).—The contents of cystine, total S, and total N of pubic and scalp hair were determined. The S content and the cystine/N ratio are greater in scalp hair, whilst the cystine and S contents of the hair of white persons are greater than those of the hair of coloured persons.

F. O. H.

Micro-determinations of purine substances in tissues. G. SCHMIDT. I. Determination of guanine. E. ENGEL (Z. physiol. Chem., 1932, 208, 225—227, 227—236).—I. A micro-method for the determination of guanine is described. The tissue is killed with liquid air and hydrolysed with 2% aq. H_2SO_4 . After addition of NaOH and removal of free NH_3 the solution is treated with guanase at pH 8.8. The NH_3 liberated determines the guanine present.

J. H. B.

Hydrolysis of nucleic acid, nucleotides, and nucleosides. Y. KOBAYASHI (J. Biochem. Japan, 1932, 15, 261—275).—The ease of hydrolysis, as shown by the rate of liberation of PO_4 and ribose, is guanine > adenine > uracil > cytosine-nucleotide. The same order is true for the case of hydrolysis of the corresponding nucleosides. Combination of the two series leads to an explanation of the rate of hydrolysis of nucleic acid.

F. O. H.

Wild animal [hedgehog, polecat] fats. A. PAWLETTA (Pharm. Zentr., 1932, 73, 417—420).—Six samples of the liquid fat (pasty at -15°) of hedgehogs were examined, having: d_{40}^{15} 0.9206—0.9259, n_D^{40} 1.4629—1.4656, sap. val. 195.2—198.2, I val. 89.2—98.4: the fatty acids had m.p. $33-34^\circ$, setting point $22.5-23.4^\circ$. Distinction between the fats of hibernating and non-hibernating hedgehogs could not be made. Polecat (*Putorius*) fat (5 samples) had: m.p. $36-39^\circ$, f.p. $24.2-24.4^\circ$, d_{40}^{15} 0.9169—0.9190,

n_D^{20} 1.4598—1.4621, sap. val. 195—199, I val. 60.6—66.4, the fatty acids had m.p. 38.5—39.0°, setting point 33.5—33.8°. E. L.

Chemical composition of fish. III. Composition of *Pleuronectes* and mackerel. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1932, 14, 178—187).—*Pleuronectes platessa* contained on the average edible matter 56%, inedible 44%; the composition of the former, as wt.-% of the fresh fish, was: H_2O 45.6%, lipins, 1.06, protein 8.56, ash 0.78, P 0.094, Cl 0.06; that of the inedible fraction was H_2O 33.3, lipins 1.43, protein 6.01, ash 3.26, P 0.4, Cl 0.11. For *Scomber scombrus* the figures were: edible matter 65.5%, composed of H_2O 47.9, lipins 4.0, protein 12.7, ash 0.9, P 0.07, Cl 0.024; the inedible portion contained H_2O 23.9, lipins 3.4, protein 5.6, ash 1.6, P 0.234, Cl 0.056. The composition of individual fish varied widely from the mean. H. F. G.

Crystalline luciferin. S. KANDA (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 1).—A conc. EtOH solution of the substance(s) previously prepared (A., 1930, 1202) is treated with saturated EtOH- $CdCl_2$ until no further pptn. occurs; the ppt. is washed repeatedly with EtOH- $CdCl_2$, the combined filtrates freed from EtOH in a vac., diluted with H_2O , and then extracted with Et_2O or C_6H_6 . Slow evaporation of the washed (with much H_2O) Et_2O or C_6H_6 extract gives cryst. *Cypridina* luciferin which still contains P. H. B.

Ash content of insects. E. B. UVAROV (Bull. Entomol. Res., 1931, 22, 453—457).—The ash of the locust, *Schistocerca gregaria*, contains SiO_2 11.9, Cu 0.13, Fe_2O_3 2.06, Mn 0.16, Na_2O 6.2, K_2O 18.2, CaO 6.2, MgO 4.9, TiO_2 0.16, Ni 0.009, P_2O_5 32.4, SO_3 2.56, Cl 0.40, C 2.4, H_2O 0.54%. Immature, actively feeding locusts contain more SiO_2 than sexually mature locusts. Most of the SiO_2 and Fe_2O_3 is contained in the tissues. Ch. Abs.

Proportion of skeletal tissues in insects. P. A. BUXTON (Biochem. J., 1932, 26, 829—832).—If the dried powdered meal worm is digested with pepsin and pancreatin the reaction stops or becomes very slow when 8.1—8.7% of the original dry material is left. The same proportion of residue is left if the material is exposed to 1% aq. KOH at 100° for 24 hr. With other insects consistent results are also obtained. In the KOH method hæmatin is dissolved in the case of blood-sucking insects. S. S. Z.

Colouring matter of cocoons of green Japanese silkworms. C. JUCCI and C. MANUNTA (Atti R. Accad. Lincei, 1932, [vi], 15, 473—477).—This colouring matter, *bombichlorin*, is readily sol. in H_2O , and slightly sol. in 95% EtOH, and gives yellow salts with alkalis. T. H. P.

Determination of cholic acid in bile. J. G. REINHOLD and D. W. WILSON (J. Biol. Chem., 1932, 96, 637—646).—Dog or human hepatic bile diluted with H_2O is heated at 70° for 8 min. in presence of 12N- H_2SO_4 and 1.3 mg. of furfuraldehyde per c.c. The resulting fluid is cooled and compared colorimetrically with a similarly treated standard solution of Na cholates, using monochromatic light of 600—690 m μ (cf. A., 1929, 1114). Human gall-bladder

bile must be previously deproteinised with EtOH. Pure conjugated and unconjugated cholic acids in equimol. amounts produce equal intensities of colour. F. O. H.

Solubility of fatty acids in bile under the action of lecithin. E. SZÖRENYI (Biochem. Z., 1932, 249, 182—188).—Lecithin has no influence on the solubility of oleic acid in solutions of conjugated bile salts. The diffusion of oleic acid dissolved in bile salt solutions is the same in presence or absence of lecithin (0.8%). Lecithin in 1% bile salt solution is not diffusible. P. W. C.

Influence of lecithin on the solubility of oleic acid in bile-salt solutions. A. MÜLLER (Biochem. Z., 1932, 249, 189—194).—Emulsions obtained by shaking bile-acid solutions with oleic acid and keeping for a long time to separate the undissolved acid, contain 2—3% of oleic acid and can be clarified by addition of a little NaCl. Only 0.5—0.6% of this acid is diffusible and the amount is not materially altered by the presence also of lecithin. P. W. C.

Yield and fat content of human milk. C. VINCENT and J. VIAL (Compt. rend., 1932, 194, 2328—2330).—The fat content of human milk given three times daily in the case examined varied considerably within wide limits and was independent of the quantity of milk. The total fat secreted showed, however, the same variations as the quantity of milk given each time. A. L.

Absorption of milk precursors by the mammary gland. III. Relation of amino-acid absorption to protein synthesis. J. H. BLACKWOOD. IV. Phosphorus metabolism of the mammary gland. J. H. BLACKWOOD and J. D. STIRLING (Biochem. J., 1932, 26, 772—777, 778—784).—III. In non-lactating cows the NH_2 -acid content of the jugular blood is lower than that of the arterial blood. The NH_2 -acid content of mammary-venous blood is slightly higher than that of arterial blood. In lactating cows the NH_2 -acid content of jugular blood also differs from that of arterial blood. The NH_2 -acid content of mammary venous blood is, however, always significantly lower than that of either jugular or arterial blood, thus confirming the view that NH_2 -acids are the precursors of milk-protein. The ratio of sugar to N absorbed by the mammary gland is different in different animals, the range of variation being identical with that of the ratio found in milk. The ratio of corpuscular NH_2 -acid to that of plasma is approx. 3:1 for the dairy cow. The NH_2 -acids of the corpuscles play no part in the exchanges between the blood and the mammary gland.

IV. The acid-sol., org. and inorg. P content of the jugular blood of lactating and non-lactating cows is lower than that of the arterial blood 4 hr. after the ingestion of food. The inorg. P content of mammary blood is higher than that of jugular blood and approx. equal to that of arterial blood in lactating and non-lactating cows. The org. acid-sol. P content of mammary venous blood is lower than that of arterial blood in lactating cows but slightly higher in non-lactating cows. The partition of org. acid-sol. P between the corpuscles and the plasma is different for lactating and non-lactating animals. S. S. Z.

Iodometric determination of lactose in milk. J. FINE (Biochem. J., 1932, 26, 569—572).—The milk is clarified with colloidal Fe and the lactose determined iodometrically in the resulting serum.

S. S. Z.

Micro-determination of vacate-oxygen. H. R. KANITZ (Biochem. Z., 1932, 249, 234—238).—The method, depending on HIO_3 oxidation of the urine, is described.

P. W. C.

Uric acid in frog's glomerular urine. J. BORDLEY (3rd) and A. N. RICHARDS (Amer. J. Med. Sci., 1931, 182, 881—882).—Folin's method has been adapted.

CH. ABS.

Classification of products of nitrogen metabolism in the urine of different species of mammals. E. TERROINE, (MLLE.) M. CHAMPAGNE, and (MLLE.) G. MOUTROT (Compt. rend., 1932, 194, 2235—2237).—The urine of different species of mammals is examined for nitrogenous substances, representative figures being tabulated. The results are discussed.

J. L. D'S.

Tryptophanuria and its significance. A. T. BRICE (Arch. Int. Med., 1932, 49, 978—980).—An improved Boltz test (A., 1931, 254) for tryptophan was positive in 33% of 525 specimens of urine from general surgical and medical cases. In some, tryptophan was present without proteinuria, whilst in others proteins were present which apparently contained no tryptophan.

W. O. K.

Relation of nutrition to contagious cattle abortion. E. B. HART, F. B. HADLEY, and G. C. HUMPHREY (Wisconsin Agric. Exp. Sta. Res. Bull., 1932, No. 112, 45 pp.).—A "poor" ration supplemented only with NaCl maintained the condition and milk-producing capacity of cows nearly as well as a high-protein ration supplemented with bone meal, cod-liver oil, and iodised salt, and did not cause any greater susceptibility to infection by *B. abortus*. Use of cod-liver oil as a source of vitamin-D depressed milk-fat production. Cows on a "poor" ration adjusted themselves to a low Ca intake, the efficiency of Ca utilisation increasing as the Ca supply in the ration decreased.

A. G. P.

Clinical significance of volume and hæmoglobin content of the red blood-cell. R. L. HADEN (Arch. Int. Med., 1932, 49, 1032—1057).—In anæmias of all types the investigation of the no., mean vol., and hæmoglobin content of the red blood-cells is important.

W. O. K.

Hyperglycæmia of cancer. G. E. WOODWARD and E. G. FRY (Biochem. J., 1932, 26, 889—897).—The average blood-sugar level in 52 untreated cancer cases as determined by the Hagedorn-Jensen method is 20 mg./100 c.c. above normal. Treated cancer cases and cases of non-malignant growths also show blood-sugar vals. higher than normal, the treated cases being on the whole almost as high as the untreated. Purely medical cases do not in general show an increase in the blood-sugar level.

S. S. Z.

Metabolism of thiol compounds in tumour tissue. A. GOERNER and M. GOERNER (Amer. J. Cancer, 1932, 16, 360—365).—Rats with Flexner-Jobling carcinoma showed a decrease in liver- and

tumour-glutathione when on a diet low in cystine. Liver tissue lost glutathione more readily than tumour tissue. On a normal diet the latter varied more widely in glutathione content than the former.

CH. ABS.

Distribution of blood-cholesterol in cancer. H. R. DOWNES and G. T. PACK (Amer. J. Cancer, 1932, 16, 290—296).—Blood-cholesterol is normal; the relationship between whole blood and plasma vals. is not const.

CH. ABS.

Blood changes in malignant diseases. C. N. MYERS and B. THRONE (Amer. J. Cancer, 1932, 16, 297—306).—Cholesterol indices have no val. for the detection of neoplasms. There is evidence of metabolic disturbance involving fats, carbohydrates, and N.

CH. ABS.

Fermentation-accelerating action of tumour extracts and its relationship with Rosenthal's activator. G. BOSTROM (Biochem. Z., 1932, 249, 239—240).—Corrections of the author's paper (this vol., 418).

P. W. C.

Blood-sugar in arsphenamine dermatitis. J. MU (Chinese Med. J., 1932, 46, 449—455).—Of 9 syphilitics suffering from arsphenamine dermatitis 8 gave an abnormally high blood-sugar curve after administration of glucose, whilst in 4 the fasting blood-sugar level was also high. The abnormality in blood-sugar was approx. parallel with the intensity of the dermatitis.

W. O. K.

Behaviour of the animal organism in pancreatic diabetes towards certain carbohydrates. III. Effect of sodium hexosediphosphate on diabetic and on normal organisms. V. S. ILJIN and J. T. KUSNETZOV (Z. ges. exp. Med., 1931, 79, 635—652; Chem. Zentr., 1932, i, 703; cf. A., 1930, 365).—Na hexosediphosphate injected subcutaneously into depancreatized cats produced a pronounced and lasting diminution of blood-sugar frequently down to the normal. The blood-sugar of normal cats is not affected. The inorg. blood-P rises in diabetic animals. Hyperglycæmia often precedes the diminution in blood-sugar. Na glycerophosphate eliminates inorg. P after subcutaneous injection. The blood-sugar content of diabetic animals is lowered neither by small nor by large poisonous doses of Na glycerophosphate, in spite of the rise in blood-inorg. P.

L. S. T.

Galactose tolerance of normal and diabetic subjects, and effect of insulin on galactose metabolism. J. H. ROE and A. S. SCHWARTZMAN (J. Biol. Chem., 1932, 96, 717—735).—Blood-galactose is determined by removing fermentable sugar with yeast, and applying the Benedict method (A., 1931, 973) to the protein-free filtrate. Blood- and urinary galactose and total blood-sugar vals. after ingestion of galactose (1 g. per kg. body-wt.) show that normal and diabetic persons have approx. the same galactose tolerance. Blood-galactose of rabbits is not influenced by insulin, and the latter is not detoxified by galactose.

Clinical significance of the atoxyl-resisting lipase of blood-serum. S. KUNOS and A. GERO (Arch. Verdauungs-Krankh., 1931, 50, 232—246; Chem. Zentr., 1931, ii, 688).—The presence of atoxyl-

resisting lipase in blood-serum can be detected with certainty when there is a pathological change in the function of the pancreas.

L. S. T.

Excretion of creatine and creatinine. Hourly excretion in normal children and in children with progressive muscular dystrophy. M. C. MAGEE (Amer. J. Dis. Children, 1932, 43, 322—326).—The excretion fluctuates; day vals. are higher than night vals. Muscular dystrophy in children is characterised by creatinine coeff. 2 and total creatinine coeff. 6.

CH. ABS.

Sodium chloride and water balance in epilepsy. F. PROESCHER and W. S. THOMAS (J. Nerv. Ment. Dis., 1931, 74, 577—597).—A tendency towards abnormal NaCl retention is observed. There is no disturbance in the renal H_2O output, but the extrarenal output varies widely. There is no relationship between the no. of convulsions, mental condition, and NaCl storage.

CH. ABS.

Distribution of calcium between blood and [cerebrospinal] fluid and carbon dioxide content of the blood in epilepsy. S. KATZENELBOGEN (J. Nerv. Ment. Dis., 1931, 74, 636—643).—The alkali reserve was 57—74; blood-Ca was 8.1—11, and cerebrospinal fluid-Ca 4.3—5.8 mg. per 100 c.c. There was no relation between the Ca vals. and convulsions or mental condition. There appears to be increased permeability to Ca of the barrier between blood and cerebrospinal fluid.

CH. ABS.

Guanidine as a factor in alimentary intoxication in infants. K. DODD, A. S. MINOT, and H. CASPARIS (Amer. J. Dis. Children, 1932, 43, 1—9).—The intoxication is characterised by increase in the blood-guanidine and -guanidine-like substances. Intramuscular or intravenous administration of Ca gluconate does not affect the vals. Animals suffering from guanidine poisoning exhibit similar symptoms and show improvement on administration of Ca salts.

CH. ABS.

Blood-urea changes in abnormal mental states after the administration of amino-acid. M. R. LOCKWOOD and D. R. DAVIES (Biochem. J., 1932, 26, 745—752).—There is no material difference from the normal in the blood- NH_2 -acid changes following the administration of gelatin or glycine to psychotic subjects of varying types. Two characteristic blood-urea curves were observed: one of agitated and simple retarded melancholia which is typified by rapid and uniform changes, the total extent of the changes showing a marked increase of the normal. There is a rapid rise to a high level followed by a rapid fall within the 5-hr. period to the fasting level. In the other curve, which is obtained during recovery from melancholia and in apathetic states generally, whilst the early changes are fluctuating, the max. reading is obtained later than in the normal, the actual changes again being larger than the normal. The rise in urea level is slow, reaching its peak at the 5th hr. of the test period.

S. S. Z.

Heart-muscle and experimental myocarditis. H. WASSERMEYER and A. ROHRBACH (Arch. exp. Path. Pharm., 1932, 166, 375—391).—Myocarditis in rabbits, induced by injection of caffeine and adren-

aline, is accompanied in the heart-muscle by none of the chemical changes typical of fatigue. F. O. H.

Posterior pituitary hormone and toxicosis of pregnancy. E. FAUVET (Klin. Woch., 1931, 10, 2125—2129; Chem. Zentr., 1932, i, 697).—The toxicosis is attributed to over-production of the hormone.

A. A. E.

Nature of urinary protein in eclampsia. N. J. EASTMEN (Amer. J. Obstet. Gynecol., 1931, 22, 756—760).—The globulin is high, urinary albumin:globulin being about 3. Ratios of 6.7 and 13.3 were obtained, respectively, in nephritis and nephrosis complicated by pregnancy.

CH. ABS.

Occurrence and aetiology of rickets. N. R. DHAR (J. Physical Chem., 1932, 36, 1846—1850).—The disturbance of the acid-base equilibrium, resulting in a change of pH of blood to the acid side, is the immediate cause of rickets. Vitamin-D is essential for the proper oxidation of fats in the body; in its absence acids accumulate, thus preventing normal pptn. of Ca from the blood. Both vitamin-D and ultra-violet light aid complete oxidation of fats. It is suggested that thyroid administration should prove useful in curing rickets.

R. B. (b)

Vitamin therapy in pulmonary tuberculosis. I. Effect of activated ergosterol on calcium and inorganic phosphorus in the blood-serum. P. D. CRDM (Amer. Rev. Tuberculosis, 1931, 23, 576—592).—The absorption of Ca and inorg. P in the gastrointestinal tract is increased. The product $Ca \times P$ is used as a criterion of the effect of activated ergosterol on the blood-serum-Ca and -P.

CH. ABS.

Serum-calcium in pulmonary tuberculosis. J. KAMINSKY and D. I. DAVIDSON (Amer. Rev. Tuberculosis, 1931, 23, 422—428).—Minimal cases and cases with quiescent lesions gave practically normal serum-Ca vals.; in active cases and cases with extensive lesions the serum-Ca tends to be low. Little difference was observed between the sexes; the age group 37—46 showed the highest and 47—64 the lowest vals. Normal or high vals. were afforded by patients receiving cod-liver oil.

CH. ABS.

Calcification of tuberculous foci in the epididymis by means of calcium diethyl ortho- and pyro-phosphate. R. TACHIKAWA (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 29—32).—Calcification was observed when rabbits inoculated with *B. tuberculosis* of the human type were subjected after 3—4 weeks to intravenous injection of 2—3% $Ca(Et_2PO_4)_2$ or $CaEt_2P_2O_7$ (1—2.7 g.).

CH. ABS.

Pulmonary concretions. M. MORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 17—18).—The concretions consist chiefly of $Ca_3(PO_4)_2$.

CH. ABS.

Phosphatase in the sputum of tuberculous persons. I. Amount of phosphatase in the sputum and its relation to the number of bacilli found. Y. IMAGAWA (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 81—83).—Phosphatase is always present in the sputum of tuberculous persons; the amount is the greater when tubercle bacilli are absent or present only in small quantities.

CH. ABS.

Phosphatase and pyrophosphatase in tubercles. I. I. HORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 1—12).—A study of the influence of p_H , temp., constituents of the phosphoric ester salts examined, time, and various drugs on the cleavage of the ester salts by phosphatase and pyrophosphatase from tuberculous rabbits. CH. ABS.

Synthesis of glucosephosphoric acid by tuberculosis phosphatase. M. MORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 19—20).—Glucosephosphoric acid was produced by an extract of tuberculous lymphomata with Na_2HPO_4 , glucose, and $\text{NH}_4\text{Cl}-\text{NH}_3$ buffer solution at p_H 8.6. CH. ABS.

Synthesis of phosphoric esters by tuberculosis phosphatase. M. MORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 33—36).—The velocity of synthesis of glycerophosphoric ester from a mixture of Na_2HPO_4 and glycerol by the extract of tuberculous lymphoma in rabbits increases until the action of the enzyme is nearly exhausted after 96 hr. The optimal is 8.3—8.9. At 60°, but not at 40°, the phosphatase is inactivated. CH. ABS.

Tuberculosis phosphatase. II. Effect of rays. I. HORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 62—74).—Sunlight has little effect on the cleavage of the Ca salts of fructosemonophosphate and sucrose- and α -glycero-phosphates by phosphatase from tuberculous lymphomata of rabbits. Ultra-violet light retards it in the first two cases. In the presence of fluorescent substances, e.g., eosin, sunlight diminishes the effect. Hg, Fe, Cu, Au, Al, and Ni salts retard, whilst Mn, Cu, and Mg salts slightly favour, the action. In the presence of K_2AsO_3 the cleavage of the sucrosephosphate is retarded; the others are almost completely hydrolysed. KH_2AsO_4 diminishes the action. Atoxyl slightly increases the cleavage of fructosemonophosphate, but decreases that of the others. CH. ABS.

Influence of X-rays on tuberculous phosphatase. M. MORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 21—22).—X-Rays (Mo anticathode) had no essential effect on the phosphatase extracted from tuberculous lymphomata. CH. ABS.

Tuberculosis pyrophosphatase and taka-pyrophosphatase. M. MORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 13—16).—Pyrophosphatase of the tuberculous tissue transforms pyrophosphates into orthophosphates. Takapyrophosphatase ppts. $\text{CaHPO}_4 \cdot 7\text{H}_2\text{O}$ from solutions of Ca Et_2 pyrophosphate. Injection of $\text{Ca}_3\text{P}_2\text{O}_7$ produces considerable deposition of $\text{CaHPO}_4 \cdot 7\text{H}_2\text{O}$ in tuberculous lymphomata. Optimal action of pyrophosphatase occurs at p_H 7.4—7.6. CH. ABS.

Calcium studies. VII. Calcium and inorganic phosphorus content of cerebrospinal fluid and blood-serum in chronic glomerulonephritis with uræmia. A. CANTAROW (Arch. Int. Med., 1932, 49, 981—993).—In 10 cases of nephritis the ratio of cerebrospinal fluid-P to serum-P lay within normal limits varying from 0.31 to 0.42 (average 0.38). The degree of hyperphosphatæmia

approx. paralleled the creatinine retention and acidosis. The serum-Ca varied from 6.84 to 9.02 mg. per 100 c.c., whilst the cerebrospinal fluid-Ca varied from 3.26 to 5.05. Low cerebrospinal fluid-Ca appeared to be associated with increased nervous irritability. W. O. K.

Oxidation by the brain. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1932, 26, 725—744).—The rates of oxidation of a no. of substrates in presence of brain-tissue of various animals, after it has become depleted of its oxidisable material, have been studied. The rate of oxidation of added substrates to the brain varies inversely with the size of the animal. Glucose, Na lactate, and Na pyruvate at equiv. concns. are oxidised at approx. the same rate by brain-tissue. Glucose is not appreciably oxidised by brain in Ringer's solution. The addition of phosphate buffer to Ringer's solution restores the rate of oxidation due to glucose. Lactate is probably completely oxidised by brain. The addition of serum increases the O_2 uptake due to brain. Iodoacetic acid inhibits the oxidation by brain of glucose, fructose, and mannose and only partly inhibits the oxidation of lactate, pyruvate, and glutamate. It has no effect on succinate oxidation. The oxidation of succinate by brain tissue varies with its content of oxidisable material. The presence of lactate "spares" the oxidation of succinate by brain, probably due to its competition with succinate for the oxidised form of a carrier. Of all the tissues investigated human grey matter is the least active toward the oxidation of succinate. S. S. Z.

Behaviour of fats during incubation of hen's eggs. K. KUSUI (J. Biochem. Japan, 1932, 15, 319—323).—Towards the end of the incubation period there is a marked decrease in the total fats of the egg. The free fatty acids attain a max. after 3 days' incubation. After 14 days the proportion of free fatty acids (to total fatty acids) in the embryo is approx. 5 times that in the remainder of the egg; further incubation results in a decrease of total and free fatty acids in both parts such that the ratio is unchanged. The fatty acids of the hen's egg are mainly unsaturated. F. O. H.

[Physiological] exclusion and utilisation of the liver. G. ROSENFELD (Arch. exp. Path. Pharm., 1932, 166, 205—210).—The blood-sugar-lowering action of diastase resembles that of insulin in being antagonised by adrenaline which, in sufficient amount, inhibits the action of diastase and favours the loss of fat from the liver of P-poisoned dogs (cf. A., 1930, 1209). Introduction of antidiastase-containing serum into P-poisoned dogs prevents fatty degeneration of the liver. The exclusion of diastatic action is equiv. to the recommencement of normal liver carbohydrate metabolism with a concomitant exclusion of fatty infiltration of the liver. F. O. H.

Physiological deposition of fat in the liver and its prevention. G. ROSENFELD (Arch. exp. Path. Pharm., 1932, 166, 211—213).—Dogs fed with sesame oil experience an increase in the liver-fat, the increase being inhibited by simultaneous administration of glucose or sucrose. F. O. H.

Experimental deposition of fat in the kidney. G. ROSENFELD (Arch. exp. Path. Pharm., 1932, 166, 214—221).—Fatty infiltration of the kidneys of dogs fed on fat occurs only to a limited extent which is not const. with either normal or phloridzinised animals. In both types the increase in fat is inhibited by simultaneous ingestion of sugar. An increase of kidney-fat is not induced by any poison such as P. The deprivation of the kidney-glycogen in the pregnant rabbit and the accumulation of glycogen by the foetus are investigated and correlated with the related phenomena of carbohydrate deprivation and fat migration. F. O. H.

Lipin excretion. VIII. Lipin content of the intestinal mucosa. W. M. SPERRY. IX. Secretion of lipins into the intestine. W. M. SPERRY and R. W. ANGEVINE (J. Biol. Chem., 1932, 96, 759—768, 769—786).—VIII. The lipin content of the mucosa of the small intestine and colon of normal dogs and dogs with ileostomies does not account for lipin excretion, since this would require a daily desquamation of about 12% of the entire intestinal epithelium.

IX. The lipin excretion of fistulas of the small intestine is greater than that found in the faeces of dogs on a lipin-free diet. Similar excretions from fistulas of the caecum are found. An appreciable amount of the large secretion of lipins into the small intestine is reabsorbed. The remainder plus a small amount of lipin secreted into the colon comprises the endogenous excretion in the faeces. A. C.

Control of carbohydrate metabolism. J. J. R. MACLEOD (Lancet, 1932, 222, 1079—1086).—A lecture. L. S. T.

Significance of bile-acids in carbohydrate metabolism. XVII. Influence of bile-acids on lactic acid metabolism. XVIII. Influence of bile-acids on blood-glycolysis and muscle-glycogenolysis. M. TERAOKA. XIX. Influence of cholic acid on the excretion of lactic acid by rabbits poisoned with hydrogen cyanide. S. SIBUYA (Biochem. Z., 1932, 249, 95—117, 118—125, 176—181).—XVII. The mean normal lactic acid vals. for fasting rabbits are for liver 0.0592%, for muscle 0.196%, and for blood 10.558 mg. per 100 g. Subcutaneous administration of small amounts of Na cholate solution to fasting rabbits decreases the liver-lactic acid and of larger amounts of deoxycholic acid solution increases the acid val. of both liver and muscle. The blood val., however, remains unchanged. Small amounts of deoxycholic acid have no effect on any of the vals. Lactic acid formation in ox liver during autolysis is decreased by small and increased by large amounts of cholic acid and is also increased by small amounts of deoxycholic acid. Lactic acid formation in autolysing muscle is always decreased whatever amount of bile-acid is added. Glycogen formation in the livers of fasting rabbits from *dl*-lactic acid, given by mouth, is increased by either subcutaneous or peroral administration of Na cholate.

XVIII.—Blood-glycolysis *in vitro* is not affected by addition of 0.001%, but is inhibited by 0.01—0.04% of bile acid. Glycogenolysis and glycolysis by muscle-enzymes *in vitro* is strongly inhibited by 0.1%

of bile acid, deoxycholic having a greater effect than cholic acid.

XIX.—Subcutaneously injected γ -lactic acid is in part excreted by rabbits after poisoning with HCN. The amount excreted is decreased by administration also of cholic acid. P. W. C.

Sugar assimilation and bile acids. II, III. H. YUKI (J. Biochem. Japan, 1932, 15, 359—371, 373—379).—II. The absorption of glucose in the intestine and its assimilation in the liver of the rabbit are increased by oral administration of $\text{PO}_4^{''}$ buffer at p_H 7.55. Oral administration of ergosterol increases the assimilation of glucose by the liver and reduces alimentary hyperglycaemia, phenomena probably dependent on increased bile acid formation under the influence of ergosterol.

III. Glycogenesis in the liver of rabbits is increased by oral administration of ergosterol, the effect being more pronounced when Na lactate is simultaneously ingested. Glycogenesis due to Na lactate alone is markedly increased if ergosterol is fed 9 hr. previously. F. O. H.

Determination of pyruvic acid. E. M. CASE (Biochem. J., 1932, 26, 753—758).—The principle of the method is based on the determination of the depth of colour produced by dissolving the 2:4-dinitrophenylhydrazones in EtOH-KOH. The method is applicable to muscle filtrates. One part in 100,000 parts of AcCO_2H can be determined in abs. amounts at least as low as 0.2 mg. S. S. Z.

Origin of pyruvic acid in muscle. E. M. CASE (Biochem. J., 1932, 26, 759—771).— AcCO_2H (I) is produced from starch or glycogen, but little from lactate, in the presence of rabbit muscle extract or of chopped muscle. Amylase or NaF completely suppresses the formation of (I) from starch. No satisfactory evidence can be obtained that the disappearance of (I) from minced muscle is due to the formation of lactic acid. (I) is formed from hexosediphosphate in presence of sulphate, but not from methylglyoxal by muscle extract. Antiglyoxalase increases the production of (I) from starch, Na hexosediphosphate, or methylglyoxal. (I) is not an intermediary in lactic acid formation and is not a product of direct oxidation of lactic acid. S. S. Z.

Determination of lactic acid production without destruction of the muscle. C. A. MAWSON and A. D. RITCHIE (Biochem. J., 1932, 26, 615—618).—The lactic acid which diffuses into the Ringer's solution surrounding the stimulated muscle is oxidised with freshly-pptd. MnO_2 in presence of MnSO_4 and H_3PO_4 ; the resulting MeCHO is received in $\text{Na}_2\text{S}_2\text{O}_3$ and determined iodometrically. Amounts of lactic acid of the order of 0.1 mg. can be determined. S. S. Z.

Formation of ammonia and decomposition of pyrophosphate in muscle. W. MOZOLOVSKI, J. REIS, and B. SOBZUK (Biochem. Z., 1932, 249, 157—160).—The formation of NH_3 and decomp. of pyrophosphate in muscle-pulp proceed side by side, but by adjustment of the p_H to 9.2 (borate buffer) the two processes can be separated, NH_3 formation being inhibited and pyrophosphate decomp. unaffected.

P. W. C.

Embryological chemistry of reptiles. IX. Behaviour of the egg-vitellin during incubation of sea-turtle eggs. K. KUSUI (J. Biochem. Japan, 1932, 15, 325—330).—The vitellin decreases during the incubation period probably due to its assimilation by the developing embryo. The chemical composition, however, remains const. F. O. H.

(a) Increase of liver-proteins on a diet of amino-acids, butter-fat, and glucose. (b) Increase of liver-proteins on a diet of amino-acids and a minimum of honey. C. GAUTIER (Bull. Soc. Chim. biol., 1932, 14, 800—803, 804—807).—(a) Frogs, fed on a mixed diet containing NH_2 -acids as the N constituent, show an increase in liver wt. of $6\frac{1}{2}$ times; the total liver-proteins doubled, whilst the % protein decreased. H. D.

(b) The liver wts. of frogs fed on a diet containing only NH_2 -acids, salts, vitamins, and a min. of honey are doubled; the protein is lowered, whilst the total protein increased by $>50\%$. H. D.

Feeding experiments with methionine. T. E. WEICHELBAUM, M. B. WEICHELBAUM, and C. P. STEWART (Nature, 1932, 129, 795).—*dl*-Methionine, added to the Sherman-Merrill diet, is almost as effective as cystine in producing increased growth in rats (cf. this vol., 83). L. S. T.

Metabolism of tryptophan. III. Availability of kynurenine in supplementing a diet deficient in tryptophan. R. W. JACKSON and W. T. JACKSON (J. Biol. Chem., 1932, 96, 697—701).—Kynurenine sulphate does not promote growth of rats on a tryptophan-deficient diet when fed in amount 5—10 times greater than the dose of tryptophan which causes sharp increase in wt. The change tryptophan \rightarrow kynurenine is therefore not reversible in the animal.

Comparative metabolism of amino-acids. V. Oxidation of phenylalanine and phenylpyruvic acid in the organism of the rabbit. J. P. CHANDLER and H. B. LEWIS (J. Biol. Chem., 1932, 96, 619—636).—Rabbits on a diet of cabbage and oats normally excrete approx. equal amounts of phenaceturic and hippuric acids. Following administration of phenylalanine or of an equiv. amount of phenylpyruvic acid considerable amounts of the latter appear in the urino, the excretion being greater with *dl*-phenylalanine than with the *l*-isomeride. Simultaneously there is an increase in the excretion of phenaceturic but not of hippuric acid. Hence with phenylalanine oxidative deamination is followed by α -oxidation to give products which are not further oxidised, whilst the opening of the Ph ring, which occurs after the oxidative deamination and before further changes in the side-chain, takes place less readily than has previously been assumed. F. O. H.

Digestibility by chickens of the constituents of the nitrogen-free extract of feeds. G. S. FRAPS (Texas Agric. Exp. Sta. Bull., 1931, No. 437, 15 pp.).—In numerous trials sugars and starch showed a high and pentosans and residual N-free extract a low digestibility. Pentosans are less digested in roughages than in concentrates. A. G. P.

Productive energy of feeds calculated from feeding experiments with sheep. G. S. FRAPS (Texas Agric. Exp. Sta. Bull., 1931, No. 436, 56 pp.).—For 1 lb. gain in wt. of fattening sheep an average of 2.60 therms of productive energy is required. The productive energy of feeding stuffs calc. from experimental data agreed reasonably well with vals. calc. from analyses and the production coeffs. of the individual constituents of rations. Revised vals. for certain production coeffs. are recorded. The productive val. of maize fodder and oat straw was greater in balanced than in unbalanced rations. The effect of a protein concentrate used to correct an unbalanced ration is greater than its actual productive energy. Grinding lucerne to a meal increased its productive energy by about 14%. A. G. P.

Relation of lime and phosphoric acid to growth and bone development of white rats. J. K. BLUM (Texas Agric. Exp. Sta. Bull., 1931, No. 441, 18 pp.).—Normal growth was produced by rations having a $\text{CaO}:\text{P}_2\text{O}_5$ ratio of 1:1 for CaO contents of 1.0—3.0%. The min. requirements for normal growth were 0.75% CaO and 1.0% P_2O_5 in the ration. Smaller proportions of either constituent reduced growth and lowered the % ash in the femur. With 6.0% CaO and 1.5% P_2O_5 , growth was normal. Rations having 6.0% P_2O_5 and 15% CaO reduced growth without an appreciable alteration of the ash content of femurs. A disproportionately high ratio of bone:total wt. was, however, produced. The ratio $\text{CaO}:\text{P}_2\text{O}_5$ in femurs bears no relationship to that in the ration. A. G. P.

Composition of growth. II. Full-term infant. W. M. SWANSON (Amer. J. Dis. Children, 1932, 43, 10—18).—The retentions of K, Na, Ca, Mg, Cl, P, and N per kg. gain in wt. are higher for cow's than for human milk diet. Addition of cod-liver oil increases the Ca and P retained. CH. ABS.

Value of an increased supply of vitamin-B₁ and iron in the diet of children. P. SUMMERFELDT (Amer. J. Dis. Children, 1932, 43, 284—290).—Addition to normal diet of a cereal mixture containing wheat germ and brewer's yeast (6.8 mg. Fe per day) produces 3.6—4.8 times the expected rate of gain in wt. CH. ABS.

Utilisation of the iron of protein foods by the albino rat. A. Comparison of growth and iron assimilation as affected by different protein foods. B. Comparison of protein foods supplementary to milk as sources of iron in nutrition. R. C. MILLER and E. B. FORBES (J. Nutrition, 1931, 4, 483—505).—A. Fe from pecans, beef muscle, eggs, arachis nuts, and walnuts was well, and from liver and kidney less well, utilised. B. Beef muscle, beef liver, and pecan $>$ kidneys, eggs, and arachis nuts $>$ walnuts and milk powder. The dry body-wt. of rats was not a significant basis of reference for Fe contents. CH. ABS.

Bromine metabolism. I. Bromine content of blood and the influence of menstruation and of oral administration of bromine. T. KURANAMI (J. Biochem. Japan, 1932, 15, 205—218).—The Br content of whole blood of men and of women during

the intermenstrual period varies between 0.51 and 0.67 mg. per 100 c.c. With menstruation the Br' level falls to a min. at the onset, rises to a val. above normal during the period, and returns to normal at its conclusion. Oral administration of 1 g. of KBr results in an increase of blood-Br', the return to normal occupying about 5 hr. The urinary Br' during this period is always less than that of the blood except for the first hr., when it is much higher. The total urinary excretion is much less than the amount ingested, the small amounts of Br' in the faeces indicating fixation in the organism. F. O. H.

Sulphur metabolism of the dog. X. Effect of isobarbituric acid on the excretion of neutral sulphur and ethereal sulphate. N. R. LAWRIE and N. W. PRIE (Biochem. J., 1932, 26, 622-623).—The acid does not cause the disappearance of the neutral S fraction from a dog's urine. It is readily conjugated with sulphate. S. S. Z.

Sulphur assimilation in wool growth. A. T. KING (Nature, 1932, 129, 938).—A discussion.

L. S. T.
Determination of sex. III. Masculinisation of *Bonellia viridis* larvae by traces of copper. C. HERBST (Naturwiss., 1932, 20, 375-379).—Addition of 0.025 mg. of Cu per 100 c.c. to cultures of these larvae in natural or artificial sea-water with or without NaHCO_3 causes a marked increase in the proportion of males. A. C.

Effect of thiol compounds on regeneration in *Podarke obscura*. S. MORGULIS and D. E. GREEN (Protoplasma, 1931, 14, 161-169).—Thio-*p*-cresol, thiophenol, thioglycolic acid, and cystine do not accelerate regenerative processes in *P. obscura*. A. G. P.

Biological significance of certain ions. VI. Action of direct current on living nerve-tissue (polarisation effect). W. W. PRÁWDICZ-NEMINSKI (Z. Biol., 1932, 92, 465-481).—The effect of d.c. on a nerve or cerebrospinal cord prep. of the frog was studied in a closed chamber. A current of 0.30-0.10 milliamp. at 6.6 volts resulted in the cathodic evolution of 0.14-5.9 mg. of NH_3 per 100 g. of nerve, a val. 2-5 times that occurring at the anode. With 0.03-0.05 milliamp. NH_3 was not evolved at the anode, the formation with higher currents being due to damage of the nerve. The surviving cerebrospinal cord prep. also evolved a greater amount of NH_3 at the cathode whether situated at the medulla or sacral end. After polarisation the region at which the cathode was applied contained a diffusible alkaline substance. The mechanism of the formation of NH_3 is discussed. F. O. H.

Permeability of frogs' skin. S. WOWSKI (Protoplasma, 1931, 14, 170-178).—The presence of NaCN reduces the permeability of frogs' skin to methylene-blue and this reduction is paralleled by decreased p.d. Exclusion of O_2 increases the permeability. A. G. P.

Behaviour of sodium deoxycholate and saponin towards membranes and tissue constituents. R. LABES and T. SCHLENKERT (Arch. exp. Path. Pharm., 1932, 166, 186-204).—Na deoxycholate

closely resembles saponin in its effect on membrane permeability. Thus it renders frog's mucous membrane permeable to substances previously not diffusible through it. At slightly acid reactions it passes into the colloidal state and loses the slight power of penetrating membranes which it exhibits at alkaline reactions. The non-toxicity of non-intravenously injected saponin and Na deoxycholate is explicable on these grounds, an additional factor being complex formation with tissue constituents. Saponin is strongly absorbed by charcoal, intestinal cells, and erythrocytes. Na deoxycholate is adsorbed by charcoal and erythrocytes, but only to a small extent by intestinal cells. The adsorption of Na deoxycholate on erythrocytes at the haemolysis point is almost as great as that for saponin, despite the greater solution concn. of the bile salt necessary for haemolysis. This is due to its adsorption being less than that of saponin. F. O. H.

"Anomalous osmosis" in animal cells. W. A. DOREMAN (Protoplasma, 1931, 14, 341-359).—Anomalous swelling occurs in frog erythrocytes and in sea-urchin eggs on treatment with small concns. of certain ions, notably Th. The action takes place in iso-, hyper-, or hypo-tonic solutions of electrolytes and non-electrolytes. In hypertonic NaCl solution, Th salts cause anomalous swelling of the erythrocyte nucleus which is more acid ($p_H < 5.8-5.9$) than the cell stroma. The effect is not apparent in hypertonic non-electrolyte solutions nor in iso- or hypo-tonic solutions of electrolytes. A. G. P.

Vanillylethylamine, vanillylmethylamine, and benzylvanillylethylamine: relation of chemical structure to pharmacological action. W. E. HAMBOURGER (J. Pharm. Exp. Ther., 1932, 45, 163-182).—4-Hydroxy-3-methoxyphenylethylamine (I) has an essentially pressor action which is, however, less than that of tyramine. 4-Benzoyloxy-3-methoxyphenylethylamine (II) has a marked depressor action, whilst the effect of 4-hydroxy-3-methoxyphenylmethylamine (III) depends on the dose, being sometimes pressor and sometimes depressor. On isolated smooth muscle, (I) and (III) are predominantly and equally stimulant, whilst (II) is definitely depressant. W. O. K.

Effect of atropine and thyroidectomy on tryptaflavine hyperglycaemia. R. MESSINA (Arch. Farm. sperim., 1932, 54, 162-175).—Tryptaflavine hyperglycaemia in rabbits is intensified by the simultaneous administration of atropine, but is diminished by thyroidectomy. Hyperglycaemia may be induced by direct stimulation of the sympathetic nerve endings as well as by exciting the excretion of adrenaline. R. K. C.

Drugs employed as antidiabetics in Chinese medicine. V. Hypoglycaemic action of phellodendronelactone. I. Action of phellodendronelactone on the normal blood-sugar content of the rabbit. II. Mechanism of the action. N. SUGIHARA and S. HIRANO (Keijo J. Med., 1932, 3, 160-167, 163-174; cf. A., 1931, 651).—I. Phellodendronelactone administered orally, subcutaneously, or intravenously into rabbits has a marked hypoglycaemic action.

II. It does not antagonise the hyperglycaemic action of adrenaline, but reduces the hyperglycaemia produced by injection of (10%) NaCl solution or of (8.6%) NH_4Cl solution. W. O. K.

Panax Ginseng. IX. Influence on the blood picture of rabbits. K. KIN and N. SUGIHARA (Keijo J. Med., 1932, 3, 1—14).—"P. Ginseng" (Ginseng extract) administered orally to rabbits increases the nos. of leucocytes and erythrocytes and also the haemoglobin in the blood. W. O. K.

Hagedorn-Jensen method of blood-sugar determination in phloridzin diabetes. S. YAMADA (J. Biochem. Japan, 1932, 15, 311—318).—Phloridzin reduces $\text{K}_3\text{Fe}(\text{CN})_6$ at room temp. and reacts with I. Hence determinations of the blood-sugar following phloridzin administration are erroneous when the methods employed depend on the use of these reagents. Thus phloridzin apparently effects a hyperglycaemia in rabbits if the blood-sugar is followed by the Hagedorn-Jensen method, but determinations by a Cu method indicate a hypoglycaemia. F. O. H.

Fat transport through the lymph system in fasting and phloridzin poisoning. H. R. RONY, B. MORTIMER, and A. C. IVY (J. Biol. Chem., 1932, 96, 737—743).—Lymph from the thoracic duct of fasting and phloridzinised dogs contains large amounts of fat; the vals. are greater than the corresponding blood-vals. Since the sugar content of such lymph is far less than that of the blood or of normal lymph, fat is not mobilised and transported as sugar. The findings favour the possibility that fat is transported through the lymph system. A. C.

Examination for narcotic drugs. COULOUA (Ann. Falsif., 1932, 25, 201—204).—The lethal dose of cocaine for guinea-pigs is 0.05 g., and for morphine 0.1 g. per 250 g. body-wt. Heroin and dionine have $[\alpha]_D^{25}$ —75° and —97°, respectively. T. McL.

Poisoning by percaine. F. RIECHEN (Z. Unters. Lebensm., 1932, 63, 557—560).—Symptoms of poisoning, distribution of the drug in the organs, chemical reactions, and distinction from cocaine are described. E. B. H.

Colloid chemistry of nervous systems. IV. W. D. BANCROFT, R. S. GUTSELL, and J. E. RUTZLER, jun. (J. Physical Chem., 1932, 36, 1521—1548; cf. this vol., 191).—Small increasing amounts of morphine were administered to dogs, and shortly before the abrupt withdrawal of morphine some of the dogs were given NaCNS (a peptising agent). Those receiving NaCNS showed no withdrawal symptoms, whilst those not receiving it showed symptoms. NaCNS may therefore be expected to counteract (in part) the effects of morphine. C. T. S. (b)

Disturbance of carbohydrate and acid-base economy and of gaseous exchange in avertin narcosis. H. FUSS and E. DERRA (Klin. Woch., 1932, 11, 19—21; Chem. Zentr., 1932, i, 1118).—Experiments in which O_2 or CO_2 were also administered are described. The CO_2 val. of arterial blood is affected in opposite directions by the fall in alkali reserve and the difficulty of breathing. Increase in blood- CO_2 diminishes the blood-lactic acid. A. A. E.

Influence of diet on carbon tetrachloride intoxication in dogs. J. T. CUTLER (J. Pharm. Exp. Ther., 1932, 45, 209—226).—Dogs on various diets, (a) poor in carbohydrate and Ca, (b) poor in carbohydrate and rich in Ca, (c) rich in carbohydrate and Ca, (d) rich in carbohydrate but poor in Ca, and (e) very rich in fat, were subjected to poisoning with CCl_4 , but exhibited no significant differences in the degree of liver damage. The degree of intoxication and the death rate, however, varied markedly according to diet, being very high with diet (a), moderate with (d) and (e), and low with (b) and (c). Ca and carbohydrate have therefore a protective action, whilst meat protein is deleterious, presumably as the result of its giving rise to guanidine (cf. A., 1931, 651). W. O. K.

Toxicology of the carbonyls. A. J. AMOR (J. Ind. Hygiene, 1932, 14, 216—221).—A review of symptoms, pathology, diagnosis, treatment, and prognosis of poisoning by $\text{Ni}(\text{CO})_4$. Safety measures are also discussed. W. O. K.

Antimony salt of sodium β -hydroxy- γ -thiolpropanesulphonate. A. LEULIER, M. JUVIN, and H. TÊTE (J. Pharm. Chim., 1932, [viii], 15, 593—597; cf. this vol., 192).—This salt injected into guinea-pigs is excreted mainly in the urine, and to a smaller extent in the faeces. Some is deposited in the liver and kidneys, considerable amounts being found in the former organ if death precedes urination. J. W. B.

[Pharmacology of the] quinoline series. II. W. HEURNER. III. Action of orally administered yatren in diseased animals. B. WEICKER. IV. Yatren. H. NAHME and K. SEELKOPF. V. Quinolinesulphonic acids. K. SEELKOPF and H. NAHME. VI. Benzenesulphonic acids. H. NAHME. VII. Carboxylic acids. F. GRABE and K. SEELKOPF. VIII. Hydroxy- and hydroxyallyl-quinoline. K. SEELKOPF, F. BENDER, H. NAHME, and E. SCHULZE. IX. Hydroxyquinolinium bases. F. GRABE, H. NAHME, and K. SEELKOPF. X. Di-iodo-derivatives. A. PALM (Arch. exp. Path. Pharm., 1932, 166, 117—122, 123—125, 126—149, 150—156, 157—160, 161—165, 166—171, 172—175, 176—185; cf. A., 1929, 214).—II. The pharmacological action of some quinoline derivatives and allied substances is discussed.

III. Oral administration of yatren to healthy rabbits produces a slight and variable change in the leucocyte count, whereas in rabbits which have previously been subcutaneously injected with turpentine there is a significant increase, the extent of which is dependent on the period between the time of administration of turpentine and that of yatren.

IV. Intravenous injection of yatren into dogs is followed by the excretion of 70—90% of the I injected, the proportions appearing in the urine and faeces being dependent on the amount administered. In the starving dog the excretion of I is slow and mainly in the faeces, the urinary I suddenly increasing on feeding with a protein-free diet. The differences between I-excretion with NaI and that with yatren indicate that with the latter I is excreted as an aromatic compound. The effect of yatren on the basal and

protein metabolism, the body temp., and the *R.Q.* of dogs is described.

V. The effect of oral administration of the following compounds on the N-excretion, basal metabolism, and *R.Q.* of dogs was investigated: 5-chloro-8-hydroxyquinoline-7-sulphonic acid; 8-hydroxyquinoline-5-sulphonic acid; 8-hydroxy-7-propylquinoline-5-sulphonic acid; and quinoline-8-sulphonic acid.

VI. The excretion of N, SO_4 , and total S following oral administration of the Na or K salts of the following sulphonic acids was determined: benzene-; phenol-*p*-; guaiacol- (a mixture of the 1-hydroxy-2-methoxy-4- and -5-sulphonic acids); and propyl-guaiacol- (a mixture of 1-hydroxy-2-methoxy-4-propyl-5-sulphonic and -5-propyl-4-sulphonic acids).

VII. The excretion of N following administration of Li 8-hydroxyquinoline-7-carboxylate, Na acetyl-8-hydroxyquinoline-7-carboxylate, and salicylic acid (for which the changes in basal metabolism and *R.Q.* were also followed) was investigated in dogs.

VIII. The changes in urinary urea, basal metabolism, and in the amount and character of the bile, due to oral administration of 8-hydroxyquinoline and its 7-allyl derivative were investigated in dogs with biliary fistula.

IX. The N excretion, basal metabolism, and *R.Q.* following oral administration of 8-hydroxyquinoline methochloride were followed in fed and starving dogs. The toxicity of this substance and also that of 8-hydroxy-7-propyl- and -7-allyl-quinoline to rats and mice were determined.

X. Oral administration of 5:7-di-iodo-8-hydroxyquinoline in rabbits is followed by the excretion of up to 90% of the I given. That the excreted I is to a certain extent differently combined in faeces and urine is shown by the difference in the partition of I on C_6H_6 extraction. Examination of the urine indicates that in the organism I is not removed from its quinoline compound, which is excreted in the form of derivatives, of which at least one is a glycuronic ester. With di-iodotyrosine the main excretion of I is in the urine, the organism retaining 10% the distribution of which is determined. With thyroxine, however, the main excretion of I is in the faeces while the body retention is greater. F. O. H.

Physiological properties of neriin and other *Nerium oleander* glucosides. H. SIMONNET and G. TANRET (Bull. Soc. Chim. biol., 1932, 14, 724—744).—Neriin is sol. in H_2O and is similar in action to the strophanthin and ouabain groups, being rapid in action and quickly eliminated. A normal dose for the dog is 0.25 mg. per kg. body-wt. The hydrolysis product of neriin, nerigenin, is more toxic. Oleandrin is insol. in H_2O , produces a rise in blood-pressure, and has a weaker diuretic and heart-slowng action. H. D.

Relationships between the Ca and K ion equilibrium and antirheumatic drugs. II. K. IN (Keijo J. Med., 1932, 3, 125—137).—After the administration of certain antipyretic drugs to infected rabbits, the Ca content of the blood rises, whilst the K content tends to fall, the original concns. being regained after several hr. W. O. K.

Changes in the blood-sugar due to various degrees of experimental shock. R. GRUN and H. REINWEIN (Arch. exp. Path. Pharm., 1932, 166, 366—370).—Anaphylactic shock induced in guinea-pigs by injections of Witte's peptone, albumin, or horse-serum is attended by a fall in the blood-sugar; the extent of which, however, is not sufficiently great to permit correlation with that of the shock but appears to depend on the substance producing it. Injection of proteins is followed by a fall in the blood-sugar of a type different from that due to guanidine and its derivatives. F. O. H.

Toxicological detection of hydrogen cyanide. J. A. KLAASSEN (Pharm. Weckblad, 1932, 69, 655—680).—For the detection of HCN the Prussian-blue reaction is recommended whenever practicable, but the microchemical AgCN reaction provides a valuable preliminary test. For determination of HCN in fresh organs, many methods are satisfactory, but when decomp. has progressed somewhat Schulek's method (BrCN formation) is the best. The reaction between reducing sugars and HCN, the formation of the latter in decaying corpses by the action of bacteria, and the conversion of HCN into CNS derivatives in living and dead organisms are discussed. H. F. G.

Biochemistry of aluminium. III. Effect of aluminium on growth and reproduction of the rat. IV. Occurrence of aluminium in the thyroid. V. Intestinal absorption of aluminium in the rabbit. K. MACKENZIE (Biochem. J., 1932, 26, 833—845).—Al additions to the diet have no perceptible influence when the diet is adequate for growth and reproduction in the rat, when the diet is insufficient for growth or maintenance, or when fed to several successive generations of rats. Al absorption from such diets is exceedingly small. Al occurs only in very small quantities in the thyroid and is not correlated with I in normal metabolism. Injection of Al salts into the intestine of rabbits does not cause appreciable absorption of Al into the blood stream. S. S. Z.

Toxicological identification of antimony. C. PALMERI (L'Ind. Chimica, 1932, 7, 567—572).—If HCl and KClO_3 are used in the oxidation of org. matter SbCl_3 is formed which on diluting and treating with H_2SO_4 to separate Pb and Ba, may be almost completely pptd. as SbOCl , thus escaping identification. Oxidation by HNO_3 and NO_2 is preferred. From the oxidised liquid PbSO_4 , BaSO_4 , and H_3SbO_4 are pptd. with dil. H_2SO_4 . The ppt. is treated with NH_4OAc and NH_3 which dissolve PbSO_4 , the residue is washed with NH_4OAc solution, suspended in dil. aq. NH_3 , and treated with H_2S , BaSO_4 is filtered off, and the filtrate, when acidified with H_2SO_4 , gives the characteristic Sb_2S_3 ppt. O. F. L.

Renal threshold for hæmoglobin in dogs uninfluenced by mercury poisoning. W. H. HAVILL, J. A. LIGHTY, jun., G. B. TAYLOR, and G. H. WHIPPLE (J. Exp. Med., 1932, 55, 617—625).—The min. or depression renal threshold for dog hæmoglobin is not modified by moderate doses of HgCl_2 . CH. ABS.

Tolerance for mercury poisoning increased by frequent hæmoglobin injections. W. H.

HAVILL, J. A. LICHTY, jun., and G. H. WHIPPLE (J. Exp. Med., 1932, 55, 627—635).—Deposition of pigment in the renal tubular epithelium resulting from injection of superthreshold amounts of dog haemoglobin permits survival of lethal doses of HgCl_2 with little evidence of renal injury. CH. ABS.

Bile acid metabolism. VII. Bile- and bile acid-secretion in cholecystography with sodium tetraiodophenolphthalein. H. MIKAMI (J. Biochem. Japan, 1932, 15, 219—228).—Intravenous injection of the substance into dogs with biliary fistulae produces a small but prolonged increase in bile secretion, whilst the amount of bile acids is decreased. The bilirubin content first decreases and then increases to a level approx. twice that of the normal. The extensive variation in the bile acid/bilirubin ratio indicates that the secretions of the two substances are in no way related. F. O. H.

Absorption of compound solution of iodine from the gastro-intestinal tract: absorption of free iodine. B. N. E. COHN (Arch. Int. Med., 1932, 49, 950—956).—In anaesthetised dogs the absorption of I from the colon or small intestine is probably preceded by its conversion into iodide. W. O. K.

Graphic correlation of radiation and biological data. F. S. BRACKETT (Smithsonian Misc. Coll., 1932, 87, No. 8, 1—7).—The transmission curves of H_2O and O_2 for light of different wave-length are correlated with corresponding curves obtained for the emission from heated bodies, from the sun, and from the Hg arc in quartz; also with those of the transmitting power of flesh, relative visibility of the human eye, relative phototropic response of oat seedlings, absorption band for ergosterol, and the erythema response of the human skin. A. L.

Recent advances in the study of enzymes. B. WOOLF (Nature, 1932, 129, 928—930).—A summary of a recent discussion. L. S. T.

Determination of enzyme action. A. K. BALLS (J. Assoc. Off. Agric. Chem., 1932, 15, 131—136).—Physico-chemical principles are discussed. W. J. B.

Dilatometric studies in enzyme action. II. Contraction constants of enzyme-substrate reactions. M. SREENIVASAYA and H. B. SREERANGACHAR (J. Indian Inst. Sci., 1932, 15A, 17—24; cf. A., 1929, 1488).—A new type of dilatometer in which the substrate and enzyme are mixed within the vessel itself is described. Immediately on mixing enzyme-substrate systems there occurs an increase or a decrease in the total vol. Following the determination of the "contraction const." for urea-urease and arginine-arginase systems, the apparatus may be applied to the determination of urea and arginine in physiological fluids and protein hydrolysates. F. O. H.

Co-enzymes, hydrogen donors, and arsenic poisoning of cell respiration. H. HANDOVSKY (Biochem. Z., 1932, 249, 195).—Criticism of the technique of Banga and Szent-Gyorgyi (this vol., 537). P. W. C.

Oxidation-reduction potential. Action of anions on succinodehydrogenase. L. PINCUSSEN

and J. GORNE (Biochem. Z., 1932, 249, 130—140).—An active sample of the enzyme can be prepared from horse flesh without use of phosphate as eluting agent. Halogens in sufficient concn. injure the enzyme, the degree of injury being $\text{Cl} < \text{Br} < \text{I}$. The action of KF cannot be compared, since this substance displaces the p_{H} into the inactive range. P. W. C.

Kinetics of fumarase. K. P. JACOBSON, J. TAPADINHAS, and F. B. PEREIRA (Biochem. Z., 1932, 249, 72—74).—An equation is given for determination of the combined velocity coeffs. of a reversible equilibrium, and some preliminary results obtained with rabbit's-liver fumarase indicate its validity. P. W. C.

o-Quinones as enzyme models. IV. Catalysts inactive at p_{H} 6—8. B. KISCH (Biochem. Z., 1932, 249, 63—71).—Quinol, benzoquinone, protocatechuic acid, pyrogallol, phloroglucinol, and homogentisic acid, although unable to effect oxidative deamination at p_{H} 6—8, cause a feeble deamination at p_{H} 9—12. At this p_{H} , resorcinol is very active and gives 50% of the theoretical amount of NH_3 from glycine. The extent of deamination decreases in the series glycine > serine > phenylglycine > leucine. Little or no deamination occurs with alanine, α -aminobutyric acid, valine, isoleucine, nor under the action of orcinol, isatin, alloxan, and ethylene glycol. P. W. C.

Decomposition of hydrogen peroxide by catalase. D. RICHTER (Nature, 1932, 129, 870).—Comparison with the photochemical decomp. indicates that the enzyme reaction is a chain reaction in which the active centres of the enzyme function only by starting the chains, which then continue in the solution or on other surfaces. The inhibition of enzyme reactions may be due in certain cases to the rupture of the reaction chains by the inhibitors. L. S. T.

Hydrogenlyases. Bacterial enzymes liberating molecular hydrogen. M. STEPHENSON and L. H. STICKLAND (Biochem. J., 1932, 26, 712—724).—These enzymes are distinct from formic dehydrogenase and from hydrogenase. In the case of *B. coli* formic hydrogenlyase is formed only when the organism is grown in the presence of formate. Its formation is not due to the partly anaerobic conditions of its production or to the p_{H} of the medium. Its optimum rate of action is at p_{H} 7 and it shows a much lower affinity than formic dehydrogenase. The enzyme is very sensitive to poisons and KNO_3 inhibits its production of H_2 . In *B. coli* it produces the theoretical amount of H_2 from formate. Formic hydrogenlyase is distinct from the hydrogenlyases liberating H_2 from the sugars. The evolution of H_2 from glucose does not occur through HCO_2H as an intermediate product. S. S. Z.

Reduction of glutathione by a liver-system. P. J. G. MANN (Biochem. J., 1932, 26, 785—790).—It is reduced by glucose in presence of glucose dehydrogenase from liver. The reaction proceeds slowly, and is greatly accelerated by an activator, sol. in H_2O , insol. in EtOH, present in the liver. S. S. Z.

Reduction of glutathione in mammalian erythrocytes. N. U. MELDRUM (Biochem. J., 1932, 26,

817—828).—In the intact erythrocyte the glutathione present undergoes a slow oxidation and a much more rapid reduction. *In vitro* the reduction takes place when glucose is added to a suspension of intact corpuscles. Other hexoses as well as maltose possess the power of reduction. Non-reducing sugars and hexahydric alcohols cause no reduction. Pentoses reduce very feebly. S. S. Z.

Structure and enzyme reactions. XI. Action of salts in the systems starch-amylase-proteins. G. BAUMGARTEN (Biochem. J., 1932, 26, 539—542).—In the case of taka-diastase considerable activation takes place with CaCl_2 at p_H 8.85. This activation is less at p_H 8.1; at p_H 6.5 there is no increase in the velocity of the reaction and at p_H 4.7 there is a retardation. The accelerating effect of CaCl_2 is much smaller in the presence of NaCl or KCl . The augmented production of reducing sugars in the presence of CaCl_2 at p_H 8.85 is relatively much greater than the augmented hydrolysis of starch under analogous conditions. NaCl alone accelerates the reaction at various p_H vals., but to a smaller extent than CaCl_2 . With salivary amylase the action of NaCl may be accelerating or retarding according to its concn. This reaction is retarded by CaCl_2 both in the presence or absence of NaCl or KCl and in the presence of either sol. or heat-coagulated egg-white. S. S. Z.

Limit of hydrolysis of starch by malt-amylase. S. PRONIN (Biochem. Z., 1932, 249, 7—10).—The limit of hydrolysis of sol. starch by malt-amylase depends on the amount of malt extract added and may amount to 74.9—95.88% (cf. Pringsheim and Schmalz, A., 1924, i, 106). P. W. C.

Influence of guanidine and its derivatives on the action of amylase. E. M. MYSTKOWSKI (Biochem. J., 1932, 26, 910—914).—Guanidine and creatine retard and creatinine accelerates enzymic amylolysis, the effect obtained being proportional to concn. of the substance studied. The effects are of the same order in the hydrolysis of starch or glycogen by vegetable or by salivary amylase. When both accelerating and retarding substances (glycine and guanidine) are present together, the resultant velocity of reaction is the mean of the velocities which would be obtained in the presence of each substance separately. S. S. Z.

Exponential analysis applied to the asymmetric hydrolysis of some β -glucosides with emulsin. S. MITCHELL and I. MACARTHUR.—See this vol., 816.

Co-enzyme system of lactic acid formation. O. MEYERHOF and K. LOHMANN (Naturwiss., 1932, 20, 387—390).—A review (cf. A., 1931, 654, 1184). A. C.

Determination of lipase. B. UMSCHWEIF (Biochem. Z., 1932, 249, 75—82).—The usual Willstatter method is critically examined and the stability of pancreatic enzyme preps. on keeping and against acid investigated. P. W. C.

Rennin. I. Purification of rennin and its separation from pepsin. II. Isolation of prorennin. H. TAUBER and I. S. KLEINER (J. Biol.

Chem., 1932, 96, 745—753, 755—758).—I. A highly-active rennin is obtained from the fourth stomach of the calf by fractional pptn. from feebly acid aq. EtOH. Its isoelectric point is p_H 5.4, Cl and P are absent, and it is irreversibly inactivated by alkali. In these and other respects it differs from cryst. pepsin, although the latter has rennin activity, and appears to be a thioprotease.

II. From the mucosa of the calf's fourth stomach an inactive precursor of rennin is obtained by pptn. from a CaCO_3 extract with MgSO_4 as a H_2O -sol. substance which is activated by HCl at p_H 1. A. C.

Intracellular enzymes of tissues and glands. I. Desmo-pepsin and desmo-cathepsin. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1932, 208, 258—272).—The COME₂-dried material (pig's intestinal mucosa) is extracted repeatedly with 100% glycerol below 3°. The residue is washed with 50% glycerol and dried with COME₂, EtOH, and Et₂O after each extraction. This removes the lyo- and leaves the desmo-pepsin. The latter is rendered sol. by 0.1% HCl or by autolysis. Desmo-cathepsin is also present in the fully active condition, no added kinase being required. Active pepsin solutions were obtained showing no reaction for protein. J. H. B.

Non-applicability of the Schütz-Borissow law in the determination of pepsin activity by Mett's method. J. PATTERSON and J. ADLER (Brit. J. Exp. Path., 1932, 13, 72—75).—The tubes (1.5 mm. diameter) should be prepared according to Christiansen's method, and very dil. pepsin solutions should be incubated for several days before the reading is taken. The pepsin concn. is proportional to the cube of the length digested. CH. ABS.

(a) Number and kind of proteolytic enzymes of pancreatic juice. (b) Proteolytic enzymes of intestinal and pancreatic juice. F. MOCOROA (Anal. Fis. Quím., 1932, 30, 302—304, 305—306).—(a) Pancreatic juice attacks scombrin and chloroacetyltyrosine directly, and caseinogen after addition of kinase, but not di- or tri-peptides. It therefore contains, apart from prokinase, only tryptic enzymes, an inactive proteinase and carboxypolypeptidase, but none of the ereptic enzymes which, although found in extracts of the gland, are endocellular.

(b) Contrary to Waldschmidt-Leitz and Waldschmidt-Graser (A., 1927, 698), only abnormal pancreatic juices contain kinase or ereptic enzymes, and intestinal secretion contains enterokinase as well as ereptic enzymes. R. K. C.

Formation of enterokinase from a precursor in the pancreas. J. PACE (Biochem. J., 1932, 26, 640—649).—The separation from pancreas extracts of a pre-stage of enterokinase, which gives rise to an enterokinase resembling that usually obtained from intestinal mucous membrane, is confirmed (Waldschmidt-Leitz and Harteneck, A., 1926, 323). The rate of formation of enterokinase agrees with that of a unimol. reaction. The optimum p_H of formation is about p_H 6.5—7.0. S. S. Z.

Enzymic degradation of guanylic acid in rabbit's liver. G. SCHMIDT (Z. physiol. Chem., 1932,

208, 185—224).—All the derivatives of guanylic acid containing guanine are deaminated by rabbit's liver; with guanylic acid the NH_2 -group of the guanine nucleus is eliminated without previous removal of the H_3PO_4 . NH_3 and purine are always formed in equiv. amounts. In the deamination of the guanine nucleus in guanylic acid, guanosine, and guanine at least two enzymes are concerned: guanase (optimum p_{H} 9.2) and an enzyme attacking guanylic acid (optimum p_{H} 5.3). The guanase was obtained free from the second enzyme by adsorption methods. The deamination of guanylic acid is inhibited by low concns. (0.0025*N*), that of guanine only by high concns. (0.1*N*) of NaF . Both guanase and adenosine-deaminase (optimum p_{H} 6.2) are highly sp. enzymes; the deamination curves up to 50% fission are linear. Guanylic acid phosphatase was separated from the liver deaminases. It is inhibited by NaF at 0.001*N* and has two p_{H} optima, 5—6 and 9. It is affected by an inhibitor in rabbit liver which is most active at about p_{H} 7. Inosic acid phosphatase has only the alkaline p_{H} optimum at 9. J. H. B.

Uricolysis. II. W. SCHULER (Z. physiol. Chem., 1932, 208, 237—248; cf. A., 1929, 217).—"Uric-oxidase," the enzyme responsible for the oxidation of uric acid in conversion of the latter into allantoin by the agency of uricase, was extracted from dried liver powder, but could not be further purified by the usual methods. The oxidised product, which was not isolated, is a stronger acid than uric acid, easily loses CO_2 in acid solution, eliminates urea in cone. AeOH solution, and gives the Fosse-Bossuyt reaction for allantoin. Uric acid riboside is not hydrolysed by urico-oxidase. J. H. B.

Is there a co-enzyme for urease? J. B. SUMNER and J. S. KIRK (Biochem. J., 1932, 26, 551—554).—A mixture of active and inactivated urease produces only slightly more NH_3 from urea than active urease alone. If traces of heavy metal are present urease is inactivated less readily in the presence of boiled urease than in its absence. When to cryst. or impure soya-bean urease dialysed urease is added in distilled water, the mixture possesses exactly the sum of the activity of the two components. The slightly higher activity of the second mixture observed by Onodera (A., 1916, i, 228) is due not to the function of a co-enzyme, but probably to the protection of urease against heavy metal impurities. S. S. Z.

Plasma-phosphatase. III. Clinical determination. H. D. JENNER and H. D. KAY (Brit. J. Exp. Path., 1932, 13, 22—27).—A colorimetric method requiring 1—2 c.c. is described. CH. ABS.

Inhibition of kidney-phosphatase by phosphate. E. JACOBSEN (Biochem. Z., 1932, 249, 21—38).—The velocity of hydrolysis in the system glycerophosphate, kidney-phosphatase, and $\text{PO}_4^{'''}$ and its dependence on the substrate- and inorg.- $\text{PO}_4^{'''}$ concns. are determined. The velocity of hydrolysis is chiefly determined by the separated $\text{PO}_4^{'''}$. P. W. C.

Influence of arsenate on phosphatase. M. MORII (Arb. anat. Inst. kais. Univ. Kyoto, 1931, III, C, No. 2, 23—25).—Addition of K_3AsO_4 promotes

the cleavage of glucosephosphate and glycerophosphate by takadiastase, but does not activate the synthetic action of the takaphosphatase on solutions of Na_2HPO_4 and glucose or glycerol. CH. ABS.

Behaviour of the phosphorus fractions during autolysis of organs. T. TÖRELL and B. NORBERG (Biochem. Z., 1932, 249, 53—62).—The direct P (phosphagen + $\text{PO}_4^{'''}$), residual acid-sol. P (adenosine triphosphate + hexosephosphate), phosphatide-P, and residual P (nucleic acid-P) fractions before and during slow autolysis (at 3—4°) of cat's gastric mucosa, liver, kidney, spleen, pancreas, heart, and striated muscle were determined. The direct P is increased at the expense of the residual acid-sol. P and the lipid P, but the residual P is scarcely or not affected. The high phosphatase content of the kidney and lecithase content of the pancreas are seen in the very rapid hydrolysis of their corresponding substrates. P. W. C.

Yeast and fermentation. C. R. BOND (Food Tech., 1932, 1, 389—392).—A description of the different yeasts, their requirements for growth, and their various uses is given. E. B. H.

Esterification of arsenic acid by yeast. A. E. BRAUNSTEIN and M. M. LEVITOV (Naturwiss., 1932, 20, 471).—In fermentation experiments in which AsO_4 replaced PO_4 , determination of AsO_4 , before and after acid hydrolysis, showed that up to 15% of As was in combination as hexosearsenic acid. $\text{CH}_2\text{Br}\text{CO}_2\text{H}$ inhibited the process. A. L.

Osmophilic yeasts. IV. N. KARABOLOFF and G. KRUMBHOLZ (Arch. Mikrobiol., 1931, 3, 113—121).—An organism (*Zygosaccharomyces gracilis*) isolated from incompletely fermented Portuguese wine tolerates higher sugar concns. than *Z. variabilis* and ferments glucose, fructose, maltose, and, to a small extent, galactose. Sucrose is fermented only by the crushed cells. A. G. P.

Degradation of aromatic and hydroaromatic compounds by moulds. I. Decomposition of quinic and hydroxybenzoic acids. K. BERNHAUER and H. H. WAELSCH (Biochem. Z., 1932, 249, 223—226).—A series of 28 strains of *A. niger* was grown on a medium containing quinic acid and a mixture of salts in order to follow its conversion by way of protocatechuic acid and pyrocatechol into $\text{H}_2\text{C}_2\text{O}_4$. Three strains on the 4th day gave a green colour with FeCl_3 which became red on adding Na_2CO_3 . Only one strain gave the reaction on the 6th day and none on the 7th. $\text{H}_2\text{C}_2\text{O}_4$ tests became positive on the 9th—10th day. Inositol, pyrocatechol, quinol, gallic and salicylic acids similarly gave rise to $\text{H}_2\text{C}_2\text{O}_4$. P. W. C.

Relation between $[\text{H}^+]$ and citric acid formation by *Aspergillus niger* and *Citromyces glaber*. A. FREY (Arch. Mikrobiol., 1931, 3, 158; cf. A., 1931, 1333).—Differences in optimum p_{H} for citric acid production recorded by the author and by Virtanen are not wider than might be anticipated for different strains of the fungus. A. G. P.

Influence of aluminium on the development of *Aspergillus niger*. G. LEVY (Bull. Soc. Chím. biol., 1932, 14, 745—757).—Al is not essential for the growth

of *A. niger*. Concn. of 0.005—200 mg. per litre of medium have no effect whilst a concn. of 350 mg. per litre completely inhibits growth. H. D.

Effect of associated growth on forms of lactic acid produced by certain bacteria. E. L. TATUM, W. H. PETERSON, and E. B. FRED (Biochem. J., 1932, 26, 846—852).—Lactic acid bacteria which when grown by themselves produce only *d*- or *l*-acid, produce *i*-lactic acid when grown in association with *Cl. acetobutylicum*. This effect is not obtained when the two organisms are separated by a viscous membrane. Closely related butyric acid bacteria or *S. cerevisiae* do not change the form of lactic acid.

S. S. Z.

Physiology and systematics of acetic acid bacteria. M. KREHAN (Arch. Mikrobiol., 1932, 3, 277—321).—In sugar-free asparagine media addition of salts of Na, K, Ca, and Mg markedly affects the oxidation of EtOH by *B. acetigenoides* and the growth of the organism. By this means AcOH production may be varied from zero to the max. (90% of theoretical), or the acid produced may be further oxidised to CO₂. In general, the ions Ca⁺⁺, Mg⁺⁺, H₂PO₄⁻, and Cl⁻ favour, and K⁺, Na⁺, and SO₄²⁻ retard AcOH production. At very low concns. all salts show optimum effects between 0.005 and 0.00001N. A. G. P.

Ergosterol content of certain species of mycobacterium and the effect of ergosterol on their growth. P. S. PRICKETT and O. N. MASSENGALE (J. Infect. Dis., 1931, 49, 297—302).—No ergosterol was found in 9 cultures of 6 species in 5% glycerol nutrient agar. Addition of unactivated ergosterol stimulated growth and pigment production; activated ergosterol in high concn. retarded growth but stimulated pigment production. Pathogenic strains of *M. tuberculosis* were more sensitive to activated ergosterol than non-pathogenic strains. CH. ABS.

Bacteriological action of certain synthetic organic acids toward *Mycobacterium leprae* and other acid-fast bacteria. XXI. W. M. STANLEY, G. H. COLEMAN, C. M. GREER, J. SACKS, and R. ADAMS (J. Pharm. Exp. Ther., 1932, 45, 121—162).—Of many Na salts of aliphatic monocarboxylic acids tested *in vitro* on *B. leprae* growing in 5% glycerol broth, the bactericidal action is most marked in those containing 15—18 C atoms. The presence of an ethylenic linking is not advantageous, but a branched chain or ring structure is favourable, rings of 3—6 C atoms being equally effective, provided the total mol. wt. remains approx. const. A Ph group with or without an additional ethylenic linking does not enhance the activity. Aliphatic amines containing 16—18 C atoms including a ring structure are active, but less so than the corresponding carboxylic acids. Some of the Na salts which are active against *B. leprae* in concns. of 1 in 150,000 to 1 in 200,000 are also bactericidal to *B. tuberculosis*, but only in concns. at least 3 times as great. The bactericidal activity is probably chiefly dependent on the physical properties of the acids and in particular is correlated with the power of the Na salts to lower the surface tension of aq. solutions. W. O. K.

3 N

Chemical and biological properties of the phosphatide from the tubercle bacillus. C. H. BOISSEVAIN and C. T. RYDER (Amer. Rev. Tuberculosis, 1931, 24, 751—756).—The separation of Anderson's phosphatide A3 from bacteria and bacterial debris is described. Intraperitoneal injection of the purified phosphatide does not cause the formation of tuberculous tissue or the appearance of cutaneous hypersensitiveness. The tissue reaction to phthioic acid is a foreign-body reaction. CH. ABS.

Bacterial derivatives. XV. Changes in chemical and biological properties of human tubercle bacillus polysaccharide MB-200 produced by mild acid hydrolysis. K. L. McALPINE and P. MASUCCI. XVI. Differential chemical changes accompanying the growth of human tubercle bacillus H 37 and bovine tubercle bacillus 523 grown on Long's synthetic medium. P. MASUCCI, K. L. McALPINE, and J. T. GLENN (Amer. Rev. Tuberculosis, 1931, 24, 729—736, 737—745).—XV. A fraction insol. in EtOH contained much mannose with little free reducing sugar; one sol. in EtOH contained most of the arabinose and much free reducing sugar. Destruction of the precipitin titre is more rapid than the cleavage of the polysaccharide into simple sugars.

XVI. Substances which react with human tubercle bacillus bacillary serum and produce a ppt. appear in the medium. Quant. differences in precipitin titre are discussed. A quant. measure of the pentose radical is an index of the precipitin titre. Some of the pentose in the bovine filtrate is probably free.

CH. ABS.

Oxygen optimum and media for "aerobic" bacteria. H. ZYCHA (Arch. Mikrobiol., 1932, 3, 194—204).—In certain media of low nutrient content, nodule bacteria and also *B. prodigiosus* exhibit a growth optimum at O₂ tensions less than atm. For such organisms the term "meso-aerobe" instead of "facultative anaerobe" is suggested. A. G. P.

Metabolic studies of streptococci. M. A. FARRELL and S. THOMAS (J. Infect. Dis., 1932, 50, 134—142).—N as NH₄, asparagine, or uric acid did not stimulate or support the growth of *S. rheumaticus*. When rhamnose, fructose, or galactose was added to a non-protein source of N growth was secured to the third transplant. Some NH₂-acids were antagonistic to growth. Glucose lessens the antagonistic action of tyrosine, tryptophan, and phenylalanine.

CH. ABS.

Nitrogen fixation by *Leguminosae*. I. Nitrogen fixation studies of *Rhizobia* apart from the host plant. P. W. WILSON, E. W. HOPKINS, and E. B. FRED (Arch. Mikrobiol., 1932, 3, 322—340).—No evidence was obtained of the fixation of N by nodule bacteria apart from the host plant, whether grown in pure culture or in association with other organisms or with respiring plant-tissue. Stimulatory effects of Mn on the organism were not confirmed.

A. G. P.

Bacteriophage and the root nodule bacteria. D. G. LARSD (Arch. Mikrobiol., 1932, 3, 159—193).—The bacteriophage is not sp. to one strain or species of *Rhizobium*. The optimum *p_H* is 7.6—8.0. Gum

produced by the bacteria inhibits bacteriolysis. Mannitol favours both gum formation and acid production. A. G. P.

Morphology and physiology of the purple and green sulphur bacteria. C. B. VAN NIEL (Arch. Mikrobiol., 1931, 3, 1—112).—In the media used the development of these organisms is dependent on the concn. of H_2S , $NaHCO_3$, and H^+ . In many cases the proportion of undissociated H_2S determines whether or not particular species can develop. The metabolism of the organisms is a true photosynthetic process, probably of the type $CO_2 + 2H_2S = CH_2O + H_2O + 2S$. Green S bacteria produce S only, but the purple species under favourable conditions oxidise H_2S , S, $S_2O_3^{2-}$, and SO_3^{2-} completely to SO_4^{2-} . This oxidation is associated with an equiv. reduction of CO_2 . In the absence of oxidisable S compounds the purple organism develops under anaerobic conditions in presence of org. matter provided it receives radiant energy. No growth occurs in presence of O_2 or in the dark. A. G. P.

Pigment related to prodigiosin in a pathogenic actinomyces. A. SARTORY, R. SARTORY, J. MEYER, and M. ANTONIOLI (Compt. rend., 1932, 194, 2339—2340).—The pigment isolated from *A. Allenbachii* by treatment of the cultures with 95% aq. EtOH, pptn. with H_2O , and extraction with Et_2O shows colour changes with aq. NH_3 and 0.1N-NaOH identical with those given by prodigiosin, and gives three absorption bands with max. at 5280, 4960, and 4700 Å. A. L.

Production of fluorescence by phytopathogenic bacteria. F. LABROUSSE (Compt. rend., 1932, 194, 2173—2175).—*B. tabacum* and *B. medicaginis* (var. *phaseolicola*) when grown on a beef extract medium give rise to a definite fluorescence, but only when Mg and phosphate are present. W. O. K.

Significance of accessory nutrients for the typhus-coli group. SUMOTO (Arch. Hyg., 1931, 106, 185—196; Chem. Zentr., 1932, i, 1111).—Growth is favoured by Na citrate, fructose, and EtOH as well as by lemon juice and an Et_2O extract of lemon peel; sp. activity of accessory materials is unlikely. A. A. E.

Quantitative basis of the specific precipitin reaction. T. J. KUROCHKIN and C. O. KRATZ (Chinese Med. J., 1932, 46, 387—403).—The reaction between the sp. carbohydrate antigen of *Monilia tropicalis* and its antigen (serum of rabbits immunised with killed *M. tropicalis*) has been followed quantitatively by determining the amount of carbohydrate left uncombined when a given concn. of carbohydrate is mixed with a given concn. of antibody. Over a certain range the results are expressed by the usual adsorption formula. W. O. K.

Immunological reactions between dextran polysaccharide and some bacterial antisera. J. ZOZAYA (J. Exp. Med., 1932, 55, 353—360).—Dextran, produced from sucrose by *Leuconostoc mesenteroides*, reacts immunologically with antisera from pneumococci, some species of *Salmonella*, and some types of *Streptococcus viridans* (Bargen). The existence of a distinct antibody produced by an active group of

the sp. bacterial polysaccharide, which is similar to or identical with that of the dextran polysaccharide, is suggested. CH. ABS.

Carbohydrate and protein fractions of meningococci. J. ZOZAYA and J. E. WOOD (J. Infect. Dis., 1932, 50, 177—184).—The polysaccharide and "nucleoprotein" obtained from meningococci, gonococci, and *N. catarrhalis* have similar immunological properties and are not type sp. There is no parallelism between the agglutination test and the polysaccharide precipitin test. CH. ABS.

Standardisation of antimeningococcic serum by the polysaccharide precipitin test. J. ZOZAYA (J. Infect. Dis., 1932, 50, 310—314). CH. ABS.

Factors affecting the yield of specific enzyme in cultures of the bacillus decomposing the capsular polysaccharide of type III pneumococcus. R. DUBOS (J. Exp. Med., 1932, 55, 377—391).—An improved method of prep. and concn. is described. CH. ABS.

Precipitin reaction. Determination of small quantities of a specific polysaccharide. M. HEIDELBERGER and F. E. KENDALL (J. Exp. Med., 1932, 55, 555—561).—A method for the micro-determination of the sp. polysaccharide of type III pneumococcus is based on the precipitin reaction. CH. ABS.

Carbohydrates adsorbed on colloids as antigens. J. ZOZAYA (J. Exp. Med., 1932, 55, 325—351).—Polysaccharides of *B. anthracis*, meningococcus, *S. viridans* (Bargen), *B. proteus*, *S. morgani*, *B. dysenteriae* (Shiga and Hiss), and pneumococcus can be rendered antigenic by adsorption on a colloid carrier. Dextran was also rendered antigenic by the adsorption method. CH. ABS.

Separation of antibodies from serum-proteins. Protein-free antibody. M. FRANKEL (Proc. Roy. Soc., 1932, B, 111, 165—174).—The serum is treated with kaolin on which all the antibody and the whole or part of the proteins are adsorbed. The complex is eluted with a 2% solution of glycine in aq. NaCl. From diphtheria antitoxin and antityphoid serum were obtained protein-free solutions containing 12—24% of the antitoxin. Ultrafiltration of antityphoid sera under pressure also yields protein-free, serologically-active fluids which, however, contain only 3—6% of the original flagellar agglutinin titre. With typhoid agglutinin the antibody can be freed from glycine and NaCl by dialysis without loss of activity. The antibody is colloidal, may be dried at room temp. and redissolved without loss of activity, contains traces of Et_2O -sol. material not associated with its serological properties, and is not affected by proteolytic enzymes. F. O. H.

Germicidal activity of aromatic sulphides. E. MONESS, W. BRAKER, and W. G. CHRISTIANSEN.—See this vol., 844.

Active principle in hog's stomach effective in pernicious anaemia. J. F. WILKINSON and L. KLEIN (Lancet, 1932, 222, 719—721).—Active extracts were obtained only when fresh stomach tissue was subjected to high pressure. EtOH pptd. from these extracts the whole of the active principle, which

appears to be enzymic in nature and is probably not identical with that present in liver. L. S. T.

Does adrenaline affect the diffusion of lactate ions in [frog's] muscles? W. M. VESSELKINA (Z. ges. exp. Med., 1931, 79, 630—634; Chem. Zentr., 1932, i, 698).—Adrenaline increases the amount of lactic acid which separates from muscles immersed in Ringer's solution and decreases that withdrawn by muscles immersed in a similar solution containing Na lactate. It increases the decomp. of glycogen in muscle. L. S. T.

Blood-sugar response to adrenaline in thyroid-fed animals. A. J. ABBOTT and F. W. VAN BUSKIRK (Amer. J. Med. Sci., 1931, 182, 610—626).—Feeding 2.55 g. of desiccated thyroid to a rabbit resulted in progressive loss of body-wt., decrease in the hyperglycemic response to adrenaline, and an absence of hyperglycemic response with fatal hypoglycemic response to adrenaline when the liver-glycogen was apparently depleted. No decrease in hyperglycemic response was observed with cats or dogs. CH. ABS.

Adrenaline blood-sugar curve during fatigue and the potassium: calcium ratio. F. V. MADON and S. GOLDBERGER (Atti R. Accad. Lincei, 1932, [vi], 15, 301—304).—Experiments on four individuals show that fatigue causes an increase of 15—20% in the K content of the blood, whereas the Ca content remains unchanged. The effect of fatigue on the action of adrenaline on blood-pressure varies irregularly and with the individual. Blood-sugar is always less after labour than during rest. T. H. P.

Effect of adrenaline on blood-iodine. A. SCHITTENHELM and B. EISLER (Klin. Woch., 1931, 11, 9; Chem. Zentr., 1932, i, 698).—Normally, or in myxoedema or vegetative stigmata the blood-I rises, but in exophthalmic goitre it falls, after injection of adrenaline. A. A. E.

Thyroxine and the central nervous system. A. SCHITTENHELM and B. EISLER (Klin. Woch., 1931, 11, 9—10; Chem. Zentr., 1932, i, 698).—The I content of the tuber cinereum but not of other parts of the central nervous system is increased by thyroxine injections. Removal of the thyroid lowers the I content of the tuber cinereum, but not of other parts of the brain. L. S. T.

Effect of thyroid preparations on biochemical changes in the muscles and liver of axolotls. S. VINOKUROV and S. ERSTEIN (Z. ges. exp. Med., 1931, 79, 747—751; Chem. Zentr., 1932, i, 698).—In muscles the total N, the inorg. and sol. P are unchanged, the non-protein-N is increased, and the $P_2O_7^{4-}$ markedly decreased by the action of thyroid preps. Liver-glycogen is diminished. L. S. T.

Comparison of the assay of total extracts of posterior pituitary gland by the isolated guinea-pig uterus method with that by the inhibition of diuresis in dogs, rats, and mice. S. GLAUBACH and H. MOLITOR (Arch. exp. Path. Pharm., 1932, 166, 243—264).—The assay of preps. of the posterior pituitary lobe can be performed as accurately by the inhibition of diuresis in the dog, rat, or mouse as by the uterus method. Subcutaneous injection of solu-

tions of proteins derived from muscle or thymus gland increases the sensitivity of some animals and decreases that of others. F. O. H.

Metabolism of animals on a carbohydrate-free diet. IV. Effect of pitressin and pitocin on the distribution of fat and glycogen in the liver and muscles of albino rats. A. HYND and D. L. ROTTER (Biochem. J., 1932, 26, 578—585).—There were no significant changes in the case of pitocin whether the animals were on carbohydrate-rich or carbohydrate-free diet. There were changes more striking with carbohydrate-fed rats when pitressin was injected. Slight hyperglycemia was accompanied by a fall in liver-glycogen, a rise in muscle-glycogen, and a simultaneous infiltration of fat into the liver. As the liver-fat content increased the I val. of the fat fell correspondingly. The liver-fat reached a max. at the 5th—7th hr. when the liver-glycogen was at a min. and the muscle-glycogen increasing. The liver-glycogen reached a max. about the 17th hr., at which time the liver-fat had returned to normal. S. S. Z.

Effect of an acid extract of anterior pituitary on the iodine concentration of blood and thyroid gland. K. CLOSS, L. LOEB, and E. M. MACKAY (J. Biol. Chem., 1932, 96, 585—592).—Injection of acid extracts of the anterior lobe of the pituitary gland into guinea-pigs produces hypertrophy of the thyroid gland and an increased basal metabolism. The distribution of org. I (i.e., EtOH-insol. or protein-I) in the animals is changed, the org. I of the blood increasing at the expense of that of the thyroid. The bearing of these results on Graves' disease in man is discussed. F. O. H.

Determination of [anterior pituitary] hormone in blood. H. O. NEUMANN and F. PETER (Klin. Woch., 1931, 10, 2086; Chem. Zentr., 1932, i, 697).—Blood is collected in Na citrate, extracted with Et_2O , the hormone pptd. with EtOH, and the ppt. dissolved in H_2O . L. S. T.

Occurrence of pituitary hormones in the urine in conditions unassociated with pregnancy. T. N. A. JEFFCOATE (Lancet, 1932, 222, 662—665).—Prolan A has been found at the menopause, after castration, and in some cases of malignant disease. Prolan B can occasionally be found in the urine of non-pregnant women, but only when living chorionic elements are present in the body. L. S. T.

Gonadotropic hormones from normal urine and urine of pregnancy. C. FUNK and P. ZEFIROV (Biochem. J., 1932, 26, 619—621).—The hormone is pptd. from the urine with quinine or benzoic acid. The ppt. is then extracted with H_2O and the solution purified by fractionation with EtOH of varying concn. and finally by fractional evaporation and separation of impurities in vac. at low temp. Five doses of 8×10^6 g. of the semi-cryst. prep. injected into rats caused a threefold increase in wt. of seminal vesicles and two-fold of the uteri. The simultaneous administration of this hormone and andronin (male sex hormone) to capons evokes less response than that of andronin alone, injections of the gonad-stimulating principle having no effect. Combined

administration of the two hormones to infantile rats showed less response than that of each substance separately. S. S. Z.

Metabolically-active extract of the ovary. K. KAUFFMANN, C. MÜLLER, and O. MÜHLBOCK (Klin. Woch., 1931, 11, 14—18; Chem. Zentr., 1932, i, 696—697).—Extracts from follicular fluid accelerate development and check growth in frog's larva. The extracts were free from sex hormones which have no such effect. Extracts from the whole ovary did not give the metabolically active material. L. S. T.

Chemistry of insulin. J. JENSEN (Science, 1932, 75, 614—618).—Mainly a summary of previous work. The actions of acids and alkalis on insulin support the view that the characteristic constituent of the insulin mol. is composed, wholly or partly, of glutamic acid and cystine. L. S. T.

Effect of insulin on the formation of blood-albumin and the influence of administration of carbohydrate and caffeine. M. TAUBENHAUS and S. ROSENZWEIG (Z. klin. Med., 1931, 118, 719—735; Chem. Zentr., 1932, i, 699).—Insulin increases the total albumin in human blood resulting from a marked increase in globulin. The ratio albumin : globulin falls markedly. Administration of carbohydrate or injection of caffeine before or at max. hypoglycæmia diminishes this increase in globulin, keeping the blood-sugar unchanged. L. S. T.

International vitamin standards. MEDICAL RESEARCH COUNCIL (Pharm. J., 1932, 129, 5).—The international standard preps. are described and the international units are defined as (i) the vitamin-A activity of 10^{-6} g. of the standard prep. of carotene, (ii) for vitamin-B₁ the antineuritic activity of 10 mg. of the standard prep. adsorbed on kaolin, (iii) for vitamin-C the antiscorbutic activity of 0.1 c.c. of fresh lemon juice, and (iv) the vitamin-D activity of 1 mg. of the standard solution of irradiated ergosterol. R. K. C.

Stock diet for rats bred for vitamin tests. K. H. COWARD, M. R. CAMDEN, and E. M. LEE (Biochem. J., 1932, 26, 679—690).—Diets suitable in some laboratories were not satisfactory when prepared from the same recipe, but necessarily of materials from different sources. A description of a new diet which is satisfactory for at least 2 generations is given. Reproduction but not the growth of the young rats shows a seasonal variation on this diet. Fluctuations in the degree of rickets appear to be correlated with the source of dried milk. S. S. Z.

Photochemistry of vitamins-A, -B, -C, -D. I. M. HEHLBRON and R. A. MORTON (Nature, 1932, 129, 866—867).—A crit. discussion. L. S. T.

Photochemistry of vitamins-A, -B, -C, -D. F. P. BOWDEN and C. P. SNOW (Nature, 1932, 129, 943).—A reply to criticism (preceding abstract). L. S. T.

Variations in growth response of rats in vitamin-A tests compared with the variation in rats growing normally. K. H. COWARD (Biochem. J., 1932, 26, 691—703).—A comparative statistical analysis of the records of many rats in each of the above groups. S. S. Z.

Oxidation of vitamin-A in vitro. Influence of the solvent. W. J. DANN (Biochem. J., 1932, 26, 666—678).—Vitamin-A in a cod-liver oil concentrate was destroyed by aeration at high temp. more rapidly in some solvents than in others. It is particularly stable in EtOH, EtOH-KOH, and EtOAc. In EtOH it is also stable towards H₂O₂. S. S. Z.

Determination of vitamin-A. G. FRANCKE (Biochem. Z., 1932, 249, 48—52).—Standardised rats should be used. P. W. C.

Relative vitamin-A and -D content of different samples of cod-liver oil. K. H. COWARD (Pharm. J., 1932, 129, 4).—Blue vals. and vitamin-A and -D potencies of 44 samples of cod-liver oil are given. The blue val. is only an approx. measure of vitamin-A potency. There is no correlation between vitamin-A and -D potencies and no estimate of vitamin-D potency can be made from blue vals. R. K. C.

Content of vitamin-A in commercial preparations. K. SCHÜBEL and W. GEHLEN (Arch. exp. Path. Pharm., 1932, 166, 354—365). F. O. H.

Chemical methods for determination of vitamins. I. The Bezssonoff reaction. F. V. von HAHN and M. WIEBEN (Z. Unters. Lebensm., 1932, 63, 481—495).—A historical survey of the reaction is given. The intensity of the colour produced does not necessarily agree with the vitamin content determined by feeding experiments on animals. The same intensity of colour was produced in cases where the vitamin content was negligible and where the activity was high. E. B. H.

Physiology of vitamins. XIX. Acid-base balance of the blood during lack of undifferentiated vitamin-B. XX. Glucose tolerance during lack of undifferentiated vitamin-B. E. BURACE and G. R. COWGILL (J. Biol. Chem., 1932, 96, 673—684, 685—696).—XIX. No marked variations occur in the serum-electrolyte concns. of dogs fed on a diet deficient in the vitamin-B complex, if the appetite is maintained. When inanition accompanies B-deficiency a slight acidosis occurs. This may be due to increased blood-lactic acid caused by polyneuritic convulsions, but cannot be ascribed definitely to fasting or lack of the vitamin.

XX. The glucose tolerance of dogs was determined by following the blood-sugar curve after glucose injection. Glucose tolerance decreases (increased blood-sugar and delayed removal) in vitamin-B-deficient dogs, but this is dependent on the extent of fasting, which was controlled. A sp. influence of vitamin-B on carbohydrate metabolism has not been demonstrated. A. C.

Hexuronic acid as the antiscorbutic factor. A. SZENT-GYÖRGYI (Nature, 1932, 129, 943).—The results previously described (this vol., 548), and now confirmed, leave no doubt of the antiscorbutic activity and the vitamin nature of the hexuronic acid. L. S. T.

Chemical nature of vitamin-C. J. L. SVIRBELY and A. SZENT-GYÖRGYI (Biochem. J., 1932, 26, 865—870).—Guinea-pigs have been completely protected from scurvy for 90 days by the administration

of 1 mg. daily of hexuronic acid. Vitamin-C is therefore a single substance and identical with hexuronic acid. S. S. Z.

Hexuronic acid as the antiscorbutic factor. S. S. ZILVA (Nature, 1932, 129, 943; cf. this vol., 657).—Guinea-pigs receiving daily 1 mg. of Szent-Gyorgyi's cryst. hexuronic acid from adrenal glands showed no macroscopic signs of scurvy after 55 days and increased in wt. regularly for the first 40 days. Although the results confirm those of Svrbely and Szent-Gyorgyi (this vol., 548) and show the presence of the antiscorbutic factor in this prep., they do not afford sufficient evidence of the identity of hexuronic acid with the antiscorbutic factor. L. S. T.

Antiscorbutic fraction of lemon juice. X. S. W. JOHNSON and S. S. ZILVA (Biochem. J., 1932, 26, 871—888).—The substance (or substances) responsible for the acceleration of the inactivation of the reducing principle and of vitamin-C in neutral autoclaved decitrated lemon juice is most probably related to pyrocatechol and is formed from the sugars of the juice during the process of autoclaving. On autoclaving decitrated lemon juice or solutions containing the same concn. of sugars, a substance is produced which is capable of oxidising $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ but not guaiacum or benzidine. Pyrocatechol and quinol do not destroy the reducing principle of lemon juice in the absence of an enzymic factor, whilst benzoquinone and the ethereal extracts from autoclaved lemon juice or sugars do so unaided. S. S. Z.

Vitamin-C content of sheep-liver with observations on the effects of freezing and storage. J. I. MILLS (Biochem. J., 1932, 26, 704—711).—About 3 g. of liver are equiv. to 1 g. of cabbage in antiscorbutic potency. Freezing and thawing of liver diminishes its vitamin-C considerably and a further loss is incurred on storage at -19° for 6 months. S. S. Z.

Experimental scurvy. XII. [Total] sulphur metabolism of guinea-pigs on a vitamin-C-free diet. XIII. [Detailed] sulphur metabolism of guinea-pigs on a vitamin-C-free diet. S. OHATA (J. Biochem. Japan, 1932, 15, 285—299, 301—310).—XII. The total S contents of various organs, faeces, and urine are not significantly different in normal and scorbutic animals.

XIII. The distribution of S in the urine of normal and scorbutic guinea-pigs is investigated. With scurvy the neutral S fraction is increased, whilst the ethereal- SO_4 fraction is decreased. F. O. H.

Influence of a diet deficient in vitamins-C and -D on the Ca : PO_4 ratio of serum in rats and guinea-pigs. H. VON EULER and M. RYDBOM (Biochem. Z., 1932, 249, 141—150).—The Ca : PO_4 ratio for serum of normal rats (0.28) is somewhat lower than for normal guinea-pigs (0.39—0.43), but in rachitic rats (0.35) corresponds approx. with that for scorbutic guinea-pigs (0.30—0.30). P. W. C.

Production of vitamin-D in a glow discharge. F. A. ASKEW, R. B. BOURDILLON, and T. A. WEBSTER (Biochem. J., 1932, 26, 814).—Vitamin-D can be produced in a glow discharge, but the yield per unit of

electrical energy is much smaller than that obtained with a Hg-vapour lamp. S. S. Z.

Formation of vitamin-D in dried beer-yeast by ultra-violet radiation. K. SCHÜBEL and W. GEBLEN (Arch. exp. Path. Pharm., 1932, 166, 348—353).—Ultra-violet irradiation of medicinal yeast (D.A.B. VI) yields a product rich in vitamin-D. The optimum wave-length is approx. 300 m μ , when the product may contain 40 clinical units per g. Such preps. retain their activity unchanged for 3 years. F. O. H.

Mode of action of vitamin-D. The parathyroid theory; clinical hypervitaminosis. L. J. HARRIS (Lancet, 1932, 222, 1031—1038; cf. A., 1931, 659).—Vitamin-D acts by permitting increased net absorption of Ca or phosphate from the gut, and tending to raise the level of blood-Ca or phosphate. The latter rise results in increased calcification in sites provided with the calcifying enzyme phosphatase. The parathyroid hormone raises the blood-Ca level by draining mineral matter from bone and not by increased net absorption from the gut. The view that vitamin-D acts normally by stimulation of the parathyroid cannot be accepted. The ill-effects on hypervitaminosis are the same in man as in experimental animals, and in the former the toxic overdose of irradiated ergosterol is not far removed from the optimal curative dose. L. S. T.

Vitamin-D content of the fat of sea perch, porpoise, and seal. S. N. MATZKO and D. A. VITAL (Z. Unters. Lebensm., 1932, 63, 495—498).—The vitamin-D contents were 100—150 units per g., <50 per g., and negligible, respectively. E. B. H.

Germination. Evolution of fatty substances and phospholipins in the early stages of development of *Lupinus albus*. A. HÉE and L. BAYLE (Bull. Soc. Chim. biol., 1932, 14, 758—782).—The lecithins of the seed grown on H_2O both in the dark and when exposed to light are largely utilised during germination for the building up of the young plant. H. D.

Biocatalysts in germination. H. VON EULER, T. PHILIPSON, and D. BURSTRÖM (Z. physiol. Chem., 1932, 208, 281—284).—The factor Z stimulating fermentation by living yeast is contained in the husks and cotyledons of barley and in leguminous seeds. J. H. B.

Presence of a growth-promoting substance in *Boletus edulis*. N. NIELSEN (Biochem. Z., 1932, 249, 196—198).—The fruit bodies of *B. edulis* do, but of the mushroom, *Psalliota campestris*, do not, contain a substance which promotes the growth of the coleoptile of *Avena*. P. W. C.

Catalase in seeds. J. STEPHAN (Jahrb. wiss. Bot., 1932, 75, 771—808).—Determinations of catalase activity by the iodometric and KMnO_4 methods give similar vals. both for shaken and unshaken preps. The manometric is preferable to the eudiometric method. The decomp. of H_2O_2 is largely dependent on the rate at which the mixture is shaken. A modification of the Nemeš-Duchon catalasometer is described. In the examination of seed materials admixture with a buffer solution before treatment with H_2O_2 is recommended. A given quantity of the

enzyme decomposes a definite amount of H_2O_2 . No simple relationship exists between the rate of decomp. of H_2O_2 and the ratio of catalase to H_2O_2 present. The reaction rate corresponds with that of a bimol. reaction only when carried out at 10° . A. G. P.

Comparative variations of some carbohydrates in *Potentilla reptans* and *P. verna*. P. GILLOT and H. WIOLAND (Bull. Soc. Chim. biol., 1932, 14, 822—831).—The stems and roots were analysed during growth and the initial reducing sugars, the sugars hydrolysable by diastase, the starchy matter, and the glucosides hydrolysable by emulsin were determined. H. D.

Metabolic physiology of green algae. II. Action of iron, zinc, and copper salts. M. ROBERG (Jahrb. wiss. Bot., 1932, 76, 311—332).—Zn stimulates in concns. up to 0.001 mg. per c.c., and is toxic at 0.05 mg. per 100 c.c. Cu stimulates slightly at very small concns. only. Toxicity is associated particularly with autotrophic and stimulation with heterotrophic and mixotrophic conditions. A. G. P.

Gas content of the cenobia of *Rivularia polyotis* (J. Ag.), Hauck. Z. DANIN (Atti R. Accad. Lincei, 1932, [vi], 15, 317—322).—The gases secreted in these cavities, like those formed in the corresponding cavities of brown and green algae, contain O_2 , which increases with the light intensity to 70%. T. H. P.

Life history of the *Xanthoria* fungi. H. BARTUSCH (Arch. Mikrobiol., 1931, 3, 122—157).—Variations in the pigmentation of *X. parietina* are attributed to the extent of pptn. of parietin. This lichen-acid is best detected by the blood-red coloration produced with $Ca(OH)_2$ or $Ba(OH)_2$. The acid is sol. in H_2SO_4 , NaOH, or KOH yielding red solutions. Micro-sublimation methods are also applicable. The intensity of coloration of the thallus depends on the no. and size of the crystals formed. A. G. P.

Liberation of hydrogen cyanide by certain fungi. M. MIRANDE (Compt. rend., 1932, 194, 2324—2326).—The secretion of HCN by *M. oreades* is localised at points midway up and on both sides of the lamellae. The carpophores, killed by boiling in H_2O , liberate HCN again on further treatment with boiling H_2O . A. L.

Hydrocyanic acid in sorghum, Sudan grass, and some hybrids. H. FINNEMORE and C. B. COX (J. Proc. Roy. Soc. New South Wales, 1931, 65, 145—152).—In all cases the HCN content is greatest in young seedlings and gradually disappears, but may persist for 130 days. The HCN content of air-dried material varies from 10 to 160 mg. per 100 g. P. G. M.

Biological decomposition of plant materials. VII. Nature of the residual hemicelluloses of rotted straw. A. G. NORMAN (Biochem. J., 1932, 26, 573—577).—Only 2 g. of hemicellulose were recovered at the close of 9 months' fermentation from 1 kg. of dry straw containing originally 230 g. of hemicellulose. There was no indication of variation in biological availability of hemicellulose or the accumulation of less available groupings. A H_2O -sol. polysaccharide containing 33% of uronic acid

anhydride, 66% of hexosan, and glucose units was isolated from the products of fermentation. S. S. Z.

Lignins from cereal straws. I. Isolation and fractionation of lignin from oat and wheat straw. L. MARION (Canad. J. Res., 1932, 6, 521—531).—Lignins isolated from oat and wheat straw by means of the Mo ether of ethylene glycol (I) and conc. HCl have been fractionated into 5 components by means of various solvents. The main fraction, sol. in $COMe_2$, isolated from oat-straw lignin has the same properties, OMe content, and composition as the corresponding fraction isolated from wheat-straw lignin. The components fractionated are compounds of lignins with (I); lignins isolated by means of unmethylated solvents (e.g., 1:4-dioxan) have lower OMe vals. The lignins isolated from other types of plants by the same method have different properties and composition from those of the straw lignins. E. S. H.

Chemical composition of the periwinkle (*Vinca minor*, L.). F. RUTISHAUSER (Compt. rend., 1932, 195, 75—77).—Addition of $Pb(OAc)_2$ to an extract of periwinkle yields a brown ppt. After removal of Pb from this a yellow laevorotatory product is obtained by fractional pptn. with EtOH. Alkaline hydrolysis of this yields protocatechuic acid; acid hydrolysis gives a product which, on dry distillation or alkali fusion, yields pyrocatechol. An amorphous laevorotatory glucoside (*vincoside*) is also obtained by acid hydrolysis (1.7 g. per kg. fresh tissue). P. G. M.

Toxic constituent of the seeds of *Tephrosia vogelii*. K. W. MERZ (Arch. Pharm., 1932, 270, 362—363).—Tephrosin, dehydrodeguelin, and deguelin have been isolated. R. S. C.

Chemical constituents of tobacco. II. Glucosides of tobacco leaf. I. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1932, 8, 1—3).—*Tabacolinin*, m.p. 227° (decomp.; brown at 175°), and *tabacilin* are isolated from Japanese tobacco leaves by extraction with hot 95% EtOH in presence of $CaCO_3$ and separated by pptn. with $Pb(OAc)_2$. On hydrolysis with dil. aq. H_2SO_4 in EtOH the former gives glycuronic acid and a yellow, cryst. *aglucone*, and the latter glucose, nicotine, and other products. H. A. P.

Essential oil in desert plants. II. Oil of *Chrysothamnus nauseosus*. M. ADAMS and L. KEHOE (J. Amer. Chem. Soc., 1932, 54, 2448—2451; cf. B., 1928, 106).—The essential oil of *C. nauseosus* contains about 3% of β -pinene, 30—40% of limonene and dipentene, 2% of cuminaldehyde, and 20% of sesquiterpenes. The occurrence of dipentene and caoutchouc in *Chrysothamnus* suggests that one may be a metabolic product of the other. C. J. W. (b)

Phytosterols: sterols of grape-seed oil. C. ANTONIANI and F. ZANELLI (Atti R. Acad. Lincei, 1932, [vi], 15, 284—286).—Acetylation and bromination by Windeus' method of the crude sterol of grape-seed oil yields only one sol. bromoacetyl derivative, the presence of stigmasterol or analogous sterols being thus excluded. The product is accompanied by a compound which, on fractional crystallisation (and debromination) from EtOH, gives a substance, m.p. 93 — 94° . The sterol appears to be mostly

sitosterol, with a small proportion of a dextrorotatory sterol.

T. H. P.

Composition of asarum oil. V. BRUCKNER and T. SZÉKI (J. pr. Chem., 1932, [ii], 134, 107—140).—The essential oil of *A. Europaeum* contains a terpene, b.p. 62.5°/23 mm. (1—2%); it is doubtful whether this is l-pinene as stated in A., 1888, 680), l-bornyl acetate (12—15%), a tricyclic (?) sesquiterpene, b.p. 78°/3 mm. (10—12%), methyleugenol (15—20%); or methylisoeugenol (?), asarone (30—35%), asaraldehyde (2—3%), and resins (10—12%). The presence of l-bornyl acetate depends on the source of the oil.

H. A. P.

Fumaric acid in the micro-sublimate from *Cetraria islandica*. I. KOFLER and H. RATZ (Arch. Pharm., 1932, 270, 338—340).—The sublimate is mainly fumaric and not lichestic acid (cf. A., 1914, ii, 153).

R. S. C.

Proteins of ragweed pollens. C. A. JOHNSON and B. Z. RAPPAPORT (J. Infect. Dis., 1932, 50, 290—309).—Giant ragweed pollen contains at least two antigens: possibly a globulin and an albumin. The pollen proteins of the giant and common ragweed and of *Iva xanthifolia*, *Ambrosia bidentata*, *Xanthium canadense*, *Franeria tenuifolia*, *A. psyllostachya*, and *F. acanthicarpa* are antigenically related. Dialysis of pollen extracts involves loss of protein, both fractions being active. The carbohydrates and crude fibre were clinically relatively inert; a lipid fraction contained 0.2—0.3% N. The active principle of ragweed pollen is probably of protein nature or clings to a protein moiety.

CH. ABS.

Alkaloids of *Leontica Eversmanii*, Bge. I. A. OREKHOV and R. KONOVALOVA (Arch. Pharm., 1932, 270, 329—334).—The nodules of *L. Eversmanii* contain leontamine (I), $C_{14}H_{26}N_2$, b.p. 118—119° [(?) dihydrochloride; dichloroplatinate, m.p. 248° (decomp.); dipicrate, m.p. 194—195°; dimethiodide, m.p. 265—268°], and leontidine (II), m.p. 116—118° [hydrochloride, m.p. 293° (decomp.) after sintering at 280°; chloroplatinate, m.p. 258—259° (decomp.)]. (I) is stable to $KMnO_4$ and is not reduced catalytically; it thus contains four saturated rings. The ratio N:Cl in the hydrochloride of (II) is 1:2.

R. S. C.

[Constituents of] root-bark of *Plumbago rosea*, L. M. C. T. KATTI and V. N. PATWARDHAN (J. Indian Inst. Sci., 1932, 15A, 9—15).—Fractional solvation of the material extracted by 90% aq. EtOH from the root-bark of *P. rosea* (chitramul) yields plumbagin, sitosterol (the properties of which support the theory that the sterol exists in three isomeric forms), a fatty alcohol (arachidyl?), oleic, linoleic, and lignoceric (?) acids, sitosterol glucoside, $C_{33}H_{56}O_6$, m.p. 259—260°, a saturated hydrocarbon, m.p. 77—78°, and glucose. Plumbagin, m.p. 75—76°, $C_{11}H_8O_3$ (cf. A., 1928, 1249, 1376), yields a CO_2Et -derivative, m.p. 108—109°, and, when treated in EtOH solution with Br, a Br-derivative, m.p. 172—173°, containing 44.4% Br. The min. lethal dose of plumbagin for rats is 110—120 mg. per kg. body-wt. when administered subcutaneously and approx. 20 and 35 mg. for guinea-pigs and frogs respectively. F. O. H.

Bog-moss. I. Composition of *Sphagnum fimbriatum*, Wils. M. SHIKATA and M. WATANABE (Mem. Coll. Agric. Kyoto, 1932, 22, 1—6).—A sample of *S. fimbriatum* from fresh Japanese tundra peat contained H_2O 19.6%, lignin 1.5%, ash 3.2%, pentosans 11.9%, galactosan 1.6%, protein 0.9%, and mannan trace. Vals. for the cellulose content varied from 30.4% (alkali-insol. residue) to 48.5% (chlorination method); the former is regarded as more probable (α -cellulose 8.8%). Both the cellulose and lignin differ in properties from those of wood.

H. A. P.

Biochemistry of the autumn fall of the leaf. S. KOMATSU and S. OZAWA (Mem. Coll. Sci. Kyoto, 1932, A, 15, 57—65).—Determinations have been made of the H_2O , ash, Et_2O -sol. matter, N, chlorophyll, carbohydrate, and crude fibre content of the leaves of the *Ginkgo biloba*, and of the pH of the sap expressed from the leaves between June and November. At the end of summer the cell-sap becomes more acid and the ratio of H_2O -sol. to H_2O -insol. N decreases, but in autumn the sol. N increases and the acidity falls sharply. The H_2O content of the leaves increases continuously until just before they fall, when it decreases suddenly. As the content of reducing sugars follows the H_2O content it is suggested that the latter plays an important part in the hydrolysis of polysaccharides. The non-reducing sol. sugars are converted into crude fibre during the summer and both the crude fibre and ash contents of the leaves increase with age. It is suggested that the most important function of the autumn leaf-fall is to enable the plant to eliminate inorg. materials the accumulation of which interferes with the metabolic changes of the tissue materials.

A. R. P.

Nitrogen compounds of the potato tuber; reaction and f.p. of the juice. S. POPEAWSKI (Rocz. Nauk. Roln. Leś., 1931, 25, 95—126; Chem. Zentr., 1932, i, 1170).—In the vegetation period the total N increases; the amide-N increases more than the NH_2 -acid-N. In warm storage the total N falls; cold-stored potatoes contain more N than warm-stored. The embryos, relatively to the tubers, contain more non-protein-N but less NH_2 -acid-N. Acidity at first rises after harvesting. On storage the sap attains a characteristic max. f.p. depression.

A. A. E.

Isolation of glutathione from potato tubers treated with ethylene chlorohydrin. J. D. GUTHRIE (J. Amer. Chem. Soc., 1932, 54, 2566—2567).—Pieces of fresh tubers are treated with 1.6% CH_2Cl-CH_2-OH , kept in a closed container for 24 hr., then planted in moist soil for 5 days. They are then washed and ground, and the juice is expressed; 1.5 litres of the starch- and protein-free filtrate give 870 mg. of the Cu^+ salt of glutathione. Glutathione could not be isolated from the juice of untreated tubers. Potatoes stored for several months gave smaller yields than fresh tubers.

C. J. W. (b)

Effect of ethylene chlorohydrin treatments on the catalase, peroxidase, pH , and thiol content of gladiolus corms. J. D. GUTHRIE, F. E. DENNY, and L. P. MILLER (Contr. Boyce Thompson Inst.,

1932, 4, 131—140).—Treatment of corms with ethylene chlorohydrin (1—3 c.c. of a 40% solution per litre for 1—3 days) increased the catalase and peroxidase activity of the expressed juice and dried tissue, and the SH' content of the expressed juice and extracts of dried tissue. The simultaneous increase in the p_H of the juice differed with different varieties. The I-reducing power of the corms was not appreciably affected by the treatment except in one case where there was a marked increase. These changes occurred in both dormant and active corms. A. G. P.

Ethylene-induced epinasty of leaves and the relation of gravity to it. W. CROCKER, P. W. ZIMMERMAN, and A. E. HITCHCOCK (Contr. Boyce Thompson Inst., 1932, 4, 177—218).—Of numerous gases examined only C_2H_4 , C_2H_2 , C_3H_8 , CO, and C_4H_8 induced epinasty in plants, their effectiveness in this respect being: 1, 500, 500, 5000, 500,000, in the order named. Activity is associated with the unsaturated linking in the mols. and was not apparent in any saturated derivatives of the above. Acetaldehyde, allyl alcohol, and isoprene did not produce epinasty, but were highly toxic to the plants. The action of the gases is not related to their solubility in H_2O , but is probably due to their ability to combine with certain constituents of the protoplasm. The epinastic response of petioles is a sensitive test for small concns. of these gases. The position of the plant in relation to the gravitational pull markedly influenced the epinastic effects. Both excised and attached leaves were affected. The downward pull of leaves following C_2H_4 treatment is 4—8 times their wt. A. G. P.

Conditions affecting nitrate reduction by plants. S. H. ECKERSON (Contr. Boyce Thompson Inst., 1932, 4, 119—130).— NO_3' reduction in the plants examined was much reduced by decreasing the light intensity or the period of exposure. Formation of reductase in plants practically ceased if either K or PO_4''' was deficient in the nutrient. When Ca was deficient plant injury occurred first in the roots and later in the stem tips. Decreased reductase activity follows the course of the injury. With SO_4''' deficiency reductase activity diminished slowly to a min. which was maintained for several weeks. No disintegration of the protoplasm was apparent. Reductase activity was not related to the amounts of NO_3' or starch present in the plant. A. G. P.

Influence of potash nutrition on the assimilation rates of wheat leaves. G. GASSNER and G. GOEZE (Ber. deut. bot. Ges. (Festschr.), 1932, 50A, 412—482).—Apparatus is described for determining assimilation rates of cut leaves. Assimilation commences immediately after exposure to light, attains its full rate after 10—15 min., and continues steadily for many hr. Deficiency of H_2O induces a premature retardation. Assimilation vals. of leaves and the susceptibility of the plants to rust vary inversely with the K content of the soil in which they are grown. Possible interrelationships of the K supply and the N economy of plants are discussed. A. G. P.

Accumulation of electrolytes. IV. Internal versus external concentrations of potassium. A. G. JAKES and W. J. V. OSTERHOUT (J. Gen. Physiol., 1932, 15, 537—550).—Lowering of the K' content of sea-water from 0.011M to 0.006M, but allowing the total concn. of NaCl+KCl to remain the same, caused a decrease in the K' and an increase in the Na' content of the cell sap of *Valonia macrophysa*. The cells ceased to grow, although there was no evidence of injury. Increase of K' in the sea-water increased the K' , halide, and total cation content and also the ratio K'/Na' of the cell sap. A. L.

[Properties of] large [vegetable] cells. W. J. V. OSTERHOUT (Austral. J. Exp. Biol., 1932, 9, 135—139).—The protoplasm of large cells (*Nitella*, *Valonia*, *Halicytis*) is probably covered with a liquid film immiscible with H_2O . Electrolytes pass through this film chiefly non-ionised, the curve of penetration being, in general, of the first order. The energy required for the accumulation of electrolytes within the cells is derived from the production of substances by them and the process takes place because an ion may pass inwards in one combination more rapidly than it can pass outwards in another. W. M.

Intake of ions from salt solutions by higher plants. II. K. PRSCHLE (Ber. deut. bot. Ges. (Festschr.), 1932, 50A, 42—60).—The amount of CO_2 evolved by roots of growing plants is large in comparison with the difference between the intake of anions and cations from sterile, neutral-salt solutions. The part played by mol. and dissociated H_2CO_3 and by H' and OH' in maintaining the electrostatic equilibrium between nutrient solutions and plant fluids is discussed in relation to the non-equivalence of the intake of anions and cations. A. G. P.

Rust diseases of cereals. IV. Mechanism of the action of mercury salts on wheat-smut spores [*Tilletia tritici*, Bjerk., Winter]. J. BODNAR and A. TERENYI (Z. physiol. Chem., 1932, 207, 78—92; cf. A., 1931, 133).—Rust spores irreversibly adsorb Hg from aq. $HgCl_2$, $HgBr_2$, and $Hg(OAc)_2$, but not from $Hg(CN)_2$. The adsorbed Hg prevents germination on aq. $Ca(NO_3)_2$, but treatment with $Hg(CN)_2$ has no effect on germination. Spores treated with $Hg(OAc)_2$ germinate in moist soil. From $HgCl_2$ and $HgBr_2$ solutions the salts are adsorbed (being lipinsol.) and kill the spores; $HgBr_2$ has the more powerful effect, as it is less dissociated. From $Hg(OAc)_2$ only metal ions are adsorbed. Germination is prevented by 3.5% Hg'' . NaCl depresses the action of $HgCl_2$, but renders $Hg(OAc)_2$ able to kill the spores, owing to the formation of $HgCl_2$. J. H. B.

Isolation of guanidine. J. A. SAUNDERS (Biochem. J., 1932, 26, 801—813).—The guanidine is first adsorbed on charcoal, from which it is removed with acid EtOH, and eventually on "doucil" (Na Al silicate), from which it is eluted with saturated NaCl solution and MeOH. It is finally pptd. as the picrate: 2 mg. of guanidine or dimethylguanidine per 100 c.c. in aq. solution can be detected. For determination in blood the proteins are removed by the method of Folin and Wu. S. S. Z.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1932.

General, Physical, and Inorganic Chemistry.

Existence of a Boltzmann distribution in the band levels of H_2 excited by electronic collision. L. S. ORNSTEIN and A. A. KRUTHOF (Z. Physik, 1932, 76, 780—781). A. B. D. C.

Peculiar phenomena of the electrodeless ring discharge through hydrogen in a long tube. B. ARAKATSU and K. KIMURA (Mem. Fac. Sci. Agric. Taihoku, 1932, 5, 15—23).—The nature of the glow, as pressure is reduced, is described and discussed. N. M. B.

Distribution of intensity in N_2 α - and NO β -bands. F. CAVALLONI (Z. Physik, 1932, 76, 527—534).— N_2 α -bands were investigated between 6700 and 5300 Å., and NO β -bands between 4900 and 2700 Å. A. B. D. C.

New forbidden absorption band system of the oxygen molecule. G. HERZBERG (Naturwiss., 1932, 20, 577).—A new absorption band system of O_2 , consisting of eight bands converging rapidly, lies between 2400 and 2600 Å. The origin of the bands is discussed and it is suggested that they are of a type hitherto unknown. W. R. A.

Spectra of incompletely bound molecules (polarisation molecules) K_2 , Na_2 , Cs_2 , and broadening of absorption lines. H. KUHN (Z. Physik, 1932, 76, 782—792).—Absorption bands due to polarisation mols. accompany the principal series due to alkali-metal vapours of high density. A. B. D. C.

Extension of "Summensatz" for alkalis and an application to the Stark effect. J. G. KIRKWOOD (Physikal. Z., 1932, 33, 521—525).—Mathematical. W. R. A.

Mean lives of the lowest metastable states in neutral oxygen, and intensities of lines arising therefrom. A. F. STEVENSON (Nature, 1932, 130, 131). L. S. T.

Mg IV and Al V spectra in the extreme ultra-violet. J. SODERQVIST (Z. Physik, 1932, 76, 756—759). A. B. D. C.

Fused silica etalons in the study of hyperfine structure. B. VENKATESACHAR and L. SIBAIYA (J. Sci. Instr., 1932, 9, 216—218).—Faint satellites of Hg I 5461 at -0.154 Å., and of Hg I 5770 at -0.173 , -0.213 , and -0.257 Å., are recorded. C. W. G.

Intensity measurements in the argon spectrum. T. BARENDs (Physica, 1931, 11, 275—281; Chem. Zentr., 1932, i, 635). L. S. T.

Fluorescence of a jet of zinc atoms. P. SOLEIL-LELET (Compt. rend., 1932, 195, 372—373; cf. this vol., 439). C. A. S.

Polarisation of fluorescence bands of cadmium vapour. L. SOSNOWSKI (Compt. rend., 1932, 195, 224—226). C. A. S.

Intensities in fluorescent spectrum of iodine. L. L. AGARBICEANU (Compt. rend., 1932, 195, 123—125; cf. this vol., 668).—In the series excited by λ 5461 the terms $+2$ and -4 have been observed. The wave-lengths of -4 , -2 , and $+2$ are respectively 5223, 5339, and 5585 Å. (cf. A., 1922, ii, 178). C. A. S.

Lines of tungsten and rhenium appearing in the spectrum of the electric furnace. A. S. KING (Astrophys. J., 1932, 75, 379—385).—75 lines for W and 19 for Re in the range 2800—6700 Å. are recorded. The Re lines show hyperfine structure. L. S. T.

Effects of temperature and nitrogen pressure on the afterglow of mercury resonance radiation. E. W. SAMSON (Physical Rev., 1932, [ii], 40, 940—963).—The decay rate of the λ 2537 afterglow from an optically excited quartz cell containing low-pressure Hg vapour, for a N_2 pressure range of 0.5—100 mm. at three temps., gave a very rapid increase of the decay coeff. with rise of temp. at high pressures. N. M. B.

Hyperfine structure and the polarisation of mercury resonance radiation. A. C. G. MITCHELL (Physical Rev., 1932, [ii], 40, 964—973; cf. Larrick, this vol., 315).—Mathematical. N. M. B.

Absorption of the resonance line λ 2537 in mercury vapour. H. MAGLIANO (Z. Physik, 1932, 76, 793—798).—Inconsistencies in recorded vals. of the absorption coeff. of this line are due to different methods of evaluation; 5.78 cm^{-1} is a lower limit for the coeff. at 20° . A. B. D. C.

Fluorescent excitation of Hg by the resonance frequency and by lower frequencies. IV. (LORD) RAYLEIGH (Proc. Roy. Soc., 1932, A, 137, 101—116).—In a moving current of vapour the resonance luminosity behaves differently from the other components of the fluorescence. The visual luminosity contains 2^3P_0 and 2^3P_2 metastable atoms, whilst the resonance luminosity contains only 2^3P_1 atoms. The complete line spectrum of Hg is present when excitation is by the resonance line only, and the spectrum thus excited is dominated, like the band spectrum, by the motion of the vapour stream. L. L. B.

Hyperfine structure of certain Hg I lines in the electrodeless discharge. T. S. SUBBARAYA and T. G. S. IYENGAR (Proc. Roy. Soc., 1932, A, 137, 216—229).—The structure of the 4916 Å. line of Hg I is found to agree with that previously given by Venkatesachar and Sibaiya (this vol., 104). On the basis of this structure the splitting of the 6^1P_1 level has been determined and the structures of a no. of lines have been obtained. The regularities found by Schuler and Keyston (*ibid.*, 2) regarding the equality of the total separations for the isotopes 199 and 201 and the relatively inverted positions of their fine levels are confirmed. L. L. B.

New light source for excitation of resonance radiation in metal vapours, particularly in mercury. F. G. HOUTERMANS (Z. Physik, 1932, 76, 474—480). A. B. D. C.

Hyperfine structure of lead spectrum. II. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 245—248; cf. this vol., 104).—An extension of previous measurements proves the existence of Pb^{210} . J. W. S.

Exciting atomic jets by high-frequency electromagnetic discharge. A. BOGROS and F. ESCLANGON (Compt. rend., 1932, 195, 368—370).—The method, which is specially suitable for investigating hyperfine structure, is a combination of the at. jet (cf. A., 1926, 874; this vol., 454) and the electrodeless discharge (cf. this vol., 245). C. A. S.

Calibration of a normal lamp with a line spectrum. L. S. ORNSTEIN and H. C. BURGER (Z. Physik, 1932, 76, 777—779). A. B. D. C.

Spectral energy distribution of the high-current vacuum tube. J. A. ANDERSON (Astrophys. J., 1932, 75, 394—406).—With a c.d. >10,000 amp. per sq. cm. a continuous spectrum appears independent of the nature of the electrode or residual gas. L. S. T.

Atomic lines in the sun-spot spectrum. C. E. MOORE (Astrophys. J., 1932, 75, 222—273, 298—336).—Lines of Lu^+ have been identified. The composition of the atm. above sun-spots has been quantitatively investigated. L. S. T.

Relative intensities of multiplet transitions in complex spectra. C. W. UFFORD (Physical Rev., 1932, [ii], 40, 974—979).—Mathematical. N. M. B.

General formula for absorption transitions. V. POSEJPAL (Compt. rend., 1932, 195, 36—39; cf. A., 1931, 665).—Assuming that a photon penetrates into an atom only as far as the level corresponding with its quantum, $h\nu$, and that only a photon of which the trajectory reaches the energy level which it cannot pass on on collision transfer all its energy to the peripheral electrons, a new formula for the absorption transition is deduced. C. A. S.

Filter difference method of exciting intense monochromatic X-rays. H. KUSTNER (Z. Physik, 1932, 77, 52—59).—An improvement of an earlier method (A., 1931, 993) gives the $\alpha\alpha'$ -doublet of great purity. A. B. D. C.

Intensity measurements in the continuous X-ray spectrum. J. BOGILD (Z. Physik, 1932, 77,

100—103).—An ionisation chamber which measures intensities between 1.4 and 0.6 Å. is described.

A. B. D. C.

Spectrography of X-rays by transmission of a non-canalised beam across a curved crystal. (MLLE.) Y. CAUCHOIS (J. Phys. Radium, 1932, [vii], 3, 320—336).—A detailed account of work already noted (this vol., 246).

Forces of linkings in the lattice and X-ray spectrum. R. GLOCKER (Naturwiss., 1932, 20, 536—539).

Theory of X-ray absorption in molecular gases. H. J. GROENWOLD (Z. Physik, 1932, 76, 766—767).—Identity of the nuclei of diat. mols. gives rise to no peculiarity in the fine structure of X-ray absorption edges. A. B. D. C.

Theory of X-ray absorption in molecular gases. H. PETERSEN (Z. Physik, 1932, 76, 768—776; cf. Kronig, this vol., 553).—The position of fine structure in absorption edges gives an estimate of inter-at. distances. A. B. D. C.

Scattering of X-rays by chlorine. H. RICHTER (Physikal. Z., 1932, 33, 587—588).—The scattering of X-rays by Cl_2 using Cu- $K\alpha$ and Mo- $K\alpha$ radiation has been determined; the results agree more closely with val. calc. according to Hartree's than according to Thomas and Fermi's method. W. R. A.

Scattering of X-rays by gases and crystals. Y. H. WOO (Physical Rev., 1932, [ii], 41, 21—23; cf. this vol., 441).—The Raman-Compton-Jauncey formula deduced classically for scattering by an atom is in agreement with the wave-mechanical result.

N. M. B.

Non-diagram lines of $K\alpha$ radiation of aluminium. E. CARLSSON (Z. Physik, 1932, 76, 471—473).—Two weak lines α_7 and α_8 have been observed in the spectrum of Al, and α_9 has been observed from Al_2O_3 . Displacement of the lines α_1 to α_6 by chemical combination was also observed. A. B. D. C.

Partial absorption of X-rays. H. HULUBEI (Compt. rend., 1932, 195, 231—233). C. A. S.

Partial absorption in the soft X-ray region. F. C. CHALKLIN and L. R. CHALKLIN (Compt. rend., 1932, 195, 374—376).—The line $K\alpha$ of C present in soft X-ray spectra obtained with the vac. spectrograph (due to grease etc.) is always accompanied by a very diffuse line of wave-length 51 Å., corresponding with 242 electron volts or $35 < K\alpha$ of C. This is attributed to expulsion of an electron from the L level by a quantum of radiation $K\alpha$, which thus loses part of its energy. C. A. S.

X-Ray absorption coefficients in the range 0.3—2.0 Å. L. H. MARTIN and K. C. LANG (Proc. Roy. Soc., 1932, A, 137, 199—216).—An ionisation balance method and a photographic method for the measurement of X-ray absorption coeffs. are described. Absorption coeffs. have been measured for Fe, Ni, Cu, and Zn over the range 0.3—2.0 Å., and for Mo, Pd, Ag, and Sn over shorter ranges. For Fe, Ni, Cu, Zn, Pd, and Ag the K jump equals E_K/E_L . L. L. B.

Disappearance of hydrogen in the presence of potassium or lithium ion sources. C. H. KUNS-

MAN and R. A. NELSON (Physical Rev., 1932, [ii], 40, 936—939).—The rate of clean-up of H was observed on K and spodumene glass surfaces, sources of K and Li ions, respectively. The effect can be explained by a reaction on or within the hot glass, probably the formation of H_2O vapour. N. M. B.

Lower sensitivity limit of technical potassium cells and their adaptation to the photo-electric measurement of α -preparations. G. A. TEVES (Ann. Physik, 1932, [v], 14, 57—79).—The determination of weak photo-electric currents can be carried out by increasing the sensitivity of the electrometer and decreasing the dark effect. Intensities of 10^{-10} erg per $cm.^2$ sec. in the spectral range 440—540 m μ may be determined. The linear dependence of photo-electric current on incident radiation is not rigid for these weak currents. The use of photo-electric cells for measurement of α -preps. is independent of the observer, and is more accurate than the scintillation method. Registration of a single α -particle is not possible with the apparatus described. A. J. M.

Ionisation and excitation by ion collision. W. WEIZEL and O. BEECK (Z. Physik, 1932, 76, 250—257).—Ionisation of inert gases by positive alkali ions sets in suddenly at high potentials (100—500 volts). The mechanism suggested is an Auger effect, i.e., a radiationless transition of energy from the excited ion to the inert gas atom. Ions are necessary only to give the required high relative velocities. A. B. D. C.

Excitation of inert gases by collision with inert gas ions. W. WEIZEL (Z. Physik, 1932, 76, 258—259).—The results of Günther-Schulze and Keller (A., 1931, 1348) are explained on the hypothesis of the preceding abstract. A. B. D. C.

Excitation function of helium. J. H. LEES (Proc. Roy. Soc., 1932, A, 137, 173—186).—An accurate method for measuring the excitation functions of He is described. Measurements of the variation of light intensity with electron current and with He pressure have been made. L. L. B.

Excitation processes in helium. J. H. LEES and H. W. B. SKINNER (Proc. Roy. Soc., 1932, A, 137, 186—198).—Theoretical. The phenomenon of spreading outside the electron beam is examined in detail, and a rough qual. picture is given of the excitation process in He. L. L. B.

Structure of thin crystal layers. F. KIRCHNER (Z. Physik, 1932, 76, 576—596).—Electron diffraction was used to study the form of thin cryst. layers of CdI_2 , Bi, Au, Ag, Tl, Pb, Se, Sb, Te, As, $CdCl_2$, Hg_2Cl_2 , $ZnCl_2$, $PbCl_2$, $HgBr_2$, HgI_2 , Hg_2I_2 , Sb_2O_3 , NH_4Cl , MgO , Zn , Cd , and MoO_3 . The layers were obtained by evaporation and condensation, and variation of the structure with rate of evaporation and layer thickness was studied. A. B. D. C.

Rectilinear propagation and diffraction of electrons. H. DE LASZLO and V. E. COSSLETT (Nature, 1932, 130, 59—60).—Experiments which show that electron beams obey the simple laws of geometrical optics are described. L. S. T.

Diffraction of electrons by single crystals: paraffin and saturated fatty acids. J. J. TRILLAT and T. VON HIRSCH (Compt. rend., 1932, 195, 215—217).—The diffraction effects obtained on passing electrons through films of paraffin and stearic acid confirm current views on structure, the unit cell of paraffin being a rhombic prism with a 7.30, b 4.84 Å.; that of stearic acid a monoclinic prism with (for the α modification) a 9.15, b 4.85 Å., for β a 5.46, b 7.30. Once a cell with a 7.30, b 5.02 Å. was observed, which may be the γ form (cf. A., 1926, 1083). C. A. S.

Elastic and inelastic electron scattering in hydrogen. A. L. HUGHES and J. H. McMILLEN (Physical Rev., 1932, [ii], 41, 39—48; cf. this vol., 442).—Energy and angular distribution of electrons scattered by H_2 mols. was investigated. N. M. B.

Scattering of electrons by mercury. W. HENNEBERG (Naturwiss., 1932, 20, 561—562).

W. R. A.

Electron diffraction and the inner potential of metals. A. BÜHL (Naturwiss., 1932, 20, 577—578).—Theoretical (cf. this vol., 554). W. R. A.

Electron diffraction and photo-electric effect for alkali metal surfaces. I. Experimental. W. KLUGE and E. RUPP (Z. Physik, 1932, 77, 82—99).—The spectral photo-electric effect is used to determine the purity of the metal; the surface can be cooled to liquid air temp. A. B. D. C.

Secondary electron emission from a nickel surface produced by positive ions of mercury. R. M. CHAUDHRI (Proc. Camb. Phil. Soc., 1932, 28, 349—355).—When a beam of positive Hg ions produced from an arc in Hg vapour is fired at a Ni surface, electrons are emitted. For a fresh untreated Ni target the emission is about 1.5% for ion energies 600 volts, and rises to 15—20% at 2000 volts. Degassing of the target at a red heat or continued bombardment with Hg ions leads to a decrease in the emission. J. W. S.

Motion of electrons in the field of excited helium. J. McDougall (Proc. Camb. Phil. Soc., 1932, 28, 341—348). J. W. S.

High-velocity positive ions. II. Disintegration of elements by high-velocity protons. J. D. COCKCROFT and E. T. S. WALTON (Proc. Roy. Soc., 1932, A, 137, 229—242).—Experiments are described showing that protons having energies above 150,000 volts are capable of disintegrating the elements Li, Be, B, C, O, F, Na, Al, K, Ca, Fe, Co, Ni, Cr, Ag, Pb, and U. The disintegration of Li has been studied in detail, and it is estimated that for a thick layer of Li, the no. of disintegrations for a voltage of 250 kv. is 1 per 10^9 protons, and for 500 kv. is 10 per 10^9 protons. Li, B, and F give the largest emission of particles, the emission varying similarly with rise of voltage. These elements are all of the $4n+3$ type, and it is supposed that the addition of a captured proton leads to the formation of a new α -particle inside the nucleus. L. L. B.

Optical study of the reflexion of hydrogen canal rays by solid bodies. E. HOROVITZ (Physikal. Z., 1932, 33, 579—582). W. R. A.

Recombination of ions in air at low pressures. E. LENZ (Z. Physik, 1932, 76, 660—678).—The coeff. of recombination of ions in air, determined between the pressures 20 and 760 mm., is proportional to the pressure, and has the val. 1.7×10^{-6} cm.³/sec.-1 at 760 mm. A. B. D. C.

Law of interaction of ions. C. PUTILOV (Z. Physik, 1932, 76, 814—825).—The effective repulsion of ions in the Mie-Born formula (Ann. Physik, 1903, 11, 657) depends both on the "architecture" of the electronic shell and on the no. of electrons in the shell. The law for the second factor is that the effective repulsion is proportional to the product of the electrons around the cation and those around the anion. A. B. D. C.

[**Measurement of ionic mobility.**] M. LAPORTE (Physikal. Z., 1932, 33, 547—548).—A reply to Stetter (this vol., 442). W. R. A.

Gaede's streaming experiment. P. CLAUSING (Ann. Physik, 1932, [v], 14, 134—138).—The results of Gaede's experiment (*ibid.*, 1913, [iv], 41, 289) on the streaming of H₂ through a slit can be made to agree with both the theory of frictional streaming and that of mol. streaming if a different slit width is assumed. A. J. M.

Molecular flow. P. CLAUSING (Ann. Physik, 1932, [v], 14, 129—133).—Mathematical. A. J. M.

Ramsauer effect for symmetrical diatomic molecules. H. C. STIER (Z. Physik, 1932, 76, 439—470).—Theoretical. The cross-section of the mol. is related to the proper functions, with their *m* and *l* vals., for individual electrons. A. B. D. C.

Inclusion of the rare earths in the periodic table. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1932, 2, 62—64).—The rare-earth elements are arranged in two periods, on the assumption that the no. of sub-groups increases to 4 in groups III to VII, and to 8 in group VIII. R. T.

Pauli's principle and the structure of the atomic nucleus. III. E. N. GAPON (J. Gen. Chem. Russ., 1932, 2, 97—102).—A classification of the elements is given, based on their at. structure, from which it follows that the isotope Ge⁷⁸ should exist, as well as Te^{126, 128}, and ¹³⁰, and the isobars Ge⁷⁸-Se⁷⁸-Kr⁷⁸, Zr⁹⁶-Mo⁹⁶-Ru⁹⁶, and Sn¹²¹-Te¹²¹-Xe¹²⁴. R. T.

Structure of atomic nuclei. I. W. HEISENBERG (Z. Physik, 1932, 77, 1—11).—Exchange and Coulomb energies are calc. for nuclear systems consisting only of protons and neutrons. The results agree with experiment; in particular, the He nucleus represents a closed shell, and an equal no. of protons and neutrons gives a min. exchange energy. β -Ray disintegration can also be explained. A. B. D. C.

Nature of the potential barrier of the nitrogen nucleus. E. C. POLLARD (Proc. Leeds Phil. Soc., 1932, 2, 324—330).—From measurements of the relationship between the range of α -particles and the no. of protons ejected from N₂, it is concluded that the manner of entry of an α -particle into a N nucleus is over the top of the potential barrier, and not by resonance at a "virtual" level of energy. The calc.

height of the barrier is not inconsistent with Gamow's hypothesis that the vol. of a nucleus is proportional to the no. of α -particles it contains. J. W. S.

Nuclear structure. J. H. BARTLETT, jun. (Nature, 1932, 130, 165).—Regularities for elements of low mass are pointed out and a possible principle for building up these elements is suggested. For the lighter elements protons and neutrons, and not α -particles, are regarded as the elementary constituents. L. S. T.

Physico-chemical study of the rare-earth sulphates. II. Theoretical conclusions. B. BRAUNER and E. ŠVAGR (Coll. Czech. Chem. Comm., 1932, 4, 239—246).—A discussion of published data (this vol., 470) and further work. The rare earths may be put in the periodic table without the usual discontinuity, Sm and Tu being in group I, Eu and Yb in group II, La, Gd, and Lu in group III, etc.; the difference between successive elements is much less than in other parts of the table. D. R. D.

Constitution and spin of atomic nuclei. F. PERRIN (Compt. rend., 1932, 195, 236—237; cf. this vol., 442, 556, 790).—A discussion. C. A. S.

Relative abundance of hydrogen isotopes in natural hydrogen. C. A. BRADLEY, jun., and H. C. UREY (Physical Rev., 1932, [ii], 40, 889—890; cf. this vol., 554).—Spectroscopic investigation showed no appreciable variation of abundance of H² in samples from various sources. N. M. B.

Concentration of the H² isotope of hydrogen by the fractional electrolysis of water. E. W. WASHBURN and H. C. UREY (Proc. Nat. Acad. Sci., 1932, 18, 496—498).—Spectroscopic examination of H₂ and O₂ from residual H₂O from commercial cells operating for 2 and 3 years showed a marked increase in abundance of H² relative to H¹. N. M. B.

Search for isotopes of hydrogen and helium. W. BLEAKNEY (Physical Rev., 1932, [ii], 41, 32—38; cf. this vol., 788; Urey, *ibid.*, 554).—Mass-spectrographic investigation indicates an abundance ratio H²/H¹=1/30,000 \pm 20% in ordinary electrolytic H₂. He³ and He⁵ were not found, indicating an abundance ratio <1/50,000. N. M. B.

Mass spectra of helium and oxygen. F. W. ASTON (Nature, 1932, 130, 21—22).—The line of He⁺⁺ has been observed. He-O₂ mixtures give stronger O lines than does pure O₂; line 32 is 268 times as intense as line 34, which is 4.2 times as intense as line 33. These are only approx. minima, since the presence of S (from grease) enhances lines 34 and 33. L. S. T.

At. wts. in 1931. E. MOLES (Anal. Fis. Quím., 1932, 30, 460—476).—A criticism of the international table of at. wts. for 1931. The work of Batuecas indicates 14.008 as the most probable at. wt. of N, whilst that of Maass and Cooper on the densities of CO₂ and SO₂ has been recalcd. to allow for the effects of adsorption. The determinations of the at. wt. of F carried out by Moles and Batuecas indicate that the true val. is >19.00. Data for Kr and Xe not considered in the official report are noted. The val. given for I, viz., 126.932, appears too high in view of the work of Honigschmid and Striebel and of Aston;

it should be 126.92, approx. Birge's work supports the val. of 1100 : 1 for the ratio $O^{16} : O^{18}$.

H. F. G.

Methyl fluoride [and at. wt. of fluorine.] T. BATUECAS (J. Chim. phys., 1932, 29, 269—279).—A reply to criticism (cf. A., 1931, 1207). E. S. H.

Constitution of tantalum and niobium. F. W. ASTON (Nature, 1932, 130, 130).—Mass-spectrum analysis of the fluorides show that Ta and Nb are essentially simple. Ta gives a strong line at 181 with a diminishing series 200, 219, . . . due to TaF , TaF_2 , . . . No other isotope could be detected. The estimated packing fraction, approx. -4, gives an at. wt. 180.89 ± 0.07 . Nb gives a single line at 93 and fluorides at 102, 121, . . . A large negative val., approx. -8, for the packing fraction appears to be probable, giving an at. wt. 92.90 ± 0.05 . The present vals. for the at. wts., 181.4 and 93.3, are too high.

L. S. T.

Radioactivity. O. ERBACHER and K. PHILIPP (Naturwiss., 1932, 20, 586—589).—A summary.

W. R. A.

Half-life period of protoactinium. A. VON GROSSE (Naturwiss., 1932, 20, 505).—The half-val. period of Pa was estimated as 32,000 years $\pm 10\%$ from determinations on pure Pa_2O_5 worked up from residues of Ra ores.

W. R. A.

[Half-life period of protoactinium.] O. HAHN (Naturwiss., 1932, 20, 505—506).—Criticism (cf. preceding abstract).

W. R. A.

Concentration of slow neutrons in the atmosphere. P. B. MOON (Nature, 1932, 130, 57—58).

L. S. T.

New evidence for the neutron. (MME.) I. CURIE and F. JOLIO (Nature, 1932, 130, 57; cf. this vol., 555).—Rays emitted by Li under bombardment by α -particles from Po have a penetrating power in Pb less than that of the γ -rays of Po and are more readily absorbed by paraffin than by Pb, showing that they cannot be electronic or electromagnetic in nature. These rays are different from known radiations and are probably neutrons. The protons ejected from Be form 2 groups. This suggests that there are also 2 groups of neutrons, not necessarily homogeneous; one group has a range of 28 cm. in air and an energy of 4.5×10^6 electron volts, whilst the other has a range of 70 cm. with energy 7.8×10^6 electron volts. The neutrons and photons from Be may be emitted simultaneously : $Be^9 + \alpha = C^{12} + n + h\nu$.

L. S. T.

Neutrons from boron excited by radon. M. DE BROGLIE and L. LEPRINCE-RINGUET (Compt. rend., 1932, 195, 88—89).—Neutrons emitted by B under the influence of Rn traverse Pb much more readily than paraffin, being scarcely at all absorbed by 5 cm. of Pb, whereas they are about half absorbed by 5 cm. of Cu or Al. This transparency of Pb is perhaps due to its re-emission of neutrons.

C. A. S.

Emission of slow neutrons by the action of α -particles on beryllium. P. AUGER (Compt. rend., 1932, 195, 234—236; cf. this vol., 443, 672).—The paths of protons ejected on passing the neutrons produced from Be by α -particles from Po into a Wilson expansion chamber containing moist H_2 have

been analysed without and with a diffuser. The results indicate great diffusion of neutrons by collision with the atoms of Cu without substantial loss of energy, resulting in a concn. in the cavity forming the chamber. More than half the protons have energies < 300 kv.-electrons, and many < 100 . These results indicate that many of the neutrons are slow.

C. A. S.

Influence of atomic groupings of radioelements on the liberation of emanation. (MLE.) C. CHAMIE (J. Chim. phys., 1932, 29, 242—247).—To explain the influence of volatile substances on the rate of evolution of emanation it is suggested that occluded atoms retain some of the latter.

C. W. G.

Magnetic spectrum of α -particles from radium. S. ROSENBLUM (Compt. rend., 1932, 195, 317—319).—Using as source $RaCO_3$ the following velocities ($\times 10^9$ cm. per sec.), based on 1.698 for α -Ra-A (cf. this vol., 671), have been determined : α -Ra 1.517, α_1 -Ra 1.48₈, α -Rn 1.623. The energy difference α - α_1 -Ra (185 electron kv.) agrees well with previous results (cf. A., 1925, ii, 9).

C. A. S.

Absorption measurements and the continuous spectrum of β -rays. J. A. CHALMERS (Proc. Camb. Phil. Soc., 1932, 28, 319—327).—The observed "kinks" in the absorption-thickness of absorber curve for heterogeneous β -radiation from any radioactive source (cf. A., 1929, 1124; 1930, 1085) are discussed theoretically.

J. W. S.

Energy problems in the continuous spectra of β -rays. J. A. CHALMERS (Proc. Camb. Phil. Soc., 1932, 28, 328—337).—Possible reasons why the β -rays from any sp. radioactive disintegration are emitted with a wide range of energies, whereas either the corresponding α -rays have equal velocities or their velocities are grouped, are discussed.

J. W. S.

Photo-electric effect of L_{II} and L_{III} electrons for γ -rays. T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 249—298).—Mathematical.

J. W. S.

γ -Radiation excited in boron and beryllium. H. BECKER and W. BOTHE (Z. Physik, 1932, 76, 421—438).— γ -Radiation emitted by Be and B under α -ray bombardment is almost uniformly distributed, and has an energy of 5×10^6 volts. The probability of excitation plotted against α -ray energy has a min., which lies at 3×10^6 volts for B. A. B. D. C.

Ionisation of air by γ -rays as a function of pressure and collecting field. I. S. BOWEN (Physical Rev., 1932, [ii], 41, 24—31).

N. M. B.

Secondary effects of penetrating corpuscular radiation. B. ROSSI (Atti R. Accad. Lincei, 1932, [vi], 15, 734—741).—The penetrating power of the secondary radiation and the behaviour of Pb and Fe screens have been studied.

H. F. G.

Anomalous absorption of penetrating radiation. B. ROSSI and B. CRINÒ (Atti R. Accad. Lincei, 1932, [vi], 15, 741—746).

H. F. G.

Atom factors. W. EHRENBERG and K. SCHAFER (Physikal. Z., 1932, 33, 575—576).—An addendum (cf. this vol., 316).

W. R. A.

Recombination of hydrogen atoms. G. E. KIDBALL (J. Amer. Chem. Soc., 1932, 54, 2396—2398).—A possible mechanism for the recombination of H atoms (cf. this vol., 449) is the collision of an H atom with a H_2 mol. to form a quasi-mol. which then collides with another H atom to form two H_2 mols. M. McM. (c)

Gravitation considered as neutral magnetism due to motion of all matter in time. A. P. MATHEWS (J. Physical Chem., 1932, 36, 1738—1743).

Equivalent chemical linkings formed by s , p , and d eigenfunctions. R. HULTGREN (Physical Rev., 1932, [ii], 40, 891—907).—Mathematical. N. M. B.

Space quantisation of atoms on impact. H. KUHN and O. OLDENBERG (Physical Rev., 1932, [ii], 41, 72—78).—Certain diffuse band max. in the spectra of Hg vapour with A or Kr are interpreted. N. M. B.

Interconversion factors for numbers in energetic and related units. C. H. D. CLARK (Phil. Mag., 1932, [vii], 14, 291—297).—Factors connecting the different units for charge, e.m.f., and those involving e , m , h , N , J , and $\nu\lambda$ are tabulated and discussed. N. M. B.

Measurements of ultra-violet solar radiation. E. PETTIT (Astrophys. J., 1932, 75, 185—221).—Atm. O_3 at Tucson is equiv. to a layer 0.18 cm. thick at n.t.p. L. S. T.

New form of a polarisation prism transparent in the ultra-violet. C. LEISS (Z. Physik, 1932, 76, 851—852).—A polarisation prism transparent to 0.185 μ is described. A. B. D. C.

Absorption spectra of solid bodies. R. PEIERLS (Ann. Physik, 1932, [v], 13, 905—952; cf. this vol., 673).—A more complete theoretical discussion of the theory put forward previously. J. W. S.

Absorptive power of black and white substances used for radiation measurements. III. E. HASCHE (Ann. Physik, 1932, [v], 14, 342—352; cf. A., 1931, 405).—The absorptive power of Ångström's pyrgeometer was investigated in the range 0.6—50 μ . A. J. M.

Band spectra of zirconium oxide. L. W. JOHNSON (Phil. Mag., 1932, [vii], 14, 286—291; cf. Lowater, this vol., 211).—Wave-lengths, frequencies, and vibrational analysis for the region $\lambda\lambda$ 4000—7000 are tabulated. N. M. B.

Predissociation spectra of triatomic molecules. J. FRANCK, H. SPONER, and E. TELLER (Z. physikal. Chem., 1932, B, 18, 88—101).—The principles followed in interpreting the predissociation spectra of diat. mols. require amplification when applied to the spectra of polyat. mols., to take into account the more complex nuclear vibrations and the fact that polyat. products of decomp. contain vibrational and rotational energy, whereas for monat. products of decomp. only electron excitation energy need be considered. The predissociation spectra of SO_2 and NO_2 are examined. Energy data show the dissociation of SO_2 into SO and O to be impossible at 2800 Å., so that the supposed predissociation in this region is merely a pressure effect (cf. A., 1930, 1383). The energy val. for the

predissociation limit at 1950 Å. exceeds the energy required thermally for dissociation into SO and O by about 13 kg.-cal., which must be divided between translational and vibrational energy. R. C.

Absorption of ozone between λ 3050 and 3400 Å. N. T. ZE and C. S. PIRAW (Compt. rend., 1932, 195, 309—311).—The coeffs. of absorption for 236 wave-lengths within the above limits are tabulated. C. A. S.

Absorption of water in visible region. B. LANGE and C. SCHUSTERIUS (Z. physikal. Chem., 1932, 160, 468).—Corrections (cf. this vol., 557). R. C.

Absorption and fluorescence spectra in mercury halide vapours. I. HgI_2 . K. WIELAND (Z. Physik, 1932, 76, 801—813).—Investigation of these spectra to 1500 Å. showed that HgI_2 dissociates into an excited HgI mol. and unexcited I, whence HgI_2 is an atom-mol. A. B. D. C.

Splitting of absorption spectra by lowering of temperature. W. KASPEROWICZ (Z. Physik, 1932, 76, 481—482).—The ultra-violet absorption spectra of C_6H_6 , $C_{10}H_8$, anthracene, and phenanthrene were investigated at temp. between 0° and –190°. Bands beyond 270 $m\mu$ were displaced towards longer wave-lengths, whilst those below this wave-length remained undisplaced as the temp. was lowered. A. B. D. C.

Ultra-violet spectrum of indene. L. SCHWARTZ (Arch. Phys. biol. Chim.-Phys. Corps Organisés, 1931, 9, 131—133; Chem. Zentr., 1931, ii, 643).—Indene in C_6H_{14} shows absorption bands at 2800, 2700, 2625, 2560, 2500, 2420 (2340?), and 2200 Å.; Beer's law holds. L. S. T.

Fluorescence of formaldehyde. Conditions for excitation and vibrational analysis. G. HERZBERG and K. FRANZ (Z. Physik, 1932, 76, 720—728).—Fluorescence, excited in the vapour of CH_2O by means of a C arc, gave two ground state vibrational frequencies 1713 and 1023 cm^{-1} , the former due to the C—O vibration and the latter to the transverse vibration of the H atoms. A. B. D. C.

Ultra-violet absorption of methyl halides. A. HENRICI (Z. Physik, 1932, 77, 35—51).—The line and continuous absorption spectra in the far ultra-violet were investigated for the Me halides, excepting Cl_4 and the fluorides. A. B. D. C.

Influence of substituent groups on the visible and ultra-violet absorption spectra of amino-acids and related substances. G. A. ANSLOW and M. L. FOSTER (J. Biol. Chem., 1932, 97, 37—46; cf. A., 1931, 718).—Absorption spectra are recorded from 6000 to 1850 Å. for cystine (I), cysteine (II), alanine, aspartic (III), glutamic (IV), succinic (V), and butyric acids in HCl solution. With (I) there is a band at 2510 Å. (cf. A., 1931, 1211) which is believed to be due to dissociation into (II) and its chloride. Similar bands for (III), (IV), and (V) are ascribed to weakening of the α - β C linking. A. A. L.

Infra-red bands in the aurora. J. KAPLAN (Nature, 1932, 130, 60—61). L. S. T.

Spectrographic observations of infra-red lines in the auroral spectrum. H. HAMADA (Nature, 1932, 130, 26). L. S. T.

Infra-red characteristic frequencies of the alkali halide crystals. M. BORN (Z. Physik, 1932, 76, 559—560).—Barnes' results (this vol., 675) are in agreement with the characteristic frequencies calc. for the alkali halide crystals by Born and Brody (Z. Physik, 1932, 11, 327). A. B. D. C.

Effect of dilution and temperature on infra-red absorption bands: molecular associations. R. FREYMAN (Compt. rend., 1932, 195, 39—41).—Experiment does not confirm that electrolytic dissociation is the explanation of the variations with concn. and temp. (cf. this vol., 6) in intensity of the OH bands in BuOH etc. solutions. This is caused by dissociation of associated mols. (cf. this vol., 445). C. A. S.

Vibration spectra [of formaldehyde and acetone]. R. TITEICA (Compt. rend., 1932, 195, 307—309).—The absorptions of CH_2O to $6.2\ \mu$ and of COMe_2 to $7.20\ \mu$ have been measured and the fundamental frequencies numbering 6 and 10, respectively, determined, in good agreement with the Raman lines and previous results (cf. A., 1925, ii, 627, 1025; this vol., 558). C. A. S.

Raman effect with gaseous ammonia. E. AMALDI and G. PLACZEK (Naturwiss., 1932, 20, 521).—A reinvestigation of the rotation Raman spectrum of gaseous NH_3 at 3 atm., excited by the 2537 Å. Hg line, shows the existence of weak $\Delta J = 1$ lines, as well as the stronger $\Delta J = \pm 2$ lines. The moment of inertia calc. (2.78×10^{-40}) is in agreement with previous vals. The following Raman frequencies are also reported: 3334.2; 933.8 and 964.3; 1922 (weak); and 2210 and 2270 cm^{-1} (very weak). J. W. S.

Fine structure of Raman bands. II. Raman spectrum of aqueous solutions of ammonia. A. LANGSETH (Z. Physik, 1932, 77, 60—71).—The NH_3 mol. is little distorted by dissolution in H_2O , and the moments of inertia of the mol. are 1.4 (about the symmetry axis) and $2.8 (\times 10^{-40} \text{ g. cm}^2)$. The Raman band investigated was that at 3300 cm^{-1} . A. B. D. C.

Smekal-Raman spectra of SiHCl_3 , CHFCl_3 , and CF_3Cl . C. A. BRADLEY, jun. (Physical Rev., 1932, [ii], 40, 908—913).—Data and classifications are recorded; 6, 8, and 9 frequency displacements, respectively, were observed. N. M. B.

Raman spectrum of nitrous oxide. A. LANGSETH and J. R. NIELSEN (Nature, 1932, 130, 92—93).— N_2O at 30 atm. gave strong shifts at 1286.5 and 2223.2 cm^{-1} ; 6 weak shifts are also recorded. L. S. T.

Raman effect in aqueous solutions of nitrates. P. GRASSMANN (Naturwiss., 1932, 20, 560—561).— $\text{Cu}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ are unique among nitrates in giving two Raman displacements near 720 cm^{-1} . The relative intensities of these two displacements depends on the $[\text{NO}_3^-]$ in the solution. W. R. A.

Raman effect and free rotation. K. W. F. KOHLRAUSCH (Z. physikal. Chem., 1932, B, 18, 61—72).—By comparison of Raman spectra the valency frequencies of the radical R in the alkyl halides, RX , and those of the linking C-X have been identified. The C-X valency frequency appears double only

with a mol. in which free rotation permits the assumption of different configurations. The effect of temp. on the relative intensity of two Raman lines of $\text{C}_2\text{H}_4\text{Cl}_2$ indicates that there are two mol. forms of this compound. R. C.

cis-trans-Isomerism in ethylenic hydrocarbons CHMe:CHR. M. BOURGUEL, (MLLE.) B. GRÉDY, and L. PIAUX (Compt. rend., 1932, 195, 129—131; cf. this vol., 676).—The Raman frequencies of three sets of lines of the *cis*- and *trans*-isomerides of Δ^2 -pentene, Δ^2 -octene, and α -phenyl- Δ^2 -propene, and of *cis*- Δ^2 -nonene and *cis*-cyclohexyl- Δ^2 -hexene (cf. A., 1928, 150) show characteristic differences between the two isomerides (cf. this vol., 706). The chief frequency of the *cis*-open-chain hydrocarbons is almost identical with that of cyclohexene, and that of the *trans*-isomeride near to that of trimethylene, in accordance with the usual stereochemical theory. C. A. S.

Determination of intensity of Raman lines. G. ELLENBERGER (Ann. Physik, 1932, [v], 14, 221—240).—A spectrophotometric method was used to determine the variation of intensity with frequency of Raman lines from CCl_4 , CH_2Cl_2 , C_6H_6 , $\text{C}_2\text{H}_2\text{Cl}_4$, and AcOH . Deviation from the theoretical law is the greater the larger is the frequency displacement of the Raman line. A. J. M.

Raman spectra and isomerism of rhodinol and citronellol. (MLLE.) B. GRÉDY (Compt. rend., 1932, 195, 313—314; cf. this vol., 676).—From a comparison of the Raman lines near 1600 cm^{-1} of β -methyl- Δ^2 -octene 1647, β -methyl- Δ^2 -octene 1677, γ -methyl- Δ^2 -nonene 1670, β -ethyl- Δ^2 -octene 1646, and γ -methyl- Δ^2 -nonene 1672, with those of commercial citronellol, 1677 strong, 1645 very weak, and rhodinol, wide line at 1675 separating on fractionation into two at 1673 and 1677, it is concluded that citronellol is almost pure $\beta\zeta$ -dimethyl- Δ^2 -octen-0-ol (I), with about 1% of $\beta\zeta$ -dimethyl- Δ^2 -octen-0-ol, whilst rhodinol consists of a mixture of (I) with a small amount of alcohols with chains ending in $\cdot\text{CH}\cdot\text{CMe}:\text{CHMe}$ and $\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CH}:\text{CH}_2$, (cf. A., 1928, 1113, 1138). C. A. S.

[Raman effect and] conjugated double linkings. M. BOURGUEL (Compt. rend., 1932, 195, 311—312; see above).—Comparison of the chief Raman frequencies for 12 compounds containing conjugated double linkings—in some cases benzenic—with the frequencies deduced from the nearest simple ethylenic compound shows some differences of about 50 cm^{-1} . The following results are new: isoprene 1640; styrene 1601, 1636; *cis*- α -phenyl- Δ^2 -propene 1599, 1642; *trans*- α -phenyl- Δ^2 -propene 1599, 1664; acraldehyde 1618, 1692; *trans*-crotonaldehyde 1642, 1690; *trans*-cinnamaldehyde 1600, 1629, 1676; $\text{CPh}\cdot\text{CH}$ 1601, 2111; $\text{CPh}\cdot\text{CMe}$ 1599, 2213, 2223. C. A. S.

Raman effect in terpenes. II. Terpenic alcohols and ketones and other substances closely related to the terpenes. G. B. BONINO and P. CELLA (Mem. R. Accad. d'Italia, 1932, 3, 5—41).—The Raman spectra of the following compounds have been measured: pulegone, carvenone, carvone, β -thujone, menthone, fenchone, terpineol, eucalyptol, citral, citronellal, citronellol, linalool, and geraniol. The

Raman lines are classified into those due to CH_2 , $\text{C}\equiv\text{C}$, and $\text{C}\equiv\text{O}$ groups. In addition, the origin of four lines below about 900 cm^{-1} , characteristic of the terpene nucleus, is discussed. O. J. W.

Light scattering in relation to molecular structure; new data for depolarisation in 39 gases. S. PARTHASARATHY (Indian J. Physics, 1932, 7, 139—157).—Visual light-scattering measurements have been made, using sunlight. A shows 0.56% and He 3% depolarisation. In compounds of the type RX_4 , the anisotropy decreases with increasing size of the X atom, and increases with increasing size of the R atom. Positive groups lower, and negative radicals increase, the depolarisation. In the paraffin series the val. increases slowly as far as C_3H_8 and then remains const. The depolarisation increases progressively in the series C_2H_6 , C_2H_4 , C_2H_2 , and HCl , HBr , HI . Cl-substituted derivatives of CH_4 show a max. val. at CH_2Cl_2 . The val. for COS is less than for CO_2 or CS_2 ; CO and NO show much smaller depolarisations than CO_2 and N_2O , respectively. J. W. S.

Raman effect. XV, XVI. Raman spectra of organic substances (*cis-trans*-isomerism). A. DADIEU, A. PONGRATZ, and K. W. F. KOHLRAUSCH. **XVII. Energy distribution in the mechanical model of a triatomic molecule.** M. RADAKOVIC. **XVIII. Raman spectra of organic substances. Poly-substituted benzenes. I.** A. DADIEU, A. PONGRATZ, and K. W. F. KOHLRAUSCH (Monatsh., 1932, 60, 205—220, 221—238, 239—252, 253—269; cf. A., 1931, 998).—XV. The Raman spectra of series of *cis*- and *trans*-isomerides of the type $\text{CHX}\cdot\text{CHY}$ have been investigated, and are discussed with reference to the structures of these isomerides. The $\text{C}\equiv\text{O}$ group can show a resonance frequency either at 1650 or at 1720 cm^{-1} . The frequency 1840 cm^{-1} observed with maleic but not with fumaric esters is explained as due to the presence of a small proportion of dihydroxylactone form in the former.

XVI. The Raman spectra of *cis*- and *trans*- $\text{CHBr}\cdot\text{CHBr}$, *cis*- and *trans*- $\text{CHPh}\cdot\text{CHPh}$, CH_2Ph_2 , $(\cdot\text{CH}_2\text{Ph})_2$, and $\text{CPh}\cdot\text{CPh}$ have been investigated, and are discussed in relation to previous data.

XVII. Mathematical.

XVIII. The Raman spectra of the six isomerides of $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$ and of $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_2$ have been investigated and the results are discussed. J. W. S.

Polarisation of light-scattering. I. S. VENKATESWARAN (Phil. Mag., 1932, [vii], 14, 258—270).—An analysis of the polarisation of the radiation of unaltered frequency separated from the Raman radiations for C_6H_6 , CS_2 , PhMe , CCl_4 , and PCl_3 supports the theory of the spinning photon. N. M. B.

Structure sensitivity of ultra-violet colouring and excitation of rock-salt crystals. H. J. SCHRÖDER (Z. Physik, 1932, 76, 608—627).—The optical properties of rock-salt are dependent on the tempering and the extent of plastic deformation of the crystal. A. B. D. C.

Additive colouring of alkali halide crystals. II. Evidence of ultramicroscopic diffusion. E. REXER (Z. Physik, 1932, 76, 735—755; cf. A., 1931,

998).—At high temp. (approx. 600°) Na diffuses along imperfections in NaCl crystals in the disperse phase. Spectral distribution of colouring in Li, Na, K, Ca, Sr, and Ba halide crystals showed that the cation is the source of the colouring. A. B. D. C.

Nature of blue rock-salt. H. LIERMANN and E. REXER (Naturwiss., 1932, 20, 561).—A continuation of previous work (cf. preceding abstract).

W. R. A.

Spectra of the excited absorption of Lenard phosphors. R. KÜHNER (Ann. Physik, 1932, [v], 13, 873—904).—The spectra of CaS-Cu , SrS-Cu , CaS-Pb , SrS-Pb , and CaS-Mn phosphors all show a more rapid increase of intensity with rise of temp. in the short-wave than in the long-wave region. The ultra-violet excitation decreases with increasing metal content, and the smaller is the latter the further does the band max. lie towards the ultra-violet region. Laws of spectra of phosphors are discussed.

J. W. S.

New photo-electric phenomenon. Q. MAJORANA (Compt. rend., 1932, 195, 226—228).—When light from a Hg or incandescence lamp falls intermittently (period 500—600 per sec.) on a film 20—100 μ thick of Ag, Au, Pt, or Sn supported on glass, and a current is passed along the film which also traverses the primary of a transformer, sounds are heard in a telephone in the secondary circuit. This is due to variation in resistance of the film by 10^{-4} to 10^{-5} of its amount caused by the incident light. Films of Al or Zn are inactive. C. A. S.

Unidirectional layer photo-effect. F. WAIBEL and W. SCHOTTKY (Physikal. Z., 1932, 33, 583—585).— Cu_2O plates which have no unidirectional layer exhibit less than 1/10,000 of the spontaneous photo-effect of plates which have a unidirectional layer. The part of the unidirectional layer photo-stream which depends on voltage (inner photo-effect) disappears when the contact surface has no unidirectional properties. W. R. A.

Role of dyes in photo-electric phenomena. (MLLE.) C. STORA (J. Chim. phys., 1932, 29, 168—183).—Electrodes of Pt, Au, Cd, C, Cu, Hg, and Zn in the CuO and Cu_2O photo-electric cells in contact with electrolytes exhibit no photo-electric effect, but if immersed in H_2O , EtOH , or collodion solutions of dyes, an adsorbed layer is formed on their surfaces which functions photo-electrically. W. R. A.

Crystal and unidirectional layer photo-electric effects. W. BULIAN and H. SCHREIBER (Naturwiss., 1932, 20, 506; cf. Scharf and Weinbaum, this vol., 560).—Discussion of the theories of the mechanism of the Cu_2O photo-electric cell. W. R. A.

Electrical and optical properties of semi-conductors. V. Determination of electrical conductivity of powders. A. VOLKL (Ann. Physik, 1932, [v], 14, 193—215).—A method of studying the electrical conductivity of semi-conductors in the form of powders is described. It is tested on Cu_2O (an electronic conductor) and on AgCl (an electrolytic conductor). A. J. M.

Electrical and optical properties of semi-conductors. VI. Conductivity determinations

with powders. P. GUILLERY (Ann. Physik, 1932, [v], 14, 216—220).—The method described by Volkl (see preceding abstract) was used to determine the electrical conductivity of a no. of powders, and the results were compared with those obtained by the pastille method. The latter is not a satisfactory method.

A. J. M.

Influence of temperature and field strength on the electrical conductivity of amber. F. SEIDL (Z. Physik, 1932, 76, 565—575).

A. B. D. C.

Structure of the naphthalene nucleus. N. NUKADA (Nia Kem., 1932, 5, 41—46).—Vals. for dipole moments for $1\text{-C}_{10}\text{H}_7\text{X}$, $2\text{-C}_{10}\text{H}_7\text{X}$, and PhX , respectively, are: $\text{X}=\text{NO}_2$, 3.88, —, 3.96; F , 1.42, 1.49, 1.45; Cl , 1.50, 1.57, 1.56; Br , 1.48, 1.69, 1.49. Hence 1-C is more aromatic than 2-C. The dipole moments of $1\text{:}4\text{-C}_{10}\text{H}_6\text{Cl}_2$ and $1\text{:}5\text{-C}_{10}\text{H}_6\text{F}_2$ are zero; C-Cl and C-F are equal in moment but opposite in direction. Other dipole moments are: $1\text{:}5\text{-C}_{10}\text{H}_6\text{BrNO}_2$, 2.495, $2\text{:}8\text{-C}_{10}\text{H}_6\text{Cl}_2$, 2.58, $1\text{:}5\text{-C}_{10}\text{H}_6(\text{NO}_2)_2$, 0.6, $1\text{:}2\text{-C}_{10}\text{H}_6\text{BrF}$, 2.34, $1\text{:}2\text{-C}_{10}\text{H}_6\text{BrI}$, 1.80, $1\text{:}8\text{-C}_{10}\text{H}_6(\text{NO}_2)_2$, 7.1 (unit 10^{18}). C_{10}H_8 , but not $2\text{:}6\text{-C}_{10}\text{H}_6\text{Cl}_2$, has a central symmetric structure.

CH. ABS.

Anomalous conductivity of pure liquids for continuous currents. H. GARRIGUE (J. Phys. Radium, 1932, [vii], 3, 248—263).—A more detailed account of work already noted (this vol., 23).

Free rotation and dipole moments of formamide, ethylene chlorohydrin, ethylene glycol, ethylenediamine, and ethyl succinate. C. T. ZAHN (Physikal. Z., 1932, 33, 525—530).—These mols. were found to be too complicated for the satisfactory deduction of their constitution from consideration of their observed dipole moments and their "axes of free rotation." The moments of all these compounds are independent of temp.

W. R. A.

Relation between optical and dielectric properties. Ionic polarisation in solids. J. ERRERA and H. KETELAAR (J. Phys. Radium, 1932, [vii], 3, 239—247).—A study of the refractive indices and dielectric const. of the alkaline-earth fluorides and of the two oxides of Ti shows that the fact discovered for the alkali halides crystallising in the cubic system, viz., that that part of the sp. inductive capacity which is due to vibration of ions is dependent on the diameter of the ions and their deformability, is a general rule. An experimental method is described for the determination of the dielectric const. of powdered substances, for which this quantity is greater than that of a liquid used for comparison.

A. J. M.

Dielectric constant of liquid and solid nitrobenzene. A. PIEKARA (Nature, 1932, 130, 93).—Measurements of the electric polarisation of PhNO_2 in C_6H_{14} show no change in the electric moment or polarising power of the PhNO_2 mol. between -4° and 30° . Density- and dielectric const.-temp. curves show no inflexions at 9.6° (cf. A., 1931, 899). A sharp fall in the dielectric const. occurs at the f.p. (5.66°) or at any lower temp. when supercooled.

L. S. T.

Electric moment and molecular structure. VIII. Complex dipoles and long-chain molecules. C. P. SMYTH and W. S. WALLS (J. Amer.

Chem. Soc., 1932, 54, 2261—2270).—The moments of several polymethylene bromides and similar mols. containing 2, 3, or 4 dipoles have been measured. Dipoles not far apart on a C chain so affect the positions of one another as to diminish the resultant moment of the mol. The free rotation about the C-C linkings gives a variety of forms to long-chain mols., some being excluded because of high mutual potential energies of the dipoles, but a more satisfactory explanation is given by the supposition of an extended zig-zag structure of the C chain with complete freedom of rotation only at the ends. A mathematical derivation of the moments is given. Some older data are revised.

H. F. J. (c)

Dielectric constants of a number of potassium salts and alkali halides. G. STEULMANN (Z. Physik, 1932, 77, 114—116).—Dielectric const. were measured for KClO_4 , KCN , KCNS , KBrO_3 , KIO_3 , K_3PO_4 , K_2HPO_4 , KH_2PO_4 , KH_2AsO_4 , KCl , KBr , KI , K_2CO_3 , KNO_3 , KClO_3 , LiBr , LiI , NaBr , and NaI .

A. B. D. C.

Dispersion of polar liquids for radio-frequencies. P. GIRARD and P. ABADIE (Compt. rend., 1932, 195, 119—121, 217—219).—Debye's equation connecting the static and optical dielectric const. with ϵ' and ϵ'' , the real and imaginary parts of the generalised dielectric const., has been tested, the results being compared with calc. curves relating ϵ' and ϵ''/ϵ' at 20° to wave-lengths of 5—600 cm. for (the figures are respectively viscosity, radius, $\alpha \times 10^8$ cm., of the mol. assumed spherical, and ratio of the vol. of a mol. deduced from α to that deduced from the kinetic theory): Pr^nOH 0.025, 2.2, 1.5; Pr^bOH 0.025, 2.1, 1.9; Bu^nOH 0.029, 2.5, 1.3; Bu^bOH 0.037, 2.5, 1.4; *n*-amyl alcohol 0.040, 2.7, 1.3; *iso*amyl alcohol 0.046, 2.6, 1.4; *s*-dichlorohydrin 0.085, 1.3, 16; *as*-dichlorohydrin 0.12, 1.2, 18.5; glycol 0.20, 0.60, 93; glycerol 4, 0.36, 530. Results for ϵ' agree with theory, but the ratio ϵ''/ϵ' is generally low. The disagreement between the vals. calc. by the two methods indicates the necessity of taking into consideration the mol. configuration before the theory can be deemed satisfactory (cf. A., 1929, 380).

C. A. S.

Absolute measurements of the high-frequency conductivity of liquids for 3 m. wave-length. H. SCHAEFER (Z. Physik, 1932, 77, 117—122).—Aq. solutions of K_2SO_4 and NaCl showed no appreciable increase in conductivity with increase in frequency, but colloidal org. solutions showed as much as 100% increase.

A. B. D. C.

Effect of intramolecular vibrations on optical activity relations of absorption bands. W. KUHN and H. L. LEHMANN (Z. physikal. Chem., 1932, B, 18, 32—48; cf. A., 1931, 1209).—The absorption, rotation, and circular dichroism of a 2% hexane solution of β -octyl nitrite have been measured. A strong absorption band at 2300 Å. makes practically no contribution to the rotation, but a weak band at 3650 Å. exhibits anomalous rotation and circular dichroism. This latter band consists of several narrower bands, within which the anisotropy factor, g , rises to a max. at the centre and falls to zero at the edges. The absorption is largely located in four of the small bands, which are analogous in the mode of variation of

g on passing from one edge to the other and the max. val. attained, showing that the optical activity relations of an absorption band depend chiefly on the electron transition and are almost independent of nuclear vibrations within the mol. The details of the activity relations of a substance may be discovered by measurements of either rotation or circular dichroism, but the latter is the more sensitive. R. C.

Magnetic rotatory power of aqueous solution of cerous chloride and the thermal variation thereof. (MLLE.) J. PERNET (Compt. rend., 1932, 195, 376—378; cf. this vol., 794).—For dil. solutions the sp. magnetic rotatory power, G , is positive and varies as $1/(T-\Theta)$, where T is the abs. temp., and Θ approx. const. = 48° . For conc. solutions $\tau=0.196$, $G=0$ at 22.6° ; for more conc. solutions it is negative. For $\tau=0.375$ GT is const. and $\Theta=0$, becoming negative for higher concn. C. A. S.

Anomalous dispersion of magnetic birefringence. R. LUCAS and M. SCHWOB (Compt. rend., 1932, 194, 2296—2299).—In solution in CCl_4 , cyclohexane, HCO_2H , and H_2SO_4 , *r*- and *d*-camphor show anomalous dispersion of magnetic birefringence, disagreeing with Havelock's formula, and dependent on the concn. and nature of the solvent (cf. A., 1928, 816; this vol., 320). C. A. S.

[Stresses in] unions of [different kinds of] glass: dilatation of glass: compensator for [measuring] birefringence. P. TARBÉS (Compt. rend., 1932, 195, 222—224). C. A. S.

Lorentz double refraction in the regular system. E. U. CONDON and F. SEITZ (J. Opt. Soc. Amer., 1932, 22, 393—401).—Double refraction predicted by the higher approximations for crystals which are optically isotropic in the classical theory, and the optical properties of the cubic system, are discussed. N. M. B.

Attendant phenomena in electro-optical Kerr effect in high-frequency fields. H. HOYER and L. PUNGS (Physikal. Z., 1932, 33, 531—534).—The striation effects observed by Sirkar and by Cotton and Mouton in Kerr fields, especially of high frequency, as well as the appearance of the additional double refraction of the Kerr cell, are explained by a heat effect arising from the dielectric loss. W. R. A.

New optical properties produced in liquids by high-frequency sound waves. P. BICQUARD and R. LUCAS (Compt. rend., 1932, 195, 121—123; cf. this vol., 799).—Light passed through excited quartz showed six or seven spectra each side of the central fringe, the quartz being the seat of stationary elastic waves. When the high-frequency waves to which a liquid is subjected are not less than 0.5 mm., and still more if greater than the width of the pencil of light, no diffraction spectra appear, but merely general spreading. This effect increases with the amplitude of the waves, length of path, and compressibility of the liquid, and is due to the influence of the varying pressure on the refractive index. C. A. S.

Diamagnetism in evidence of ionisation potential of radon. S. C. BISWAS (J. Indian Chem. Soc., 1932, 9, 233—236).—Diamagnetic susceptibility of

groups of elements having similar outer electronic shells varies with ionisation potential. Comparison of the sp. susceptibilities of the inert gases suggests that the ionisation potential of Rn is $>$ that of Xe (11.5 volts). E. S. H.

Influence of light on paramagnetic susceptibility. C. J. GORTER (Nature, 1932, 130, 60).—The diminution of magnetic susceptibility previously observed (A., 1931, 670) is confirmed; it is due to temp. rise. L. S. T.

Magnetic properties of magnetite crystals at low temperature. C. H. LI (Physical Rev., 1932, [ii], 40, 1002—1012).—The magnetic properties changed abruptly at -160° , the temp. at which the sp. heat increases suddenly to a max. X-Ray photographs at room and liquid air temp. show no change in the distribution of the points of diffraction. N. M. B.

Magnetic susceptibility of samarium sulphate. F. H. SPEDDING (J. Amer. Chem. Soc., 1932, 54, 2593—2597).—The discrepancies between the calc. and observed vals. of the susceptibility, χ , of Sm^{+++} are ascribed to the presence of electronic isomerides of undetermined configurations. If on exciting a rare-earth ion a $4f$ electron jumps through the $5s5p$ completed shells to a $6d$ or $5g$ orbit and the basic level of Sm^{+++} is $^6\text{H}_{5/2}$ calculations for $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ give vals. of χ agreeing closely with the observed vals. up to 150° abs. At higher temp. other terms probably become effective. The electronic configuration of the excited isomeride is described. W. W. S. (c)

Ferromagnetism and related problems of the theory of electrons. P. S. EPSTEIN (Physical Rev., 1932, [ii], 41, 91—109).—Mathematical. N. M. B.

Interpretation of the Curie-Weiss law. C. J. GORTER (Physikal. Z., 1932, 33, 546—547).—The relative merits of three possible interpretations of the Curie-Weiss law [$\chi = C/(T-\Theta)$] are discussed. W. R. A.

Ferromagnetism and electrical properties. V. Thermomagnetic effect in a longitudinal magnetic field in nickel and iron. H. BROILI (Ann. Physik, 1932, [v], 14, 259—272).—The c.m.f. produced at the ends of a ferromagnetic wire down which there is a given temp. gradient when it is magnetised is investigated. It remains const. if the temp. difference is const. and the wire is saturated, and also if the magnetisation is const., the lower temp. is const., and the upper temp. is above the Curie point. A. J. M.

Gyromagnetic ratio and the magnetic moment of paramagnetic salts. E. C. STONER (Proc. Leeds Phil. Soc., 1932, 2, 309—318).—Experimental data for the magnetic moments (p vals.) of ions with 19 to 27 electrons are collected, together with the gyromagnetic ratios (g) for salts containing these ions. The p and g vals. are calc. for ideal limiting cases corresponding with close coupling of the spin (s) and orbital moment (l) vectors, with independent s and l , and with suppression of the l moment. The g vals. are in good accord with the interpretation previously given of the p vals. S

Possibility of a thermal effect accompanying sudden changes in the magneton numbers in

cupric chloride and nickel sulphate. D. S. KOTHARI (Proc. Camb. Phil. Soc., 1932, 28, 338—340).

—If there is any sudden change in the magneton no. p with change of temp. it should be accompanied by a thermal effect. No effect corresponding with a temp. change as great as 0.1° could be detected with either CuCl_2 or $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; hence either the change in magneton nos. must be spread over a temp. range or the difference in energy levels between the two vals. of p must be <2 and 14 cm^{-1} , respectively.

J. W. S.

Influence of variations of the molecular field on the magnetic properties of substances. L. NEEL (Ann. Physique, 1932, [x], 18, 5—105).—A theory of the mol. field is developed leading to an interpretation of the difference between the para- and ferro-magnetic Curie points, the abnormal increase in sp. heat of ferromagnetics above the Curie point, magnetisation and hysteresis curves, the const. paramagnetism, magnetic moment, and mol. field of metals, and the variation of susceptibility with temp. Experimental data for β -Fe, Fe-Sn, Fe-Si, Co-Pt, and Ni-Pd are recorded.

N. M. B.

Permeability of vacuum and Chipart's theorems. J. CAYREL (Compt. rend., 1932, 195, 366—368).

C. A. S.

Interaction of lattice vibrations and free electrons in metals. H. JONES (Proc. Camb. Phil. Soc., 1932, 28, 367—385).

J. W. S.

Tetrahedral field of action of atoms. II. Nature of secondary valencies. R. REINICKE (Ann. Guebbard-Severine, 1931, 7, 174—202; cf. this vol., 563).—Crystal structures of the type BN, graphite, diamond, ZnS , and AlN are discussed and illustrated in detail.

N. M. B.

Analogies of carbon and germanium. A. TCHAKIRIAN (Bull. Soc. chim., 1932, [iv], 51, 846—853).—A review.

E. S. H.

Valencies and co-ordination of carbon. G. URBAIN (Bull. Soc. chim., 1932, [iv], 51, 853—862).—A lecture, in which the co-ordination theory is applied to org. compounds. Derivatives of CO probably have a principal valency 2 and a co-ordination valency 3.

E. S. H.

Spectroscopy and valency. I. The periodic groups of atoms and ions. C. H. D. CLARK (Proc. Leeds Phil. Soc., 1932, 2, 336—346).—The relationship between valency and the symmetry of the resultant electron spins of atoms is discussed. Transitional elements tend to build up d electrons with increasing at. no. more rapidly than the symmetry rule requires as the centres and ends of the groups are reached. This is often associated with high resultant spin and large valencies in the first half of the groups and low resultant spins in the second half of the electron groups. Ions of transitional elements conform to no configurations represented by the ground states of other atoms.

J. W. S.

Quantum theory contribution to the problem of aromatic and unsaturated compounds. III. E. HUCKEL (Z. Physik, 1932, 76, 628—648).—The method previously described (A., 1931, 1000, 1356) is applied to C_{10}H_8 , anthracene, phenanthrene, Ph_2 , and

unsaturated ring systems of the form C_nH_{n+2} . The symmetry of the various states is determined, and evaluation of the resonance energies gives the least energy of excitation. Only the condensed ring systems and Ph_2 have closed electron groups, and the binding energy per electron is almost equal to that for C_6H_6 ; the least energy of excitation gives a measure of the ease with which these systems form additive compounds with an alkali metal, and the resulting order is anthracene, C_{10}H_8 (conjugated double linking), Ph_2 , C_6H_6 .

A. B. D. C.

Valency fields of ammoniates. G. BECK (Z. anorg. Chem., 1932, 206, 416—424; cf. A., 1929, 1219).—The total kinetic energy of the valency electrons in a compound is calc. from the expression $QV_a/(V_a - V_e) = i + Q$, where Q is the heat of formation, V_a the mol. vol. of the compound, and V_e the corresponding vol. before reaction. The necessary data have been determined for a no. of compounds. To form an ionised compound the kinetic energy of the valency electrons must exceed 117 kg.-cal. in the case of the ammoniates of univalent metals; otherwise a mol. space lattice is formed instead of an ionic lattice. In bivalent metals ionised ammoniates are formed when the energy exceeds 234 kg.-cal. This condition is reached in the tetrammines of Be and Pd and the hexammines of other metals; lower amines have a mol. lattice. Tervalent metals require a total electronic energy of 351 kg.-cal., which is reached in the hexammines. The Cr pentammines do not reach this crit. val., but the energy suffices for two-stage ionisation. Four types of ammoniates are distinguished: (1) those formed from strong electrolytes, in which the valency field has reached its max. val.; (2) those formed from compounds which are originally feebly ionised (e.g., Al, Be); these are decomposed by acids; (3) ammoniates in which the valency of the cation complex is a linear function of the no. of neutral mols.; these include the ammoniates of Au, Cr, Co, Pd, Rh, Ir, and Pt, and they are not decomposed by acids; (4) ammoniates of compounds with very weak valency fields (e.g., PCl_5 , BCl_3 , and SnCl_4); these are decomposed by H_2O .

E. S. H.

Relations between b.p. and chemical constitution. III. Association in liquid and vapour states. K. BILLIG (Svensk Kem. Tidskr., 1932, 44, 169—172).—In hydrocarbons $\text{C}_n\text{H}_{2n+2}$, the % of polymols. in the vapour phase increases with increasing mol. wt.; in the liquid phase it diminishes. Both in this series and in the noble gases the interval between the crit. temp. and the b.p. increases with increasing mol. wt., but the crit. pressure rises in the latter series, whereas it falls in the former. Comparison of the above temp. interval with the crit. pressure is a guide to association in the vapour phase.

A. G.

Additivity of the energies of normal covalent linkings. L. PAULING and D. M. YOST (Proc. Nat. Acad. Sci., 1932, 18, 414—416).—Empirical evidence for H_2 , the halogens, the H halides, the halogen halides, and the mols. KNa and LiH indicates that the energies are additive. The relatively ionic or covalent character of the linkings is discussed.

N. M. B.

Relation between the atomic arrangement in certain compounds, groups, and molecules and the number of valency electrons. W. H. ZACHARIASEN (Physical Rev., 1932, [ii], 40, 914—916).—Rules for the displacement of the atom A from the centre of the polyhedron formed by the surrounding atoms X in compounds of the type $(A_mX_n)^{-p}$ are given. The total no. of valency electrons per stoichiometric mol. or group is $v=8n+2m$. Interpretations in terms of ionic theory and the theory of electron pair linkings are discussed. N. M. B.

Complex salts containing co-ordinated atoms or groups of various kinds. Complexes with co-ordination number 6. I. Salts $(NH_4)_2[VF_5(H_2O)]$; $Rb_2[VF_5(H_2O)]$; $Tl_2[CrF_5(H_2O)]$. R. PIRANI (Gazzetta, 1932, 62, 380—387).—The above three compounds (*Rb* and *Tl* compounds are new) crystallise in the cubic system with the space-groups T^3 , O^3 , O_h^2 . The vals. of *a*, *v*, and *d*, respectively, for the three compounds are: (NH_4) 8.42 ± 0.01 Å., 596.9×10^{24} c.c., 2.45; (*Rb*) 8.42 ± 0.01 , 596.9×10^{24} , 3.52; (*Tl*) 8.41 ± 0.005 , 594.5×10^{24} , 6.39. The H_2O group occupies a position in the lattice equiv. to that of the F^- ions. O. J. W.

Possible form of electronic binding in crystal surfaces. I. TAMM (Z. Physik, 1932, 76, 849—850).—An electron moving in a periodic potential may effectively form a linking in a one- or two-dimensional crystal. A. B. D. C.

Electronic structures of polyatomic molecules and valency. II. General considerations. R. S. MULLIKEN (Physical Rev., 1932, [ii], 41, 49—71; cf. this vol., 562).—A consideration of present-day views of electronic structures of mols., sharing of electrons, and mol. orbitals. N. M. B.

Constitution of pyrosulphates, pyrosulphuric acid and its monohydrate. P. BAUMGARTEN (Z. anorg. Chem., 1932, 207, 111—112; cf. A., 1931, 921).—Polemical against Hantzsch (this vol., 572). J. W. S.

Space chemistry. I. Low-boiling fluorides. O. RUFF, F. EBERT, and W. MENZEL (Z. anorg. Chem., 1932, 207, 46—60).—From the mol. vols. of volatile fluorides in the liquid and gaseous states the at. radii in these mols. have been calc. The results are discussed with reference to previous vals. J. W. S.

Electronic structure of the normal nitrous oxide molecule. L. PAULING (Proc. Nat. Acad. Sci., 1932, 18, 498—499; cf. this vol., 562).—Possible vals. of the moment of inertia and corresponding structure are discussed. N. M. B.

Distribution of electrons in carborundum. J. HENGSTENBERG and J. GARRIDO (Anal. Fis. Quím., 1932, 30, 409—415).—Mathematical. The application of Fourier analysis to the determination of the charge distribution within a lattice having no centre of symmetry is discussed. The observed electronic distribution in the 001 plane of carborundum is in close agreement with that calc. on the assumption of a lattice composed of neutral atoms. H. F. G.

Determination of the energy levels of molecules from kinetic data. E. N. GAPON (J. Gen.

Chem. Russ., 1931, 1, 1177—1178).—The energy levels of mols. may be deduced from the energies of activation in those cases in which the mol. is capable of reacting in more than one direction. R. T.

Calculation of electron distribution in a diatomic molecule by the method of Thomas and Fermi. F. HUND (Z. Physik, 1932, 77, 12—25).—The potential due to a diat. mol. can be represented as the sum of two potentials due to spherical distributions of charge. A. B. D. C.

Molecular and atomic volumes. XLI. Density of crystalline hydrogen fluoride and of crystalline fluorides at low temperatures. L. LE BOUCHER, W. FISCHER, and W. BILTZ (Z. anorg. Chem., 1932, 207, 61—72).—The densities of HF , BF_3 , CF_4 , SiF_4 , GeF_4 , SF_6 , SeF_6 , and TeF_6 in the cryst. state at low temp., and in the liquid state at the m.p. and b.p., have been measured and the corresponding zero vols. calc. The results are discussed with reference to data for the other halogen compounds (cf. this vol., 322). J. W. S.

Molecular volume and density at absolute zero. Calculation of the volume correction, *b*, in van der Waals' equation. (MISS) G. L. CHABORSKI (Bul. Chim. Soc. Romane Stiinte, 1929, 31, 53—66, 119—132).—From the density and val. of *b* at any temp., the mol. vol. at 0° abs. can be calc. Data are given for 38 simple org. liquids, Hg , H_2O , Br_2 , PCl_3 , $AsCl_3$, $POCl_3$, $SiCl_4$, $TiCl_4$, and $SnCl_4$, and compared with published data. Conversely, from the density at any temp. and the mol. vol. at 0° abs., *b* can be calc. For any one substance, *b* is approx. a linear function of temp. Hence, from the above data, *b* can be calc. for any temp. Data are given for Cl_2 , Br_2 , O_2 , N_2 , Hg , NH_3 , SO_2 , PCl_3 , $POCl_3$, $AsCl_3$, $SiCl_4$, $TiCl_4$, $SnCl_4$, and 79 org. compounds. D. R. D.

Radiometric forces in low-pressure gases. G. SPIWAK (Z. Physik, 1932, 77, 123—125).—Variation of radiometric force with plate separation was used to determine boundary effects in a Knudsen manometer; for large plate separations the force is inversely proportional to the square of the separation.

Curved-crystal monochromator for powder X-ray photography. (MLLE.) Y. CAUCHOIS (Compt. rend., 1932, 195, 228—231; cf. this vol., 146, 553). C. A. S.

Intensity of reflexion of X-rays by perfect crystals. G. W. BRINDLEY (Proc. Leeds Phil. Soc., 1932, 2, 271—279).—Ewald's theory of reflexion of X-rays based on the theory of optical dispersion leads to divergent results when applied to the intensity of reflexion of X-rays from highly perfect diamond crystals where the angle of reflexion is $>45^\circ$. If the at. structure factor, neglected in Ewald's theory, is taken into account (after slight correction for zero point energy), the theoretical predictions agree with observation for all angles of reflexion. A. J. M.

Refraction of X-rays by perfect crystals. G. W. BRINDLEY (Proc. Leeds Phil. Soc., 1932, 2, 319—323).—Introduction of the at. scattering factor into Ewald's theory of X-ray reflexion leads to vals. of the variation of the intensity of reflexion with angle which

agree better with experimental data (cf. preceding abstract). J. W. S.

Bloch's integral equation in the electronic theory of metals. J. WINTER (Compt. rend., 1932, 195, 33—34; cf. A., 1929, 247; 1930, 141).

C. A. S.

Evidence of mosaic crystals in copper and platinum. F. W. CONSTANT (J. Elisha Mitchell Sci. Soc., 1932, 47, 25). CH. ABS.

Structure of products of action of alkali metals on graphite. A. SCHLEEDF and M. WELLMANN (Z. physikal. Chem., 1932, B, 18, 1—28).—The brown substance formed by the action of K on graphite (cf. A., 1929, 410) has a layer lattice, K planes alternating with the basal planes of the graphite. When the metal planes are complete the composition corresponds with the formula C_8K . By removal of alternate K planes by heating at a higher temp. a black substance is formed in which every two graphite planes are followed by a K plane; the composition is $C_{16}K$. The brown and black products formed by Rb and Cs are similar to the above. The formation of all these substances is explained by adsorption in stoichiometric proportions by the individual C surfaces of the layers of graphite. R. C.

Formation of layer lattices. H. ARNFELT (Arkiv Mat., Astron., och Fysik, 1932, 23, B, No. 2, 1—6).—During the process of graphitisation of coke, X-ray interference lines appear successively as broad diffuse bands which gradually sharpen into lines. Similar behaviour is observed in the cases of MoS_2 , CdI_2 , SnS_2 , $Ni(OH)_2$, and BN . In each case the amorphous substances crystallise into a layer lattice, accelerated greatly by foreign substances. J. W. S.

X-Ray investigation of the role of crystal water in zeolite. B. LENGYEL (Z. Physik, 1932, 77, 133—138).—The H_2O in zeolite is not bound to the lattice. A. B. D. C.

Rhenium trioxide. III. Crystal structure. K. MEISEL (Z. anorg. Chem., 1932, 207, 121—128).— ReO_3 has a cubic structure with 1 mol. in the unit cell, the lattice being analogous to that of WO_3 . $a_w = 3.734 \pm 0.006 \text{ \AA}$, $d_r = 7.43 \pm 0.04$. The radius of the O^{2-} ion is 1.32 \AA . and that of the Re^{6+} ion 0.55 \AA . J. W. S.

Crystal structure of rhombic ammonium nitrate. C. D. WEST (J. Amer. Chem. Soc., 1932, 54, 2256—2260).—The space-group is V_h^a . The NO_3 groups are probably triangles of side 2.10 \AA , with their planes parallel to b . The double refraction is probably due to an arrangement of NO_3 groups in layers in the ac plane. L. W. (c)

Crystal structure of ammonium hexabromoselenate. L. SIEG (Z. anorg. Chem., 1932, 207, 93—96).— $(NH_4)_6SeBr_6$ crystallises in the face-centred O^3 or O_h^3 system, with 4 mols. in the unit cell. The structure is similar to that of K_2PtCl_6 . Each Se atom is surrounded by 8 Br ions, the distance Se—Br being 2.51 — 2.63 \AA . Hence the radius of the Se^{4+} ion is 0.55 — 0.67 \AA . J. W. S.

Crystal lattice of germanous sulphide, GeS . W. H. ZACHARIASEN (Physical Rev., 1932, [ii], 40, 917—922).—Dimensions of unit cell, a 4.29 ± 0.01 ,

b 10.42 ± 0.03 , c $3.64 \pm 0.01 \text{ \AA}$; 4 mols. per unit cell; d_{calc} . 4.24 ; space-group V_h^a . Crystals are orthorhombic bipyramidal. The Ge atom, surrounded by distorted octahedra formed by S atoms, is displaced towards one of the octahedral faces. The distances Ge—S are 2.58 for three of the S atoms, and for the other three 2.97 \AA . Min. distance between S atoms is 3.55 \AA . N. M. B.

Crystal lattice of potassium pyrosulphite, $K_2S_2O_5$, and the structure of the pyrosulphite group. W. H. ZACHARIASEN (Physical Rev., 1932, [ii], 40, 923—935).— a 6.95 , b 6.19 , c 7.55 \AA , β $102^\circ 41'$, d_{calc} . 2.31 , 2 mols. per monoclinic unit cell; space-group C_{2h}^2 . Parameter vals. for 16 degrees of freedom were determined. The K atoms are surrounded by 9 or 7 O atoms at average distances, respectively, of 3.01 and 2.78 \AA . The distance S—S is 2.18 , and the average S—O 1.46 \AA . N. M. B.

Structure and symmetry relationships of complex cyanides of the potassium ferricyanide type. G. NAGELSCHMIDT (Veroff. Kaiser Wilhelm-Inst. Silikatforsch., 1931, 4, 27—56; Chem. Zentr., 1932, i, 629).— a , b , c , and N (no. of mols. per unit cell), respectively, are: $K_3Fe(CN)_6$ 13.42 , 10.40 , 8.38 , 4 ; $K_3Cr(CN)_6$ 13.55 , 10.60 , 8.6 , 4 ; $K_3Mn(CN)_6$ 13.56 , 10.60 , 8.5 , 4 ; $K_3Ir(CN)_6$ 13.70 , 10.53 , 8.34 , 4 ; $Cs_3Fe(CN)_6$ 11.8 , 10.1 , 7.0 , 2 . The space-groups of the cyanide and the positions of the heavy metal atoms have also been determined; symmetry relationships are discussed. L. S. T.

Lattice constants of the spinels $MgAl_2O_4$ and $ZnAl_2O_4$. V. M. GOLDSCHMIDT (Z. physikal. Chem., 1932, B, 18, 29—31).—Polemical against Clark (this vol., 798). R. C.

Confirmation of the space-group of epsomite. W. H. BARNES and R. G. HUNTER (Nature, 1932, 130, 96).—X-Ray data for epsomite give a_0 11.94 , b_0 12.03 , c_0 $6.86(5)$, with 4 mols. per unit cell; space-group Q^4 (cf. A., 1927, 297). L. S. T.

Existence of high-temperature form of cristobalite at room temperature, and crystallinity of opal. J. W. GREIG (J. Amer. Chem. Soc., 1932, 54, 2846—2849).—The failure of small cristobalite crystals embedded in a medium to invert when cooled through the inversion temp. is a more probable explanation of the existence of the high-temp. modification of cristobalite in opals (cf. this vol., 451) than the crystallisation of the high-temp. form at temp. at which the low-temp. form is more stable.

C. J. W. (c)

Inversion of cristobalite. R. B. SOSMAN (J. Amer. Chem. Soc., 1932, 54, 3015—3016).—Experiments on quenching free cristobalite from a temp. above its high-low inversion point have always shown inversion without delay. C. J. W. (c)

Cristobalite structures. II. Low-cristobalite. T. F. W. BARTH (Amer. J. Sci., 1932, [v], 24, 97—110).—Interfacial angles corresponded with those of a cubic crystal, but no cubic arrangement was found which accounted for the observed (X-ray) intensities. In selecting possible tetragonal or orthorhombic arrangements it was assumed that the structure consisted of the usual Si—O chains with direc-

tions in space nearly the same as in high-cristobalite. A suitable orthorhombic arrangement is the space-group $p2_12_12_1$ —(V^4). $a:b:c=1.00:1.00:1.00+0.01$; length of the unit (pseudo) cube of 8 mols. SiO_2 . 7.00 Å., $d_{\text{calc.}}$ 2.30. (Cf. this vol., 564.) A. G.

Crystal structure of stephanite. R. SALVIA (Anal. Fis. Quím., 1932, 30, 416—420).—Stephanite, Ag_5SbS_4 , has a 7.85 ± 0.02 , b 12.48 ± 0.02 , c 8.58 ± 0.02 Å.; 4 mols. in the unit cell; space-group V_1^7 . H. F. G.

Large-scale crystalline structure in certain glasses of exceptional composition. (LORD) RAYLEIGH (Proc. Roy. Soc., 1932, A, 137, 55—61).—The doubly refracting structure of a quasi-cryst. nature formerly observed in pure Si glass has now been found also in highly siliceous glasses down to 80% Si content, and in phosphatic glasses such as "corex" and boracic glasses such as fused $\text{Na}_2\text{B}_4\text{O}_7$ and fused B_2O_3 . L. L. B.

Occurrence and properties of crystalline alumina in silicate melts. H. B. BARLETT (J. Amer. Ceram. Soc., 1932, 15, 361—364).—The cryst. habits of α - and β - Al_2O_3 are described together with those of a new form, ζ - Al_2O_3 (d 3.6, n 1.736, unit cube, probably face-centred, 7.90 Å.) occurring in melts containing Li_2O . J. A. S.

Spacing of non-polar molecules in crystal lattices. Atomic domain of hydrogen. New feature of structure of benzene ring. E. MACK, jun. (J. Amer. Chem. Soc., 1932, 54, 2141—2165).—The radius of the at. domain of H in a crystal, i.e., half the average distance between H nuclei, is found empirically to be 1.29 Å. It is suggested that the C_6H_6 ring is flat, like that of graphite, and that the unsaturation is manifested as "bulges" or "domes," perpendicular to each face. A stereochemical theory of the structure of C_6H_6 , C_6Me_6 , anthracene, and C_{10}H_8 is advanced. L. W. (c)

[Crystal] structure of quinhidrone. O. R. FOZ and J. PALACIOS (Anal. Fis. Quím., 1932, 30, 421—425).—Quinhidrone forms monoclinic crystals having a 3.85, b 6.04, c 10.9 Å.; $d_{\text{calc.}}$ 1.416; 1 mol. in the unit cell; space-group C_{2h}^2 . In the cryst. state the symmetrical mols. are linked into a chain structure by means of H atoms. H. F. G.

X-Ray study of mannitol, dulcitol, and mannose. T. C. MARWICK (Nature, 1932, 130, 96).—A correction (cf. A., 1931, 897). L. S. T.

Layer-chain structures of thallium dialkyl halides. H. M. POWELL and D. M. CROWFOOT (Nature, 1932, 130, 131—132).—Crystal structures of compounds TlR_2X have been studied. The TI dimethyl halides are tetragonal; others are orthorhombic, pseudo-tetragonal, and all show the NaCl type of structure. Layers of TIX parallel to the ab plane are spaced out at distances dependent on the length of the alkyl chains which are attached to the TI ions perpendicularly to these layers. a and b are practically independent of the alkyl group and vary between 4.29 Å. (chloride) and 4.76 Å. (iodide). These spacings agree with other indications that the chains in these compounds do not rotate. L. S. T.

Crystallography of sucrose. II. III. G. VAVRINECZ (Magyar Chem. Fol., 1931, 37, 145—157; Chem. Zentr., 1932, i, 1362, 1362—1363; cf. A., 1928, 110).—II. A statistical study and classification into 3 types.

III. Morphological properties of sucrose crystallised from solvents such as H_2O , EtOH , MeOH , EtOAc , moist COMe_2 , etc. are given. Sucrose is insol. in C_6H_6 , PhMe , CS_2 , CCl_4 , CHCl_3 , PhNO_2 , dry COMe_2 , PhBr , MeOAc , petroleum, and turpentine.

L. S. T.
[X-Ray] structure of highly nitrated cellulose nitrate films. DESMAROUX and MATHIEU (Compt. rend., 1932, 195, 242—243; cf. this vol., 798).—Comparison of films formed from solutions of the same concn. of cellulose nitrate heated at 130° for 12 hr. in H_2O with films from the same cellulose nitrate not so treated shows that crystallinity is decreased by autoclaving. The changes, and the great decrease in viscosity, indicate that the effect of autoclaving is to break up the elementary threads of glucose residues.

C. A. S.
Intumescence as a cause of the characteristic lack of sharpness of the Röntgen spectrum of cellulose acetate. I. J. R. KATZ and A. WEIDINGER (Rec. trav. chim., 1932, 51, 847—852).—Cellulose acetate I, prepared from ramie fibre by acetylating with Ac_2O in C_6H_6 and a trace of H_2SO_4 , gives a sharp X-ray spectrum. The sharpness is destroyed on washing with H_2O . It is suggested that C_6H_6 , Ac_2O , or AcOH mols. form part of the lattice; on their removal, the regularity of the structure is destroyed.

D. R. D.
Structure sensitiveness of magnetism in metals. F. W. CONSTANT and F. E. LOWANCE (J. Elisha Mitchell Sci. Soc., 1932, 47, 24—25).—Changes in magnetic susceptibility of Cu, Ag, Bi, and Pt when subjected to cold working are recorded. CH. ABS.

Piezo-electric experiments using the method of Giebe and Schiebe. A. HETTICH and H. STEINMETZ (Z. Physik, 1932, 76, 688—706).—The presence or absence of piezo-electric properties in many compounds was determined by the method of Giebe and Schiebe (*ibid.*, 1925, 33, 760). A. B. D. C.

Hall effect in bismuth crystals. H. VERLEGER (Z. Physik, 1932, 76, 760—765).—The Hall effect was measured in a single crystal of Bi. A. B. D. C.

Magnetic properties of thin metal layers. W. ELENBAAS (Z. Physik, 1932, 76, 829—848).—The magnetic properties of Fe and Ni layers of thickness 0.2—20 μ were studied before and after tempering; the magnetic curves show evidence of fibre structure. A. B. D. C.

Effect of gases on Barkhausen oscillations. H. RINDFLEISCH (Ann. Physik, 1932, [v], 14, 273—298).—The effect of He and Ne is studied. A. J. M.

Mechanism of plasticity. N. SELJAKOV (Z. Physik, 1932, 76, 535—536).—Stereoscopic photographs of NaCl compressed by 8—10% indicated that the deformed crystal is of the monoclinic type.

A. B. D. C.
Polymorphism of long-chain saturated monobasic acids. Influence of temperature. J. THI-

BAUD and F. D. LA TOUR (J. Chim. phys., 1932, 29, 153—167).—The fatty acids crystallise in stratified layers giving single crystals of two types, α and β ; β crystals change to the α type at the transition temp., but the inverse transformation was not obtained. The transition temp. for $C_{12}H_{24}O_2$, $C_{14}H_{28}O_2$, $C_{16}H_{32}O_2$, $C_{18}H_{36}O_2$, and $C_{27}H_{54}O_2$ lie between 6° and 80° . α Crystals of palmitic acid and β crystals of stearic acid were examined by physical methods.

W. R. A.

Germanium. XXXIX. Polymorphism of germanium dioxide. A. W. LAUBENGAYER and D. S. MORTON (J. Amer. Chem. Soc., 1932, 54, 2303—2320).—The sol. and insol. modifications are enantiotropic, the transition temp. being $1033 \pm 10^\circ$. The stable m. p. of the sol. form is $1116 \pm 4^\circ$, and the metastable m.p. of the insol. form $1086 \pm 5^\circ$.

M. McM. (c)

Non-existence of two modifications in liquid nitrobenzene and carbon disulphide. E. MURAKAMI (Bull. Chem. Soc. Japan, 1932, 7, 216—221).—The heating curve of $PhNO_2$ from 8.25° to 10.25° , the change of d from 7° to 11° and of n from 8.25° to 19.3° , and the heating curve of CS_2 from -100° to -85° are continuous, and the liquid is homogeneous throughout. These liquids do not give two modifications (cf. this vol., 329).

R. S. C.

Temperature variations of the density and mol. wt. of molten bismuth. A. JOUNIAUX (Bull. Soc. chim., 1932, [iv], 51, 677—681).—The following relationship between sp. vol. v_t and temp. t has been deduced from d measurements of molten Bi at 420 — 1100° : $v_t = 0.1011 + 128 \times 10^{-7}(t - 420)$. Cryoscopic data for solutions of Bi in Co, Ni, Cu, Ag, Mg, Te, Zn, and Pb are also given. Data for d , surface tension, v.-p. and f.-p. lowering indicate that the mol. wt. of Bi below 420° diminishes as the temp. rises; between 420° and 1400° it equals the at. wt., and above 1400° the mol. wt. increases up to 1500° , goes through a max., and decreases until it is again equal to the at. wt. at about 2100° .

M. S. B.

Method for determining the velocity of sound in solids. W. T. RICHARDS (Science, 1932, 76, 36—37).

L. S. T.

Heat conductivity, Wiedemann-Franz-Lorenz number, and thermo-electric force of single crystals of mercury. H. REDDEMANN (Ann. Physik, 1932, [v], 14, 139—163).—The prep. of single crystals of Hg, together with the above determinations, is described.

A. J. M.

Electrical and heat conductivity of zinc and cadmium crystals. E. GOENS and E. GRUNEISEN (Ann. Physik, 1932, [v], 14, 164—180).—Both Zn and Cd show increase in heat conductivity as the temp. is lowered in the two principal crystal directions. The Wiedemann-Franz-Lorenz ratio was determined.

A. J. M.

Measurements with the aid of liquid helium. XIX. Investigations of the alloy series lead-thallium and lead-bismuth in relation to superconductivity. W. MEISSNER, H. FRANZ, and H. WESTERHOFF (Ann. Physik, 1932, [v], 13, 967—984).—The conductivities of these alloys at temp. of 1.5 —

20° abs. have been investigated. The superconductivity temp. of Pb-Tl alloys are similar to those found with other systems. By extrapolation of the data for Pb-Tl mixed crystals, the val. for β -Tl is calc. and found to be considerably lower than that for α -Tl. The superconductivity curve for Pb-Bi alloys corresponds with the phase diagram deduced from X-ray measurements by Solomon and Jones (A., 1931, 676). The elevation of the superconductivity temp. by addition of Bi probably arises from the fact that the latter is cubic or hexagonal in solution, not rhombohedral as in the pure state.

J. W. S.

Mechanism of superconductivity. J. DORFMAN (Nature, 1932, 130, 166—167).—A discussion.

L. S. T.

Superconductivity of argon and neon. A. GUNTHER-SCHULZE and F. KELLER (Naturwiss., 1932, 20, 592).—The gradient in A and Ne is very small and may probably arise from impurities.

Agreement of the ordinary with the thermodynamic scale of temperature. W. HEUSE and J. OTTO (Ann. Physik, 1932, [v], 14, 181—184).—The scales were compared between 0° and -183° . The ordinary scale is slightly higher than the thermodynamic in this range, the max. deviation being 0.04° at about -80° .

A. J. M.

Gas thermometer determinations of some fixed points below 0° with pressure and resistance thermometers. II. W. HEUSE and J. OTTO (Ann. Physik, 1932, [v], 14, 185—192).—Using a He thermometer in conjunction with a resistance thermometer, the v.-p. curves of some gases in the neighbourhood of atm. pressure were investigated, and extrapolated to 760 mm. The following results were obtained (temp. on thermodynamic scale): normal b.p. of N_2 , -195.814° ; normal b.p. of CO, -191.484° ; normal b.p. of O_2 , -182.963° ; normal sublimation temp. of CO_2 , -78.471° .

A. J. M.

Physical properties of sulphur, selenium, and tellurium hexafluorides and carbon tetrafluoride. W. KLEMM and P. HENKEL (Z. anorg. Chem., 1932, 207, 73—86).—The m.p., v.d., and sp. gr. in both liquid and solid states of these compounds have been determined. The b.p. and v.p. of SF_6 , SeF_6 , and TeF_6 have also been measured and the heats of sublimation, vaporisation, and fusion calc. The results are in good agreement with previously recorded vals.

J. W. S.

Specific heats of five organic liquids from their adiabatic temperature-pressure coefficients. W. T. RICHARDS and J. H. WALLACE, jun. (J. Amer. Chem. Soc., 1932, 54, 2705—2713).—The sp. heats of C_6H_6 , PhMe, CCl_4 , $CHCl_3$, and C_7H_{16} have been determined with a precision of 0.5% by measuring the change of temp. with pressure under adiabatic conditions. The pressure range was 15 — 30 atm. and the temp. range 20 — 50° . The results confirm existing data.

E. J. R. (c)

Spectroscopic determination of the specific heat of gases at high temperatures. E. JUSTI (Forsch. Gebiet Ingenieurwesens, 1931, A, 2, 117—124; Chem. Zentr., 1932, i, 1344).—Einstein's theory

is valid for diat. gases and CO_2 at high temp. Vibration frequencies can be determined from spectra and the increase in sp. heat calc. from the tables given.

L. S. T.

Heat capacity and entropy of carbon monoxide. Heat of vaporisation. Vapour pressures of solid and liquid. Free energy up to 5000° abs. from spectroscopic data. J. C. CLAYTON and W. F. GIAUQUE (J. Amer. Chem. Soc., 1932, 54, 2610—2626).—The heat capacities from 13° to the b.p., $81.61 \pm 0.05^\circ$ abs., of the liquid and the two cryst. forms, transition point $61.55 \pm 0.05^\circ$, m.p. $68.09 \pm 0.05^\circ$ abs., and the v.p. of the solid and liquid have been measured. The mol. heats of transition, vaporisation, and fusion are 151.3 ± 1 , 1443.6 ± 1.0 , and 199.7 ± 0.2 g.-cal., respectively. The observed entropy of the gas at 81.61° abs. is about $R \log_e 2$ below the corr. calc. val., 37.2; an explanation is suggested. The entropy at 298.1° abs., calc. from mol. spectra, is 47.313. The free energy has been calc. up to 5000° abs. from spectroscopic data. Combination of these results with similar data for O_2 and calorimetric data for graphite gives ΔF° up to 3000° abs. for the reaction $\text{C}_{\text{graphite}} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$. The free energy of formation of CO from β -graphite and O_2 at 298.1° abs. is -33 kg.-cal.

G. M. M. (c)

Density of pyridine between 0° and 90° . R. MÜLLER and H. BRENNIS (Z. Elektrochem., 1932, 38, 450—451).—The density of $\text{C}_5\text{H}_5\text{N}$ falls linearly from 1.0031 at 0° to 0.9111 at 90° .

H. F. G.

Adiabatic expansion of saturated vapours and the formation of mists. N. A. KOLOSOVSKI and V. V. UDOVENKO (J. Gen. Chem. Russ., 1931, 1, 1245—1248).—Saturated vapours, the mols. of which contain <10 atoms, have a negative sp. heat, and therefore condense on adiabatic expansion. This rule is verified for a no. of org. liquids.

R. T.

Vapour pressure of chlorine heptoxide. C. F. GOODEVE and J. POWNY (J.C.S., 1932, 2078—2081).— Cl_2O_7 (improved prep.) has b.p. 80° , m.p. $-91.5 \pm 2^\circ$.

A. J. M.

Conception of relative humidity, particularly at high temperatures. H. EBERT (Z. Physik, 1932, 76, 163—171).—The ordinary definition of relative humidity fails at high temp., particularly when the total pressure of gases present is less than the saturation v.p. of H_2O at the given temp.; for these temp. a formula is deduced giving the ratio of the mass of H_2O to the mass of air in any given vol., and this replaces the definition by partial pressures which is valid at lower temp.

A. B. D. C.

Application of Knudsen's law to the evaporation of water. T. ALTY (Nature, 1932, 130, 167—168).—When the temp. of an evaporating surface layer of H_2O is accurately measured there is still a discrepancy between calc. and experimental vals. for the rate of evaporation (cf. A., 1931, 904).

L. S. T.

Free energy, heat content, and entropy of iodine monochloride. J. McMORRIS and D. M. YOST (J. Amer. Chem. Soc., 1932, 54, 2247—2256).—The equilibrium between I_2 , Cl_2 , and ICl has been investigated at 368 — 473° by measurement of the reaction of Cl_2 under const. pressure with I_2 , and at

136 — 179° by the reaction of NOCl and I_2 . The free energy, ΔF° , of the reaction $\frac{1}{2}\text{I}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) = \text{ICl}(\text{g})$ is $-3125 - 1.77T$, which agrees with the val. derived from spectral data.

A. F. (c)

Entropy of bromine from spectroscopic data. W. G. BROWN (J. Amer. Chem. Soc., 1932, 54, 2394—2396).—The entropies in the standard state of Br_2° , $\text{Br}_2^{29.81}$, and Br_2^{31} , calc. from analysis of the fine structure of the visible bands, are 58.56, 60.01, and 58.70, and for the 1:2:1 mixture the val. is 59.32. These vals. agree with sp. heat data. For gaseous Br_2 , a correction for the entropy of 'mixing' yields $S_{298.1}^\circ = 58.63$.

H. F. J. (c)

Isotherms of water from 350° to 480° and for pressures up to 600 kg./cm.² C. J. VAN NIEUWENBURG and (MISS) H. B. BLUMENDAL (Rec. trav. chim., 1932, 51, 707—714).—The relations between p , v , and t have been investigated in detail over the range indicated. $v_c = 226$ kg./cm.², $v_c = 3.06$ cm.³/g., $t_c = 374^\circ$.

D. R. D.

Equation of state of a non-ideal Einstein-Bose or Fermi-Dirac gas. G. E. UHLENBECK and L. GROPPER (Physical Rev., 1932, [ii], 41, 79—90).—Mathematical.

N. M. B.

Van der Waals' equation of state. I. K. JABLONSKI (Physikal. Z., 1932, 33, 536—543).—The coeffs. a and b of the van der Waals equation can be calc. independently from the pv^2 min. At pv^2 min. the min. vol. $v = 2b$. b is const. over a wide temp. range, but a is dependent on temp. and vol. Vals. of a and b are calc. from experimental data on CO_2 , CO , C_2H_4 , N_2 , H_2 , O_2 , and He . Vals. for crit. vol., pressure, and temp. have been calc.; they are not in agreement with observed data.

W. R. A.

Equation of state for gases at low densities. D. LE B. COOPER and O. MAASS (Canad. J. Res., 1932, 6, 596—604).—A new equation of state is developed for gases at low densities, using a new function for the change in viscosity with temp. Satisfactory agreement is obtained with experimental results for CO_2 .

J. W. S.

Internal friction and density in flames. A. BECKER and K. VOGT (Ann. Physik, 1932, [v], 14, 241—258).—The internal friction and density in flames in relationship to the hydrodynamic resistance imposed by cylinders and spheres in the flame are investigated.

A. J. M.

Diffusion of hydrogen through palladium. V. LOMBARD and C. EICHNER (Compt. rend., 1932, 195, 322—324; cf. this vol., 685).—Measurements at 275 — 595° and 70 — 772 mm. indicate that the rate of diffusion/temp. curve is approx. exponential. For a plate 0.051 mm. thick and 410° the rate of diffusion is proportional to $p^{0.62}$. There is some evidence that Pd undergoes a change of state at 460° .

C. A. S.

Diffusion of mercury drops on rolled tin foils. F. W. SPIERS (Proc. Leeds Phil. Soc., 1932, 2, 280—288).—When Hg drops fall on Sn foil elliptical diffusion areas are formed; the amalgam has an approx. const. composition (11.8 at.-% Hg), and shows a hexagonal cryst. structure. The amalgam may be an inter-metallic compound, HgSn_3 .

A. J. M.

Influence of temperature on the diffusion velocity of solid metals (the zinc-copper system). C. MATANO (Mem. Coll. Sci. Kyoto, 1932, A, 15, 167—180).—By determining the change in resistance with time of metal foil composed of alternate layers of Zn and Cu, when immersed in a const.-temp. bath, the velocities of diffusion, V , at different temp. (87—302°) have been compared. $V = Be^{-\alpha/T}$, where B and α are consts. X-Ray photographs confirm that diffusion occurs. D. R. D.

Transformation of the β -phase in copper-zinc alloys. P. A. SALDAU and I. V. SCHMIDT (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 201—222).—The β -phase of Cu-Zn alloys heated at 440° during 84 days does not decompose with formation of α - and γ -phases. During this period the limits of the β -phase extend towards higher Zn content. At 480° the β -phase exists between 56.01 and 51.39 at.-% Cu, these limits widening as the temp. rises. R. T.

Lead-rich alloys of the system lead-antimony examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1932, 28, 567—569).—Equilibrium data are consistent with coexisting solid and liquid phases containing Pb_2Sb in monat. Pb. This result is at variance with X-ray data. J. G. A. G.

Dia- and para-magnetism in series of metallic mixed crystals. E. VOGT (Ann. Physik, 1932, [v], 14, 1—39).—The dependence of magnetic susceptibility on the concn. of the mixed crystals Au-Ag, Au-Pd, and Pt-Pd and the effect of the adsorption of H_2 by these alloys has been investigated. The magnetic properties are most rationally explained by the concept of at. susceptibility. This quantity shows marked deviations from the mixture rule in the diamagnetic direction for the series Au-Pd and Pt-Pd, which may be explained by supposing that the valency electron of the added metal causes the paramagnetic Pd^+ ions to change into the uncharged diamagnetic Pd atoms. Pd also loses its paramagnetism when it takes up H_2 , presumably for the same reason. A. J. M.

Existence of resistance limits in mixed crystals with haphazard atomic distribution. R. GLOCKER (Ann. Physik, 1932, [v], 14, 40—50).—It is shown theoretically that there must be a sharp resistance limit. A. J. M.

System aluminium-magnesium-silicon. L. LOSANA (Metall. Ital., 1931, 23, 367—382; Chem. Zentr., 1932, i, 1425).—Thermal analyses of 150 alloys have been made. A ternary eutectic with 5.5% of Mg and 14% of Si occurs at 559°. The field of solid solutions is limited. Alloys rich in Mg have their hardness increased slightly by the first additions of Si. Si alloys containing even 0.5–1% Mg are very brittle. L. S. T.

Ternary alloys of aluminium with silicon and copper. G. G. URAZOV, S. A. POGODIN, and G. M. ZAMORUEV (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 157—200).—Alloys containing up to 24% Si and 40% Cu consist of a mixture of Si, $CuAl_2$, and solid solutions of Cu in Al. The solubility of Cu in Al increases with the Si content; at the same time the tempering qualities of the alloy diminish. The

hardest alloy is the ternary eutectic Al-Si- $CuAl_2$, m. p. 525°, containing 5% Si, 27% Cu, and 68% Al. R. T.

Structure of some ternary alloys of aluminium, copper, and iron. K. YAMAGUCHI and I. NAKAMURA (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 815—833).—From the thermal analysis and microstructure of these alloys the phase diagram for the system Al-Cu-Fe has been evolved. The ternary phase usually designated " N " is an intermetallic compound of composition Cu_2FeAl_7 which appears to form a solid solution sparingly. It is formed by a peritectic reaction $2CuAl_2$ (liq.) + $FeAl_2$ (liq.) \rightarrow Cu_2FeAl_7 (solid). Another ternary phase, richer in Cu than " N ," has been recognised. Its form is polygonal and it gives a brown colour with aq. $Fe(NO_3)_3$ or HNO_3 . J. W. S.

Copper-nickel-silicon alloys rich in copper. E. CREPAZ (Metall. Ital., 1931, 23, 711—716; Chem. Zentr., 1932, i, 1426—1427).—The reduction in mixed crystal formation between Cu and Si with a fall in temp. is confirmed; at 750° the solubility of Si is 6.7% compared with 2.7% at room temp. The solubility of Ni and Si in Cu has been determined, together with the Brinell hardness of the quenched and tempered alloys. Hardness changes suddenly at the ratio 2Ni : Si. L. S. T.

Influence of silicon on copper-nickel alloys containing little tin. L. GUILLET, M. BALLAY, and A. LE THOMAS (Compt. rend., 1932, 195, 89—92).—The effect of Si when added to ordinary bronze or Ni-Sn alloys is similar to that in Cu-Ni alloys. In the case of Cu-Ni alloys with small Ni content the compound Ni_2Si appears if more than 1% Si is present, but with >50% Ni, 3% Si may be added without this result. C. A. S.

Change of austenite into martensite in iron-nickel alloys under load. E. SCHEL (Z. anorg. Chem., 1932, 207, 21—40).—The amount of martensite formed in Fe-Ni steel at any temp. is increased considerably by tension. Plastic deformation of steel, however, leads to martensite formation only over a definite temp. range above the transition temp. Slip-plane formation decreases the transition tendency. Spontaneous martensite formation may be due either to internal tension or, more probably, to mechanical instability of the austenite. J. W. S.

Diffusion and segregation in solid solutions. A. SMEKAL (Z. Metallk., 1932, 24, 121—124).—Hane-mann and Schroder's theory of the mechanism of diffusion in and separation of segregates from solid solutions is not in accordance with known facts. The orientation of segregates is determined not so much by the presence of free lines of movement for the atoms of the segregate in the lattice of the solid solution as by the presence of internal stresses which usually concentrate along planes of slip, twinning, or cleavage; with a high rate of pptn. of a constituent from a solid solution the segregates collect along these planes, but with a low rate of pptn. the stresses set up are at first insufficient to promote orientation of the segregates, and as soon as the first slip plane appears new nuclei of the segregate become visible along it. If the rate of diffusion of the segregates themselves exceeds the

rate of pptn., then the shape of the segregates may change appreciably without further pptn. The shape and orientation of segregates are also influenced by the nature of the solid solution lattice as well as by that of the lattice of the new constituent. A. R. P.

Diffusion and segregation in solid solutions. M. VON SCHWARZ (Z. Metallk., 1932, 24, 124—126).—Evidence in support of the above considerations is afforded by examination of Si-Cu solid solutions under the polarising microscope after various heat-treatments. A. R. P.

Formation and properties of precipitates. Theory of co-precipitation. VIII. I. M. KOLTHOFF (Chem. Weekblad, 1932, 29, 442—448).—Mixed crystal formation, resulting from adsorption during the growth of a ppt., is discussed. The extent to which true co-pptn. takes place is dependent on the degree of displacement of the adsorption equilibrium during growth of the ppt. A ppt. resulting from coagulation of a colloid carries impurities only as an adsorbed film on the surface of the particles; penetration never occurs. Occluded impurities are gradually removed if a freshly-formed ppt. is allowed to remain in contact with its mother-liquor. H. F. G.

Solubility of hydrogen in water at 25° from 25 to 1000 atmospheres. R. WIEBE, V. L. GADDY, and C. HEINS, jun. (Ind. Eng. Chem., 1932, 24, 823—825).—The solubility, S , rises from 0.0178 c.c. per g. of H_2O at 1 atm. to 15.20 at 1000 atm. (calc. as at s.t.p.). Over the range 50—1000 atm., $S=0.0244+0.01712p-0.00000196p^2$. D. R. D.

Solubility of antimony trisulphide and stannic sulphide in ammonia and ammonium carbonate. P. A. EPIK (Z. anal. Chem., 1932, 89, 17—23).— Sb_2S_3 is appreciably sol. (about 1.28%) in aq. NH_3 , especially on warming, but almost insol. in aq. $(NH_4)_2CO_3$. SnS_2 is readily sol. in aq. NH_3 and slightly sol. (about 0.17%) in aq. $(NH_4)_2CO_3$. These results invalidate the quant. separation of As from Sb and Sn by the different solubilities of their sulphides in aq. NH_3 and $(NH_4)_2CO_3$. E. S. H.

Interdependence of curves representing one and the same property of a binary system, expressed as molar concentrations, and as concentrations by weight. V. A. ANOSOV (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 143—150).—Property-composition curves vary in shape according to whether the composition is expressed in mol.-% or in wt.-%. R. T.

Shape of curves representing properties of binary systems in the case of undissociated compound formation. V. A. ANOSOV (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 151—156).—Theoretical. R. T.

Freezing points of ternary alcohol mixtures. D. S. DAVIS (Chem. Met. Eng., 1932, 39, 345).—A nomograph, based on an empirical equation, is given to enable Aldrich and Quercfeld's (A., 1931, 901) f.-p. data for the system $MeOH-EtOH-H_2O$ to be interpolated. C. I.

Sorption of condensible vapours by porous solids. I. Application of the capillary theory.

A. G. FOSTER (Trans. Faraday Soc., 1932, 28, 645—657; cf. A., 1929, 389; this vol., 16, 697).—Theoretical. One or two layers of strongly adsorbed mols. fill the small pores, but in larger pores capillary condensation ensues in certain cases, and it is suggested that the hysteresis previously observed (*loc. cit.*) is due to retarded meniscus formation. The influence of temp. on the desorption equilibria accords with the Kelvin equation which enables isothermals for different liquids and the same adsorbent to be reduced to a uniform scale. Systems with completely reversible isothermals afford no evidence of condensation. Isothermals of this type are attributed to layer adsorption and the sp. properties of the sorbed liquid markedly affect their shape, whilst in capillary adsorption the shape of the isothermals is governed largely by the size of the pores. J. G. A. G.

Solubility and activated adsorption. E. W. R. STEACIE (Trans. Faraday Soc., 1932, 28, 617—618; cf. A., 1931, 904).—Polemical against Taylor (this vol., 331). J. G. A. G.

Sorption velocity of gases by porous solids. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1932, 7, 177—188).—The velocity of sorption of gases by porous solids at const. pressure and temp. is discussed. The sorption proceeds in two stages, the velocity of the first being given by $dx/dt=K(S-x)/x^r$, where x denotes the amount sorbed at time t , and K , S , and r are consts. The velocity of the second stage is given by $x-\alpha \log t=k$, where α and k are const. O. J. W.

Adsorption with silica gel at low temperatures. W. D. UREY (J. Physical Chem., 1932, 36, 1831—1845).—Below a temp. near the crit. temp., T_c , He , A , O_2 , and CH_4 partly undergo capillary condensation, but at higher temp. there is surface adsorption. Within the gel pores T_c seems to be abnormally high. An automatic Toepler pump is described. C. A. (c)

Selective adsorption by silica gel from ammoniacal solutions of heavy metals. BERTHON (Compt. rend., 1932, 195, 384—386).—Ammoniacal solutions of the sulphates of Cu, Zn, Cd, and Ni have been examined with reference to the adsorption which occurs in contact with Patrick's SiO_2 gel. C. A. S.

Adsorption of metallic cations by cellulose. P. PASCAL and (MLLE.) J. HANSOT (Compt. rend., 1932, 195, 349—351).—The adsorption from solutions of $Pb(NO_3)_2$, $TiNO_3$, and $PbCl_2$ buffered at pH 4.8 has been examined. C. A. S.

Adsorption of dyes on diamond, charcoal, and artificial silk. H. LACHS and S. PARNAS (Z. physikal. Chem., 1932, 160, 425—444).—Paneth and Radu's experiments (A., 1924, ii, 606) have been repeated by an improved method, and their results confirmed. In the adsorption by diamond and acetate silk, the measured surface area of the adsorbent shows the adsorbed film to be unimol., and although the other adsorbents have greater adsorptive power, this is due to the existence of a large internal adsorbing surface in addition to the observed surface, and there is no evidence of the formation of multimol. films. The internal surface of viscose is $>$ that of cuprammonium silk. R. C.

Light absorption and adsorption energy. J. H. DE BOER (*Z. physikal. Chem.*, 1932, B, 18, 49—52).—The adsorption energy of an adsorbed mol. will change when the mol. is excited by absorption of light. The absorption bands will consequently be displaced by adsorption in a direction determined by the relation between the adsorption energies of the excited and normal mol. Colour changes accompanying the formation of mol. compounds may be explained similarly. R. C.

Attraction and repulsion between the plates in Schultze's "gorge" method. S. RAY (*Kolloid-Z.*, 1932, 60, 77).—Theoretical. The effect described (this vol., 112) is independent of the geometrical form, but not of the material, of the plates. E. S. H.

Capillary behaviour of glycine. R. JONES and W. C. M. LEWIS (*Biochem. J.*, 1932, 26, 638—639).—The surface tension of glycine dissolved in H_2O has a max. val. at the isoelectric point. S. S. Z.

Light-sensitive surface layers. II. F. WEIGERT and E. EBERIUS (*Kolloid-Z.*, 1932, 60, 13—23; cf. this vol., 460).—The red-sensitive surface layer formed at the surface of AgBr-gelatin emulsions by slow drying is followed by a second layer, which is sensitive to green light. The thickness of the layer is $< 700 \text{ \AA}$., and it probably consists of a unimol. layer of gelatin oriented with the long axes of the mols. perpendicular to the surface. E. S. H.

Significance of interfacial reactions. E. HEYMANN (*Allgem. Oel- u. Fett-Ztg.*, 1932, 29, 389—393).—A discussion of adsorption phenomena. E. L.

Protein monolayers. A. H. HUGHES and E. K. RIDEAL (*Proc. Roy. Soc.*, 1932, A, 137, 62—77).—Protein films on liquid surfaces, previously examined, are probably not homogeneous, and a method is described whereby a film of protein of known wt. can be spread directly from the solid protein on to the surface. Such films have been examined quantitatively by measurement of the surface pressure and surface potential, and qualitatively by means of the dark-field ultramicroscope, on 0.01N-HCl and -NaOH, and on a phosphate buffer, 5.9. Homogeneous films of gliadin were obtained with a thickness of 3 \AA ., and the change from a liquid to a gelatinous film has been detected by both methods. A general structure is assigned to protein films on the assumption that the basic polypeptide chains are stretched flat on the surface of the liquid in the most expanded state of the film. L. L. B.

Influence of temperature on structure of cellulose nitrate films. DESMAROUX and MATHIEU (*Compt. rend.*, 1932, 195, 383—384).—The discrepancy between the authors' results (cf. this vol., 798) and those of Trillat (cf. this vol., 683) is attributed to the circumstance that the film used by the latter was evaporated at 70° instead of at room temp.; such high-temp. films exhibit well-developed cryst. character. C. A. S.

Magnetic birefringence of aqueous solutions of salts of rare earths. C. HAENNY (*Compt. rend.*, 1932, 195, 219—222; cf. this vol., 10). Data are recorded for solutions of the nitrates. C. A. S.

Preparation of colloidal gold solution. A. R. BONHAM (*Canad. Pub. Health J.*, 1932, 23, 92—94).—Freshly doubly distilled H_2O (1200 c.c.) and 1% $K_2C_2O_4$ solution (15 c.c.) are heated to the b. p. and treated with 15.6 c.c. of a mixture of 1% $AuCl_3$ (50 c.c.) and 1% KOH (15 c.c.). When a red colour develops the heat supply is diminished, and at a ruby shade is stopped. After 5 min. the solution is placed in the dark. CH. ABS.

Radius of particles in a disperse system. R. AUDUBERT (*Compt. rend.*, 1932, 195, 306—307; cf. this vol., 911).—For suspensions of gamboge, mastic, As_2S_3 , and Fe_2O_3 calc. vals. of the radii are in fair agreement with the results of counting and weighing, but not of fractional centrifuging. C. A. S.

Dependence of light scattering in aerosols on the particle size and the wave-length. I. D. GUREVITSCH and G. P. LUTSCHINSKI [with V. F. MICHAÏLOV] (*Kolloid-Z.*, 1932, 60, 24—34).—The formulæ of Rayleigh and of Clausius, which are derived for isodisperse systems, do not hold for the aerosols investigated (cf. A., 1927, 9). The intensity of the scattered light I for const. wave-length can be expressed by either (a) $I - Knd^2$ or (b) $I - Knd^3$ (where n is the no. of particles per unit vol., d the diameter of the particle, and K a const.), according to the structure of the disperse particles. Formula (a) holds for dense spheres (oil and tobacco smoke) and (b) for loose aggregates (MgO and Na_2O_2 smokes). The constancy of $I\lambda^4$ in Rayleigh's equation is only a special case of the general constancy of $I\lambda^n$, where n increases with decreasing mean particle size. E. S. H.

Viscosity of suspensions. II. Viscosity of gold hydrosol. (MLLE.) D. SACHS (*J. Chim. phys.*, 1932, 29, 280—286).—The val. of K in the Einstein viscosity formula is 35 for Au hydrosols prepared by electro-dispersion, thus differing widely from theory. The application of this formula is regarded as unjustifiable (cf. A., 1931, 1367). E. S. H.

Osmotic pressure of solutions of cellulose acetate. J. GRARD (*J. Chim. phys.*, 1932, 29, 287—296).—Apparatus and technique applicable to solutions of cellulose acetate in $COMe_2$ at 20° are described. The osmotic pressure increases more rapidly than the concn.; the apparent mol. wt. decreases correspondingly with increasing concn. For 3% solutions the mol. wt. varies between 23,000 and 34,000 according to the source of the material. There is no exact relation between the osmotic pressure of different samples and their sp. viscosity, but in general high osmotic pressure accompanies low viscosity. E. S. H.

Importance of cryolysis for enzymic processes and formation of emulsions. F. F. NORD, O. M. VON RANKE-ABONYI, and G. WEISS (*Ber.*, 1932, 65, [B], 1148—1170).—A lyophile-colloidal zymase solution, after freezing and thawing, shows a temporarily enhanced activity due to an increase of surface. Certain compounds which increase the enzymic activity in various cell systems by increasing the cell permeability are destroyed by lyophile-colloidal particles which can therefore exert a protective action. It follows that the adsorptive may exercise a twofold

function in biologically important reactions. Measurements of surface tension, drop no., viscosity, electrical conductivity, or cataphoretic rate of migration show that lyophilic colloids in solution or emulsion undergo an irreversible physical change under the influence of frost. If viscosity measurements are excluded, the direction of change is similar for all colloids in dilute systems. In more conc. solutions or emulsions a different kind of change is observed with ovalbumin. Emulsions prepared with emulsifiers which have been frozen are somewhat more stable than those obtained without this pre-treatment. It appears that the functions of a colloid carrier depend on its physical condition. H. W.

Thermodynamics of solvation equilibrium in colloidal solutions. G. V. SCHULZ (Z. physikal. Chem., 1932, 160, 409—424).—An equation has been derived for the mol. potential, μ_1 , of the free solvent in a sol by assuming that μ_1 can be treated as equiv. to the mol. potential of the solvent in a true solution. Similarly, an expression for the mol. potential, μ_2 , of the solvent bound by the disperse phase has been obtained by regarding μ_2 as equiv. to the mol. potential of the solvent in a gel. These equations lead to the osmotic pressure relations established experimentally (this vol., 225, 570) and make it possible to calculate from osmotic and swelling pressure data the mol. free energy of the bound solvent in any state of a colloidal system. R. C.

Electrical properties of oil-water emulsions, with special reference to the structure of the plasmatic membrane. II. H. H. DIXON and T. A. BENNET-CLARK (Sci. Proc. Roy. Dublin Soc., 1932, 20, 211—226; cf. *ibid.*, 1930, 19, 35).—Emulsions of olive oil in H_2O containing Na oleate as emulsifier are unstable and not truly reversible when the H_2O -phase ratio is $>30\%$. Application of a small e.m.f. causes columns of the H_2O phase to form throughout the emulsion by elongation of the droplets; hence a large increase in electrical conductivity occurs and the permeability of the emulsion to H_2O -sol. substances is increased. Homogenised emulsions automatically recover the original resistance. H_2O -in-oil emulsions may remain polarised after the passage of an electrical current, the p.d. being retained for a considerable time. With a suitably adjusted Na : Ca ratio in the emulsion, very small e.m.f. may bring about the puncturing of the oil layer by the deformed H_2O phase. Within limits the sensitivity of the emulsions decreases with decreasing Na : Ca ratio; the sensitivity increases rapidly with rise of temp. and varies with the age of the emulsion. The points of similarity between the electrical behaviour of H_2O -in-oil emulsions and the plasmatic membrane are summarised. E. S. H.

Electric charge on an oil droplet in an emulsion. W. C. M. LEWIS (Trans. Faraday Soc., 1932, 28, 597—607).—Theoretical. The total electric charge density is calc. on certain assumptions (cf. Knapp, *ibid.*, 1921, 17, 457). The charge density is independent of droplet size and equilibrium is therefore possible in a polydisperse system. In oil emulsions, the charge responsible for electrophoresis is only a small fraction of the total charge, but in the case of air bubbles

in H_2O , the total charge is electrophoretic. The pressure relations inside droplets are considered.

J. G. A. G.

Action of light on the flocculation of colloidal solutions in a fluorescent medium. A. BOUTARIC and J. BOUCHARD (Bull. Soc. chim., 1932, [iv], 51, 757—760).—The flocculation of As_2S_3 hydrosols by electrolytes is accelerated by visible light in the presence of eosin, fluorescein, or erythrosin. Ultra-violet light has a stronger accelerating influence. This effect occurs only with fluorescent substances; it has been observed with many colourless fluorescent compounds under the influence of ultra-violet light, but not with non-fluorescent dyes, and the accelerating effect increases with the fluorescent power. The apparent flocculation val. of the electrolyte is lowered. E. S. H.

Electrolyte coagulation of silicic acid sols. J. POSTMA (Rec. trav. chim., 1932, 51, 726—738).—The coagulation of neutral and alkaline SiO_2 sols and aq. Na_2SiO_3 has been examined. For $BaCl_2$ and $CaCl_2$, the coagulation concn. decreases with increasing alkalinity; for $NaCl$, NH_4Cl , and $Al_2(SO_4)_3$, the reverse is the case. The limiting concn. of $BaCl_2$ becomes smaller and the quantity of Ba^{++} adsorbed by the ppt. becomes the greater the older is the solution. The results are discussed theoretically. D. R. D.

Application of physico-chemical analysis to the investigation of peptisation. A. DUMANSKI (Kolloid-Z., 1932, 60, 39—52).—A procedure for determining peptising effect and representing the results in a triangular diagram is described. The experimental results show the solid-phase effect in the peptisation of $Fe(OH)_3$ by $FeCl_3$, the amount peptised being a max. for medium amounts of peptiser. Addition of electrolytes to this system reduces the amount of peptisation, the effect of cations being in the order $Li^+ > Na^+ > Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++}$; the effect of Cl^- or Br^- is negligible, but SO_4^{--} is a powerful anti-peptiser. Results are also given for the systems: $Fe(OH)_3$ -mannitol-NaOH; $Fe(OH)_3$ -Na tartrate-NaOH; $Cu(OH)_2$ -K Na tartrate-NaOH; $CaCO_3$ -sucrose-NaOH. E. S. H.

Polymorphism of substances of high mol. wt. III. **Mutarotation of gelatin in correlation with the change in its Röntgen spectrum on coagulation.** J. R. KATZ (Rec. trav. chim., 1932, 51, 835—841).—A discussion of published data. D. R. D.

Influence of anions on the diffusion velocity of OH^- ions in gelatin jellies. V. V. ERIMOV (Kolloid-Z., 1932, 60, 78).— HCO_3^- , HPO_4^{--} , and $H_2PO_4^-$ reduce markedly the diffusion velocity of OH^- in gelatin gels (cf. this vol., 807). E. S. H.

Rôle of acids in the gelation of pectin sols. S. GLÜCKMANN (Kolloid-Z., 1932, 60, 52—59).—The increased gelation tendency of pectin sols in the presence of acids is due to the liberation of pectic acid from the cation with which it is combined. A buffering effect is shown only by samples of pectin which have a high ash content; the ash gives a measure of the cation combined with pectic acid and the buffering effect is a simple exchange between the pectin salt and the added acid. When an excess of

acid is added, no increase in gelation tendency occurs until high acid concns. are reached, when a further increase is caused by chemical alteration of the disperse phase. E. S. H.

Cresol-soap systems. III. Gelating powers of isomeric cresols with sodium salts of the acetic acid series. S. JENCIC [with H. BUBERL] (*Kolloid-Z.*, 1932, 60, 59—71; cf. B., 1927, 494, 563).—Na salts of fatty acids containing an even no. of C atoms form gels with *m*- and *p*-cresol. The concn. required for gelation in absence of H₂O for the series Na stearate to Na hexoate increases progressively over the range 1.6—10% for *m*-, 1.0—8.7% for *p*-, and 0.3—1.2% for *o*-cresol. Gels in *o*- and *p*-cresol contain the cresol as an under-cooled melt, which is stable for about a month and then crystallises. The m.p. and setting points of gels of equal %-composition rise with increasing mol. wt. of the fatty acid. The gels undergo syneresis, particularly those containing the lower fatty acid radicals. E. S. H.

Physico-chemical studies on proteins. VI. Effect of salts on caseinogen-sodium hydroxide and casein-sodium hydroxide equilibria. A. D. ROBINSON, R. A. GORTNER, and L. S. PALMER (*J. Physical Chem.*, 1932, 36, 1857—1881).—Determination of the p_H of caseinogen and casein solutions of high alkalinity shows the amount of alkali "bound" per g. of protein, w , to increase indefinitely with the p_H , and the binding of alkali in amounts exceeding stoichiometrical proportions is therefore ascribed to adsorption. w apparently increases with the protein concn., but as the same effect occurs with alanine solutions of p_H 9.7, it is probably not significant. The proteinate ion is assumed to have the same activity as Cl'. Uni-univalent salts always reduce the p_H , and more so at p_H 6—9 than at p_H 11—12.5. The caseinogen and casein preps. used showed no difference in alkali-binding power, and added salts had almost the same effect on both. K. V. T. (c)

Physico-chemical behaviour of lecithin. II. Capillary activity of lecithin-cholesterol dispersions. R. JONES and W. C. M. LEWIS (*Biochem. J.*, 1932, 26, 633—637).—The position of the isoelectric point identified with that of the surface-tension max. (A., 1929, 1381) is altered by the addition of cholesterol from p_H 2.6, characteristic of pure lecithin, to p_H 4. Filtration experiments show that the large particles of lecithin which give turbidity to the dispersion are the capillary-active units; particles of colloidal or mol. dimensions are not active. S. S. Z.

Dehydration of zeolite gels by freezing. P. G. BRID (*Ind. Eng. Chem.*, 1932, 24, 793—794).—On freezing a zeolite or other gelatinous ppt., the solid separates in distinct clusters, separated by ice. On melting, the H₂O is easily drained away. When dried in this way, zeolite had a higher base-exchange val. than when dried in an oven at 55°. A dynamic method for testing this capacity is described. D. R. D.

Effect of ultrasonic waves on thixotropic gels. H. FREUNDLICH, F. ROGOVSKI, and K. SOLLNER (*Z. physikal. Chem.*, 1932, 160, 469—472).—Thixotropic Fe₂O₃ gels are liquefied by ultrasonic waves (cf.

Wood and Loomis, *Phil. Mag.*, 1927, [vii], 4, 418), the change starting at the air-gel interface. The time of setting of the liquefied gel is the same as when it has been liquefied by shaking in the hand. The sound waves have no further action after liquefaction is complete. Thixotropic Al₂O₃ gels behave similarly. The colour changes on liquefaction suggest that the thixotropy of gels of the hydrated oxides is closely related to coagulation. R. C.

Organic thixotropic system with microscopically visible particles. H. VON RECKLINGHAUSEN (*Kolloid-Z.*, 1932, 60, 34—36).—Disperse systems of mercaptobenzthiazole, containing particles of microscopic dimensions, in C₆H₆, PhMe, EtOH, CCl₄, PhNO₂, and light petroleum are thixotropic. The time required for re-setting of the shaken gel in each medium bears no clear relation to other properties of the liquids. E. S. H.

Swelling of wool fibres in water and in aqueous solutions of sodium hydroxide, as shown by the change in cross-sectional area. M. H. NORRIS (*Trans. Faraday Soc.*, 1932, 28, 618—626).—Apparatus for determining to within 0.001 mm. the diameters of fibres immersed in a fluid is described. Results obtained with NaOH solutions are correlated with X-ray data which indicate permanent penetrations of the fibre micelles by NaOH. Stretched and steamed fibres (β -keratin) swell more than unstretched fibres in H₂O and 0.05N-NaOH. The cross-sectional diameter ratios are unchanged by swelling or by subsequent contraction. J. G. A. G.

Crystallo-polyamphiphonic theory of solutions, colloids, and plastics. V. Y. KURBATOV (*Plast. Mass.*, 1931, No. 1—2, 36—46).—The theory postulates associations (formed with elimination of H₂O) of ions carrying an equal no. of positive and negative charges. CH. ABS.

Homogenisation of glass melts as a diffraction process. H. JEBSEN-MARWEDEL (*Kolloid-Z.*, 1932, 60, 37—38).—The striæ of glass melts are discussed in terms of Ostwald's conception of diffraction systems (A., 1931, 906). The particles are probably thread-like, consisting of chains of SiO₂ mols. E. S. H.

The Debye-Hückel theory and electrophoresis. R. AUDUBERT (*Compt. rend.*, 1932, 195, 210—212).—For suspensions of gamboge, mastic, Fe₂O₃, and As₂O₃ in solutions of electrolytes of valencies 1—6, it is found that the change in the cataphoretic velocity (u_0-u) and in the electrokinetic potential ($\psi_0-\psi$) is proportional to the square root of the ionic strength at low concns. At higher concns. deviations occur which increase with the valency of the electrolyte (cf. A., 1925, ii, 115). C. A. S.

Variability of electrokinetic potential difference. G. ETTISCH and A. ZWANZIG (*Z. physikal. Chem.*, 1932, 160, 385—408).—The measurements previously reported (A., 1930, 697) have been amplified. It is now found that the electrokinetic potential, ζ , for the pure aq. NaCl solution increases in abs. val. with the pressure, p , up to about 20 cm. and then becomes const. In presence of alcohols the variability of ζ with p is more pronounced, and extends to higher pressures.

The val. of ζ calc. by Helmholtz's equation is therefore, in general, not uniquely determined by the state of the phase boundary, and cannot serve to characterise it.

R. C.

Equilibrium of para- and ortho-hydrogen. R. W. HARKNESS and W. E. DEMING (J. Amer. Chem. Soc., 1932, 54, 2850—2852).—The ratio of para- to ortho-H and percentage of para-H at 20—273° abs. have been calc. by Dennison's formula. E. J. R. (c)

Theoretical derivation of van 't Hoff's dilution law. J. ŠEBOR (Chem. Listy, 1932, 26, 234—235).—Theoretical. R. T.

Ionisation constants of acids in aqueous-alcoholic solutions on the basis of catalytic effects. H. M. DAWSON and A. KEY (Proc. Leeds Phil. Soc., 1932, 2, 296—300).—A reaction velocity method, based on the catalytic effect of an acid, for the determination of ionisation consts. of acids in aq. or EtOH-H₂O solution is described. The effect of dilution on the ionisation of CH₂Cl·CO₂H in 75% EtOH is satisfactorily represented by the law of mass action. The val. of K for this acid in the above solvent is 4.0×10^{-5} .

A. J. M.

Dissociation of salts in water. IV. Bi-bivalent salts. R. W. MONEY and C. W. DAVIES (Trans. Faraday Soc., 1932, 28, 609—614; cf. A., 1931, 1126).—The degree of dissociation and dissociation const. of sulphates and oxalates of bivalent metals have been calc. from conductivity data. Evidence of appreciable complex anion formation amongst oxalates of transitional metals is found only with Fe⁺⁺ and Ni⁺⁺ (cf. A., 1931, 66). The dissociation consts. of the alkaline-earth oxalates increase from Mg to Ba.

J. G. A. G.

Polyhalides. III. Behaviour in solution. H. W. CREMER and D. R. DUNCAN (J.C.S., 1932, 2031—2042).—Aq. solutions of the polyhalides of the series RIBr₂, RIBrCl, and RICl₂ are characterised by equilibria of the type $5\text{IBr}_2 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{I}_2 + 10\text{O}_3' + 10\text{Br}^- + 6\text{H}^+$. The solutions also contain IOH, but no IBr, ICl, Br₂, or Cl₂. In aq. RICl₂, the main equilibrium is $5\text{ICl}_2 + 9\text{H}_2\text{O} \rightleftharpoons \text{I}_2 + 3\text{IO}_3' + 20\text{Cl}^- + 18\text{H}^+$. R has no influence on the degree of hydrolysis as determined by partition experiments with CCl₄, except in the case of HIBrCl and HICl₂, which are less hydrolysed than their salts. IBr, ICl, and ICl₂ are more hydrolysed than the polyhalides derived from them. Absorption spectra are recorded for solutions of IBr, RIBr₂, and C₅H₅N·IBr, in various solvents. The reactions of the above polyhalides in aq. solution have been examined in detail. *Iodine mononitrate and trinitrate* are formed by the reactions $\text{IBr} + \text{AgNO}_3 = \text{AgBr} + \text{INO}_3$; $2\text{INO}_3 + \text{AgNO}_3 = \text{AgI} + \text{I}(\text{NO}_3)_3$, in MeOH solution.

D. R. D.

Alkali arsenites. I. R. CERNATESCU and A. MAYER (Z. physikal. Chem., 1932, 160, 305—326).—The conductivity and f.-p. depression of aq. As₂O₃ neutralised with NaOH have the same vals. as for a solution of NaAsO₂ of the same concn. Conductivity data suggest that the K salt formed on neutralisation must also be KAsO₂. The dissociation const. of arsenious acid, deduced from the hydrolysis consts. of NaAsO₂ and KAsO₂, is 9×10^{-10} . From a mixture of

equiv. amounts of KOH and As₂O₃ a salt may be crystallised which according to f.-p. measurements appears to be represented by the formula K₂As₂O₄ in aq. solution. The conductivity of aq. K₃AsO₃ differs from that of a mixture of aq. As₂O₃ and KOH in the mol. ratio 1 : 6.

R. C.

Changes of salts of tervalent metals in solution. III. Equilibrium between the violet and green forms of potassium chromium alum. C. MONTE-MARTINI and E. VERNAZZA (L'Ind. Chimica, 1932, 7, 857—865; cf. this vol., 351, 708).—Violet solutions tend to turn green even at 0°. Solutions turned green by boiling become violet on cooling, but the change is never complete. At any temp. between 0° and 100°, both green and violet solutions reach the same equilibrium, which is almost independent of the concn. between 20% and 4%. Below 35°, the violet \rightarrow green change and above 35° the green \rightarrow violet is the faster. At 19°, 50% of each is present, but at 42° only 17% of the violet form. The velocities are almost independent of the concn. between 5 and 20%.

T. H. P.

Activity coefficient of potassium chloride in aqueous solution from b.-p. data. B. SAXTON and R. P. SMITH (J. Amer. Chem. Soc., 1932, 54, 2626—2636).—The b.-p. elevations for concns. up to 7.8M have been measured, and the activity coeffs. calc. Two new arrangements for measuring b.-p. elevation are described.

G. M. M. (c)

Activity coefficients of sulphuric acid in anhydrous acetic acid. V. K. LAMER and W. C. EICHELBERGER (J. Amer. Chem. Soc., 1932, 54, 2763—2766).—Previous e.m.f. measurements of these coeffs. (A., 1931, 1127) can be accounted for on the basis of the Gronwall, LaMer, and Sandved extension of the Debye-Huckel theory (A., 1928, 841) by assuming that H₂SO₄ is a binary electrolyte in this solvent with an α val. of 11 Å. at 0.0025—0.038M.

G. M. M. (c)

F. p. of aqueous solutions. I. F.-p. apparatus. G. SCATCHARD, P. T. JONES, and S. S. PRENTISS. **II. Potassium, sodium, and lithium nitrates.** G. SCATCHARD, S. S. PRENTISS, and P. T. JONES. **III. Ammonium chloride, bromide, iodide, nitrate, and sulphate.** G. SCATCHARD and S. S. PRENTISS (J. Amer. Chem. Soc., 1932, 54, 2676—2690, 2690—2695, 2696—2705).—I. Differential measurements were made, temp. being measured with a multiple-junction thermocouple and concn. by conductivity. The solutions were kept saturated with N₂ under 1 atm., the effect of dissolved gas being shown to be approx. proportional to the square of the salt concn. A precision of 0.042° is claimed.

II. The results are consistent with a size for NO₃⁻ between those of Br⁻ and I⁻. The theory that for ions of the noble gas type the size is the only factor which need be considered in calculating the properties of aq. solutions of alkali halides has been tested.

III. With these salts a factor is operative which is negligible for other uni-univalent salts and similar in effect to association.

A. S. S. (c)

Individual differences in the osmotic coefficients of strong electrolytes. G. KARAGUNIS (Praktika, 1930, 5, 314—319; Chem. Zentr., 1932, i,

1347).—The order of the osmotic coeffs. for chlorides is different from that for fluorides. The coeffs. depend on the solubilities, and the minima required by Fajans' solubility rule are reflected in the osmotic coeffs. L. S. T.

Solving higher degree equilibrium equations with polyphase duplex slide rule. M. J. POLISSAR (Ind. Eng. Chem. [Anal.], 1932, 4, 332—334).—Mathematical. E. S. H.

Transformation of the constituents of binary and ternary systems. I. I. STEPANOV (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 57—74).—Theoretical. R. T.

Singular tensimetric diagrams of the system water-acetic anhydride. K. P. MISCHTSCHENKO and S. I. TSCHERBOV (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 47—56).—The v.p. shows a min. at 50 mol.-%, corresponding with formation of AcOH. R. T.

Phosphates of carbamide and guanylcarbamide. A. COCHET and J. HOUDIN (Compt. rend., 1932, 195, 324—326; cf. B., 1932, 636).—The 20° isotherm for the system $\text{CO}(\text{NH}_2)_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ shows that $\text{CO}(\text{NH}_2)_2\text{H}_3\text{PO}_4$ is the only solid phosphate of carbamide. The composition at the invariant point is $\text{CO}(\text{NH}_2)_2$ 53.30, H_3PO_4 23.14, H_2O 23.56%. *Guanylcarbamide phosphate* ($\text{B}_2\text{H}_3\text{PO}_4$), prepared by heating at 100° H_3PO_4 and a solution of dicyanodiamide, has m. p. 178°. C. A. S.

Fusion diagrams of highly-refractory oxides. IV. Aluminium oxide. H. VON WARTENBERG and H. J. REUSCH (Z. anorg. Chem., 1932, 207, 1—20; cf. A., 1931, 567).—The m. p. of Cr_2O_3 , La_2O_3 , and Ga_2O_3 are 2275°, 2315°, and 1740°, respectively. M.-p. data for mixtures of Al_2O_3 with BeO , MgO , SrO , BaO , NiO , CoO , Cu_2O , TiO_2 , ThO_2 , CeO_2 , La_2O_3 , Mn_2O_3 , Fe_3O_4 , Ga_2O_3 , and Cr_2O_3 are recorded. J. W. S.

Lowering of eutectic points. J. MULLER (Compt. rend., 1932, 195, 240—242; cf. this vol., 692).—Further measurements of the lowering of the eutectic point in the system $\text{H}_2\text{O-KNO}_3$ on the addition of acids, bases, and salts have been made. C. A. S.

System $\text{HgBr}_2\text{-KBr-H}_2\text{O}$. (MLLE.) M. PERNOT (Compt. rend., 1932, 195, 238—240; cf. A., 1931, 695).—Between 0° and 80° the system is similar to $\text{HgI}_2\text{-KI-H}_2\text{O}$: the only compound formed is $\text{HgBr}_2\text{KBr.H}_2\text{O}$. $\text{HgBr}_2\text{.2KBr}$ (cf. A., 1925, ii, 887) is probably a mixture of this and KBr . C. A. S.

System magnesium oxide-magnesium chloride-water. C. R. BURY and E. R. H. DAVIES [with G. GRIME] (J.C.S., 1932, 2008—2015).—At 25° the stable solid phases are: $\text{Mg}(\text{OH})_2$ (I), shown by X-ray analysis to have the brucite structure; $3\text{MgO.MgCl}_2.11\text{H}_2\text{O}$ (II); $\text{MgCl}_2.6\text{H}_2\text{O}$. Under certain conditions, gels are formed, composed of cryst. needles of (II) with solution in the interstices. The conditions of formation of magnesian cement [shown by chemical and X-ray analysis to be a mixture of (I), (II), and solution], have also been determined. On weathering, the cement becomes covered with a layer of MgCO_3 , which retards the decomp. and deliquescence of (II) in damp

air. Nevertheless, it is advisable to impregnate the surface with oil or wax. D. R. D.

System $\text{NiSO}_4\text{-CaSO}_4\text{-H}_2\text{O}$. A. N. CAMPBELL and N. S. YANICK (Trans. Faraday Soc., 1932, 28, 657—661).—Solubility data at 45°, 75°, and 90° show that $\text{CaSO}_4.2\text{H}_2\text{O}$ is present throughout and that the max. in the solubility curve is smooth and does not correspond with double salt formation. J. G. A. G.

System water-alcohol-ether at low temperatures. A. LALANDE (Compt. rend., 1932, 195, 133—136).—The equilibria at 0° and -15° have been examined (cf. A., 1911, ii, 26; B., 1923, 201A).

C. A. S.
Ternary system allylthiocarbimide-aniline-benzene. N. S. KURNAKOV and E. F. PLAKSINA-SCHISCHOKINA (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 29—46).—The compound, $\text{C}_3\text{H}_5\text{NCS.NH}_2\text{Ph}$, m.p. 99°, is formed. R. T.

Reversibility of the reactions between sulphur dioxide and calcium oxide and between sulphur and calcium oxide. J. ZAWADZKI, C. Z. MORGENTERN, T. SIBERA, and S. BRETSZNAJDER (Rocz. Chem., 1932, 12, 457—467).—The equilibrium pressures of the systems CaS-CaSO_4 , CaO-SO_2 , and CaO-S have been measured at different temp. R. T.

Salicylic acid as a secondary standard substance in calorimetry. P. E. VERKADE (J. Chim. phys., 1932, 29, 297—301).—A reply to Keffler (this vol., 23). The val. preferred for the heat of combustion of salicylic acid is 5237.7 g.-cal. (15°) per g. (weighed in vac.). E. S. H.

Energy of dissociation of nitrogen. T. C. SUTTON (Nature, 1932, 130, 132).—Using the val. -20.6 for the heat of formation of N_2O , Datta's val. for the energy of dissociation of N_2 becomes 9.0 volts or 208 kg.-cal. (cf. this vol., 799). L. S. T.

Heat of formation of nitrous oxide. T. C. SUTTON (Phil. Mag., 1932, [vii], 14, 275—285).—Calorimetric data for the reaction $\text{H}_2+\text{N}_2\text{O}\rightarrow\text{H}_2\text{O}+\text{N}$, lead to -20.5 ± 0.3 kg.-cal. N. M. B.

Heats of formation of the hydrates of manganous oxalate. M. L. SMITH and B. TOPLEY (J.C.S., 1932, 1977—1979).—Measurements of the heat of dissolution of MnC_2O_4 and its hydrates in HNO_3 indicate that $\text{MnC}_2\text{O}_4+2\text{H}_2\text{O}$ (liq.)= $\text{MnC}_2\text{O}_4.2\text{H}_2\text{O}+6247$ g.-cal.; $\text{MnC}_2\text{O}_4+3\text{H}_2\text{O}$ (liq.)= $\text{MnC}_2\text{O}_4.3\text{H}_2\text{O}+7800$ g.-cal. D. R. D.

Heats of dilution and other thermochemical data for bi-univalent salts. III. Magnesium, strontium, and barium nitrates in water at 15°. H. HAMMERSCHMID and E. LANGE (Z. physikal. Chem., 1932, 160, 445—465; cf. this vol., 23).—From measurements of the heats of dilution up to 0.1M the differential and integral heats of dissolution, Φ_m and V_m , and the apparent and partial relative mol. heat capacities at 20° have been calc. The relations of Φ_m and V_m to the concn. correspond with the Debye-Hückel limiting law only at the highest dilutions, whereas with the heat capacities the theoretical relations are approx. realised up to 0.1M. For all the magnitudes, however, the individuality of the

salt is perceptible in the concn. curve. The residual thermodynamic effects, *i.e.*, the heat effect, work done, and entropy change in the transition from the state of unit activity to the particular real concn., have been calc. for the $\text{Ba}(\text{NO}_3)_2$ solutions at 15° and 25°, and the "real" effects, ascribable to interionic forces and association, have been calc. for all three salts. The constituent elements of the dilution process responsible for the sign, magnitude, individuality, and variation with temp. of the real effects are qualitatively discussed. R. C.

Heat absorption in the cooling of salt solutions. A. STEINBACH (Forsch. Gebiet Ingenieurw., 1931, A, 2, 105—108; Chem. Zentr., 1932, i, 1344).—Data are given for CaCl_2 solutions. L. S. T.

Essential oils and heat absorption. H. NICOL (Biochem. J., 1932, 26, 658—665).—The absorption of radiant heat is chiefly due to H_2O vapour and only secondarily to the odoriferous constituents. S. S. Z.

Transference numbers of aqueous solutions of potassium, sodium, lithium, and hydrogen chlorides at 25° by the moving-boundary method. L. G. LONGSWORTH (J. Amer. Chem. Soc., 1932, 54, 2741—2758).—Measurements were made at 0.001—0.2*N*. With dil. solutions a correction for the conductivity of the H_2O is important. An interpolation formula connecting transference nos. with concn. is derived. E. J. R. (c)

Determination of electrolytic resistances at high frequencies by the bridge method. W. GEYER (Ann. Physik, 1932, [v], 14, 299—320).—Various errors in the bridge method are eliminated, and measurements recorded for MgSO_4 and NaCl solutions; the results agree with Debye's theory. A. J. M.

Conductivity of dielectric liquids. A. NIKURADSE (Physikal. Z., 1932, 33, 553—575).—A summary of the present position of the subject. W. R. A.

Limiting equivalent conductances of several univalent ions in water at 25°. D. A. MACINNES, T. SHEDLOVSKY, and L. G. LONGSWORTH (J. Amer. Chem. Soc., 1932, 54, 2758—2762).—Using an extension of Onsager's equation with new transference and conductance data the limiting equiv. conductance of Cl^- is calc. to be 76.32, from which the following limiting conductances have been calc.: K^+ , 73.50; Na^+ , 50.10; H^+ , 349.72; Ag^+ , 61.90; Li^+ , 38.68; NO_3^- , 71.42; OAc^- , 40.87. E. J. R. (c)

Determination of the mobilities of anions of weak acids. C. W. DAVIES (Trans. Faraday Soc., 1932, 28, 607—609; cf. A., 1928, 22).—The solvent correction to be applied to conductivity data for salts of weak acids is evaluated for a particular case (A., 1931, 66). The use of the "normal" correction leads to serious errors in the conductivities. J. G. A. G.

Conductivity measurements with aqueous solutions of alkylammonium picrates. P. WALDEN and E. J. BIRR (Z. physikal. Chem., 1932, 160, 327—336).—From measurements at 18° at dilutions up to 6000 litres the mobilities of the cations have been calc. From the vals. of the product of the

mobility and the viscosity of the solvent NMe_4^+ and NPr_4^+ appear to be unsolvated in H_2O and other solvents, whilst the partly alkylated ions are solvated. R. C.

Basic salts. I. Basic zinc chloride. E. HAYEK (Z. anorg. Chem., 1932, 207, 41—45).—Conductivity measurements for the systems ZnO-HCl and ZnO-ZnCl_2 indicate the existence of the basic salts $4\text{ZnO} \cdot \text{ZnCl}_2 \cdot 5\text{H}_2\text{O}$ and $\text{ZnO} \cdot \text{ZnCl}_2 \cdot \text{H}_2\text{O}$ (cf. A., 1930, 436). The salts have been isolated and analysed. J. W. S.

Complex nature of polonium ions. M. HAISINSKY (Compt. rend., 1932, 195, 131—133; cf. this vol., 701).—The relative amounts of Po carried to the cathode and anode in the electrolysis of acid and alkaline solutions show that in alkaline solution the Po is probably present as polonite, but in the acid solutions as a complex, *e.g.*, $[\text{Po}(\text{NO}_3)_6]^-$, $[\text{Po}(\text{C}_6\text{O}_4)_3]^{3-}$ (cf. A., 1931, 697). C. A. S.

Conductivity measurements in pyridine. P. WALDEN, L. F. AUDRIETH, and E. J. BIRR (Z. physikal. Chem., 1932, 160, 337—365).—Measurements at 25° with solutions of org. and inorg. salts show marked differences in the ionisation of various solutes. In the order of diminishing strength the cations form the series $\text{Ag} > \text{Li} > \text{K} > \text{Na}$ and the anions the series $\text{picrate} > \text{ClO}_4 > \text{I} > \text{NO}_3 > \text{Br} > \text{Cl}$. Kohlrausch's square-root law is valid, being applicable to strong and moderately strong electrolytes when $v > 8000$ litres, and the validity of the principle of independent ionic migration has been established for several of the solutes. For the tetra-alkylammonium salts the val. of the product of the equiv. conductivity at infinite dilution and the viscosity of the solvent is considerably higher for $\text{C}_5\text{H}_5\text{N}$ than for other solvents, an abnormality which is apparently traceable to the cations. There are no grounds for postulating a Grotthus conductivity for the pyridinium ion in $\text{C}_6\text{H}_5\text{N}$. R. C.

Potentials of ferromanganese and of ferrochromium anodes at different current densities and hydrate concentrations. M. DE K. THOMPSON and R. B. MORRISSEY (Trans. Amer. Electrochem. Soc., 1932, 61, 259—266).—Single potentials of Fe-Mn and Fe-Cr anodes in aq. NaOH or KOH have been measured at various c.d. At higher alkali concns. the potential for a given c.d. is almost independent of the concn., although the current efficiencies for the individual anode products (permanganate or chromate, O_2 , and oxides) change notably over this range. H. J. T. E.

Variation of potential of electrolytic iron with p_{H} of the medium. A. TRAVERS and J. AUBERT (Compt. rend., 1932, 195, 138—139).—The limiting potential (relative to the HgCl electrode) of electrolytic Fe in $N\text{-HCl}$, $\text{-H}_2\text{SO}_4$, $\text{-H}_3\text{PO}_4$, or -HClO_4 is -0.51 to -0.52 volt, and -0.730 in 1% Na_2SO_4 . Addition of a depolariser, *e.g.*, MnO_2 , has no effect, but if the Na_2SO_4 solution is deprived of O_2 by bubbling H_2 through it, and the current of H_2 maintained, the potential falls to -0.78 volt, and in a N -alkali solution similarly treated to -1.050 volt. The H electrode thus formed is not reversible. An Fe electrode used for a few min. as cathode gives

immediately on being withdrawn potentials of -0.91 volt in 1% Na_2SO_4 and -1.14 in $N\text{-NaOH}$.

C. A. S.

Mercury sulphates and standard cells. R. B. ELLIOTT and G. A. HULETT (J. Physical Chem., 1932, 36, 2083—2086).—The e.m.f. of Cd and Zn cells prepared with Hg_2SO_4 which has crystallised on slow reduction with SO_2 of a half-saturated solution of HgSO_4 in $1:6\text{H}_2\text{SO}_4$ is fairly const., and is lowered by covering the crystal surfaces with finely-divided Hg.

L. P. H. (c)

Glass electrodes. S. I. SOKOLOV and A. H. PASSINSKI (Z. physikal. Chem., 1932, 160, 366—377).—The deviation of the potential of an electrode of Li, Na, or K glass in a strongly alkaline solution of an alkali hydroxide from the val. corresponding with a reversible H electrode is greatest if the cation present in solution is the same as that in the glass or has a lower at. no. If the at. no. is higher, the deviation is much smaller and the slope of the potential- p_{H} curve never changes in sign. The deviations are ascribed to the migration into the glass of the external metal ion in preference to H^+ . The readiness with which this occurs will depend on the size of the anhyd. ion, the space occupied in the glass by its cation, and the phase boundary potential.

R. C.

Rate of autoxidation of oxidation-reduction systems and its relation to their free energy. E. S. G. BARRON (J. Biol. Chem., 1932, 97, 287—302).—The autoxidation by mol. O_2 of a no. of reversible oxidation-reduction dyes (cf. A., 1930, 639) has been studied electrometrically. At const. p_{H} and in absence of catalysts a linear relationship exists, with a few exceptions, between E'_0 (the e.m.f. when oxidant/reductant equals 1) and the logarithm of the time required to oxidise the dye from 2 to 50% oxidation. The same relation holds for the rate of oxidation of single oxidation-reduction systems. With some dyes the rate indicates a reaction of the first order.

F. O. H.

Oxidation-reduction potential of hexuronic acid. I. D. GEORGESCU (J. Chim. phys., 1932, 29, 217—237).—Hexuronic acid extracted from orange juice establishes a definite potential corresponding with $r\text{H}_2$ 15 ± 0.5 .

C. W. G.

Theory of electrolytic polarisation. H. FRICKE (Phil. Mag., 1932, [vii], 14, 310—318).—Mathematical.

N. M. B.

Influence of high-frequency currents on polarised electrodes. I. S. GLASSTONE and G. D. REYNOLDS (Trans. Faraday Soc., 1932, 28, 582—596).—The decrease of polarisation of a Pt or Pb cathode resulting from applied high-frequency currents (H.F. effect) is approx. proportional to the high-frequency c.d. At high polarising c.d. the H.F. effect is small and almost independent of the gas saturating the electrolyte, and the magnitude, for a given high-frequency c.d., is approx. proportional to the high-frequency e.m.f. With low polarising c.d. the H.F. effect is very large in solutions saturated with air or O_2 , but small for H_2 or N_2 . Although high-frequency oscillations do not affect the min. H_2 overvoltage, the residual current is increased, especially in the presence of O_2 . These H.F. effects and the mechanism of the

“electrolytic detector” are accounted for on the view that high-frequency currents exert their depolarising effect by increasing the rate of diffusion of active material from, or depolariser to, the electrode. The magnitude and mechanism of the H.F. effect are probably the same at both anode and cathode.

J. G. A. G.

Alternating-current capacities of electrolytic condensers. F. W. GODSEY, jun. (Trans. Amer. Electrochem. Soc., 1932, 61, 331—345).—Anode films in electrolytic condensers are readily formed in a.c. circuits if two anodes of equal area are used. The capacity of such an anode differs widely from the d.c. capacity at similar voltage, when the effective a.c. formation voltage is taken as the max. voltage which appears across the anode film during the formation period. If, however, the effective formation voltage on a.c. is calc. from measured electrolyte potentials, a close agreement is obtained. The film behaves as if it consisted of two parts, an inner rectifying layer and an outer layer penetrated by the ions and solvent mols. of the electrolyte solution, the relative dimensions of these parts depending on the operating conditions. Such a structure corresponds with the author's adsorbed liquid theory.

H. J. T. E.

Potential gradients in anodic films. F. W. GODSEY, jun. (Trans. Amer. Electrochem. Soc., 1932, 61, 347—357).—Potential gradients for anode films in electrolytic condensers calc. on the basis of theories of film structure range from 160×10^6 to 2×10^6 volts per cm. The gas oxide theory is rejected because of the high gradients required, and the solid oxide theory because of the extremely high dielectric const. which must be postulated for the film. It is inferred that the film contains a certain proportion (probably 30 vol.-%) of the electrolyte solvent, held either by adsorption or absorption (cf. preceding abstract).

H. J. T. E.

Electrolytic valve action and electrolytic rectifiers. E. NEWBURY (Proc. Roy. Soc., 1932, A, 137, 134—145).—The behaviour of various valve and rectifying electrodes has been investigated by using the cathode-ray oscillograph. Valve action depends on the formation of an adherent insulating anodic film which is permeable to H^+ but not to the anions present; rectifying action occurs when such a film is irreducible by electrolytic H_2 and not further oxidisable by discharged anions. The film responsible for the rectifying action of an Al electrode is the oxide only, the presence of hydroxide being a marked disadvantage. The action of the Ta rectifier is similar to that of Al.

L. L. B.

Unimolecular decomposition of simple molecules. R. MECKE (Z. physikal. Chem., 1932, B, 18, 53—60).—Examination of the decomp. of CO_2 and CH_2O (cf. this vol., 680) by means of the theory previously advanced (*ibid.*, 559) shows that, according to the mode of decomp., either normal or excited atoms may be formed.

R. C.

Initiation of gaseous explosions by small flames. J. M. HOLM (Phil. Mag., 1932, [vii], 14, 18—56).—A theoretical relation between the limiting diameters for the propagation of flames in small tubes and const. of the combustible mixture is deduced,

assuming extinction to be due primarily to the cooling effect of unburnt gases. Methods of determining limiting diameters and the conditions for ignition through apertures in metal plates are described. There was no evidence that a min. time of contact with a flame is necessary for ignition. H. J. E.

Oxidation of carbon monoxide. G. HADMAN, H. W. THOMPSON, and C. N. HINSHELWOOD (Proc. Roy. Soc., 1932, A, 137, 87—101).—The oxidation of moist CO takes place at a rate which is proportional to the concn. of CO and H_2O and inversely proportional to that of O_2 . In cylindrical bulbs it is proportional to the square of the diameter. These facts are consistent with the assumption that the primary process is the interaction of CO and H_2O , the H_2 produced setting up reaction chains, and the retarding action of O_2 breaking the chains by an oxidation process at the vessel wall and not by a "poisoning" of the primary process. The chain length is of the order 10^6 in a 7.5 cm. diameter Si vessel at 600° . The efficiency of collisions in propagating the chain is as high as 1 in 100. The kinetics of the dry reaction are quite different, confirming the view that direct oxidation takes place independently of traces of H_2O . With dry gases at lower pressures there is an explosive region bounded by limits outside which the reaction is very slow. L. L. B.

Velocity of dissociation of nitrogen tetroxide by method of sound waves. W. T. RICHARDS and J. A. REID (J. Amer. Chem. Soc., 1932, 54, 3014—3015).—The velocity coeff. at 25° and 260 mm. is approx. 4.8×10^4 and the activation energy closely approximates to the heat of dissociation of N_2O_4 . It may be assumed, therefore, that the velocity of association of N_2O_4 has little if any temp. coeff. C. J. W. (c)

Kinetics of chemical change in solution. E. A. MOELWYN-HUGHES (Phil. Mag., 1932, [vii], 14, 112—130).—The rates of many bimol. reactions in dil. solution between neutral solute mols., or between a neutral solute mol. and an ion, agree with those calc. from the no. of collisions with energy $>$ the energy of activation E . The rate of hydrolysis of esters, amides, and substituted glycines catalysed by H^+ in aq. solution is expressed by a similar relation, but different expressions must be used in calculating the no. of collisions and E . Discrepancies in certain more complicated reactions in solution are accounted for by assuming additional degrees of freedom. H. J. E.

Kinetics of the reversible reaction between arsenious acid and iodine. E. JÓZEFOWICZ (Rocz. Chem., 1932, 12, 441—456).—Roebuck's results (A., 1903, ii, 14; 1906, ii, 76) have been confirmed. The heat of the reaction $I_3' \rightleftharpoons I' + I_2$ is -4300 g.-cal., and of $I_2 + H_2O \rightarrow HIO + H' + I'$ is $-23,200$ g.-cal. R. T.

Saponification of acetamide and acetanilide by a base. (Mlle.) J. M. A. HOEFLAKE and F. E. C. SCHEFFER [with M. J. R. H. VAN NOUHUYS and (Mme.) J. C. POSTHUMUS-BRUYN] (Rev. trav. chim., 1932, 51, 673—691).—The rates of saponification of NH_2Ac and $NHAcPh$ by aq. KOH have been measured at various temp. and the results explained thermodynamically. The concn. of NH_3 in the partly hydro-

lysed NH_2Ac was determined by bubbling air through the solutions, the val. of p_{NH_3} in air/ c_{NH_3} in solution having been determined for aq. KOH, KOAc, and NH_2Ac . The degree of saponification of $NHAcPh$ was determined by back-titration of the chilled solution with alkali after adding excess of H_2SO_4 . D. R. D.

Kinetics of thiocyanate-brominated fatty acid reactions. V. K. LAMER and J. GREENSPAN (J. Amer. Chem. Soc., 1932, 54, 2739—2741).—After 1500 min. interfering reactions obscure the kinetics of the halogen replacement by CNS' in the halogenated fatty acids. Halogen in the β -position in an ion is more reactive than in the α -position. E. J. R. (c)

Semicarbazone formation. J. B. CONANT and P. D. BARTLETT (J. Amer. Chem. Soc., 1932, 54, 2881—2899).—A quant. study of the factors affecting the equilibrium and rates of semicarbazone formation. The extent of hydrolysis of a given semicarbazone is a function of the acidity of the solution; an equation is derived for its expression. The formation of semicarbazones is subject to general acid catalysis and a fairly satisfactory formulation is developed in terms of the effect of acidity on the amount of semicarbazide reacting and acid catalysis. The equilibria and rates of semicarbazone formation for a variety of ketones and aldehydes are measured under comparable conditions. Velocity coeffs. for formation and hydrolysis are reported as follows: MeCHO 361, 1040; PhCHO 2.05, 0.62; furfuraldehyde 0.73, 0.55; $CMe_3 \cdot CHO$ 20, 37; $AcCO_2H$ 7.37, 3.8; CMe_2 6.02, 1800; cyclohexanone 36, 7600; pinacolone 0.068, 86. There is no apparent relation between the speed of formation of the semicarbazone and its stability. Certain relations between structure and equilibria and rates of semicarbazone formation are pointed out. C. J. W. (b)

Rate of absorption of carbon dioxide in water and in alkaline media. J. W. PAYNE and B. F. DODGE (Ind. Eng. Chem., 1932, 24, 630—637).—Air or H_2 with different proportions of CO_2 was passed up a packed glass tube in countercurrent to H_2O , solutions of Na_2CO_3 , NaOH, $Na_2CO_3 + NaHCO_3$, and sucrose. The average over-all absorption coeff. is independent of the CO_2 concn. A 4-fold increase in gas rate has no effect on the coeff. Increase in liquid rate increases the coeff. very materially. A 16-fold variation in Na_2CO_3 concn. has no significant effect on the coeff. Rise in temp. greatly increases the coeff. The absorption coeff. is less for aq. Na_2CO_3 than for pure H_2O . Addition of $NaHCO_3$ to aq. Na_2CO_3 decreases the coeff. Addition of small amounts of sucrose and CH_2O to aq. Na_2CO_3 increases the coeff. slightly. The coeff. for dil. NaOH is $>$ for aq. Na_2CO_3 . The rate of absorption in dil. $NaHCO_3$ is appreciably less than in pure H_2O . The absorption rate for aq. Na_2CO_3 is practically const. throughout the tower and does not diminish with falling partial pressure of CO_2 . The diffusion theory of absorption is discussed; chemical reaction rate must also be taken into account. H. I.

Velocity of dissolution and sublimation of a solid rotating in a liquid. V. GIAMBALVO (Nuovo Cim., 1931, 8, 246—257; Chem. Zentr., 1932, i, 1332).

—Results obtained when a rotating solid gradually dissolves in different conc. solutions or sublimates in air are discussed. L. S. T.

Reduction of cupric oxide by carbon monoxide and hydrogen. A. JULIARD (Bull. Soc. chim. Belg., 1932, 41, 289—308).—The results previously reported (this vol., 577) can be explained by assuming that the velocity of reduction of CuO is determined at each moment by the velocity of diffusion of the reducing gas through the envelope of reduced material to the CuO surface. Mathematical equations developed to represent the course of reaction are shown to be in accordance with experimental results. E. S. H.

Adsorption and reflexion processes in the interaction of hydrogen and metals. K. F. BONHOEFFER and A. FARKAS (Trans. Faraday Soc., 1932, 28, 561).—A correction. The discontinuities attributed to surface hydride formation (this vol., 568) are due to a non-uniform temp. distribution along the wire (cf. Busch, Ann. Physik, 1921, 64, 401). J. G. A. G.

Reaction regions. XXI. Reaction regions Al-MoO₃-CaF₂, Al-MoO₃-CaF₂, Al-S-B₂O₃, and Si-Cu-PbO. W. P. JORISSEN and A. H. BELINFANTE. **XXII. Prevention of explosive reactions in gas and vapour mixtures by small amounts of various substances.** W. P. JORISSEN, J. BOOY, and J. VAN HEININGEN (Rec. trav. chim., 1932, 51, 853—867, 868—877).—XXI. The ranges of composition within which the reactions propagate themselves throughout the mass when they have been started by means of a mixture of powdered Fe and S have been determined. The results, which are expressed by means of triangular diagrams, show a striking analogy to the explosion regions of three-component gas mixtures.

XXII. Explosion regions are given for mixtures of air and CH₄ with BuⁿCl, PrBr, EtI, SO₂Cl₂, SiCl₄, and SiHCl₃. < 1% of POCl₃ is sufficient to render all mixtures of air and CH₄ non-explosive. D. R. D.

Linear velocity of crystallisation of copper at the cathode in electrolysis of copper sulphate. A. GLAZUNOV and A. ROSKOT (Chem. Listy, 1932, 26, 308—311).—The velocity of crystallisation, *V*, of Cu is 10—20 times that of Ag under similar conditions; *V* diminishes in the presence of gelatin and with increasing concn. of CuSO₄. As the c.d. is increased, *V* rises at first rapidly and then more slowly. R. T.

Reaction kinetics in heterogeneous systems. Oxidation of anthracene with chromic acid. V. MAJER and V. MARECEK (Z. physikal. Chem., 1932, 159, 181—193).—In the oxidation of anthracene suspended in aq. K₂Cr₂O₇ and H₂SO₄ at 60—100° the rate of disappearance of the chromic acid follows the unimol. law, although for a short time after reaction has begun the velocity coeff., *k*, rises slowly. *k* increases with the rate of stirring, the amount of anthracene suspended in unit vol. of liquid, the ratio anthracene : CrO₃, and the interfacial area in such a way as to suggest that the reaction is a surface reaction in which diffusion plays an important part, although certain features of the reaction, in particular the fact that *k* remains const. as the reaction proceeds and the

interfacial area therefore diminishes, suggest a more complicated mechanism. *k* increases by 11% for 1° rise in temp. Addition of AcOH increases *k*, apparently because the solubility of the anthracene is increased. R. C.

Homogeneous catalysis of gaseous reactions. Catalytic decomposition of nitrous oxide by halogens. F. F. MUSGRAVE and C. N. HINSHELWOOD (Proc. Roy. Soc., 1932, A, 137, 25—36).—The thermal decomp. of N₂O is catalysed by halogens, the free halogen atom probably being the catalyst. As the concn. of the catalyst increases, the rate reaches a limiting val. The reactions are homogeneous and unimol. with respect to the N₂O. L. L. B.

Comparison of catalytic effects produced by acids in aqueous and in aqueous-alcoholic solution. H. M. DAWSON and G. V. HALL (Proc. Leeds Phil. Soc., 1932, 2, 289—295).—The catalysing powers of CH₃Cl·CO₂H and AcOH in EtOH-H₂O mixtures were determined. The catalytic activity of the undissociated acid is reduced, whilst that of the acid anion is increased, by replacing H₂O by EtOH. It is probable that this effect is directly connected with the diminution of the ionisation consts. caused when aq. EtOH is used instead of H₂O as a solvent. A. J. M.

Fenton's reaction. IV. A. T. KUCHLIN (Rec. trav. chim., 1932, 51, 887—913).—Oxidation of glucose by FeSO₄ and H₂O₂ yields (1) at 30° in dil. solution, osone, and α-keto- and αβ-diketo-gluconic acids; (2) at 30° in conc. solution, CH₂O; (3) at 70° in conc. solution, CO₂, CH₂O, H₂C₂O₄, glycollic, tartronic, and glyceric acids, and probably unidentified lower ketonic acids. The FeSO₄ catalyses oxidation of the secondary alcohol groups, whereas HNO₃, KMnO₄, and aq. Br without catalysts oxidise the end C atoms. The influence of the concn. of H⁺, Fe²⁺, Fe³⁺, and glucose on the initial velocity of oxidation has been investigated. β-Glucose and -mannose are oxidised more rapidly than the α-forms. The catalytic action of Fe²⁺ is not due to complex formation nor to the formation of any peroxide of Fe; it is probable that the electric field due to the Fe²⁺ ions causes a deformation of the sugar mols. which favours oxidation of certain OH groups. Fe³⁺ does not act similarly, although complex formation occurs to a greater extent. D. R. D.

Slow hydrolysis of zinc acetate. J. GUERON (Compt. rend., 1932, 195, 150—152; cf. A., 1887, 767).—The hydrolysis of 0.0015*M*-Zn(OAc)₂ has been examined potentiometrically and the result is shown by *p_H*-time curves. Equilibrium is attained after varying times at *p_H* 5.9—6.0. Hydrolysis is accelerated by CO₂ in the solution, the time for half variation of *p_H* varying from 1 to 50 hr., and, also by increase, relative to vol., of the glass surface, e.g., by introducing glass wool (cf. this vol., 481). C. A. S.

Chain reactions in enzymic catalysis. J. B. S. HALDANE (Nature, 1932, 130, 61; cf. this vol., 880).—A discussion. L. S. T.

Chain reactions in enzymic catalysis. D. RICHTER (Nature, 1932, 130, 97).—A discussion (cf. preceding abstract). Christiansen's energy chain mechanism affords a more satisfactory explanation of

the observed facts in enzymic reactions than does the chain mechanism proposed by Haber and Willstätter.

L. S. T.

Catalytic oxidation of uric acid. Z. DOBROWOLSKA (Biochem. J., 1932, 26, 543—550).—Thioglycollic acid, dithioglycollic acid, cysteine, or cystine is without influence on the oxidation of uric acid either in the presence or absence of salts of Fe or Cu. Monohydrated Na urate separates from systems containing uric acid and thioglycollic acid at p_H 10.5—11.5. Methylene-blue catalyses the oxidation of uric acid under aerobic but not anaerobic conditions, the velocity of the reaction varying with p_H . The reaction is inhibited according to the p_H of the medium by Cu salts (0.0001M-CuSO₄) and to a slight extent by 0.004M-KCN over the range p_H 6—10. The catalytic activity of solutions of methylene-blue rises considerably during the first few weeks, especially when alkaline.

S. S. Z.

Influence of various sulphur compounds on the precipitation of a mixture of silver iodide and bromide [from silver nitrate] by a mixture of alkali iodide and bromide. E. CALZAVARA (Bull. Soc. Franç. Phot., 1932, 19, 13—15).—Only thioacetic acid, thiosinamine, and K selenotrichionate show well-defined sulpholysis (or selenolysis), which is retarded, in the last two cases, by gelatin. Activators containing S retard the pptn. of AgBr and AgI, even when sulpholysis is not perceptible, both in neutral and in alkaline media; gelatin alone also retards the pptn., but in many cases tends to check the retardation caused by the activators. The activators displace the equilibria in favour of iodide pptn. Intermediate compounds, e.g., Ag β -thiolactate, can sometimes be detected.

J. L.

Catalysis in Deacon's process. (Mlle.) A. E. KORVEZEE (Rec. trav. chim., 1932, 51, 815—834).—The stability of the Cu compounds formed in Deacon's process (CuCl₂, CuO, Cu₂OCl₂) in presence of Cl₂, H₂O, HCl, and O₂ has been studied at 450° and total pressure 0.5 atm. The catalysis is chemical in character, depending on the formation of intermediate compounds.

D. R. D.

Nitrogen, iron, and contact catalysis. H. H. GRAY (Chem. and Ind., 1932, 537—538).—Sieverts' view (A., 1907, ii, 741) that gaseous N₂ is insol. in α -Fe was corrected by himself (A., 1931, 1120) and numerical vals. of solubility were given together with the assertion of the formation of a definite nitride. The evidential val. of the activated adsorption interpretation is not accepted.

C. A. K.

Dispersity of catalyst and catalytic activity. K. YOSHIKAWA (Bull. Chem. Soc. Japan, 1932, 7, 201—210).—The hydrogenation of C₂H₂ using Ni and Pd catalysts containing varying amounts of kieselguhr has been studied. The quantity of kieselguhr added to the catalyst influences the activity of the resulting mixture. By passage over Ni or Pd distributed on a suitable amount of kieselguhr, C₂H₂ is hydrogenated almost entirely to C₂H₄ instead of to C₂H₆. A possible mechanism of the reaction is suggested.

O. J. W.

Photolysis of hydrogen peroxide in aqueous solution. L. J. HEIDT (J. Amer. Chem. Soc., 1932, 54, 2840—2843).—In the photolysis at 28 \pm 2° in very intense light of wave-length 3130 Å. the quantum yield approaches 1 as the H₂O₂ concn. decreases.

G. M. M. (c)

Quantum yield in photochemical decomposition of gaseous hydrazine. R. R. WENNER and A. O. BECKMAN (J. Amer. Chem. Soc., 1932, 54, 2787—2797).—In the decomp. in light of wave-length 1990 Å. and under pressures of 2—14 mm. the quantum yields range from 1 at the lower to 1.7 at the higher pressure. A reaction mechanism is proposed.

G. M. M. (c)

Photochemical, mercury-sensitised reactions between hydrogen, oxygen, and carbon monoxide. M. BARAK and H. S. TAYLOR (Trans. Faraday Soc., 1932, 569—581; cf. A., 1931, 1136).—The combination of H₂ and O₂ in a static system at 14° under the influence of excited Hg is autocatalytic in 2H₂:O₂ and H₂-rich mixtures, but with mixtures rich in O₂ or containing CO the rate of reaction is approx. const. With equal concn. of H₂ and CO, the H₂ is oxidised 5 times as rapidly as the CO. The average velocity is max. with 2H₂:O₂ mixtures (300 mm.) and this is unaffected by CO, but excess of O₂ has a greater retarding effect than excess of H₂. The rate of interaction of H₂ and CO is about 18% of that between 2H₂ and O₂ under similar conditions. The mechanism of H₂O formation is discussed. The data are consistent with an almost exclusive initial formation of H₂O₂ and a reaction sequence involving short chains.

J. G. A. G.

Photodichroism and photoanisotropy. XI. Production of photodichroic mirrors. F. WEIGERT and F. STIEBEL. XII. Technique. F. WEIGERT (Z. physikal. Chem., 1932, B, 16, 113—122; 18, 73—87; cf. A., 1931, 1378).—XI. On development of grainless Lippmann plates after exposure to red light the Ag separates in a highly reflecting form, originating in a thin layer on the surface of the emulsion which can readily be wiped off and has a spectral sensitivity distribution quite different from that of the interior, the sensitivity to red being particularly pronounced. Exposure to green or blue light has a similar, but very much less marked, effect. The mirrors produced after exposure to polarised light exhibit photodichroism and photodireflexion.

XII. A modified polarimeter with monochromator enabling photoanisotropic effects to be measured rapidly and very accurately, and a method for the simultaneous determination of photodichroism and photo-double refraction, utilising a quarter-wave mica plate, are described.

R. C.

Action of X-rays on ferrous sulphate solutions. N. A. SCHISCHAKOV (Phil. Mag., 1932, [vii], 14, 198—203; cf. A., 1929, 408).—The action of X-rays on aq. FeSO₄ containing H₂SO₄ in presence and absence of O₂ produces, in addition to direct oxidation, a reaction between FeSO₄ and H₂SO₄ forming Fe₂(SO₄)₃ and H₂.

H. J. E.

Action of radon on some unsaturated hydrocarbons. II. Propylene and cyclopropane. G. B. HEISIG (J. Amer. Chem. Soc., 1932, 54, 2328—

2332; cf. A., 1931, 1252).—In the radon polymerisation of propylene at an initial pressure of 675.8 mm. and of cyclopropane at 683.5 mm. the $-M/N$ ratios are 4.9 and 3.3, respectively. Low vals. of $\Delta(H_2 + CH_4)/-\Delta H_C$ are associated with higher $-M/N$ vals.

W. E. V. (c)

Behaviour of metals towards salts, especially ammonium salts in presence and in absence of ammonia. H. EHRLIG (Z. anorg. Chem., 1932, 206, 385—397).—The conditions under which metals, deposited electrolytically from ammoniacal solutions, tend to redissolve in the electrolyte have been investigated. The metals examined include Cu, Bi, Pb, Ni, Co, Fe, Cd, Zn, and Mg in solutions of NH_3 , NH_4NO_3 , NH_4Cl , $(NH_4)_2SO_4$, and $NaNO_3$ with and without addition of NH_3 . Cd, Zn, and Mg dissolve readily in these solutions; Cu in smaller degree, and chiefly when the wet electrode is exposed to the air and replaced in the electrolyte. Cd, Zn, and Mg reduce NH_4NO_3 to NH_4NO_2 , N_2O appearing in the gases evolved from Zn and Mg. The dissolution of Cd is not completely prevented by applying a cathodic potential. Addition of NH_3 to aq. NH_4NO_3 accelerates the dissolution of Zn, increases slightly that of Cd, and retards the dissolution of Mg. These effects bear a relation to the solubilities of the corresponding hydroxides in the solutions concerned. E. S. H.

Hydrazinates of some silver salts. H. GALL and H. ROTH (Z. anorg. Chem., 1932, 206, 369—377).—The compounds $AgCNS.N_2H_4$, $AgCN.N_2H_4$, $AgNO_3.N_2H_4$, and $Ag_2SO_4.3N_2H_4$ have been isolated. The thermal decomp. temp. of the last two have been determined. Hydrazinates of Ag salts containing O in the acid radical undergo irreversible decomp. in the solid phase below room temp., forming Ag; those containing halogen or similar acid radicals have a wider temp. region of existence. E. S. H.

Pyrogenic decomposition of calcium sulphite. I. TRIFONOV (Z. anorg. Chem., 1932, 206, 425—426).—The reactions $4CaSO_3 = 3CaSO_4 + CaS$ and $2CaSO_3 = 2SO_2 + 2CaO$ are followed at high temp. by the reaction $CaS + 2SO_2 = CaSO_4 + 2S$. The complete change at high temp. may be represented: $3CaSO_3 = 2CaSO_4 + CaO + S$. E. S. H.

Theory of mercurammonium salts (bromides, and chlorides). Crystallisation of dimercurammonium bromide and hydrated dimercurammonium chloride. M. FRANÇOIS (Ann. Chim., 1932, [x], 17, 254—269).—All the mercuric halides form compounds with NH_3 corresponding with the formula $HgX_2.2NH_3$; by the further action of NH_3 , they give mono- and di-mercurammonium halides, HgH_2NX and Hg_2NX , respectively. There is no chloride or bromide, however, to correspond with the iodide $3HgI_2.4NH_3$ obtained by the action of NH_3 under reduced pressure. From this can be obtained the compound $Hg_3N_4I_6$. There is a corresponding Br compound, $Hg_3N_4Br_6$, but no Cl compound. Methods for the prep. of the different compounds are given, and also for the prep. of cryst. specimens of Hg_2NBr and $Hg_2NCl.H_2O$. M. S. B.

Chemistry of boron. A. STOCK (Bull. Soc. chim., 1932, [iv], 51, 697—712).—A lecture.

Preparation of ultramarine and similar substances from aqueous alkali aluminium silicates by the action of sulphide solutions. E. GRUNER (Fortschr. Min. Kryst. Petr., 1931, 16, 73—74; Chem. Zentr., 1932, i, 1213—1214).—Aq. alkali Al silicates and alkali sulphide solutions produce blue colours which on drying or washing disappear with formation of H_2S and S. At 21° permutites can take up 2.5—5 atoms of S per 3 mol. Permutites retain air tenaciously. After evacuation, the material no longer produces a blue colour; air-free permutite takes up 2 S per 3 mol.: $2NaOH, 2Na_2O, 3Al_2O_3, 6SiO_2, 6H_2O$ affords $2NaSH$ (or Na_2S_2), $2Na_2O, 3Al_2O_3, 6SiO_2, 6H_2O$. At room temp. or up to 150° the blue colorations show no X-ray interference patterns; when prepared at 250° they give those of pyrogenic ultramarines, and react as true ultramarines. A. A. E.

Reactions and properties of nitric oxide and its compounds. II. Salts of nitric oxide-sulphurous acid. H. GEHLEN (Ber., 1932, 65, [B], 1130—1140; cf. A., 1931, 922).—Addition of solutions of $K_2SO_4.N_2O$ to solutions of the requisite salts gives the compounds $K_4Zn(SO_4.N_2O)_3.2H_2O$; $K_4Mn(SO_4.N_2O)_3.2H_2O$; $K_2Co(SO_4.N_2O)_3.2H_2O$; $K_4Cd(SO_4.N_2O)_2.2H_2O$. An analogous Na salt could not be prepared. The salts appear to be complex compounds. They decompose slowly in cold, rapidly in warm, H_2O , immediately in presence of acid with production of SO_4^{2-} and N_2O . When gently heated they evolve H_2O followed by a mixture of Na and NO_2 , leaving K_2SO_4 and the sulphite of the heavy metal which decomposes partly into SO_2 and oxide. They may be preserved for several weeks in vac. over KOH. $Tl_2SO_4.N_2O$ is obtained by the action of NO on alkaline solutions of Tl_2SO_3 . The same rate of absorption of NO is shown by equiv. solutions of Li_2SO_3 , Na_2SO_3 , K_2SO_3 , and Tl_2SO_3 in presence of the corresponding hydroxide. Selenites and tellurites do not absorb NO. Decomp. of solutions of $K_2SO_4.N_2O$ by dil. H_2SO_4 is a suitable method for the prep. of N_2O , which is obtained pure after washing with 4N-KOH and H_2O . Similarly purified N_2O obtained by thermal decomp. of NH_4NO_3 at 229—231° and 247—249° has a max. purity of 99.08% and 99.37%, respectively. H. W.

Arsenic bromosulphide. H. B. VAN VALKENBURGH and S. F. DAVIS (J. Colo. Wyo. Acad. Sci., 1929, 1, No. 1, 51).—When H_2S is passed over $AsBr_3$ at 150°, $AsSBr$, m.p. 118° (approx.), is formed.

CH. ABS.

Precipitation of the hydrofluoric acid solution of protoactinium and tantalum by ammonia. F. REYMOND and CHENG DA-CHANG (Compt. rend., 1932, 195, 144—146; cf. A., 1931, 1021, 1026).—The method previously used to recover Pa and Ta from HF solution leads to loss of Pa. To a solution containing, e.g., 0.2 g. Ta_2O_5 should be added 10 drops of H_2SO_4 , and the mixture heated until white fumes appear; on cooling and diluting, the Ta_2O_5 is completely pptd. by NH_3 . Or the mixture containing H_2SO_4 may be directly calcined (in absence of H_2SO_4 some Ta is volatilised), but in this case some Ta_2O_5 adheres irremovably to the side of the crucible.

C. A. S.

Synthesis of chromium thiocyanate complexes of heavy metals. D. ISAMADOS (Praktika, 1930, 5, 61—64; Chem. Zentr., 1932, i, 1353; cf. this vol., 133).—The compounds $\text{Sn}_3[\text{Cr}(\text{CNS})_6]_2 \cdot 2\text{H}_2\text{O}$, $\text{As}[\text{Cr}(\text{CNS})_6]$, and $\text{Cd}_3[\text{Cr}(\text{CNS})_6]_2 \cdot 2.5\text{H}_2\text{O}$, are described.

L. S. T.

Concentration of polonium (Ra-F) from active lead nitrate. C. KULLE (Coll. Czech. Chem. Comm., 1932, 24, 247—258).—On shaking $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ with a neutral solution of active $\text{Pb}(\text{NO}_3)_2$ and NH_4NO_3 , the Po is adsorbed. From the $\text{Al}(\text{OH})_3$ the Po is conc. electrolytically; from the $\text{Fe}(\text{OH})_3$, by distillation. Alternatively, the hydroxides may be dissolved in HCl and the Po pptd. on a rotating Ag plate. A method is given for the determination of radioactive substances in solutions by direct measurement of the ionisation effect, without evaporation.

D. R. D.

[Reactions of iodine.] E. ANGELESCU and V. D. POPESCU (Z. physikal. Chem., 1932, 160, 466—467).—A reply to criticism (this vol., 585).

R. C.

Structure and polymerisation of brown ferric orthohydroxide. A. KRAUSE and M. CIOKÓWNA (Rocz. Chem., 1932, 12, 468—477).—The ratio Ag : Fe in the product obtained by addition simultaneously of $\text{Fe}(\text{NO}_3)_3$ and AgNO_3 to boiling aq. NaOH is 3 : 4, whilst when the solution is boiled 3 min. before addition of AgNO_3 and 30 min. after, the ratio approaches 1 : 1. This is explained on the assumption that the ppt. has the structure $(\text{HO})_2(\text{Fe}-\text{FeO}_2\text{H})_n \cdot \text{O} \cdot \text{FeO}$ in the first case, 3 H atoms being replaceable by Ag, and $(\text{HO})_2 \cdot \text{Fe} \cdot (\text{FeO}_2\text{H})_n \cdot \text{O} \cdot \text{FeO}$ in the second, $n-1$ H atoms being replaceable.

R. T.

Metal carbonyls. XV. Derivatives of iron carbonyls with *o*-phenanthroline. W. HIEBER and F. MUHLBAUER. **XVI. Derivatives of cobalt and nickel carbonyls.** W. HIEBER, F. MUHLBAUER, and E. A. EHMANN (Ber., 1932, 65, [B], 1082—1089, 1090—1101).—XV. When gently heated, a solution of $\text{Fe}(\text{CO})_5$ and *o*-phenanthroline monohydrate in COMe_2 becomes intensely blue at 60° owing to the formation of an additive product; at $65-70^\circ$, the solution becomes red, CO is evolved, and the compound $\text{Fe}(\text{CO})_3 \cdot \text{C}_{12}\text{H}_8\text{N}_2$ is deposited. The production of the additive product is a time reaction, apparently conditioned by a rearrangement of the five CO groups initially enclosing the Fe atom. $\text{Fe}(\text{CO})_5$ and *o*-phenanthroline in pyridine at 90° afford the substance $\text{Fe}_2(\text{CO})_6 \cdot (\text{C}_{12}\text{H}_8\text{N}_2)_2 \cdot \text{C}_5\text{H}_5\text{N}$, from which pyridine is slowly evolved at 120° . If the solution is heated at 100° and subsequently cooled, the product $\text{Fe}_3(\text{CO})_{7.5}(\text{C}_{12}\text{H}_8\text{N}_2)_2$ separates. $\text{Fe}_3(\text{CO})_6(\text{C}_{12}\text{H}_8\text{N}_2)_2$ is obtained by the action of *o*-phenanthroline on $\text{Fe}_2(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_3$ in anhyd. MeOH . The compounds are pyrophoric. Their dark colour is attributed to the org. complex. With undiluted NO slow reaction occurs: $2\text{Fe}(\text{CO})_3(\text{C}_{10}\text{H}_8\text{N}_2) + 2\text{NO} = \text{Fe}_2(\text{CO})_5(\text{NO})_2(\text{C}_{10}\text{H}_8\text{N}_2)_2 + \text{CO}$. The behaviour towards acids resembles that of other carbonyl derivatives except that the stable $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]^{++}$ is immediately produced; the other phenomena are explained by the production of $\text{Fe}(\text{CO})_4$, and, particularly, of $\text{Fe}(\text{CO})_4\text{H}_2$.

XVI. $[\text{Co}(\text{CO})_4]_2$ (mol. wt. determined in freezing

C_6H_6) loses CO at $55-60^\circ$ with production of $[\text{Co}(\text{CO})_3]_4$ [mol. wt. determined in $\text{Fe}(\text{CO})_5$]. The Co carbonyls are distinguished by great tendency towards polymerisation and high chemical activity. With pyridine there is a ready evolution of CO and production of $\text{Co}_2(\text{CO})_8 \cdot 4\text{C}_5\text{H}_5\text{N}$, whilst *o*-phenanthroline in dil. MeOH affords $\text{Co}(\text{CO})_3(\text{C}_{10}\text{H}_8\text{N}_2)$. The compounds are decomposed by Br with evolution of CO. With acids reaction occurs: $2\text{Co}(\text{CO})_3 + 2\text{H}^+ = \text{Co}^{++} + \text{Co}(\text{CO})_3$ [polymeride] + $3\text{CO} + \text{H}_2$; $3\text{Co}(\text{CO})_3 + 2\text{H}^+ = \text{Co}^{++} + \text{Co}(\text{CO})_3$ [polymeride] + $\text{Co}(\text{CO})_4$ [dimeride] + $2\text{CO} + \text{H}_2$; a volatile Co carbonyl is evolved. When gently warmed with the requisite alcohol, $\text{Co}(\text{CO})_4$ evolves CO and yields $\text{Co}_2(\text{CO})_8 \cdot \text{MeOH}$ and $\text{Co}_2(\text{CO})_8 \cdot 1.5\text{EtOH}$. $\text{Ni}(\text{CO})_4$ is appreciably more stable than $\text{Co}(\text{CO})_4$ towards chemical reagents. In pyridine in absence of air and moisture a yellow coloration is observed at 40° . Partial substitution of CO by pyridine is beset with difficulty, since the equilibrium $\text{Ni}(\text{CO})_4 + x\text{C}_5\text{H}_5\text{N} = \text{Ni}(\text{CO})_{4-x} + x\text{CO}$ ($x < 4$) is readily displaced towards the left when the solutions are cooled and $\text{Ni}(\text{CO})_4$ is re-formed. CO must be continuously removed. The primary products are $\text{Ni}_2(\text{CO})_4 \cdot 3\text{C}_5\text{H}_5\text{N}$ and $\text{Ni}(\text{CO})_2 \cdot \text{C}_5\text{H}_5\text{N}$. If the solution is subjected to continuous distillation in high vac., the substance $\text{Ni}_2(\text{CO})_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ is readily prepared (apparatus described). Similarly, substituted Ni carbonyls are not obtained under like conditions with MeOH or anhyd. $\text{C}_2\text{H}_4(\text{NH}_2)_2$. In pyridine, COMe_2 , or anhyd. EtOH , *o*-phenanthroline and $\text{Ni}(\text{CO})_4$ at room temp. afford the relatively stable $\text{Ni}(\text{CO})_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$, stable to NO but decomposed by Br with quant. evolution of CO. It is decomposed by acids: $\text{Ni}(\text{CO})_2 + 2\text{H}^+ = \text{Ni}^{++} + 2\text{CO} + \text{H}_2$ and $2\text{Ni}(\text{CO})_2 + 2\text{H}^+ = \text{Ni}(\text{CO})_4 + \text{Ni}^{++} + \text{H}_2$. The amounts of CO and H evolved are less than those corresponding with the Ni^{++} produced; since fixation of H to Ni does not appear to occur, it is probable that CO and nascent H react with one another under the experimental conditions.

H. W.

Recommended specifications for analytical reagent chemicals. W. D. COLLINS and collaborators (Ind. Eng. Chem. [Anal.], 1932, 4, 347—350).—Specifications and tests are recommended for C_6H_6 , $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Pb subacetate, phenolphthalein, KNO_3 , NaF , NaNO_2 , PhMe , and $\text{C}_6\text{H}_4\text{Me}_2$. Corrections are made to former specifications for MoO_3 , CuO , KI , and NaHCO_3 .

E. S. H.

Removal of colour from solutions to be examined by colour comparisons. P. L. HIBBARD (Ind. Eng. Chem. [Anal.], 1932, 4, 283).—The colour of soil extracts, plant extracts, solutions of dyes or indicators, etc. may be removed by adding saturated aq. Br, decolorising with NaOH , adding HCl to liberate Br again, and finally removing the Br by adding Na_2SO_3 .

E. S. H.

Technique of colorimetry. N. E. PESTOV (Z. anal. Chem., 1932, 89, 9—17).—The sources of error in colorimetry and the choice of conditions for comparison are discussed. A technique for reading is recommended.

E. S. H.

Thermometric titration. T. SOMIYA (J.S.C.I., 1932, 51, 135—140).—Mainly a summary of published

work (cf. B., 1927, 329, 439; A., 1928, 858; B., 1929, 274, 670; 1930, 674, 777). The reaction between Ac_2O and NH_2Ph is also suitable for the analysis of salts of NH_4Ph by thermometric titration.

E. S. H.

Microanalysis of extremely hygroscopic substances. D. F. HAYMAN (Ind. Eng. Chem. [Anal.], 1932, 4, 256).—The substance is stored in a small bottle in a vac. desiccator, stoppered and weighed immediately. When mixed quickly with dry, powdered CuO , it does not become sticky and can be transferred to Pregl's micro-Dumas apparatus. In a second procedure, N_2 is passed over the material at 100° for 90 min. before weighing.

E. S. H.

Simple basic indicators. I. Acidity functions of mixtures of sulphuric and perchloric acids in water. L. P. HAMMETT and A. J. DEYRUP (J. Amer. Chem. Soc., 1932, 54, 2721—2739).—For certain mixtures of conc. acids and H_2O basic indicators are desirable. Basic org. substances suitable for determining the acidity of mixtures containing 0—100% H_2SO_4 and 0—70% HClO_4 are enumerated.

W. T. H. (c)

Use of the quartz lamp in quantitative analysis. A. JERMSTAD (Dansk Tidsskr. Farm., 1932, 6, 141—148).—Illumination with a quartz lamp permits the use of fluorescent indicators for 0.1—0.001*N*-acid-alkali titrations.

R. S. C.

Use of mixed indicators in acidimetry. P. BRUERE (Ann. Falsif., 1932, 25, 325—328).—The advantages of using more than one indicator are discussed. The sulphonephthaleins are more satisfactory than litmus.

T. McL.

Standardisation of *N*-hydrochloric acid with solid sodium thiosulphate. J. BICKER (Z. anal. Chem., 1932, 88, 414—417).— $\text{Na}_2\text{S}_2\text{O}_3$ (2—5 g.) is dissolved in a little H_2O , the solution treated with 3 g. of KI and 20 c.c. of 4% aq. KIO_3 , and the mixture titrated with the HCl using starch as indicator.

A. R. P.

Rapid determination of moisture in seeds and other granular substances. R. M. DAVIES.—See B., 1932, 685.

Determination of water in presence of alcohols, aldehydes, and acetals. J. ROSS (J.S.C.I., 1932, 51, 121—122r).—The mixture is heated at 110 — 120° for 12 hr. with a known wt. of previously evaluated Bz_2O . From the amount of BzOH and unchanged Bz_2O the amount of H_2O originally present may be calc. CH_2O forms $\text{CH}_2(\text{OBz})_2$, which is weighed and a correction applied. A little $\text{CHMe}(\text{OH})_2$ may be present. The method is applicable with appropriate corrections to mixtures containing HCO_2H , AcOH , MeOAc , and EtOAc .

A. A. L.

Microchemical detection of hydrogen peroxide and of other peroxides by means of lead sulphide. R. KEMPF (Z. anal. Chem., 1932, 89, 88—90).—Photographic printing paper, after being fixed, is treated with 0.05% $\text{Pb}(\text{OAc})_2$ solution followed by saturated H_2S solution. The decolorising of the resulting PbS by H_2O_2 can be used to detect as little as 0.0005 mg. of the latter.

O. J. W.

Argentometric determination of chloride, especially in the presence of bromide and iodide, using diphenylamine-blue as indicator. R. LANG and J. MESSINGER (Z. anal. Chem., 1932, 88, 336—342).—The Br' is removed by boiling the solution (40 c.c.) with 5 c.c. of H_3PO_4 (*d* 1.7) and 0.2 g. of KIO_3 . If I' is also present this is first removed with KIO_3 and 10 c.c. of 10% AcOH ; no loss of Cl' occurs in either process. An alternative procedure for removing both Br' and I' consists in adding H_2SO_4 and COMe_2 followed by a slight excess of KBrO_3 . In all cases the Cl' is titrated with AgNO_3 , using diphenylamine-blue as indicator.

A. R. P.

Determination of chlorine and bromine in a mixture of chloride and bromide. J. BOUGAULT and E. CATTELAIN (Ann. Chim. Analyt., 1932, [ii], 14, 289—291).—The method of pptg. and weighing as AgCl and AgBr , and reducing the mixed ppt. with Zn and dil. H_2SO_4 and weighing as Ag gives accurate results when Zn of high purity is used.

E. S. H.

Determination of active oxygen in lead oxides. M. LE BLANC and E. EBERIUS (Z. anal. Chem., 1932, 89, 81—88).—An improved form of apparatus in which the Pb_3O_4 is treated with HCl and the liberated Cl_2 passed into a solution of KI is described.

O. J. W.

Iodometric determination of polysulphide sulphur. P. SZEBERENYI (Z. anal. Chem., 1932, 88, 433—435).—In the method previously described (this vol., 710) the reaction between NaOI and polysulphide S is facilitated by immersion of the vessel in boiling H_2O . Heating the mixture over a free flame results in the production of IO_3' , which converts the polysulphide into polythionate instead of into SO_4'' .

A. R. P.

Preservation and determination of sodium thiocyanate. J. GREENSPAN (J. Amer. Chem. Soc., 1932, 54, 2850).—To prevent mould formation in CNS' solutions 1 drop of PhMe is added to 100 c.c. of solution. In oxidising CNS' with I_2 a borax buffer is advantageous.

W. T. H. (c)

Standards [for colorimetric determination of ammonia by Nessler's reagent]. R. DANET (J. Pharm. Chim., 1932, [viii], 16, 68).—A solution containing 0.8 c.c. of 0.1% K_2CrO_4 and 22 c.c. of 0.1% $\text{Co}(\text{NO}_3)_2$ per 100 c.c. is suitable.

R. S. C.

Colorimetric determination of nitrate with diphenylamine or diphenylbenzidine. K. PFELSTICKER (Z. anal. Chem., 1932, 89, 1—8).—Riehm's method (B., 1930, 1149) is recommended; with slight variations in procedure it is useful for determining NO_3' in solutions containing 0.02—10 mg. per litre. With increasing dilution of the H_2SO_4 the influence of temp. and Cl' content increases. The concn. and rate of addition of the reagents are controlled.

E. S. H.

Colorimetric determination of dilute solutions of azoimide. G. LABRUTO and D. RANDISI (Annali Chim. Appl., 1932, 22, 319—324).— HN_3 in dil. solution can be determined accurately by the colour developed with FeCl_3 .

E. W. W.

Combustion in micro-elementary analysis. A. FRIEDRICH (Angew. Chem., 1932, 45, 476—478).—The

substance is weighed out in a small glass tube (4 cm. long and 7 mm. diam.) closed at one end, which is introduced into the combustion tube with the open end facing the Pt contact. The tube is heated first at the open end, the burner being then gradually moved towards the closed end, *i.e.*, in the direction opposed to the stream of O_2 . By this procedure the danger of incomplete combustion is avoided.

A. B. M.

Determination of carbon dioxide and titratable base in sea-water. D. M. GREENBERG, E. G. MOBERG, and E. C. ALLEN (*Ind. Eng. Chem. [Anal.]*, 1932, 4, 309—313).—A semi-micro-method for determining the total CO_2 content of sea-water with a portable manometric apparatus is described. The method is suitable for work on board ship and the results are reproducible to within 1%. The differential titration method for determining $CO_3^{''}$, HCO_3' , and free CO_2 in sea-water has been studied. When phenolphthalein and Me-orange are used as indicators the results are reproducible to within 1%, and the total CO_2 agrees to about 1% with that obtained with the above apparatus. For sea-water having $p_H > 7.8$, the difference between the base titration val. and the total CO_2 gives the $CO_3^{''}$ content.

E. S. H.

Direct titration of normal oxalates in neutral solution using fluorescein as an adsorption indicator. A. W. WELLINGS (*Trans. Faraday Soc.*, 1932, 28, 565—566).—The 0.1—0.05*M*-oxalates are titrated quantitatively with $Pb(OAc)_2$. Acid and alkali interfere.

J. G. A. G.

Determination of silica in silicates. N. A. TANANAEV and F. I. PERTSCHIK (*Z. anal. Chem.*, 1932, 88, 348—352).—The method depends on the decomp. of the silicate with HF , followed by evaporation with $H_2C_2O_4$, heating of the residue at 190—200° to remove excess of $H_2C_2O_4$, and finally fusion with a weighed quantity of $NaPO_3$. The difference between the sum of the wt. of sample and $NaPO_3$ and the wt. of the phosphate glass obtained gives the SiO_2 . The method is applicable to silicates containing Fe_2O_3 , TiO_2 , CaO , MgO , K_2O , Na_2O , and <15% Al_2O_3 .

A. R. P.

Determination of sodium potassium cobaltinitrite, and use [of the latter] for determination of potassium. L. CUNY (*J. Pharm. Chim.*, 1932, [viii], 16, 55—58).—0.25—8 mg. of K can be determined by pptn. as $Na_2K[Co(NO_2)_6]$, evaporation with conc. HCl , and volumetric determination of Cl' in the residue.

R. S. C.

Atomic mass of sodium. I. End-point of sodium chloride-silver titration. C. R. JOHNSON (*J. Physical Chem.*, 1932, 36, 1942—1949; cf. A., 1931, 584).—To eliminate arbitrary factors in the determination of the end-point comparison was made nephelometrically or potentiometrically with standard solutions prepared with concns. of salts and acids such as should be present at the end-point of the analysis proper.

L. P. H. (c)

Detection of caesium, rubidium, and thallium by the drop method. N. A. TANANAEV (*Z. anal. Chem.*, 1932, 88, 343—347).—With a solution of equimol. amounts of $PdCl_2$ and $AuCl_3$ in dil. HCl solutions of $CsCl$, $RbCl$, and $TlCl$ yield brown to black

compounds of the type $M_2AuPdCl_7$. Tl and Cs yield red to brown ppts. with $KBiI_4$, but Rb gives no such ppt. $Cs_2AuPdCl_7$ and $Rb_2AuPdCl_7$ are sol. in $NaOH$, but the Tl compound is blackened due to reduction of the Au and Pd by the $TlOH$. The application of these tests to the detection of Cs , Rb , and Tl in the presence of one another and of other cations is discussed.

A. R. P.

Determination of silver in solutions of potassium argentocyanide. A. WOGGINZ (*Z. anal. Chem.*, 1932, 89, 120—121).— Ag is pptd. from solutions of $KAg(CN)_2$ by Al , collected, dissolved in HNO_3 , and titrated with NH_4CNS .

O. J. W.

Micro-electrolytic determination of silver, mercury, and cadmium in ammoniacal solution. (Determination of copper, cobalt, and nickel in organic substances.) A. OKÁČ (*Z. anal. Chem.*, 1932, 89, 106—112; cf. this vol., 590, 712).—The micro-electrolytic method for the determination of Cu , Co , and Ni already described can be applied to the determination of Ag , Hg , and Cd , but not to Zn . By means of a two-fold separation Cu , Co , and Ni can also be determined with sufficient accuracy in presence of org. radicals.

O. J. W.

Iodometric titration of colloidal silver. E. EINECKE (*Z. anal. Chem.*, 1932, 89, 90—95).—Excess of I solution is added to the colloidal Ag solution and titrated back with $Na_2S_2O_3$. The reaction between Ag and I is complete after 2 hr., and can be carried out in daylight.

O. J. W.

Use of acidimetric indicators in argentometry. F. J. GARRICK (*Proc. Leeds Phil. Soc.*, 1932, 2, 301—302).—The usual acidimetric indicators (Me-orange, Me-red, bromophenol-blue) may be used satisfactorily in argentometry.

A. J. M.

Determination of small amounts of lime in presence of large amounts of magnesia. R. HEILINGÖTTER (*Chem.-Ztg.*, 1932, 56, 582—583).—For the analysis of magnesite, SiO_2 , silicates, Fe , and Al are removed by the usual methods, Ca is pptd. by $(NH_4)_2C_2O_4$, the ppt. dissolved in dil. HCl and repptd. repeatedly until a const. wt. is obtained. Mg is determined by difference.

E. S. H.

Micro-determination of barium. E. J. KING (*Biochem. J.*, 1932, 26, 586—589).—The Ba is pptd. by an excess of standard H_2SO_4 and the excess of H_2SO_4 determined by pptn. with benzidine and titration of the benzidine sulphate with $NaOH$.

S. S. Z.

Composition of analytical barium sulphate precipitates. F. L. HAHN and R. KEIM (*Z. anorg. Chem.*, 1932, 206, 398—406).—When equiv. solutions of $BaCl_2$ and K_2SO_4 are mixed under conditions such that neither reagent is in excess during any part of the mixing, but KCl is also present, the pptd. $BaSO_4$ has a slight excess of $SO_4^{''}$. The excess is shown to be present partly as K_2SO_4 and partly as H_2SO_4 .

S H

Quantitative precipitations at extreme concentrations. III. V. NJEGOVAN and V. MARJANOVIĆ (*Z. anal. Chem.*, 1932, 89, 112—120; cf. A., 1930, 1544).—Further details are given concerning the

quant. pptn. of Mg as phosphate and the application of the method to the determination of PO_4^{3-} .

O. J. W.

Direct titration of magnesium and manganous sulphate using fluorescein as an adsorption indication, and the extension of the method to the direct titration of other soluble sulphates and alums. A. W. WELLINGS (Trans. Faraday Soc., 1932, 28, 561—564).—In the absence of acid, Cl^- , and NO_3^- , fluorescein indicates, by the colour change yellow \rightarrow pink \rightarrow dark orange (after shaking), the quant. pptn. of 0.1—0.05M- MgSO_4 and - MnSO_4 by $\text{Ba}(\text{OH})_2$. Similarly, other sol. sulphates, which do not yield deeply-coloured hydroxides, may be titrated quantitatively in the presence of $\text{Mg}(\text{OAc})_2$ or $\text{Mn}(\text{OAc})_2$. Elevation of temp. obscures the endpoint.

J. G. A. G.

Rinmann's-green test for zinc. A. A. BENEDETTI-PICHLER (Ind. Eng. Chem. [Anal.], 1932, 4, 336—337).—A drop of the test solution is placed on a piece of filter-paper previously impregnated with $\text{K}_3\text{Co}(\text{CN})_6$ and the paper is then ignited. A disc of green ash on the spot where the drop was added is produced by 0.0006 mg. of Zn. The test solution is best prepared by dissolving in HNO_3 the ZnS pptd. in a separation. Sn and Sb also give a green ash, and the presence of Ti, Mn, Fe, Ni, Co, or Cd interferes with the test.

E. S. H.

Determination of zinc oxide in presence of zinc sulphide. C. V. BORDEIANU.—See B., 1932, 677.

Separation and determination of copper in presence of aluminium by means of 8-hydroxyquinoline. J. CALVET (Compt. rend., 1932, 195, 148—150; cf. A., 1927, 848).—Unless present in very great excess Cu is accurately separated from Al by 8-hydroxyquinoline (3% solution) in presence of Na tartrate and AcOH or NH_3 at 70—80°; AcOH should be \geq 6—7%. The dried ppt. is $\text{Cu}(\text{C}_9\text{H}_6\text{NO})_2$. Fe in small quantities, Mg, Be, Mn, Zn, and Cd do not interfere; but Ni and Co must be absent. C. A. S.

Macro-electroanalysis and separation of copper and nickel. J. GUZMAN (Anal. Fis. Quím., 1932, 30, 433—440).—Macro-electroanalysis is defined as the quant. deposition of 1 g. or more of metal, which may be effected economically and at low c.d. by the use of a large Cu cathode, the (rotating) anode being a passive Fe wire or a Pt spiral. Details of the determination of Cu and Ni in acid and ammoniacal solution are given; the results differ by not more than 0.05%. The following procedure is recommended for analysis of Cu-Ni alloys (about 75% Cu): the sample (1 g.) is dissolved in 8 c.c. of HNO_3 (d 1.12) and 1 g. of $(\text{NH}_4)_2\text{SO}_4$ is added; the Cu is deposited on a Cu cathode of area 212 sq. cm. within 20 min. by electrolysis at 1.4 amp. per sq. dm. The solution is then neutralised with aq. NH_3 , 10 g. of $(\text{NH}_4)_2\text{SO}_4$, 5 g. of Na_2SO_3 , and 25 c.c. of aq. NH_3 (d 0.92) are added, and the Ni is deposited under the same conditions as the Cu, except that an Fe anode may be employed.

H. F. G.

Gasometric determinations by means of the ureometer. II. G. D'ESTE (Boll. Chim. farm., 1932, 71, 437—445).— Cu^{II} salts: 10 c.c. of a solution containing about 0.25 g. of Cu, 0.5 c.c. of aq. FeCl_3 ,

and 10 c.c. of a 1.5% solution of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ are thoroughly shaken in the reaction chamber (this vol., 550) with 10 c.c. of 20% aq. KOH. N_2 is quantitatively liberated in 5 min.; 8.8 c.c. N_2 (at 0° and 760 mm.) = 0.100 g. Cu. Hg^{II} salts: 0.5 g. of HgCl_2 and 0.5 g. of NaCl are dissolved in 15 c.c. of H_2O , 10 c.c. of 1.5% aq. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ are added and shaken with 5 c.c. of 10% aq. KOH; 40.8 c.c. N_2 = 1.00 g. HgCl_2 . Iodates: 10 c.c. of 1% iodate solution are allowed to react with a mixture of 10 c.c. of 1.5% aq. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ and 5 c.c. of H_2SO_4 (1:4); 1 c.c. N_2 = 0.007643 g. KIO_3 . Bromates: to 10 c.c. of a 1% bromate solution are added 0.3 g. of KBr and treated as the iodate; 1 c.c. N_2 = 0.00497 g. KBrO_3 . Hypochlorites and hypobromites: 10 c.c. of a 2% hypochlorite or hypobromite solution are treated with 5 c.c. of 1.5% aq. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ neutralised with KOH. By this method N_2H_4 salts may be determined: 1 c.c. N_2 = 0.00581 g. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$. Na_2O_2 : about 0.1 g. of Na_2O_2 is allowed to react with 5 c.c. of NaOBr solution diluted with 10 c.c. H_2O or 10 c.c. of fresh solution of 10% $\text{K}_3\text{Fe}(\text{CN})_6$; 28.7 c.c. O_2 = 0.100 g. Na_2O_2 .

O. F. L.

Detection and nephelometric determination of small quantities of mercury. J. GOLSE and M. JEAN (Bull. Soc. Pharm. Bordeaux, 1931, 3, 168—176; Chem. Zentr., 1932, i, 1272).—1 c.c. of the solution, containing \leq 2 mg. Hg per litre, is treated with 0.1 c.c. of 2.5% strychnine sulphate solution and 0.1 c.c. of 0.5% KI solution, and the turbidity is compared with that produced by known quantities of Hg. For solutions containing 2—0.2 mg. per litre, 25 c.c. are treated with 0.1 c.c. of a solution of 1 g. As_2O_3 and 5 c.c. N -NaOH per litre, and the As and Hg are pptd. by Bougault's reagent. The centrifuged and washed ppt. is dissolved with Br, and excess of Br is removed in a current of air. 1 drop of a solution of 0.01 g. of phenolphthalein and 1 c.c. NaOH in 100 c.c. H_2O , 1 drop of N -NaOH, and 0.1N- H_2SO_4 to slight acidity are added; H_2O is added to 1 c.c., and the determination continued as above, the comparison sample being treated similarly.

A. A. E.

Determination of small quantities of mercury. M. JEAN (Bull. Soc. Pharm. Bordeaux, 1931, 3, 176—183; Chem. Zentr., 1932, i, 1271—1272).—Hg is pptd. with CH_2O and dissolved in 0.02N-I; excess of I is removed at 100° and the I combined as HgI_2 determined by Bernier and Peron's method with KMnO_4 or by conversion into iodate with Br and titration with 0.02N- $\text{Na}_2\text{S}_2\text{O}_3$ after addition of KI and AcOH.

A. A. E.

Determination of aluminium and excess acid in aluminium salts. H. L. DAVIS.—See B., 1932, 677.

Occurrence and determination of iron in sea-water. T. G. THOMPSON, R. W. BREMNER, and I. M. JAMIESON (Ind. Eng. Chem. [Anal.], 1932, 4, 288—290).—The presence of org. compounds, Cl^- , NO_3^- , NO_2^- , and F^- in sea-water interferes with the determination of Fe by KCNS. These substances are removed by evaporating the sample with H_2SO_4 . The interference due to SO_4^{2-} is obviated by using a large excess of KCNS. Surface sea-water shows a seasonal variation of Fe content, which is diminished at times

of max. diatom growth. The Fe content generally increases with the depth. E. S. H.

Analysis of alloy steels. P. L. BLANKEN.—See B., 1932, 680.

Potentiometric titration of sodium and potassium ferrocyanide. K. MASAKI (Bull. Chem. Soc., Japan, 1932, 7, 188—200).—Potentiometric titrations at 25° of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{Na}_4\text{Fe}(\text{CN})_6$ solutions with HgCl_2 , NiSO_4 , and CoSO_4 solutions, using Pt as the indicator electrode, show that the following reactions take place: $2\text{Hg}^{++} + \text{Fe}(\text{CN})_6^{4-} = \text{Hg}_2\text{Fe}(\text{CN})_6$; $2\text{Ni}^{++} + \text{Fe}(\text{CN})_6^{4-} = \text{Ni}_2\text{Fe}(\text{CN})_6$; $2\text{Co}^{++} + \text{Fe}(\text{CN})_6^{4-} = \text{Co}_2\text{Fe}(\text{CN})_6$. Similar reactions occur with FeCl_3 and with AgNO_3 . O. J. W.

Electrolytic micro-determination of nickel and cobalt. A. OKÁČ (Z. anal. Chem., 1932, 88, 431—433).—The metals are deposited together by electrolysis in aq. NH_3 , the solution being stirred with a current of CO_2 . The weighed deposit is dissolved in HNO_3 and the Ni pptd. with dimethylglyoxime, the Co being determined by difference. A. R. P.

Titration with dichromate and an internal indicator, and its applications. F. SIERRA and F. BURRIEL (Anal. Fis. Quím., 1932, 30, 441—444).— $\text{Fe}(\text{CN})_6^{4-}$ may be determined as follows: to 50 c.c. of the solution [1% $\text{K}_3\text{Fe}(\text{CN})_6$] are added 25 c.c. of 2*N*-HCl and 1 c.c. of 0.4% benzidine acetate solution, and the whole is diluted to 100—150 c.c. and titrated slowly and with vigorous stirring with 0.1*N*- $\text{K}_2\text{Cr}_2\text{O}_7$; at the end-point a greenish-yellow to dark brown coloration, accompanied by a violet ppt., is produced as a result of oxidation of the indicator. The error is about $\pm 0.5\%$. H. F. G.

Separation of uranium-X from uranium. H. HERSZFINKIEL and J. TOŁWINSKA (Rocz. Chem., 1932, 12, 426—440).—Suitable adsorbents for removing U-X from aq. UO_2^{++} are $\text{Fe}(\text{OH})_3$, CeF_3 , and BaSO_4 . Adsorption is increased by adding salts which form double compounds with UO_2^{++} , thereby diminishing its concn., but do not combine with Th. Such salts are NaF, NH_4HCO_3 , and K_2CrO_4 ; $\text{Na}_4\text{P}_2\text{O}_7$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ combine with both UO_2^{++} and Th^{4+} . Better results are obtained by adding $\text{Fe}(\text{OH})_3$ or BaSO_4 to the solution than by pptg. them in presence of the UO_2^{++} salt. R. T.

Low-temperature thermostat. F. O. LUNDSTROM and C. W. WHITTAKER (Ind. Eng. Chem. [Anal.], 1932, 4, 294—295).—Heat is conducted away from the bath to the cooling agent by means of a Cu rod soldered through the wall of the bath, which is also made of Cu, thus rendering a cooling coil in the bath unnecessary. Ice is used as cooling agent for maintaining temp. between room temp. and 7°, and liquid NH_3 is used for temp. between 7° and -25° . E. S. H.

Mercury-vapour lamp for laboratory use. I. BALINKIN and D. A. WELLS (Rev. Sci. Instr., 1932, [ii], 3, 388—391).—Hg is contained in the lower limbs of an h-shaped Pyrex tube, and an arc is started by tilting. Connexion to 60—120 volts is made through sealed-in W electrodes. C. W. G.

Microscope-centrifuge and some of its uses. E. N. HARVEY (J. Franklin Inst., 1932, 214, 1—23).

Trichromatic colorimeter. J. ZERNICKE (J. Opt. Soc. Amer., 1932, 22, 418—421).

X-Ray reflexion spectrograph. H. KERSTEN (Rev. Sci. Instr., 1932, [ii], 3, 384—387). C. W. G.

Photovoltaic cell as indicator in precise titrometry. H. M. PARTRIDGE (Ind. Eng. Chem. [Anal.], 1932, 4, 315—317).—The application of the photovoltaic cell to titrations is described. A few readings are taken and the end-point is determined by interpolation. In acid-alkali titrations, using phenolphthalein as indicator, an accuracy of 1 in 1000 is obtained. E. S. H.

Photometric eyepiece for visual quantitative spectrum analysis. F. TWYMAN (Trans. Optical Soc., 1932, 33, 176—181).—A spectrum is split into halves, and a selected line in one half is brought vertically above a selected line in the other half. The intensity of the brighter line is reduced to that of the other by means of a neutral wedge. In analyses of Pb-Cd alloys an error of 11% was obtained in the Cd content, of which 7% was due to irregularities in the wedge. C. W. G.

F/1.8 quartz monochromator-spectrograph. J. W. PERRY (Trans. Optical Soc., 1932, 33, 159—175).—The design of large monochromators and spectrographs is discussed, and a combined instrument (*F*/1.6 at 0.185μ to *F*/2.0 at 1.2μ) is described. C. W. G.

Use of thermopiles for absolute measurement of radiant energy. P. A. LEIGHTON and W. G. LEIGHTON (J. Physical Chem., 1932, 36, 1882—1907).—A line thermopile of the many-junction type and the galvanometer system required have been investigated in respect of construction, drift, calibration, auxiliary resistances, effects of diverging light, surface variations in sensitivity, and integration. L. P. H. (c)

Determination of relative humidities by means of thermocouples. J. H. LANNING (Ind. Eng. Chem. [Anal.], 1932, 4, 286—287).—Two small thermocouples are used, one having a small drop of H_2O surrounding it. The difference of temp. caused by the evaporation of the drop is recorded electrically. E. S. H.

Hydrogen electrode and apparatus for the determination of p_{H} . P. L. DU NOUY (Science, 1932, 75, 643—644). L. S. T.

Methods. XVII. Electrometric apparatus. L. PINCUSSEN and J. GORNE (Biochem. Z., 1932, 249, 126—129).—An electrode designed for the rapid determination of p_{H} of small amounts of fluid and an example of the use of electrometric methods in the micro-determination of Ca are described. P. W. C.

Specification for burettes. W. MORSE (Ind. Eng. Chem. [Anal.], 1932, 4, 263).—A few distinctive graduation marks below the lowest usual mark on a burette obviate the inconvenience of running past the mark. E. S. H.

Apparatus for accurately reading burettes. A. J. SCHATTENSTEIN (Z. anal. Chem., 1932, 88, 435—436).—The device comprises a glass tube 2 cm. long, which slides smoothly over the burette tube and can

be held in any position by a metal clip. On the upper portion of the tube are engraved a thin line encircling the tube and a thick black line extending only half-way round. On the other side of the tube to the black line there are 10 subdivisions below the circular line corresponding with nine divisions of the burette and thus providing a vernier scale. The black line at the back serves to render the bottom of the meniscus more conspicuous.

A. R. P.

Electrically operated burette tap. R. KOPPEN (Chem. Fabr., 1932, 273).—The lower end of the burette is closed by a ground cylindrical glass bulb which rests on the shoulder of the constriction and encloses an Fe armature. Surrounding the burette is a coil of wire, so placed that on passage of current the armature, and with it the bulb, rises and permits the liquid to flow from the burette. No grease is necessary.

H. F. G.

Micro-burette. R. B. DUSTMAN (Ind. Eng. Chem. [Anal.], 1932, 4, 345—346).—The apparatus can be read to 0.01 c.c.

E. S. H.

Removing "frozen" plugs from stopcocks. H. W. BAILEY (Ind. Eng. Chem. [Anal.], 1932, 4, 324).—Two key removers are described.

E. S. H.

Nitrometer. R. POGGI and B. BALDI (Annali Chim. Appl., 1932, 22, 317—319).—A nitrometer tube is narrow in its upper half and wide below, continuously graduated, and suitable for both macro- and semi-micro-determinations.

E. W. W.

Experiments with a high-temperature ozoniser. R. P. ALLEN (J. Physical Chem., 1932, 36, 1601—1648).—Treatment of EtOH, MeCHO, COMe₂, and AcOH in an ozoniser operated by a Tesla coil and heated externally gave results essentially the same as those of former workers. Some evidence was obtained of photosensitisation by heat.

C. A. (c)

Magnetic damping, oil- or air-damping for analytical balances? F. SARTORIUS (Chem.-Ztg., 1932, 56, 583).—Magnetic damping of the swinging balance suffers through the difficulty of excluding traces of Fe from the balance materials. Oil-damping leads to inaccuracy through the different resistance offered by the liquid under changing temp. and humidity. Air-damping is free from objection; an apparatus is recommended, depending on the air-friction between two Al cylinders in relative motion.

E. S. H.

Calibration of a McLeod gauge in a vacuum system. K. H. RAMASWAMY (Phil. Mag., 1932, [vii], 14, 96—99).—A method of calibrating without dismounting the gauge is described.

H. J. E.

Pressure pump for circulating gases in a closed system. E. B. KESTER (Ind. Eng. Chem. [Anal.], 1932, 4, 298).—The apparatus is actuated by a H₂O-pump through a Hg medium and has no solid moving parts or bearing surfaces. It circulates 6—20 litres per hr. and operates continuously. It is devised for overcoming the strong resistance offered by a column of viscous liquid, such as tar.

E. S. H.

Pressure control with automatic liquid-leveling device. J. V. VAUGHEN (Ind. Eng. Chem. [Anal.], 1932, 4, 346).—A Hg reservoir, suspended by

a suitable spring, maintains a const. flow of Hg, which displaces liquids at a const. rate into a reaction vessel.

E. S. H.

Apparatus for reactions in liquid phase at elevated temperatures and pressures. H. ADKINS (Ind. Eng. Chem. [Anal.], 1932, 4, 342—345).—Apparatus for reactions involving the agitation of a liquid and a solid in presence of a gas at temp. and pressures above normal is described. The apparatus is suitable for org. hydrogenations.

E. S. H.

Apparatus for pressure control in vacuum distillations. L. M. ELLIS, jun. (Ind. Eng. Chem. [Anal.], 1932, 4, 318—319).

E. S. H.

Safety device for high-vacuum pumps operated for periods without supervision. W. PUPP (Physikal. Z., 1932, 33, 530—531).

W. R. A.

Apparatus for study of changes in alloys. Isothermal microdilatometer. Registering thermomagnetometer. P. CHEVENARD (J. Phys. Radium, 1932, [vii], 3, 264—280).—The micro-dilatometer is for the study of the instability of alloys, and measures, as a function of the log. of the time, the spontaneous variation in length of a specimen at const. temp. In most cases the curves are semi-rectilinear, and the angle of the curve is taken as an index of the instability of the alloy. The thermo-magnetometer registers variations of magnetisation of ferro-magnetic bodies as a function of time.

A. J. M.

Electronic tubes. A. DAUVILLIER (J. Phys. Radium, 1932, [vii], 3, 229—238).—A description of four types of discharge tube useful for studying diffraction of electrons, crystal structure, X-ray spectra of gases, and the production in air of soft X-rays, up to 8 Å. in wave-length, respectively.

A. J. M.

Micro-mol. wt. determinations by the method of molar depression of the m.p. II. J. PIRSCH (Ber., 1932, 65, [B], 1227—1229; cf. this vol., 713, 714).—In addition to the solvents previously used (*loc. cit.*), bornylamine is recommended. Camphene dibromide has a very high mol. depression, but is not sufficiently stable and does not give const. vals. for the mol. depression with different standard substances.

H. W.

Automatic apparatus for intermittent washing. B. H. CARROLL (Ind. Eng. Chem. [Anal.], 1932, 4, 323—324).—The distinctive feature of the apparatus is a two-way tap, which is turned intermittently by a small motor, actuated by clock contacts. The apparatus is devised particularly for washing photographic films.

E. S. H.

Unit for removal of solid particles from gas streams. R. C. STRATTON, J. B. FICKLEN, and E. W. KRANS (Ind. Eng. Chem. [Anal.], 1932, 4, 334).—A modified gas-washing bottle is described, in which the gas enters the absorption liquid through a Gooch crucible, closed at the top by a rubber stopper. The apparatus is very efficient for ordinary gas-absorption purposes.

E. S. H.

Accurate air separator. P. S. ROLLER (Ind. Eng. Chem. [Anal.], 1932, 4, 341).—The apparatus formerly described (A., 1931, 706) has been improved by adding an automatic tapper.

E. S. H.

Ashing apparatus for samples containing traces of iodine. G. M. KARNs (Ind. Eng. Chem. [Anal.], 1932, 4, 299—300).—The apparatus obviates the necessity for using the rapid stream of O_2 generally recommended. E. S. H.

Movable hot-ring for evaporation of saline solutions in gravimetric analysis. K. LESCHEWSKI (Z. anal. Chem., 1932, 89, 50—51).—The device obviates loss through spurting during evaporation. The solution is placed in a boiling-tube, and outside the tube, at the level of the liquid surface, is placed a ring of asbestos paper wrapped with an electrically-

heated Ni-Cr coil. As evaporation proceeds the hot-ring is gradually lowered. E. S. H.

Reciprocal lattice projecting ruler and chart. L. J. B. LACOSTE (Rev. Sci. Instr., 1932, [ii], 3, 356—364).—A simple rapid graphical method of interpreting secondary spectra of oscillating crystal photographs is described. C. W. G.

Apparatus for counting sand grains. J. E. APPEL (Science, 1932, 76, 58—59).—A simple apparatus for the rapid counting of small particles is described. L. S. T.

Geochemistry.

Evidence for the constitution of the ether. J. MACKEY (J. Franklin Inst., 1932, 214, 73—98).

Determination of the radioactivity of the atmosphere. G. ALIVERTI (Nuovo Cim., 1931, 8, 233—245; Chem. Zentr., 1932, i, 1335).—A modification of Gerdien's method is described. L. S. T.

Italian natural gases. III. Determination of higher hydrocarbons by analysis by condensation. M. G. LEVI, C. PADOVANI, and M. BUSI (Annali Chim. Appl., 1932, 22, 380—392).—Various Italian natural gases have been analysed; most contain some hydrocarbons higher than CH_4 .

E. W. W.

Determination of carbonaceous waste gases and soot in the air. J. HIRSCH (J. State Med., 1932, 40, 300—302).—The air (Berlin) was passed over heated CuO after removal of CO_2 ; more CO_2 was produced. C particles may be collected on a filter and then heated with CuO to produce CO_2 . CH. ABS.

Chemistry of the water and silt of Lake Agigea. P. PETRESCU (Bul. Soc. Chim. Romania, 1931, 13, 57—81).—The compositions of the dissolved and suspended matter in the H_2O of Lake Agigea are tabulated. The particle size in the latter has also been investigated. J. W. S.

Analysis of rains and snows at Mount Vernon, Iowa. S. F. WILLIAMS and O. K. BEDDOW (Chem. News, 1932, 145, 40—43).

"Ferrosilite" as a name for the normative molecule $FeSiO_3$. H. S. WASHINGTON (Tsch. Min. Petr. Mitt., 1932, 43, 63—66).—The name ferrosilite (fs), first proposed by the author in 1903, for the mol. $FeSiO_3$ in the calculation of rock analyses, is preferable to hypersthene suggested by Barth (A., 1931, 1390).

L. J. S.

"Doctoring" of the norm. C. E. TILLEY (Tsch. Min. Petr. Mitt., 1932, 43, 68—69).—Further criticism of Barth (A., 1931, 1390). L. J. S.

Magmatic and non-magmatic silicate systems. F. LOEWINSON-LESSING (Tsch. Min. Petr. Mitt., 1932, 43, 45—62).—A comparison of the chemical and mineral composition of igneous rocks with that of stony meteorites, contact-metamorphic rocks (hornfels), and slags shows certain essential differences. In the latter types differentiation has played no part as in igneous magmas. L. J. S.

Petrology and chemistry of a titaniferous amphibolite from Ribeira, Galicia. I. PARGA-PONDAL (Anal. Fis. Quím., 1932, 30, 426—432).—The mineral contains hornblende 58%, plagioclase and quartz 30.6%, titanite 6.1%, ilmenite 4.3%; or SiO_2 47.9%, Al_2O_3 13.08%, and TiO 5.29%. It appears to be an ortho-amphibolite. The manner of formation is discussed. H. F. G.

Geochemistry of scandium. V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss., Göttingen, 1931, 257—279; Chem. Zentr., 1932, i, 1356—1357).—An exhaustive review of the occurrence of Sc. Results of spectro-analytical examination of numerous minerals and rocks are tabulated. Most of the Sc in rocks is present in the Mg and Fe^{II} silicates.

A. A. E.

Igneous history of the Buckskin Gulch stock, Colorado. Q. D. SINGEWALD (Amer. J. Sci., 1932, [v], 29, 52—67).—A detailed account of the petrology is given, and the crystallisation-differentiation is discussed. C. W. G.

Garnet rock near West Redding, Conn. W. M. AGAR and P. KRIEGER (Amer. J. Sci., 1932, [v], 29, 68—80).—Petrological and mineralogical descriptions and an analysis are given. C. W. G.

Origin of circulating sulphate solutions in rocks and soils. E. BLANCK and H. EVLIA (Chem. Erde, 1932, 7, 298—319).—The presence of free SO_3 , as well as CO_2 , in ground-water is of importance in rock weathering. Free SO_3 in soils has been attributed to the decomp. of pyrite, but it appears that the decay of albuminous substances from plants is more important. Determinations were made of the total S and the SO_3 portion present in plants and in the soil during each month of the year. L. J. S.

Vanadium content of sedimentary rocks. K. JOST (Chem. Erde, 1932, 7, 177—290).—The amounts of V present in sedimentary rocks of various kinds and of different geological ages are tabulated from the literature, and many new determinations are also given. Determinations were made by the potentiometric method of Zintl and Zaimes (B., 1928, 525). The average amount in clays and shales is 0.012%, in sandstones 0.002%, and still less in limestones and dolomites. Larger amounts are present in laterites and bauxites (including sedimentary Fe ores and Mn

ores) as in rocks containing org. remains, bitumen, coal, and oil. The V from the weathering of igneous rocks (average V 0.018%) goes mostly with the clays, and in the presence of org. matter there is a further enrichment from solution due to reduction, especially in arid climates. L. J. S.

Form of the calcium carbonate in the shells and skeletons of recent and fossil organisms. F. K. MAYER (Chem. Erde, 1932, 7, 346—350).—X-Ray powder photographs show that the material consists in some cases of calcite and in others of aragonite. L. J. S.

Ore-bearing diabbases of the Dill district. R. MOSEBACH (Chem. Erde, 1932, 7, 320—345).—Analysis of an olivine-dolerite shows NiO 0.22%, and the rock contains small nests of sulphide minerals—pyrite, pyrrhotine, pentlandite, and chalcopyrite. These have been formed by hydrothermal action, the Fe and Ni being derived mainly from the olivine of the rock. L. J. S.

Classification of sedimentary clays. J. DE LAPPARENT (Compt. rend., 1932, 195, 257—258).—Of these there are three chief types: (1) halloysite clays (type, the grey plastic clay of the Paris basin): felted lamellæ of halloysite with small crystals of rutile and anatase; (2) montmorillonite clays (type, oligocene clays of Algiers and Oran): minute lamellæ of montmorillonite, free from Ti; and (3) kaolinite clay (type, tonstein of the Sarre basin): essentially kaolin, free from Ti. (1) has been formed from granite decomposed elsewhere and accumulated by H₂O action, (2) and (3) were formed *in situ*, probably from feldspars, (2) in a dry, (3) in a moist climate. C. A. S.

Meteorite from the Black Hills, Wyoming. C. C. O'HARA (Science, 1932, 76, 34).—Unoxidised drillings from a new meteorite (Bear Lodge meteorite) contain 91.70% Fe and 8.12% Ni. L. S. T.

Process of peat formation. G. KEPPELER (Angew. Chem., 1932, 45, 473—476).—Formulae are deduced relating the true degree of conversion (x) of the initial plant material into peat with the glucose val. and with the amount of the acid-insol. residue (cf. B., 1920, 394A). The formulae when applied to a peat "profile" and to various peat samples gave

concordant vals. of x which, however, are much higher than those previously assumed. The glucose vals. for a no. of peat-forming plants varied from 36.7% to 69.3%, and corresponding variations occurred in the acid-insol. residues. The significance of the formulae used is discussed. A. B. M.

Anomalous heat effects of certain radioactive minerals. A. DORABIALSKA (Rocz. Chem., 1932, 12, 416—425).—The heat effects of orangite and monazite are considerably greater than would follow from their content of radioactive elements. This effect is not due to adsorption of H₂O or to chemical processes or morphological changes taking place in the crystals. The continuous evolution of heat is associated with the La and Yt fractions, being absent from the Ca and Er fractions. Heat effects of the same order of magnitude are given by La and Yt derived from other sources. R. T.

Volcanic ash from Guatemala. E. DEGER (Chem. Erde, 1932, 7, 291—297).—An account is given of the eruption on Jan. 21, 1932, of the Fuego volcano, and analyses of the ash are recorded. L. J. S.

Phosphate beds in the Cioclovina caves. E. GEORGACOPOL and (Mlle.) M. DAVIDESCU (Bul. Chim. Soc. Romane Stiinte, 1929, 31, 3—22).—The beds, which have been formed by the fossilisation of bones, contain (1) Ca(H₂PO₄)₂, sol. in H₂O; (2) CaHPO₄, insol. in H₂O, sol. in ammoniacal NH₄ citrate; (3) Ca₃(PO₄)₂, insol. in the above; (4) Ca₃(PO₄)₂.CaO, sol. in 2% citric acid; (5) Fe and Al phosphates. (1), (2), and (4) are immediately assimilable by plants, (3) dissolves slowly under the action of CO₂, (5) are insol. and valueless as fertilisers. The effect of soil, humidity, etc. on fertilising val. is considered. D. R. D.

Laterite and laterite soils. ANON. (Imp. Bur. Soil Sci. Tech. Comm., 1932, No. 24, 30 pp.).—The characteristics of true laterites are discussed. In tropical areas, intense leaching leads to the formation of laterites *in situ*. The product contains Al₂O₃ (in excess of that requisite to combine with the SiO₂) in the form of gibbsite. Special methods of analysis and an extensive bibliography are appended. A. G. P.

Organic Chemistry.

Significance of X-ray structure in organic chemistry. J. HENGSTENBERG and H. MARK (Naturwiss., 1932, 20, 539—544).

Number of structural isomerides of homologues of methane and methyl alcohol. D. PERRY (J. Amer. Chem. Soc., 1932, 54, 2918—2920).—The no. of primary, *sec.*-, and *tert.*-isomeric alcohols for C₂₁ to C₃₀, and structurally isomeric paraffins for C₁₉ to C₃₉ and for C₆₀, are calc. by Henze and Blair's method (A., 1931, 1147, 1148). C. J. W. (b)

Separation of normal long-chain hydrocarbons by fractional distillation in high vacuum. (Miss) H. S. GILCHRIST and (Miss) B. KARLIK (J.C.S., 1932, 1992—1995).—An electrically heated apparatus is

described (cf. Müller, A., 1928, 1176). Mixtures of eicosane (1.3—50%) and triacontane (50—98.7%) and of tetracosane (3%) and triacontane (97%) are separable as shown by X-ray examination of the fractions obtained. H. B.

Action of radon on some unsaturated hydrocarbons. II. Propylene and cyclopropane. G. B. HEISIG.—See this vol., 918.

Mechanism of polymerisation of unsaturated compounds. R. ŌDA (Nia Kem., 1932, 5, 47—53).—Mols. of unsaturated compounds are considered to tend to become arranged so as to have a min. electric moment; union of chemical linkings then takes place. CH. ABS.

Formation of various organic sulphur compounds from ethylenic hydrocarbons. A. MAILHE and M. RENAUDIE (Compt. rend., 1932, 195, 391—393).—In presence of SiO_2 gel at 650—725° H_2S and C_2H_4 , propylene, Δ -*n*-butene, or isoamylene give H_2 , CH_4 , mercaptans (I), aromatic, ethylenic, and saturated hydrocarbons, neutral sulphides (II), thiophen and its homologues (III), and CS_2 . (II) are formed by decomp. of (I), and (III) from (II). Bu_2S or BuSH in presence of SiO_2 gel at 700° gives thiophen. More CS_2 is formed at the higher temp. R. S. C.

New isomeride of benzene. Hexa- Δ^{α} -diene- $\Delta\gamma$ -inene. LESPIEAU and GUILLEMONAT (Compt. rend., 1932, 195, 245—247).— $\alpha\beta$ -Dibromoethyl ether with the Mg_2 derivative of C_6H_2 affords α -bromo- γ -ethoxy- $\Delta\gamma$ -butinene (I), b.p. 47—48°/14 mm., and $\alpha\zeta$ -dibromo- $\beta\delta$ -diethoxy- $\Delta\gamma$ -hexinene in two stereoisomeric forms, b.p. 158—162°/14 mm. [Br_2 -derivatives (II), m.p. 113—114° and 70—70.5°]. With Zn dust in BuOH at 110° (I) affords mainly vinylacetylene. The mixture (II) similarly affords hexa- Δ^{α} -diene- $\Delta\gamma$ -inene, b.p. 84.5—85° (hexabromide, m.p. 105—106°). J. L. D.

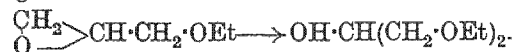
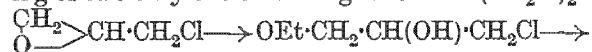
Detection of chloropicrin. E. V. ALEXEEVSKI (J. Chem. Ind., Russia, 1931, 8, No. 20, 50—51).—Reduction in aq. solution with Ca affords HNO_2 , which is detected with $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ and H_2SO_4 . CH. ABS.

Determination of small amounts of ethyl iodide. R. D. COOL (J. Biol. Chem., 1932, 97, 47—52).—Oxidation is effected with Cl_2 or Br with HIO_3 , which is determined with KI and $\text{Na}_2\text{S}_2\text{O}_3$, after removal of excess Cl_2 or Br with PhOH . A. A. L.

Oxidation of alcohols by chromic acid. L. SEMICHON and M. FLANZY (Compt. rend., 1932, 195, 254—256).—Primary and sec. alcohols with dil. CrO_3 afford acids and ketones rapidly and nearly quantitatively. CMe_3OH is incompletely oxidised under similar conditions after 125 hr. isoButyric acid suffers graded oxidation to COMe_2 and EtCO_2H . Glycerol and the sugars afford CHO and HCO_2H . J. L. D.

Microchemical detection of methyl alcohol in presence of ethyl alcohol. C. KOLLO and N. CRISAN (Bul. Soc. Chim. Romania, 1932, 13, 82—88).—By oxidation with Beckmann's reagent, condensation of the aldehydes with 5:5-dimethyl-dihydroresorcinol, and separation of the products by fractional micro-sublimation, small quantities of MeOH in min. concn. of 0.5% can be detected in presence of EtOH . R. S. C.

Partial esterification of polyhydric alcohols. XII. Function of ethylene oxide rings. A. FAIRBOURNE, G. P. GIBSON, and D. W. STEPHENS (J.C.S., 1932, 1965—1972).—The production of glycerol $\alpha\gamma$ - Et_2 ether (I) (0.72 mol.) from $\alpha\gamma$ -dichlorohydrin (II) (1 mol.) and NaOH (2.2 mols.) in EtOH involves four reactions, viz., the formation and opening of two ethylene oxide rings: $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2 \longrightarrow$



The conditions governing these reactions are investigated

and modified so that each intermediate can be isolated. Ring formation occurs under the action of NaOH , whilst fission of the ring (leading to the β -OH compound) is accomplished by acid or alkali (not in neutral solution). Gradual addition of aq. NaOH (1 mol.) to (II) at 75—80° gives 0.86 mol. of epichlorohydrin (III), which with $\text{EtOH}\cdot\text{H}_2\text{SO}_4$ affords α -chlorohydrin γ -Et ether, the detection of which during the prep. of (I) from (II) is difficult owing to its decomp. by $\text{EtOH}\cdot\text{NaOH}$ at approx. the same rate as it is produced. This is converted by 27% NaOH at 80—100° into glycidyl Et ether, which with 1% $\text{EtOH}\cdot\text{H}_2\text{SO}_4$ gives (I). The prep. of glycerol $\alpha\gamma$ - Ph_2 ether (IV) from (II) is similarly investigated. (III) heated with NaOPh gives (IV), but with PhOH (2 mols.) at 110°, α -chlorohydrin γ -Ph ether results. Treatment of a mixture of (II) and PhOH with 27% NaOH at 70—80° and then at 100° gives glycidyl Ph ether (63% yield), converted by PhOH and a little alkali into (IV).

The compounds described by Suzuki and Inoue (A., 1930, 736) are not the di-*p*-nitrobenzoates of glycerol α - and β -Me ethers (A., 1931, 599); the structure of the " β "-chlorohydrin used is unproven. H. B.

Partial esterification of polyhydric alcohols. XIII. Glycerol α -phenyl ether. XIV. Iodo-hydrins. A. FAIRBOURNE and D. W. STEPHENS (J.C.S., 1932, 1972—1973, 1973—1977).—XIII. Glycerol α -Ph ether exists in two forms, m.p. 54° and 68°. $\alpha\gamma$ -Di-*o*-tolylxy- β -acetoxyp propane has m.p. 36° (cf. A., 1931, 599).

XIV. Di-*p*-nitrobenzoates of specimens of α -iodohydrin obtained from different sources are identical; β -iodohydrin is unknown. $\alpha\beta$ -Di-iodohydrin, m.p. 43°, is prepared from allyl alcohol and I; its *p*-nitrobenzoate, m.p. 66—67° (decomp.), laurate, m.p. 38—39°, palmitate, m.p. 55°, and stearate, m.p. 55—56°, are similarly obtained from the allyl esters. $\alpha\gamma$ -Di-iodohydrin *p*-nitrobenzoate, m.p. 81—82°, palmitate, m.p. 48—49°, and stearate, m.p. 49—50°, are prepared by acylation of $\alpha\gamma$ -di-iodohydrin (from $\alpha\gamma$ -dichlorohydrin and KI). Comparison of the above and related pairs of esters shows that the m.p. of the *as*-compound may be higher than, the same as, or lower than the m.p. of the *s*-isomeride (cf. Robinson *et al.*, this vol., 364). The glyceryl palmitate, m.p. 69°, of Bergmann and Carter (A., 1930, 1555) is the β -ester. H. B.

Equilibrium in binary systems with erythritol as component. N. A. PUSHIN and M. DEZELIC (Monatsh., 1932, 60, 431—437).—Thermal analysis shows that erythritol does not give definite compounds or solid solutions, but only mechanical mixtures with *o*- and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, $\text{CCl}_3\cdot\text{CO}_2\text{H}$, mannitol, or SbBr_3 . Palmitic, stearic, oleic, elaidic, and picric acid do not mix with erythritol when molten and form two liquid layers. Mannitol and glycerol resemble erythritol in their behaviour towards the two and three first-named acids, respectively.

H. W.

Partly acylated sugar alcohols. I. Treatment of benzoylated mannitol $\alpha\zeta$ -di-iodohydrin with silver fluoride. II. The dibenzoylmannitol of Einhorn and Hollandt. A. MÜLLER (Ber.,

1932, 65, [B], 1051—1055, 1055—1059).—I. *d*-Mannitol is converted by successive treatment with CPh_3Cl and BzCl in pyridine into $\alpha\zeta$ -ditriphenylmethylmannitol $\beta\gamma\delta\epsilon$ -tetrabenzoate, m.p. 183—184°, $[\alpha]_D^{20} +42.62^\circ$ in CHCl_3 (or $+2\text{EtOH}$, m.p. 141—142°), transformed by HBr-AcOH into *d*-mannitol $\beta\gamma\delta\epsilon$ -tetrabenzoate (I), m.p. 145—147° after softening, $[\alpha]_D^{20}$ about -0.5° in CHCl_3 , from which $\alpha\zeta$ -diacetyl-*d*-mannitol $\beta\gamma\delta\epsilon$ -tetrabenzoate, m.p. 146°, $[\alpha]_D^{19} +40.38^\circ$ in CHCl_3 , and *d*-mannitol hexabenzoate, m.p. 149—150°, $[\alpha]_D^{19} +53.97^\circ$ in CHCl_3 , are derived. (I) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in pyridine yield $\alpha\zeta$ -di-*p*-toluenesulphonyl-*d*-mannitol $\beta\gamma\delta\epsilon$ -tetrabenzoate, m.p. 171° or, more usually, m.p. 166°, $[\alpha]_D^{19} +36.98^\circ$ in CHCl_3 , which with NaI in COMe_2 at 100° affords $\beta\gamma\delta\epsilon$ -tetrabenzoyl-*d*-mannitol $\alpha\zeta$ -iodohydrin (II), m.p. 70—71°, $[\alpha]_D^{19} +31.93^\circ$ in CHCl_3 (additive compound with 1 mol. of dioxan, $[\alpha]_D^{19} +32.05^\circ$ in CHCl_3). (II) and AgF in pyridine give a small yield of substance, m.p. 147—148°, $[\alpha]_D^{20} +45.79^\circ$ in CHCl_3 , which does not add Br or reduce Fehling's solution. The formation of a double linking by the action of AgF on the iodohydrins of sugar alcohols appears evidence of the immediate proximity of the I atom to an O ring.

II. The mannitol dibenzoate of Einhorn and Hollandt does not react with CPh_3Cl in pyridine, thus confirming the $\alpha\zeta$ -structure (cf. Brigl and Grüner, this vol., 598); tetra-acetyl- α -mannitol $\alpha\zeta$ -dibenzoate has m.p. 125—126°, $[\alpha]_D^{17} +41.64^\circ$ in CHCl_3 . Tri-*p*-toluenesulphonyl-*d*-mannitol $\alpha\zeta$ -dibenzoate, m.p. 133—134°, $[\alpha]_D^{17} +43.56^\circ$ in CHCl_3 , is transformed by NaOAc and Ac_2O in a complex manner into a product, m.p. 135°, which yields *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Na}$ with NaI in COMe_2 at 175—180°, but not at 110°, giving an I-free product, m.p. 140—142°, $[\alpha]_D^{19} +54.39^\circ$ in CHCl_3 . Mannitol $\alpha\zeta$ -dibenzoate is converted by COMe_2 and H_2SO_4 into $\gamma\delta$ -isopropylidene-*d*-mannitol $\alpha\zeta$ -dibenzoate, m.p. 94—95°, transformed by $\text{NH}_3\cdot\text{MeOH}$ into $\gamma\delta$ -isopropylidenemannitol, m.p. 84°, $[\alpha]_D^{19} +27.66^\circ$ in H_2O , identical with the $\alpha\beta$ -isopropylidenemannitol of Irvine and Patterson (J.C.S., 1914, 105, 989), the constitution of which follows from its conversion into $\alpha\zeta$ -ditriphenylmethyl- $\gamma\delta$ -isopropylidene-*d*-mannitol $\beta\epsilon$ -diacetate, m.p. 143°, $[\alpha]_D^{19} \pm 0^\circ$, by successive treatment with CPh_3Cl and Ac_2O in pyridine. α -Sorbitol benzoate, m.p. 140°, $[\alpha]_D^{18} +1.85^\circ$ in pyridine, from *d*-sorbitol and BzCl in pyridine, did not react with CPh_3Cl .

H. W.

Component of *Polygala tenuifolia*. J. SHINODA, S. SATO, and D. SATO (Ber., 1932, 65, [B], 1219—1223).—Continued extraction of *P. tenuifolia* with MeOH , evaporation of the extract to dryness after addition of MgO and H_2O , and subsequent treatment with EtOH and Et_2O affords polygaritol (I), m.p. 142—143°, $[\alpha]_D^{20} +47.81^\circ$ in H_2O , which does not reduce Fehling's solution or react with $\text{NHPh}\cdot\text{NH}_2$, Br , or KMnO_4 . It appears identical with the product isolated from *P. amara*, L., and *P. vulgaris*. The Ac_4 derivative has m.p. 73—75°. (I) is reduced by P and HI (d 1.7) to hexyl iodide, b.p. 167°. Oxidation of (I) with H_2O_2 followed by treatment with $\text{NHPh}\cdot\text{NH}_2$ affords glucosazone, m.p. 208°, whereas after oxidation with NaOBr an osazone, m.p. 184°, is obtained identical with that derived from styracitol

and from hydroxyglucal. (I) is therefore $\alpha\epsilon$ -anhydro-mannitol.

H. W.

Reaction between diethyl ether and phosphorus pentachloride. W. S. GUTHMANN (J. Amer. Chem. Soc., 1932, 54, 2938—2940).— PCl_5 (7 g.) boiled with 30 c.c. of Et_2O for 48 hr. gives an oil, not completely miscible with Et_2O , stable at room temp. in absence of moisture, and hydrolysed to MeCHO , HCl , H_3PO_4 , H_3PO_3 , and unidentified stable organo-P compounds.

C. J. W. (b)

Synthesis and enzymic decomposition of galactose 6-phosphate. B. HVISTENDAHL (Svensk Kem. Tidskr., 1932, 44, 156—162).—The synthesis of galactose 6-phosphate from diisopropylidenegalactose is described (cf. A., 1931, 1393). Enzymes derived from bones hydrolyse galactose 6-phosphate five times as rapidly as those present in the kidneys, but in both cases the velocity of the reaction is less than half that which results when a glycerophosphate solution is employed. Fermentation experiments using treated and untreated yeast and galactose 6-phosphate, with or without added phosphate, tended to show that this ester does not play any part as intermediate product in the fermentation of galactose.

H. F. H.

Compounds of fructosediphosphoric acid. C. NEUBERG and M. SCHEUER (Biochem. Z., 1932, 249, 478—482).—The prep. and properties of the benzidine salt of fructosediphosphoric acid, $\text{C}_6\text{H}_{10}\text{O}_4(\text{PO}_4)_2\cdot\text{B}_3$ (B =benzidine), are described. Impure Zn and Cd salts can be prepared from the Mg salt. The uranyl compound is insol. in H_2O .

W. McC.

Thionitrates. I. *tert*-Butyl thionitrate, $\text{CMe}_3\cdot\text{S}\cdot\text{NO}_2$. H. RHEINBOLDT and F. MOTT (Ber., 1932, 65, [B], 1223—1224).—*tert*-Butyl thionitrate, m.p. -12° , b.p. 54—54.5°/13 mm., decomp. about 150°, is prepared by oxidising *tert*-butyl thionitrite in AcOH with fuming HNO_3 .

H. W.

Detection and determination of dichloroethyl sulphide by combustion. M. MAXIM (Chem.-Ztg., 1932, 56, 503).—Determinations of this substance by the action on it of HI and titration of the liberated I , and by reduction of H_2SeO_3 and weighing the Se , are not sp. Since S is not usually present in the impurities associated with the compound, it is better to determine S by the Carius method or by combustion of the gas in an open tube, leading the products through H_2O_2 and BaCl_2 , and determining the S as BaSO_4 . A cloudiness or ppt. in the collecting vessel indicates the presence of dichloroethyl sulphide.

B. P. R.

Industrial synthesis of sodium moniodomethanemonosulphonate. G. AUBRISCHIO (L'Ind. Chimica, 1932, 10, 714—716).— $\text{CHI}_3\cdot\text{SO}_3\text{Na}$ was prepared by direct sulphonation of 20% aq. CHI_3 by Na_2SO_3 under reflux condenser for >5 hr. CHI_3 is formed as intermediate product. NaI formed is decomposed by Cl_2 , and the residual Cl_2 displaced by CO_2 . The neutralised liquid is evaporated on the water-bath. NaCl is separated by treating the residue with EtOH . The product is recrystallised from EtOH . The yield is almost quant.

O. F. L.

Oxidation of acetic acid and acetate by persulphate. F. FICHTER and L. PANIZZON (Helv.

Chim. Acta, 1932, 15, 996—1008).—The principal initial product of the oxidation of acetate in alkaline and acid solution by $K_2S_2O_8$ appears to be Ac_2O_2 , which hydrolyses to Ac_2O_2H , although in acid solution part breaks down to C_2H_6 ; during the hydrolysis $MeOH$, C_2H_4 , and/or CH_4 and CH_2O are formed. Simultaneously with the main reaction, succinic acid is formed by direct oxidation. The main reaction is identical with that which takes place during anodic oxidation of $AcOH$ and during photolysis of uranyl acetate. H. F. G.

Special case of allylic isomerism. RAMBAUD (Compt. rend., 1932, 195, 389—391).—Et vinylglycollate (I) and PBr_3 give Et γ -bromocrotonate (II) and an inseparable mixture of unchanged (I) and Et α -bromovinylacetate, which isomerises partly to (II) when distilled. Me vinylglycollate and PBr_3 give only Me γ -bromocrotonate. (I) and $SOCl_2$ give Et α -chlorovinylacetate, b.p. $67.5^\circ/23$ mm., which with $CaBr_2$ yields (II). R. S. C.

Choleic acids. V. Separation of optical antipodes by means of co-ordination compounds. H. SOBOTKA and A. GOLDBERG (Biochem. J., 1932, 26, 905—909).— $CHMeEt\cdot CO_2H$, $CHPhEt\cdot CH_2OH$, dipentene, and camphor have been resolved by this method. S. S. Z.

Electrolysis of a mixture of two fatty acids. M. MATSUI and S. ARAKAWA (Mem. Coll. Sci. Kyoto, 1932, A, 15, 189—194).—The hydrocarbons formed at the anode on electrolysing aq.-alcoholic solutions of binary mixtures of fatty acids, approx. neutralised with K_2CO_3 , at 70 — 75° and 12—13 amp. per 15 sq. cm. with Pt electrodes, have been investigated. A mixture of $AcOH$ and $C_{15}H_{31}\cdot CO_2H$ yields $C_{16}H_{34}$ and $C_{30}H_{62}$ (*n*-paraffins); $AcOH$ and $C_{17}H_{35}\cdot CO_2H$ yield $C_{18}H_{38}$ and $C_{34}H_{70}$; $EtCO_2H$ and $C_{15}H_{31}\cdot CO_2H$ yield $C_{17}H_{36}$ and $C_{30}H_{62}$; $Pr\cdot CO_2H$ and $C_{15}H_{31}\cdot CO_2H$ yield $C_{18}H_{38}$ and $C_{30}H_{62}$; $CH_2Cl\cdot CO_2H$ and $C_{15}H_{31}\cdot CO_2H$ yield $C_{16}H_{33}Cl$ and $C_{30}H_{62}$; $CH_2Ph\cdot CO_2H$ and $C_{15}H_{31}\cdot CO_2H$ yield $PhCHO$, $C_{30}H_{62}$, and (?) $C_{16}H_{33}\cdot Ph$; $CCl_3\cdot CO_2H$ is decomposed at the temp. employed. The regularity of the results, which is shown also in the approx. quant. equality of the yields, suggests that the fatty acids and $CH_2Cl\cdot CO_2H$ all give analogous primary products, the varying stability of which determines the nature of the final products. D. R. D.

Reactions of olefinic compounds. I. Additivity of olefinic acids towards hypochlorous acid and ethyl hypochlorite: orientation in relation to additive mechanism. G. F. BLOOMFIELD and E. H. FARMER (J.C.S., 1932, 2062—2071).— Δ^7 -Hexenoic acid in Et_2O and aq. $HOCl$ (Cl-free but containing $CaCl_2$) give after 55—60 hr. at 0° about 95% of δ -chloro- γ -hexolactone, b.p. 115 — $116^\circ/5$ mm., and <5% of (probably) γ -chloro- δ -hydroxyhexoic acid. Δ^8 -Hexenoic acid and $HOCl$ afford about 20% of (probably) γ -chloro- β -hydroxyhexoic acid, m.p. 83 — 84° , and nearly 80% of a mixture of β -chloro- γ -hexolactone, b.p. $80^\circ/5$ mm., and a non-volatile stereoisomeride (which when kept for 1 year gives cryst. material, $C_6H_9O_2Cl$, m.p. 175°). Δ^a -Hexenoic acid combines with $HOCl$ much more slowly than its isomerides; the resultant product contains much unchanged material, α -chloro- β -hydroxyhexoic acid (I),

m.p. 82° , and an impure stereoisomeride (II) of (I) (free from any detectable amount of β -chloro- α -hydroxyhexoic acid). (I) is oxidised by $K_2Cr_2O_7-H_2SO_4$ to $PrCO_2H$, whilst the impure acetate of (I) on reduction (Na-Hg), subsequent hydrolysis ($EtOH-KOH$), and oxidation (alkaline $KMnO_4$) gives small amounts of $H_2C_2O_4$ and $PrCO_2H$. (II) is oxidised ($K_2Cr_2O_7-H_2SO_4$) to fumaric and fatty acids (containing much $PrCO_2H$); its acetate is degraded (as above) to $H_2C_2O_4$ and $PrCO_2H$. Crotonic and sorbic acids give very small amounts of additive compounds with $EtOCl$. Of the three hexenoic acids, only the Δ^8 -acid reacts smoothly with $EtOCl$ in CCl_4 or Et_2O ; at least 93% of a mixture of isomeric β -chloro- γ -hexolactones and <1% of (probably) γ -chloro- β -ethoxyhexoic acid are formed in Et_2O ; it is assumed that the production of the lactones involves the loss of

OEt after the inception of addition. The similarity in the results with $HOCl$ and $EtOCl$ suggests that aq. $HOCl$ reacts in mol. condition (as does $EtOCl$);

the polarisations are $\overset{\delta+}{Cl}\overset{\delta-}{OH}$ and $\overset{\delta+}{Cl}\overset{\delta-}{OEt}$. The addition of Cl to Δ^8 -hexenoic acid can be represented analogously to that of $EtOCl$ and $HOCl$, since chlorination in Et_2O or hexane at -8° gives solely β -chloro- γ -hexolactone and HCl (liberated from the outset of reaction); addition in all three cases is initiated mainly or wholly at C_8 . The main activations (δ -) of Δ^a - and Δ^7 -hexenoic acids are at C_a and C_8 , respectively. The chlorination of cinnamic acid in $EtOH$ is discussed briefly. H. B.

Conjugated compounds. XVIII. Addition of hypochlorous acid to sorbic acid. G. F. BLOOMFIELD and E. H. FARMER (J.C.S., 1932, 2072—2078).—Sorbic acid in Et_2O and aq. $HOCl$ give a solid mixture (A) of 80% of δ -chloro- γ -hydroxy- Δ^a -hexenoic acid (*Ag* salt) and 20% of its lactone together with a stereoisomeric δ -chloro- γ - Δ^a -hexenolactone (I), decomp. above $140^\circ/5$ mm. (yielding sorbic acid), and (probably) the γ -lactone (II) of $\alpha\delta$ (or $\beta\delta$)-dichloro- $\beta\gamma$ (or $\alpha\gamma$)-dihydroxyhexoic acid; A, (I), and (II) represent 50—60, 20—25, and 15—30%, respectively, of the sorbic acid used, and practically the whole of the acid suffers attack at C_8 . Reduction of A (H_2 , colloidal Pd, H_2O) affords a little unidentified chloro-hydroxyhexoic acid, m.p. 141 — 142° , and (mainly) δ -chloro- γ -hexolactone, b.p. $120^\circ/9$ mm., m.p. about 11.5° , which is reduced by Na-Hg in aq. $EtOH$ to γ -hexolactone and a trace of Cl-free acid and is oxidised ($K_2Cr_2O_7-H_2SO_4$) to small amounts of $AcOH$, succinic acid, and an oil. A is oxidised by O_3 to $H_2C_2O_4$ and an aldehyde (oxidised by H_2O_2 to a Cl-free substance, m.p. 87 — 94°), by neutral $KMnO_4$ to $H_2C_2O_4$ and an oily Cl-acid (see below), and by $K_2Cr_2O_7-H_2SO_4$ to fumaric acid, a trace of $AcOH$, and an oily Cl-acid (consisting largely of $CHClMe\cdot CO_2H$). Reduction (H_2 , colloidal Pd, aq. $COMe_2$) of (I) gives unidentified acidic material and (probably) a mixture of γ -hexolactone and δ -chloro- γ -hexolactone, whilst oxidation (neutral $KMnO_4$) affords $H_2C_2O_4$, a trace of $AcOH$, and $CHClMe\cdot CO_2H$. (II) is also oxidised ($KMnO_4$) to $CHClMe\cdot CO_2H$ and $AcOH$. $HOCl$ could not be added to A, suggesting that (II) arises by addition of $HOCl$ to the primarily formed $\alpha\delta$ -chloro-

hydrin or by simultaneous attack at both the double linkings of sorbic acid.

Solid (*B*) and liquid (*C*) (mainly lactic) products are also formed from β -vinylacrylic acid and HOCl; oxidation of *B* and *C* gives $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$. The mode of addition suggested by Muskat and Hudson (A., 1931, 1148) does not apply to *B* or to a large proportion of *C*. Consequently the hypothesis of Muskat and Northrup (A., 1930, 1553) is untenable. H. B.

Solid glycerides of sardine oil. K. KINO (J. Soc. Chem. Ind. Japan, 1932, 35, 247B—249B).—The following are isolated by fractional crystallisation, using COMe_2 , CHCl_3 -EtOH, and EtOH-Et₂O as solvents: α -*dimyricto*- β -*palmitin*, m.p. 59.8—60°; α -*β*-*dimyricto*- γ -*palmitin*, m.p. 53°; β -*myristo*- α -*γ*-*dipalmitin*, m.p. 58.5—59°; α -*myristo*- β -*γ*-*dipalmitin*, m.p. 55.5°, and a *myristodipalmitin*, m.p. 51°. Unsaturated fatty acid derivatives are also present.

H. A. P.

Autoxidation of the fatty acids. I. Oxygen uptake of elaidic, oleic, and stearic acids. G. W. ELLIS (Biochem. J., 1932, 26, 791—800).—The uptake by the first two acids of more than 20% of O in 24—48 hr. can be caused by a moderate rise of temp. (50—75°) in presence of Co oleate and by high dispersion of the acids. Stearic acid is liable to appreciable oxidation under these conditions at 75°. H₂O and CO₂ are evolved during the autoxidation. Their formation appears to be due to secondary reactions. In the case of elaidic acid under the most advantageous conditions for an initial oxidation process, 3 to 4 atoms of O are absorbed; 2 or 3 of these are retained by the non-volatile autoxidation product. S. S. Z.

Esters of orthoformic acid. P. P. T. SAH and T. S. MA (J. Amer. Chem. Soc., 1932, 54, 2964—2966).—The following trialkyl orthoformates are prepared from CHCl_3 , the appropriate alcohol, and Na in about 30% yield: Me, b.p. 103—105°; Et; *Pr*^β, b.p. 166—168°; *Pr*^α; Bu^β, b.p. 224—226°; Bu^α, b.p. 245—247°, and isoamyl, b.p. 265—267°. Numerous physical data are given.

C. J. W. (b)

Decomposition of valerolactone. R. W. THOMAS and H. A. SCHUETTE (J. Amer. Chem. Soc., 1932, 54, 3008—3009).—The partial decomp. of valerolactone as it approaches the b.p. is due (mainly) to the formation of a polymerisation product. C. J. W. (b)

Chemical examination of flowers of the mullen. L. SCHMID and E. KOTTER (Monatsh., 1932, 60, 305—316; cf. this vol., 501).—The pale yellow material separable from the α -croctinglucoside (*loc. cit.*) by means of C₆H₆ is identified as thapsiaic acid, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_{14}\cdot\text{CO}_2\text{H}$, containing a small amount of α -croctetin. Separation cannot be effected by crystallisation from C₆H₆, EtOAc, or MeOH, but isolation is readily accomplished by hydrogenation of the crude product (Pd or PtO₂) after oxidation with HNO₃ (*d* 1.38) at 100° or by treatment with 5% NaOH at 50°. The acid, m.p. 124°, is further identified by the Ag salt, anhydride, m.p. 70.5°, Et₂ ester, m.p. 37—38°, and Me₂ ester, m.p. 52°.

H. W.

Reactions and reagents for detecting organic compounds. I. E. EEGRIWE (Z. anal. Chem., 1932, 89, 121—125).—Tests for identifying tartaric,

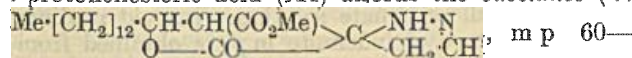
malic, glycollic, and oxalic acids in presence of other org. acids are described.

O. J. W.

Formation of ethyl triacetylacetate. F. SEIDEL (Ber., 1932, 65, [B], 1205—1211).—The action of AcCl on Et sodioacetoacetate in anhyd. Et₂O affords AcOH, Et acetoacetate (I), Et diacetylacetate (II), and a small amount of Et triacetylacetate (III), b.p. 97—105°/14 mm., identified by conversion into Et 4-acetyl-3 : 5-dimethylpyrazole-4-carboxylate (IV), m.p. 188° (readily isolated from accompanying products on account of its insolubility in H₂O). The Ac₃ derivative does not appear to be formed by the action of AcCl and K₂CO₃ on (II) at 100° or from the Na derivative of the latter and AcCl at room temp., whilst at 200° complete decomp. ensues. (IV) and NHPH·NH₂ afford colourless crystals, m.p. 210—215°, or straw-yellow needles, m.p. 248°. Titration with Br shows (II) to contain 86.0—86.5% of the enolic form, depending considerably on temp. and concn. The method is applicable to the examination of the mixture of (I), (II), and (III). The product of the action of Ac₂O on (I) at 170—180° is converted by N₂H₄ into 3 : 5-dimethylpyrazole; the existence of Et β -acetoxyisocrotonate appears therefore to be doubtful.

H. W.

Constitution of protolichestic acid and lichestic acid. M. ASANO and T. KANEMATSU (Ber., 1932, 65, [B], 1175—1178).—Lichestic acid (I), m.p. 123.5°, is obtained by extracting Iceland moss from Tateyama with Et₂O, shaking the extract with aq. K₂CO₃, acidifying the alkaline solution, and boiling the ppt. with Ac₂O. When heated with excess of 0.1N-KOH (I) yields lichesterylic acid (II), m.p. 83—84° (semicarbazone, m.p. 125°). With diazomethane, *l*-protolichestic acid (III) affords the substance (?)



61°, whereas (I) yields *Me l*-lichesterylate, m.p. 53—54°, [α]_D²⁰ —28.07° in CHCl₃. Oxidation of (I) by KMnO₄ gives myristic acid, m.p. 54°. The constitutions

$\frac{\text{CMe}\cdot\text{CO}}{\text{O}\cdots\text{CO}}>\text{O}$, $\text{COR}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, and $\text{CH}_2\cdot\text{C}\cdot\text{CO}\cdot\text{CHR}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (R=Me·[CH₂]₁₂) are assigned to (I), (II), and (III), respectively. H. W.

α -Hydroxy- β -methoxysuccinic acid, its complexes with copper, and their circular dichroism. J. GIUNTINI (Compt. rend., 1932, 195, 125—127).— α -Hydroxy- β -methoxysuccinic acid (cf. J.C.S., 1915, 107, 15) dissolves Cu(OH)₂ to a max. of 1.5Cu(OH)₂ per mol. Observation of [α] indicate compounds containing per mol. of acid 1 and 1.5CuO (cf. A., 1925, ii, 15), the latter forming intense bluish-green crystals. The impossibility of obtaining a complex similar to TCu₂ (T=tartaric acid residue) when one alcoholic function is blocked shows that in the attachment (to the asymmetric C atoms) of the Cu atoms of the group (TCu₂T)^{IV} in Cu-T complexes the alcohol functions play an essential part.

C. A. S.

Alginate acid : its mode of occurrence and its constitution. T. DILLON and (Miss) A. McGUINNESS (Sci. Proc. Roy. Dublin Soc., 1932, 20, 129—133).—Fresh *Laminaria* fronds do not evolve CO₂ with aq. Na₂CO₃ and do not, therefore, contain free alginic acid (I). The ash content (Ca and Fe) of impure (I)

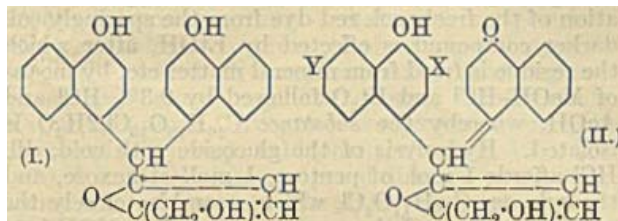
their max. efficiency. The gradual improvement is attributed to the removal as $\text{Fe}(\text{CO})_5$ of Fe present originally in the pumice. Ageing of the contact, caused by deposition of C, can be overcome by ignition in air. In all cases the optimal temp. of reaction is $670\text{--}680^\circ$. Further increase in the yield of (I) is rendered difficult by the accentuated decomp. induced by higher concn. of (I). This can be repressed only by use of a large excess of COMe_2 , which protects the (I) from further decomp. A further source of loss lies in the tendency of (I) to polymerise. The re-condensed COMe_2 invariably contains marked amounts of polymerisate, which remains as a resin on evaporation. The yields of (I) calc. on the CH_4 evolved ($\text{COMe}_2 = \text{CH}_2\cdot\text{CO} + \text{CH}_4$) are approx. 10% higher than those calc. by titration with alkali hydroxide. The difference is attributed to the formation of polymericides. H. W.

ψ -Halogenes. XX. Triacetyl- and diacetylmethane. L. BIRCKENBACH, K. KELLERMANN, and W. STEIN (Ber., 1932, 65, [B], 1071—1079).—Triacetylmethane, b.p. $104^\circ/19$ mm. (*K*, decomp. about 180° ; *Cs*, decomp. about 170° ; *Ag* salts), is prepared by the action of AcCl on Na acetylacetonate in Et_2O or of AcCl and AlCl_3 on acetylacetone in CS_2 . Hydrolysis with H_2O and NaOH follows the respective courses: $\text{CHAc}_3 + \text{H}_2\text{O} = \text{AcOH} + \text{CH}_2\text{Ac}_2$ and $\text{CHAc}_3 + 2\text{NaOH} = 2\text{NaOAc} + \text{COMe}_2$. The *Ag* salt is transformed by the requisite halogen in Et_2O at -10° into triacetylmethyl chloride, m.p. $20\cdot3^\circ$, bromide, m.p. $47\cdot9^\circ$, and iodide, m.p. $44\cdot9^\circ$. Hydrolysis with H_2O leads to CHAc_3 and hypohalogenous acid and thence to trihalogenomethane. With NaOH , KI , and KCN reaction occurs: $3\text{CAc}_3\text{Hal} + 7\text{NaOH} = 7\text{NaOAc} + 2\text{COMe}_2 + \text{CHHal}_3$; $\text{CAc}_3\text{Hal} + 2\text{KI} = \text{KCAc}_3 + \text{KHal} + \text{I}_2$; $\text{CAc}_3\text{Hal} + \text{KCN} = \text{KCAc}_3 + \text{CNHal}$. Electrolysis of CHAc_3 and its salts affords oxidising anodic solutions, indicating the primary production of ψ -halogenes. The optical behaviour of CHAc_3 and its salts establishes the existence of ketonic and enolic forms; the equilibrium mixture contains only two components. Nef's observation of the existence of a non-acidic component in the product of the action of AcCl on CHNaAc_2 (see above) is due to the necessity of a large excess of KOH for the dissolution of CHAc_3 . The *Ag* salt of CH_2Ac_2 yields diacetylmethyl chloride, b.p. $152^\circ/708$ mm. bromide, m.p. $23\text{--}24^\circ$, and iodide, m.p. 31° . They are hydrolysed by H_2O and NaOH respectively to CH_2Ac_2 and HOHal , whence CHHal_3 and COMe_2 , NaOAc , and CHHal_3 . KI and KCN react with elimination of I and production of CNHal , respectively. SO_2 reduces quantitatively to CH_2Ac_2 and Hal' . With $\text{Cu}(\text{OAc})_2$ in C_6H_6 or AcOH the salts $\text{Cu}(\text{ClAc}_2)_2$, $\text{Cu}(\text{BrAc}_2)_2$, and $\text{Cu}(\text{IAc}_2)_2$, decomp. above 180° , are produced. H. W.

Precipitation of sugars and polyhydroxy-compounds by metallic hydroxides in alkaline solution. I. General character of the precipitation. P. FLEURY and J. COURTOIS (J. Pharm. Chim., 1932, [viii], 16, 97—109).—Considerable pptn. occurs when various heavy metals, best Fe, are used in 10% solution in presence of NaOH (I), $\text{Ba}(\text{OH})_2$, or aq. NH_3 [best (I)]. Acetates are more efficient than nitrates. Sometimes the ppt. redissolves in

excess of alkali. Methods of analysis and decomp. of the ppt. are described. R. S. C.

Molisch reaction. II. H. BREDERECK (Ber., 1932, 65, [B], 1110—1113; cf. this vol., 145).— α -Naphthol and 5-hydroxymethylfurfuraldehyde in presence of 10% NaOH at 100° afford *di-1-hydroxy-4-naphthyl-5-hydroxymethyl-2-furylmethane* (I), $+\text{Et}_2\text{O}$, m.p. 148° after softening at 136° , $+\text{H}_2\text{O}$, m.p. about 178° after slow decomp. above 135° (*Ac* derivative, m.p. 180° after softening at $162\text{--}163^\circ$). With conc.



H_2SO_4 at 17° , (I) affords the monosulphonic acid (II; $\text{X}=\text{SO}_3\text{H}$, $\text{Y}=\text{H}$), whereas at 100° the disulphonic acid (II; $\text{X}=\text{Y}=\text{SO}_3\text{H}$) is obtained. In the Molisch reaction the pentose or hexose is converted into furfuraldehyde or 5-hydroxymethylfurfuraldehyde, which condenses with α -naphthol to the triarylmethane derivatives. This is oxidised and then sulphonated by the H_2SO_4 to a degree dependent on the temp. attained at the zone of contact of acid and reagent, thus giving the observed dye. H. W.

Fenton's reaction. IV. A. T. KÜCHLIN.—See this vol., 917.

Optical crystallographic description of the phenylosazones and other derivatives of sugars. V. H. MORRIS (J. Amer. Chem. Soc., 1932, 54, 2843—2846).—The optical properties of the phenylosazones of glucose, galactose, arabinose, xylose, and maltose, and of K H saccharate, fructosephenylmethylosazone, mannosephenylhydrazone, mucic acid, arabinosedi-phenylhydrazone, and CdBr_2 xylonate have been determined with the petrographic microscope by the immersion method. Vals. of n_a , n_b , and n_γ , the optical character, optic axial angle, sign of elongation, optical orientation, and crystal habit are given. The above phenylosazones can be identified by immersion in liquids with definite refractive indices. F. W. Z. (b)

Synthesis of *d*-talose from *d*-galactose. T. KOMADA (Bull. Chem. Soc. Japan, 1932, 7, 211—216).—Acetobromogalactose and Zn dust in cold 50% AcOH give galactal triacetate, b. p. $138\text{--}140^\circ/0\cdot2\text{--}0\cdot3$ mm. [absorbs 1 mol. of Br or H_2 (in abs. Et_2O in presence of Pt-black)], hydrolysed by Zemlen's method (not by $\text{NH}_3\text{--MeOH}$) to impure galactal, m.p. $95\text{--}100^\circ$ (decomp.). This with BzO_2H in CHCl_3 at 0° gives *d*-galactose and *d*-talose, separated by crystallising the phenylmethylhydrazones from MeOH and regeneration of the sugars by PhCHO . R. S. C.

Oxidation products of fructose in ammoniacal solution by methylene-blue and atmospheric oxygen at room temperatures. J. PARROD (Compt. rend., 1932, 195, 285—286).—An aq. solution containing fructose (1 mol.), methylene-blue free from Zn (0.4 mol.), and NH_3 (16 mols. 20%) with air at room temp. during 1 month affords 4-methoxy-

glyoxaline, *d*-4-arabinotetrabutoxyglyoxaline, and the amide, m. p. 214°, of glyoxaline-4-carboxylic acid. Absence of methylene-blue affects the reaction mainly by altering the proportions of the products of oxidation.

J. L. D.

Dye of *Papaver rhæas*. II. L. SCHMID and R. HUBER (Monatsh., 1932, 60, 285—294).—The blossoms are extracted with AcOH and the dyes are pptd. with Et₂O-HCl. EtOH is added to the solid dissolved in H₂O, and the filtrate treated with Et₂O. Separation of the freely-sol. red dye from the sparingly-sol. darker compound is effected by EtOH, after which the residue is freed from mineral matter etc. by means of MeOH-HCl and Et₂O followed by 0.3% HCl and AcOH, whereby the substance C₂₆H₂₉O₁₃Cl₂H₂O is isolated. Hydrolysis of the glucoside with cold, dil. HCl affords 1 mol. of pentose, 1 mol. of hexose, and the aglucone C₁₅H₁₁O₄Cl, which resembles closely the anthocyanidins. It is converted by molten KOH into protocathechuic acid; the phenolic component could not be identified.

H. W.

Inulin and inulinase. XII. H. PRINGSHEIM and P. OHLMEYER (Ber., 1932, 65, [B], 1242—1248).—The results described previously (A., 1931, 941) are vitiated by the presence in *A. niger* of mannitol which does not pass into solution until the enzyme is extracted with the buffer solution (*p*_H 3.8) and thus appears among the products of the hydrolysis of inulin. The "difructose anhydride acetate" is identified as mannitol acetate. Adsorption of inulinase is best effected with Willstätter's Al(OH)₃ B and elution with phosphate buffer (*p*_H 6.8), or preferably with aq. NH₃. The purified enzyme is much more efficient than the crude extract in the hydrolysis of inulin. The inulinase unit is defined as that amount of enzyme which hydrolyses 150 mg. of inulin to the extent of 30% in 1% solution during 3 hr. at 37°. With the purified enzyme inulin is hydrolysed to the extent of 95%. The difference between the results of titration with Fehling's solution and hypiodite indicates the presence of a small amount of glucose, usually about 1.5% of the inulin. Removal of 83% of the fructose in the cryst. form from the hydrolysate and examination of the residue confirms this val. The presence of at least 3% of glucose, as found after acid hydrolysis, could not be demonstrated. Whilst it is possible that glucose is present in the non-hydrolysed inulin residue, it is probable that enzymic hydrolysis does not follow the same course as acid hydrolysis.

H. W.

Action of sodium triphenylmethyl on inulin in liquid ammonia. L. SCHMID and R. FALKE (Monatsh., 1932, 60, 295—304).—*p*-Benzhydryltetraphenylmethane, m.p. 226—227° (identified also as the carbinol, OH·CPh₂·C₆H₄·CPh₃, m.p. 219—220°), is obtained by the action of NaCPh₃ on inulin in liquid NH₃. Although the carbohydrate is quantitatively recovered unchanged, the hydrocarbon is not obtained in good yield in its absence. It cannot be prepared from CPh₃ or NaCPh₃ in liquid NH₃ and inulin could not be replaced by sol. starch.

H. W.

Glycogen. II. Methylation and acetylation. G. K. HUGHES, A. K. MACBETH, and F. L. WINZOR (J.C.S., 1932, 2026—2031; cf. A., 1924, i, 1046).—

The results of Haworth *et al.* (A., 1930, 72) on the methylation of glycogen triacetate are confirmed. Six treatments of glycogen with Me₂SO₄ and aq. NaOH give a product (OMe 36%), which on repeated methylation (as before) affords a product (OMe 40.8%), hydrolysed by 1.5% MeOH-HCl to (mainly) 2 : 3 : 6-trimethylmethylglucoside and a dimethylmethylglucoside. Repeated methylation in presence of COMe₂ gives, however, a product containing 44% OMe, but methylation proceeds much less readily than with glycogen triacetate. Glycogen and methylglycogen (OMe about 36%) could not be depolymerised in glycerol at 190° and 200—210°, respectively.

Glycogen is acetylated readily by Ac₂O and conc. H₂SO₄ at room temp., but "treated" glycogen (pptd. from a boiling aq. solution by EtOH) is similarly acetylated only with difficulty. On the other hand, "treated" starches (potato, rice, wheat, maize) are acetylated more readily than the original materials (which also react at different rates). In all the experiments, depolymerised EtOH-sol. triacetates, m.p. 150—155° (hydrolysed by MeOH-HCl to α- and β-methylglucosides), are produced.

H. B.

Polymorphism of substances of high mol. wt. IV. Attempted explanation of the isomerism of polysaccharides (cellulose, starch). J. R. KATZ and A. WEIDINGER (Rec. trav. chim., 1932, 51, 842—846).—The different forms of starch and cellulose are definite chemical isomerides with different constitutional formulæ. The difference probably lies in the spatial arrangement of the atoms in the C₆H₁₀O₅ units.

D. R. D.

Chain length of natural celluloses and of acetylxylan from deciduous trees. E. SCHMIDT, K. MEINEL, W. JANDEBEUR, and W. SIMSON [with K. BETZ, R. SCHNEGG, and M. HECKER] (Cellulosechem., 1932, 13, 129—139).—Cellulose from different sources contains 0.28% CO₂H independently of whether it has been isolated by treatment with ClO₂ and dil. NaOH or whether, as with cotton cellulose, this treatment has been unnecessary. The scission products of the skeleton substance of wood consist of 78.4% of cellulose (I) and 21.6% of de-acetylated xylan (II), corresponding with the ratio 3C₆H₁₀O₅ to 1C₅H₈O₄. The CO₂H content of the mixture is 0.66%, of which 0.22% is in (I) and 0.44% in (II). The calc. CO₂H content of the latter is thus 2.05%, and that found after separating it from (I) with 5% NaOH is 1.86%. Conductometric titration also indicates 0.28% CO₂H in (I). It is concluded that the chains of natural (I) and of acetylxylan (III) contain 96 and 16 units, respectively, or multiples of these. It is probable that in wood (I) and (III) are combined to form an ester and the proportion 3C₆H₁₀O₅ to 1C₅H₈O₄ suggests that the actual chain length of (III) is 32 units, containing 2CO₂H.

A. G.

Wood cellulose. I. Methylation of the α-cellulose. III. The depolymerised celluloses of wood and cotton. III. "Resistant portions." D. J. BELL (Biochem. J., 1932, 26, 590—597, 598—608, 609—614).—I. The max. OMe contents attained in 5 specimens of wood celluloses were 36.3—39.1% against 44.3% reached in a specimen of standard cotton cellulose treated under the same conditions.

Both cotton and wood celluloses when fully methylated are partly sol. in CHCl_3 ; $[\alpha]_D$ in CHCl_3 cotton -10° , Thiriena pulp (wood) $+2.5^\circ$. The methylated wood celluloses each contained a fraction incompletely methylated and completely resistant to hydrolysis. These isolated resistant fractions of about 28% OMe content could not be methylated above 32% OMe. The non-resistant portions are constructed wholly of glucose residues having free OH groups in positions 2, 3, and 6.

II. Triacetates of different wood α -celluloses prepared under standard conditions, showed sp. rotations varying from -19° to 0° . Simultaneous deacetylation and methylation led to the formation of fully methylated depolymerised cellulose (OMe 39.2%), $[\alpha]_D -2.3^\circ$ in CHCl_3 . The empirical composition was the same as that of the corresponding intact cellulose. Cleavage of the above methoxide yielded 2:3:6-trimethylmethylglucoside and a resistant portion with 29.9% OMe. The cleavage products of the depolymerised and methylated cellulose, but not of the intact cellulose, contained a small amount of 2:3:4:6-tetramethylglucose. Acetylation also effected depolymerisation, the trimethyl-depolymerised cellulose showing $[\alpha]_D -1.2^\circ$ in CHCl_3 . Cleavage of this material was complete and no tetramethylglucose was found. Cleavage of depolymerised cotton methylated to the extent of 38.6% OMe was complete, no resistance being encountered; a small amount of tetramethylglucose was found in this case. There is definite relationship between optical activity in CHCl_3 of wood cellulose acetates and the proportion of resistant material from corresponding methylated intact celluloses.

III. The fractions of wood celluloses cannot be methylated beyond a stage at which their composition corresponds with that of a dimethylcellulose. Their Ac derivatives seem to be identical. The resistant material from the cleavage products of fully methylated depolymerised wood cellulose possesses properties very similar to those of the resistant portions of the corresponding intact methylated cellulose. Cotton cellulose methylated to 30% of OMe yields an Ac derivative with properties which are not common to the acetates of the "resistant portions." The cleavage products of the Ac derivatives of the latter are a mixture of 2:3:6-trimethylglucoside, dimethylmethylglucosides, and monomethylmethylglucosides. In the case of Thiriena-pulp cellulose the mixture of dimethylmethylglucosides consists mainly of the 2:6- and 3:6- with a little of the 2:3-dimethylmethylglucosides. There are indications of the presence of 6-monomethylmethylglucoside in the residual material. S. S. Z.

Reaction between diethylamine and ethylene oxide. W. H. HORNE and R. L. SHRINER (J. Amer. Chem. Soc., 1932, 54, 2925—2930).—Dry NH_4Et_2 does not react with $(\text{CH}_2)_2\text{O}$. β -Diethylaminoethyl alcohol (I), b.p. $42-44^\circ/8$ mm., $163^\circ/760$ mm. [*p*-nitrophenylurethane, m.p. $59-60^\circ$ (corr.); hydrochloride, decomp. $200-210^\circ$], results in 75% yield when $(\text{CH}_2)_2\text{O}$ is passed into $\text{MeOH}-\text{NH}_4\text{Et}_2$ at $45-60^\circ$. The high-boiling fractions from the prep. of (I) contain β -(β -diethylaminoethoxy)ethyl alcohol, b.p. $92-95^\circ/7$ mm. [*p*-nitrophenylurethane hydrochloride, m.p. $152-153^\circ$

(corr.)] [also formed from $(\text{CH}_2)_2\text{O}$ and (I) in MeOH], β -(diethylaminoethoxyethoxy)ethyl alcohol, b.p. $123-128^\circ/7$ mm. [*p*-nitrobenzoate, m.p. $121.5-122^\circ$ (corr.)], and the diethylamino-alcohols, $\text{NEt}_2 \cdot [\text{CH}_2 \cdot \text{CH}_2\text{O}]_n \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, where $n=3$ and 4, b.p. $164-172^\circ/7$ mm. and b.p. $190-200^\circ/7$ mm., respectively. C. J. W. (b)

Syntheses of glucopeptides of d -glucosamine (N -glycyl- and N - d -alanyl- d -glucosamine). M. BERGMANN and L. ZERVAS (Ber., 1932, 65, [B], 1201—1205).—Glucosamine tetra-acetate and benzylcarbonatoglycyl chloride in presence of CHCl_3 and pyridine at -10° afford N -benzylcarbonatoglycyl- β - d -glucosamine tetra-acetate, m.p. 165° (corr.), hydrolysed by NaOMe in anhyd. CHCl_3 to N -benzylcarbonatoglycyl- d -glucosamine (I), m.p. 181° (corr.), decomp. 193° , $[\alpha]_D^{20} +40.0^\circ$ in MeOH (also prepared directly from glucosamine hydrochloride). Catalytic hydrogenation of (I) in presence of Pd-black and MeOH gives N -glycyl- d -glucosamine hydrochloride, darkening above 170° , $[\alpha]_D^{20} +29.7^\circ$ in H_2O (equilibrium val.). N -Benzylcarbonato- d -alanyl- β - d -glucosamine tetra-acetate, m.p. 172° (corr.), similarly yields N -benzylcarbonato- d -alanyl- d -glucosamine, m.p. 232° (corr.), and d -alanyl- d -glucosamine hydrochloride, decomp. about 155° after softening at 150° , $[\alpha]_D^{20} +40.9^\circ$ in H_2O (equilibrium val.). H. W.

Kinetics of the degradation of polymeric-homologous chains. Rate of hydrolysis of derivatives of amino-acids. W. KUHN, C. C. MOLSTER, and K. FREUDENBERG (Ber., 1932, 65, [B], 1179—1183).—Measurement of the rate of hydrolysis of glycine anhydride (I), glycylglycine, di- and tri-glycylglycine by N - NaOH at 20° and by $0.1N$ - NaOH at 20° and 34° in the case of (I) are recorded. The rate of alkaline hydrolysis of the peptides of glycine increases with increasing no. of members. The tetrapeptide suffers fission mainly at the central linking. H. W.

General method for the synthesis of peptides. M. BERGMANN and L. ZERVAS [with, in part, O. F. LEINERT] (Ber., 1932, 65, [B], 1192—1201).—The NH_2 group of the NH_2 -acid is protected by the introduction of the $\text{CH}_2\text{Ph} \cdot \text{O} \cdot \text{CO} \cdot$ group, which can be removed, without rupture of the peptide linking, by catalytic hydrogenation in open vessels:

$\text{CH}_2\text{Ph} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHR} \cdot \text{CO}_2\text{H} \rightarrow \text{PhMe} + \text{CO}_2\text{H} \cdot \text{NH} \cdot \text{CHR} \cdot \text{CO}_2\text{H} \rightarrow \text{CO}_2 + \text{NH}_2 \cdot \text{CHR} \cdot \text{CO}_2\text{H}$. Benzylloxycarbonyl chloride (I), which decomposes when distilled into CH_2PhCl and CO_2 , is obtained in sufficient purity by addition of $\text{CH}_2\text{Ph} \cdot \text{OH}$ to COCl_2 in PhMe at 0° , removal of excess of COCl_2 by dry N_2 or CO_2 and of solvent below 60° . Glycine, (I), and $4N$ - NaOH afford N -benzylcarbonatoglycine, m.p. 120° (corr.), transformed by PCl_5 in anhyd. Et_2O into the corresponding chloride, m.p. 43° (decomp.). The following are analogously prepared: N -benzylcarbonato- d -l-alanine, m.p. $114-115^\circ$ (corr.); d -alanine, m.p. 84° , $[\alpha]_D^{20} -14.3^\circ$ in AcOH (corresponding, non-cryst. chloride); d -l-serine, m.p. 125° (corr.); NN - d -benzylcarbonato- l -cystine, m.p. 123° (corr.), $[\alpha]_D^{20} -91.7^\circ$ in AcOH , whence the corresponding chloride, m.p. $67-68^\circ$, and d -benzylcarbonato- l -cystylidiglycine Et ester, m.p. 166° (corr.); N -benzylcarbonato- d -glutamic acid, m.p. 120° , $[\alpha]_D^{20} -7.1^\circ$ in AcOH (NaOH replaced

by MgO in prep.), whence by means of Ac_2O at 100° , the corresponding *anhydride*, m.p. 94° , $[\alpha]_D^{25} -44.1^\circ$ in AcOH , which, in anhyd. CHCl_3 with NH_3 in Et_2O , affords *N*-benzylcarbonato-*d*-isoglutamine, m.p. 175° (corr.), transformed (H_2 , spongy Pd, MeOH) into *d*-isoglutamine, $[\alpha]_D^{25} +21.1^\circ$ in EtOH. *N*-Benzylcarbonato-*d*-glutamine has m.p. 137° (corr.). *N*-Benzylcarbonato-*l*-aspartic acid, m.p. 116° , $[\alpha]_D^{25} +9.6^\circ$ in AcOH , gives the corresponding *anhydride*, m.p. 84° , $[\alpha]_D^{25} -39.8^\circ$ in AcOH , and thence *N*-benzylcarbonato-*l*-isoasparagine, m.p. 164° (corr.), $[\alpha]_D^{25} +6.9^\circ$ in AcOH , and *l*-isoasparagine ($+1\text{H}_2\text{O}$), $[\alpha]_D^{25} +15.5^\circ$ in $0.1N\text{-HCl}$. *N*-Benzylcarbonato-*l*-asparagine, m.p. 165° (corr.), $[\alpha]_D^{25} +7.6^\circ$ in AcOH , and its *Me* ester, m.p. 150° (corr.), $[\alpha]_D^{25} -2.0^\circ$ in AcOH , are described. *N*-Benzylcarbonato-*dl*-phenylalanine has m.p. 103° . *N*-Benzylcarbonato-*l*-tyrosine, m.p. 101° , $[\alpha]_D^{25} +11.1^\circ$ in AcOH (*Et* ester, m.p. 78° , $[\alpha]_D^{25} -4.7^\circ$ in EtOH), *N*-*d*-arginine, m.p. 175° (corr.), $[\alpha]_D^{25} -9.2^\circ$ in $0.5N\text{-HCl}$, and *l*-histidine, m.p. 209° (corr.), are described. Glycine anhydride, (I), and $2N\text{-NaOH}$ give benzylcarbonatoglycylglycine, m.p. 178° . Benzylcarbonato-*d*-glutamic anhydride and *Et*, *d*-glutamate in anhyd. CHCl_3 afford *Et*, *N*-benzylcarbonato-*d*-glutamyl-*d*-glutamate, m.p. 137° (corr.), hydrolysed to the free acid, m.p. about 176° (corr.) after softening at 145° , whence *d*-glutamyl-*d*-glutamic acid, m.p. 205° (corr.), $[\alpha]_D^{25} +19.9^\circ$ (as hydrochloride in H_2O), which is readily hydrolysed by pancreas extract. *l*-Tyrosine *Et* ester hydrochloride and benzylcarbonato-*l*-aspartic anhydride in pyridine at room temp. give benzylcarbonato-*l*-asparagyl-*l*-tyrosine *Et* ester, m.p. 203° (corr.), whence the free acid ($+1\text{H}_2\text{O}$), m.p. 110° , and *l*-asparagyl-*l*-tyrosine, decomp. about 230° , $[\alpha]_D^{25} +60.1^\circ$ (as hydrochloride in H_2O). H. W.

Syntheses of derivatives of amino-acids. K. FREUDENBERG, H. EICHEL, and F. LEUTERT (Ber., 1932, 65, [B], 1183—1191).—Aminoacetonitrile is converted by HCl-EtOH into *Et* β -amino- α -iminoethyl ether hydrochloride; the free base, b.p. $42\text{--}43^\circ/13\text{ mm.}$, is converted by $\text{NH}_3\text{-EtOH}$ into aminoacetamide dihydrochloride. Similarly, benzamidoacetonitrile affords the non-cryst. *Et* β -benzamido- α -iminoethyl ether (hydrochloride, decomp. about 134° when rapidly heated) and benzamidoacetamidine hydrochloride, m.p. 184° . 2-Cyanothiophen and HCl-EtOH give the imino-ether $\text{C}_4\text{H}_3\text{S}\cdot\text{C}(\text{NH})\cdot\text{OEt}\cdot\text{HCl}$, decomp. $123\text{--}126^\circ$ according to the rate of heating, and thence the amidine, $\text{C}_4\text{H}_3\text{S}\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{HCl}$, m.p. 176° (slight decomp.). Thiophenamidoacetonitrile, m.p. $129\text{--}130^\circ$, from 2-thiophenoyl chloride, aminocetonitrile sulphate, and dil. NaOH in presence of C_6H_6 , yields successively *Et* β -2-thiophenamido- α -iminoethyl ether hydrochloride, decomp. $117\text{--}120^\circ$, and thiophenamidoacetamidine hydrochloride, decomp. about 275° . Chloroacetamidacetonitrile (I), m.p. $90\text{--}91^\circ$, affords *Et* β -chloroacetamido- α -iminoethyl ether hydrochloride, decomp. 122° . (I) and NaN_3 in boiling aq. EtOH give azidoacetamidacetonitrile, b.p. $148\text{--}153^\circ/0.3\text{ mm.}$; azidoacetonitrile has b.p. $53^\circ/12\text{ mm.}$ *p*-Toluenesulphonamidoacetonitrile, m.p. 136° , is converted through the imino-ether hydrochloride into *p*-toluenesulphonamidoacetamidine hydrochloride, decomp. about 185° . α -Azidopropionyl chloride, glycine, and *N*-

NaOH yield α -azidopropionylglycine, reduced by Al-Hg in aq. NH_3 to *dl*-alanylglycine, m.p. 224° (2-naphthalenesulphonyl derivative, m.p. $141\text{--}142^\circ$). *Ph* α -azidopropionate, b.p. $76^\circ/0.2\text{ mm.}$, from the chloride and PhOH in pyridine, is reduced by Al-Hg in moist Et_2O to *Ph* α -aminopropionate hydrochloride, m.p. 131° . $\text{CH}_3\text{N}_3\cdot\text{COCl}$ and *Et* lactate in presence of CHCl_3 and pyridine yield *Et* α -azidoacetoxypionate, b.p. $79^\circ/0.2\text{ mm.}$ *p*-Azidoacetoxypionate, m.p. 160° after softening at 157° , azidoacetoxysalicylic acid (II), m.p. 104° , and α -azidoacetoxypionic acid, (III), m.p. 52° , are prepared from the requisite acid and $\text{CH}_3\text{N}_3\cdot\text{COCl}$ in CHCl_3 -pyridine. Reduction of (II) with Al yields non-cryst. products, whereas hydrogenation (spongy Pt in MeOH) yields a compound, m.p. $164\text{--}166^\circ$, which is not the expected glycylsalicylic acid. (III) and H_2 in presence of H_2O and spongy Pt give α -aminoacetoxypionic acid, m.p. 161° (trihydrate, m.p. 148°). Azidoacetic anhydride, b.p. $110^\circ/0.2\text{ mm.}$, is obtained from $\text{CH}_3\text{N}_3\cdot\text{CO}_2\text{Ag}$ and $\text{CH}_3\text{N}_3\cdot\text{COCl}$ in anhyd. EtOH. Glycylglycine is prepared from glycine anhydride and 10% NH_3 at 100° . H. W.

Synthesis of α -amino- β -dihydroxy-*n*-butyric acid. H. O. L. FISCHER and L. FELDLMANN (Ber., 1932, 65, [B], 1211—1214).—Unimol. glyceraldehyde in anhyd. MeOH is treated successively with HCN and NH_3 . The aminonitrile is hydrolysed by conc. HCl . α -Amino- β -dihydroxy-*n*-butyric acid, decomp. $215\text{--}216^\circ$ (corr.) after softening at about 180° , is isolated as the *Cu* salt. α -Phenylcarbamido- β -dihydroxy-*n*-butyric acid, m.p. 163° (corr., decomp.) after softening, and α -2-naphthalenesulphonamido- β -dihydroxy-*n*-butyrolactone, m.p. 177° (corr.), are described. H. W.

Action of sulphite on cystine. H. T. CLARKE (J. Biol. Chem., 1932, 97, 235—248).—Cystine in NaOH with Na_2SO_3 gives cysteine and *S*-cysteinylsulphonic acid, isolated as the *Na* salt after removal of cysteine with Cu_2SO_4 as the substance $6\text{C}_3\text{H}_5\text{O}_2\text{NSCu}_2\cdot 2\text{Cu}_2\text{SO}_4$. The NH_4 salt is obtained by evaporation of cystine in aq. NH_3 with $(\text{NH}_4)_2\text{SO}_3$. Alkaline cystine gives a little benzylcysteine by prolonged action of CH_3PhCl , but gives $60\text{--}80\%$ in the presence of Na_2SO_3 after 5 hr. The above salts give H_2SO_4 and cysteine with hot HCl , Na_2SO_3 with NaOH , BaS_2O_3 by prolonged action of $\text{Ba}(\text{OH})_2$, and H_2SO_4 and cysteic acid with Br . The rotation of alkaline cystine solution is partly stabilised by excess of Na_2SO_3 , and depends on the concn. of NaOH and Na_2SO_3 owing to the reversibility of the above reaction. The variations of colour intensity with time are recorded for some colour reactions with cystine (this vol., 206). A. A. L.

Preparation and properties of the normal barium salt of *l*-cystine. C. J. B. THOR and R. A. GORTNER (J. Amer. Chem. Soc., 1932, 54, 3009—3011).—The *Ba* salt, darkens at about 250° , $[\alpha]_D^{25} -61.9^\circ$, of *l*-cystine is prepared in 96.5% yield from $\text{Ba}(\text{OH})_2$ and cystine in H_2O at 0° and (after filtering) subsequent addition of 95% EtOH. The salt is partly decomposed by boiling with H_2O . C. J. W. (b)

Compounds of carbamide and urethane with acids and phenols. N. A. PUSHIN and I. I. RIKOVSKI (Monatsh., 1932, 60, 438—448).—Thermal

analysis shows that carbamide (I) yields the following compounds: $\text{CO}(\text{NH}_2)_2 \cdot 2\text{AcOH}$, m.p. 41° ; $\text{CO}(\text{NH}_2)_2 \cdot 2\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$, m.p. 37° ; $\text{CO}(\text{NH}_2)_2 \cdot \text{CHCl}_2 \cdot \text{CO}_2\text{H}$, m.p. 63.5° ; $\text{CO}(\text{NH}_2)_2 \cdot o\text{-C}_6\text{H}_4(\text{OH})_2$, $\text{CO}(\text{NH}_2)_2 \cdot \text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$, m.p. 40° (decomp.); $\text{CO}(\text{NH}_2)_2 \cdot 2\text{CHCl}_2 \cdot \text{CO}_2\text{H}$, m.p. 47.5° (decomp.). With 2:4-dinitrophenol (I) does not give a compound but forms solid solutions with a max. concn. of 60 mol.-% (I). Towards strong acids, (I) functions as a monacid base, but as a diacid base towards weak acids; with acids of medium strength, both types of compound are possible. Urethane does not combine with AcOH , but yields compounds of the unimol. type with mono-, di-, and tri-chloroacetic acid. In the series AcOH , mono-, di-, and tri-chloroacetic acid the stability of the equimol. compound with (I) or urethane increases with the no. of Cl atoms in the acid mol.

H. W.

Iodometric titration of semicarbazide. P. D. BARTLETT (J. Amer. Chem. Soc., 1932, 54, 2853—2858).—Semicarbazide (1 mol.) reacts quantitatively with 4 atoms of I in dil. aq. solution. The reaction is bimol.; its rate is proportional to the non-ionised fraction of the semicarbazide up to p_{H} 5, but is considerably accelerated at p_{H} 7. At p_{H} 7 reaction is rapid enough to provide a suitable titration method. The basicity (pK_{A}) of semicarbazide, determined potentiometrically, is 3.66 at 24° and 4.40 at 0° .

C. J. W. (b)

Transformations of cyanogen. Polymerisation and action of potassium carbonate and sodamide. A. PERRET and A. KRAWCZYNSKI.—See this vol., 820.

Asymmetric synthesis with the aid of catalysts. II. G. BREDIG and M. MINAEFF.—See this vol., 967.

Behaviour of aliphatic diazo-compounds with derivatives of metals. I. Mercuri-organic derivatives and mercuric salts with diazomethane. Reaction of mercuric chloride with diphenyldiazomethane. L. HELLERMAN and M. D. NEWMAN (J. Amer. Chem. Soc., 1932, 54, 2859—2869).— HgCl_2 and a mol. equiv. of diazomethane in Et_2O give N_2 and a quant. yield of *Hg chloromethyl chloride*, $\text{CH}_2\text{Cl} \cdot \text{HgCl}$ (I), m.p. 131° (corr.), decomposed by conc. NaOH with the formation of Hg ; with 2 equivs. of diazomethane there results *Hg di(chloromethyl)*, $\text{Hg}(\text{CH}_2\text{Cl})_2$, (II), m.p. $37\text{--}40^\circ$, converted by $\text{EtOH} \cdot \text{HgCl}_2$ into (I) and HgCl , and by EtOH -conc. HCl into (I) and MeCl . $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{HgCl}$ and Et_2O -diazomethane give $\text{Hg}(\text{C}_6\text{H}_4\text{Me})_2$ and (II), whilst HgPhCl affords HgPh_2 ; in the last case, an intermediate liquid product ($\text{HgPh} \cdot \text{CH}_2\text{Cl}$?), converted by $\text{EtOH} \cdot \text{HCl}$ into (I), is produced. $\text{CH}_2\text{Ph} \cdot \text{HgCl}$ gives *Hg benzyl chloromethyl*, liquid, converted by $\text{EtOH} \cdot \text{HCl}$ into PhMe and (I), and by HgCl_2 into HgCl , $\text{CH}_2\text{Ph} \cdot \text{HgCl}$, and (I). HgI_2 and 1 or 2 mol. equivs. of diazomethane give a small quantity of (probably) *Hg di(iodomethyl)*, m.p. $82\text{--}84^\circ$. Diazomethane does not react with $\text{Hg}(\text{CN})_2$, HgPh_2 , or Hg p -ditolyl. Diphenyldiazomethane and HgCl_2 in Et_2O give (probably) the amorphous *chlorodiphenylmethylmercuric chloride*, $\text{CPh}_2\text{Cl} \cdot \text{HgCl}$, which decomposes in moist air into COPh_2 , HCl , and HgCl , and in moist Et_2O into HgCl and $(\text{CPh}_2\text{Cl})_2$. Aliphatic diazo-compounds

react also with other types of Hg compounds and with certain salts and org. derivatives of metals other than Hg . An electronic interpretation of the reaction is given. Minute quantities of (I) and (II) cause a dermatitis of the skin; (II) is a powerful vesicant.

C. J. W. (b)

Synthesis of derivatives of amino-acids containing phosphorus. E. AUBEL and W. S. REICH (Compt. rend., 1932, 195, 183—185).— $\text{Et } \alpha$ -aminopropionate and Br in abs. EtOH at low temp. give impure *Et N-bromoaminopropionate* (I), decomp. 200° . Pb H phosphite and EtI at 400° give *Et₂ H phosphite*, which with Na in Et_2O gives H , and *Et₂ Na phosphite* (II). (I) and (II) form *alanine-N-phosphorous acid*, $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{NH} \cdot \text{PO}(\text{OH})_2$, purified by the *Ba* salt. Et glutamate gives similarly the *Ba* salt of the *-phosphorous acid*.

R. S. C.

Esters of arsenious acid. P. PASCAL and A. DUPIRE (Compt. rend., 1932, 195, 14—16).—The following are prepared by heating together vitreous As_2O_3 , the appropriate alcohol, and a hydrocarbon (e.g., C_6H_6 , PhMe , $\text{C}_6\text{H}_4\text{Me}_2$) to entrain and remove the H_2O produced, if necessary under reduced pressure (cf. J.C.S., 1908, 93, 1364): Pr^a , b.p. $96^\circ/10$ mm.; Bu^a , b.p. $145^\circ/15$ mm.; Bu^s , b.p. $125^\circ/15$ mm.; *sec.-butyl*, b.p. $109^\circ/15$ mm.; *isoamyl*, b.p. $159^\circ/12$ mm.; *8-methyl- β -amyl*, b.p. $160^\circ/11$ mm.; *glycol*, b.p. $184^\circ/6$ mm.; *methoxyethyl*, b.p. $160^\circ/10$ mm.; *ethoxyethyl*, b.p. $195^\circ/10$ mm.; *butoxyethyl*, b.p. $266^\circ/10$ mm.; *chloroethyl*, b.p. $170^\circ/8$ mm.; *cyclohexyl*, b.p. $209^\circ/5$ mm.; *4-methylcyclohexyl*, b.p. $225^\circ/10$ mm.; *glyceryl*, b.p. $110^\circ/2$ mm.; *benzyl*, b.p. $290^\circ/35$ mm., and *cinnamyl arsenites*. EtOH and MeOH were not esterified under the conditions used. Vals. of n_D and $M[\omega]$ are given.

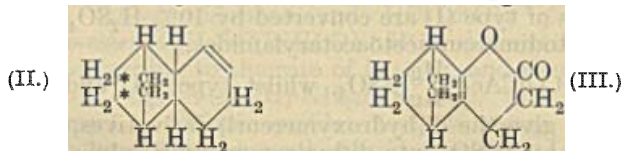
H. A. P.

Mercuration of compounds containing the reactive methylene group by mercuric acetate. K. G. NAIK and R. P. PATEL (J. Indian Chem. Soc., 1932, 9, 185—192).—Acetoacetylarnides [and $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$ and $\text{CH}_2(\text{CO}_2\text{Et})_2$] and $\text{Hg}(\text{OAc})_2$ in MeOH give di(acetoxymercuri)acetoacetylarnides, $\text{NHAr} \cdot \text{CO} \cdot \text{CAc}(\text{Hg} \cdot \text{OAc})_2$ (I), whilst malonamarylarnides [and $\text{CH}_2(\text{CO} \cdot \text{NH}_2)_2$] afford hydroxymercuri-acetoxymercurimalonamarylarnides, $\text{NHAr} \cdot \text{CO} \cdot \text{C}(\text{CO} \cdot \text{NH}_2)(\text{Hg} \cdot \text{OH})(\text{Hg} \cdot \text{OAc})$ (II). Compounds of type (I) are converted by 10% H_2SO_4 into sulphatodimercuriacetoacetylarnides, $\text{NHAr} \cdot \text{CO} \cdot \text{CAc} \langle \text{Hg} \rangle \text{SO}_4$, whilst type (II) and aq. NaOH give the di(hydroxymercuri)-derivatives, converted by H_2SO_4 into di(hydroxymercuri)sulphatodimercuridi(malonamarylarnides), $[\text{NHAr} \cdot \text{CO} \cdot \text{C}(\text{CO} \cdot \text{NH}_2)(\text{Hg} \cdot \text{OH})\text{Hg}]_2\text{SO}_4$; both types are decomposed by 0.25N- HCl (with regeneration of the amide), H_2S , and KI (original amide and KOH produced). The following are described: *di(acetoxymercuri)acetoacet-anilide*, m.p. 204° (decomp.), *-o-toluidide*, m.p. 184° , *-m-toluidide*, m.p. 194° (decomp.), *-p-toluidide*, m.p. $181\text{--}182^\circ$, *- α -naphthylarnide*, m.p. 200° (decomp.), *- β -naphthylarnide*, m.p. 197° , *-1:3:4-xylidide*, m.p. 192° , *-1:4:5-xylidide*, m.p. 204° , and *-m-nitroanilide*, decomp. above 200° ; *Et di(acetoxymercuri)acetoacetate*, m.p. 300° ; *Et di(acetoxymercuri)malonate*, m.p. 300° (decomp.); *hydroxymercuriacet-*

oxymercurimalonam-anilide, decomp. 300° , *-o-toluidide*, decomp. above 270° , *-m-toluidide*, m.p. 300° (turns yellow above 260° and brown above 290°), *-p-toluidide*, becomes reddish-brown above 280° , *-α-naphthylamide*, m.p. 278° (decomp.), *-β-naphthylamide*, m.p. 275° (decomp.), *-1:3:4-xylidide*, m.p. 270° (decomp.) (yellow above 250°), and *-1:4:5-xylidide*, becomes yellow above 260° and brown at 275° ; *hydroxymercuriacetoxymercurimalonamide*, m.p. 300° [converted by Br into $\text{CBr}_2(\text{CO}\cdot\text{NH})_2$]; *sulphatodimercuriacetoacetanilide*, m.p. 300° (brown at 240°), *-o-toluidide*, turns brown above 240° , and *-p-toluidide*, m.p. 300° (brown above 250°); *Et sulphatodimercuriacetoacetate*, becomes yellow above 200° and reddish-brown at 230° ; *di(hydroxymercuri)sulphatodimercuri-di(malonamanilide)*, becomes yellow above 250° and brown at 265° , and *-di(malonamide)*, decomp. 300° . *Malonam-1:3:4-*, m.p. 166° , and *-1:4:5-*, m.p. 197° , *-xylidides* are prepared by a modification of Whiteley's method (J.C.S., 1903, 83, 24). H. B.

Isomerisation of hexamethylene to methylpentamethylene and dimethyltetramethylene under the influence of aluminium chloride or bromide. N. D. ZELINSKI and M. B. TUROVA-POLLAK (Ber., 1932, 65, [B], 1171—1174).—Treatment of cyclohexane with AlCl_3 or AlBr_3 and dehydrogenation of the product by Pt-C gives methylcyclopentane and C_6H_6 (absorbed by fuming H_2SO_4) and dimethylcyclobutane containing small amounts of a saturated hydrocarbon. AlBr_3 dehydrogenates 1:2-dimethylcyclobutane to 1:2-dimethyldicyclo-[0:1:1]-butane, which adds H with production of 1:2:3-trimethylcyclopropane. H. W.

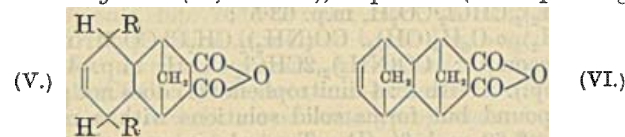
Polymerisation of cyclic hydrocarbons. II. Constitution of dimeric $\Delta^{1:3}$ -cyclohexadiene. K. ALDER and G. STEIN. **III. α - and β -Tricyclopentadienes.** K. ALDER and G. STEIN [with J. REESE and W. GRASSMANN] (Annalen, 1932, 496, 197—203, 204—251; cf. A., 1931, 473).—II. Partial reduction (H_2 , Pd, EtOH) of dicyclohexadiene (I) gives the *dihydro*-derivative (II), b.p. 107 — $108^\circ/16$ mm., oxidised by KMnO_4 in COMe_2 to the liquid β -2-keto-3:6-endoethylenecyclohexylpropionic acid (*Me* ester *oxime*, m.p. 85 — 86°), which is dehydrated by boiling Ac_2O to the *lactone* (III), m.p. 68 — 69° .



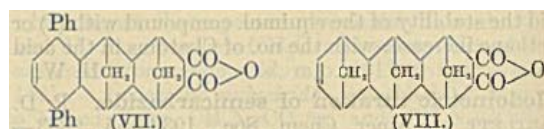
Alkaline hydrolysis of (III) regenerates the keto-acid, whilst oxidation with HNO_3 in AcOH gives *cis*-hexahydroterephthalic acid, thus confirming the structure (II, with double linking between **) assigned to (I) by Hofmann and Damm.

III. The suggestion (A., 1931, 473) that tricyclopentadiene results by 1:4-addition of cyclopentadiene to dicyclopentadiene is supported by the following reactions with analogously constituted substances. Butadiene and 3:6-endomethylene- Δ^4 -tetrahydrophthalic anhydride (IV) in C_6H_6 at 140 — 150° give the *anhydride* (V; $\text{R}=\text{H}$), m.p. 208° (free acid, m.p. about 190°); an analogous anhydride (free acid, m.p.

151°) is similarly prepared from isoprene. *trans-trans-αδ*-Diphenylbutadiene and (IV) at 145° afford the *anhydride* (V; $\text{R}=\text{Ph}$), m.p. 290° (corresponding



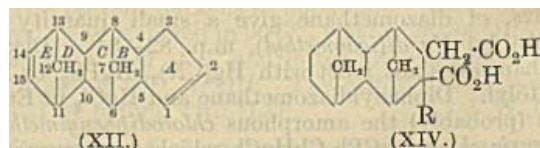
*Me*₂ ester, m.p. 170 — 171°), whilst anthracene and (IV) at 170° give an *adduct*, not melted at 355° (corresponding *Me*₂ ester, $\text{C}_{25}\text{H}_{24}\text{O}_4$, m.p. 230°). *cyclopentadiene* (1 mol.) and (IV) in C_6H_6 at 140 — 150° yield the *anhydride* (VI), m.p. 178° , which with $\alpha\delta$ -diphenylbutadiene affords the *anhydride* (VII), m.p.



301° . *cyclopentadiene* (2 mols.) and (IV) give the *anhydride* (VIII), m.p. 280° , and other additive compounds [including (VI)].

Reduction (H_2 , Pd, H_2O) of (VI) (as Na salt) affords *cis*-1:4:5:8-diendomethylenedecahydronaphthalene-2:3-dicarboxylic acid (IX), m.p. 174° (decomp.) (*anhydride*, m.p. 159 — 160°), rearranged by conc. HCl at 180 — 200° to the *trans-isomeride*, m.p. 247° . Bromination (Hell-Volhard) of (IX) gives a Br_2 -derivative (*anhydride*, m.p. about 173°) and (by dehydrogenation) unsaturated material; the latter is oxidised (KMnO_4 - COMe_2) to *cis*-4:7-endomethylenecyclohexadiene-1:3-dicarboxylic acid (X), m.p. 217° (*anhydride*, m.p. 154° ; *Me*₂ ester, m.p. 74°), a small amount of which is converted by conc. HCl at 200° into the *trans-isomeride* (+ H_2O) (XI), m.p. 226° (*Me*₂ ester, m.p. 96°). Bromination of (X) gives a little (*trans*-) *Br*-derivative, m.p. 245° [reduced by Zn dust and AcOH to (XI)], and a product which when oxidised (KMnO_4 - COMe_2) affords a saturated *hydroxy-acid*, $\text{C}_{12}\text{H}_{16}\text{O}_5$, m.p. 240° (decomp.), and unsaturated acids; energetic oxidation (KMnO_4 - COMe_2) of the latter yields *cyclopentane*-1:3-dicarboxylic acid.

The (α)-tricyclopentadiene (XII), m.p. 68° (lit. 60°) (modified prep. given), of Staudinger and Bruson (A., 1926, 719) forms an *adduct*, m.p. 206 — 208° , with $\alpha\delta$ -diphenylbutadiene and is partly reduced (H_2 , Pd, MeOH) to the 14:15-*dihydro*-derivative (XIII), b.p. 145 — $146^\circ/13$ mm., m.p. 36° (*cis*-1:2-*dibromide*, m.p. 107°), which is reduced further to tetrahydro- α -tricyclopentadiene, m.p. 49° (lit. 43°). Energetic oxidation of (XIII) with KMnO_4 in COMe_2 gives a mixture of (X), the *cis-acid* (XIV; $\text{R}=\text{H}$), m.p. 183° [*anhydride*, m.p. 151° ; *Me*₂ ester, m.p. 46° , hydrolysed by MeOH - NaOMe to the *trans-acid*, m.p. 186°]



(*Me*₂ ester, m.p. 50°), and the (crude) *cis-hydroxy-acid* (XIV; $\text{R}=\text{OH}$), m.p. 110 — 120° [*Me*₂ ester, m.p.

73° (acetate, m.p. 128—129°); acetate anhydride, m.p. 204°, which when heated passes into the corresponding γ -lactonic acid, m.p. 206° (*Me* ester, m.p. 130—131°). The production of (X) from (XIII) and (IX) shows that rings *B—E* of (XII) and the corresponding rings of (VI) [(IX) in text] are structurally and sterically identical. The formulated arrangement of rings *D* and *E* of (XII) is confirmed by the degradation (above) of (X) to cyclopentane-1 : 3-dicarboxylic acid.

During the prep. of (XII), an isomeride (termed β -tricyclopentadiene) (XV) is also produced. A mixture, b.p. 137—145°/15 mm., of (XII) and (XV) treated with PhN_3 gives the additive compound, m.p. 196°, of (XV) and that (*loc. cit.*) of (XII), whilst partial reduction affords (XIII) and dihydro- β -tricyclopentadiene (XV), m.p. 88—89° (regenerated from its *cis*-, m.p. 124°, and *trans*-, m.p. 106°, -1 : 2-dibromides), separable through their dibromides. Further reduction of (XVI) yields tetrahydro- β -tricyclopentadiene, m.p. 99—100°, whilst oxidation (KMnO_4 - COMe_2) gives a *cis*- β -dicarboxylic acid, $\text{C}_{15}\text{H}_{26}\text{O}_4$ [isomeric with (XIV; $\text{R}=\text{H}$)], m.p. 207° [anhydride, m.p. 110—111°; Me_2 ester, m.p. 108—109°, hydrolysed by $\text{MeOH}-\text{NaOMe}$ to the *trans*-acid, m.p. about 223° (Me_2 ester, m.p. 57°)], which when treated successively with Br and red P, aq. $\text{EtOH}-\text{KOH}$, KMnO_4 , dil. H_2SO_4 , and KMnO_4 affords (X), thus showing that (XII) and (XV) are stereoisomerides and that the atoms C_6 to C_{15} of both compounds possess the same spatial configuration. (XII) and (XV) represent the two possible *cis*-unions of ring *A* to C_4 and C_5 , and are considered to be formed by the addition of cyclopentadiene to two dicyclopentadienes. The configurations assigned to the dibromides of (XIII) and (XVI) are from measurements of dipole moments; dihydrodicyclopentadiene dibromide, m.p. 66°, is a *cis*-compound.

Tetracyclopentadiene and PhN_3 give an additive compound, m.p. 222°. H. B.

Compound of nitrobenzene and *m*-dinitrobenzene, $2\text{PhNO}_2 \cdot m\text{-C}_6\text{H}_4(\text{NO}_2)_2$. K. LEHMSTEDT (Ber., 1932, 65, [B], 1218—1219).—Determinations of the temp. of solidification of mixtures of PhNO_2 and $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ confirms the existence of the compound $2\text{PhNO}_2 \cdot m\text{-C}_6\text{H}_4(\text{NO}_2)_2$. The results of Hammick and others (this vol., 228) are attributed to untrustworthy experimental procedure based on measurement of m.p. H. W.

Structure of the bromination product of *o*-nitrotoluene. D. L. YABROFF (J. Amer. Chem. Soc., 1932, 54, 3011—3012).—In the action of Br on $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, oxidation-reduction occurs first and the anthranilic acid formed is then brominated to the 3 : *o*- Br_2 -derivative; continued action of Br on this gives $s\text{-C}_6\text{H}_2\text{Br}_3\cdot\text{NH}_2$. C. J. W. (b)

Action of reducing agents on iodonitro-compounds. C. D. NENITZESCU and D. A. ISACESCU (Bul. Soc. Chim. Romania, 1932, 13, 89—93).— $\omega\omega$ -Iodonitrotoluene (I) and 20% aq. NaHSO_3 give *aci*-phenylnitromethane and phenylhydroxamic acid. *p*-Chloro- $\omega\omega$ -iodonitrotoluene (II) affords similarly *aci*-*p*-chlorophenylnitromethane (III), m.p. 87—88° (lit. 64°). 9-Iodo-9-nitrofluorene (IV) gives *aci*-9-

nitrofluorene (V). (I) and $\text{NHPh}\cdot\text{NH}_2$ give ω -nitrobenzaldehydephenylhydrazone, and (II) gives the corresponding *p*-Cl-compound, m.p. 130°; with *p*-nitrophenylhydrazine (II) gives *p*-chloro- ω -nitrobenzaldehyde-*p*-nitrophenylhydrazone, m.p. 158—160°, also obtained from diazotised $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and (III). (IV) gives with $\text{NHPh}\cdot\text{NH}_2$ the $\text{NHPh}\cdot\text{NH}_2$ salt, m.p. 198°, and with N_2H_4 the N_2H_4 salt, m.p. 168°, of (V), whilst with $\text{NH}_2\text{OH}\cdot\text{HCl}$ $\alpha\beta$ -dinitro- $\alpha\beta$ -di-diphenylene-ethane is formed. The following mechanism of the reactions is suggested : $\text{CHIPh}\cdot\text{NO}_2 \longrightarrow \text{CHIPh}[\text{NH}(\text{OH})\cdot\text{O}] \text{ (A)} \longrightarrow \text{CHPh}\cdot\text{N}(\text{OH})\cdot\text{O}$, and $\text{(A)} \longrightarrow \text{CHIPh}\cdot\text{NO} \longrightarrow \text{CHPh}(\text{OH})\cdot\text{N}\cdot\text{OH}$.

R. S. C.

Splitting of the sulphonic group from the aromatic ring by electrolytic reduction. M. MATSUI and G. SAKURADA (Mem. Coll. Sci. Kyoto, 1932, A, 15, 181—188).— SO_3H groups attached to an aromatic nucleus may frequently be reduced to H at a Pb (or Hg) cathode in NaOH solution. Optimum conditions for removing the SO_3H groups of various compounds are as follows. Unless otherwise stated, the solution (usually 2—3%) in 10% aq. NaOH was electrolysed with c.d. 4.0 amp. per sq. dm. (area of electrodes 60 sq. cm.). PhSO_3H in 20% NaOH at 15°, 60.0% reduction after 3 hr. *o*-Sulphobenzoic acid in 5% NaOH at 19° and 2.0 amp. per sq. dm., 77% after 6 hr. Metanilic acid in 20% NaOH at 25°, 37.0% after 2 hr. *m*-Sulphobenzoic acid in 5% NaOH at 25°, 38% after 1.5 hr. *p*-Sulphobenzoic acid in 5% NaOH at 25° and 2.0 amp. per sq. dm., 77% after 2 hr. $1\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ in 10% NaOH with 20% EtOH at 55°, 52%. $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ in 10% NaOH with 50% EtOH at 25°, 14.0%. α -Naphthol-4- and -5-sulphonic acids, 10%. Naphthionic acid at 60°, 81% after 4 hr. α -Naphthylamine-5-sulphonic acid at 65° and 2.5 amp. per sq. dm., 73% after 4 hr. β -Naphthylamine-5-sulphonic acid at 16—45°, 12% after 2.5 hr. Sulphanilic, *p*-phenol-, α -naphthol-2-, β -naphthol-6-, α -naphthylamine-6- and -7-, β -naphthylamine-6-, 6-amino- β -naphthol-4-, 8-amino- α -naphthol-3 : 6-di-, and naphtholdi-sulphonic acids were not appreciably reduced. D. R. D.

Benzenesulphonyl fluoride derivatives. W. DAVIES and J. H. DICK (J.C.S., 1932, 2042—2046).—*o*-Chlorosulphonylbenzoyl chloride (I) and ZnF_2 in C_6H_6 or light petroleum give a little *o*-sulphobenzoic anhydride, whilst the *p*-dichloride (II) similarly (or with ZnCl_2) affords *pp'*-bischlorosulphonylbenzoic anhydride, m.p. 197°. (I) is completely hydrolysed by boiling aq. 70% KF, whereas (II) yields *p*-fluorosulphonylbenzoic acid. Chlorination of $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{F}$ at 140—175°/57 hr. causes partial elimination of S (probably thus : $\text{RCl} + \text{SO}_2\text{ClF} \longleftarrow \text{RSO}_2\text{F} + \text{Cl}_2 \longrightarrow \text{RF} + \text{SO}_2\text{Cl}_2$), giving a mixture of ω -chloro-*o*-toluenesulphonyl fluoride (III), m.p. 69° (also produced in moderate yield by rapid chlorination at 180—200°), the $\omega\omega$ - Cl_2 -derivative, and a S-free F-compound (oxidised by KMnO_4 to $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$). Chlorination of $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ at 92—93°/36 hr. gives $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHCl}_2$ (73.5% yield), whilst at 110—130°/5.5 hr. in presence of a trace of PCl_3 , $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{Me}$, $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Cl}$, and 6% of ω -chloro-*o*-toluenesulphonyl chloride, b.p. about 175°/22 mm., m.p. 146°, are produced. Chlorination

of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{F}$ occurs with practically no loss of S; $\omega\text{-chloro-}p\text{-toluenesulphonyl fluoride}$, b.p. 148—152°/20 mm., m.p. 56°, is obtained in 62.4% yield at 160—210°/7 hr. (III) and NaI in COMe_2 give $\omega\text{-iodo-}o\text{-toluenesulphonyl fluoride}$, m.p. 85—86°, converted by Ag_2O in aq. EtOH into the $\omega\text{-hydroxy-derivative}$, b.p. 128—130°/1 mm. (which could not be oxidised), and the *sultone*, m.p. 112—113°, of $\omega\text{-hydroxy-}o\text{-toluenesulphonic acid}$. $\omega\text{-Iodo-}p\text{-toluenesulphonyl fluoride}$, m.p. 106°, is similarly converted into the $\omega\text{-hydroxy-derivative}$, b.p. 157—160°/1 mm., oxidised ($\text{CrO}_3\text{-AcOH}$) to $p\text{-fluorosulphonylbenzoic acid}$. $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{F}$ and cold CrO_2Cl_2 give impure *benzaldehyde-}o\text{-sulphonyl fluoride}, b.p. 143—155°/1 mm. (2 : 4-dinitrophenylhydrazones, m.p. 216—218°), oxidised slowly by atm. O_2 to a product, m.p. 65° (decomp.), readily hydrolysed by H_2O at 0° to $o\text{-sulphobenzoic acid}$; oxidation of the CHO group by the ordinary methods results in hydrolysis of the SO_2F group. Saccharin and PCl_5 at 120—130° give $o\text{-CN-C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$, which with aq. 70% KF and xylene at 100° (bath) affords $o\text{-cyanobenzenesulphonyl fluoride}$, m.p. 88—89°; the CN group of this is not affected by cold acid hydrolytic agents or by HCl, HBr, or HI in Et_2O . $o\text{-Nitrobenzenesulphonyl fluoride}$, m.p. 60°, is prepared from the chloride and 70% KF. One or other of the groups in the above $o\text{-substituted benzenesulphonyl fluorides}$ exhibits anomalous behaviour.*

H. B.

Directive influence of the alkylsulphonamido- and dialkylsulphonamido-groups. R. L. SHRINER, M. T. GOEBEL, and C. S. MARVEL (J. Amer. Chem. Soc., 1932, 54, 2470—2476).—The directive effect of the mono- and di-sulphonamido-groups in the C_6H_5 ring is predominantly $o\text{-}p$. Nitration of methanesulphonanilide (I) gives the 2 : 4-(NO_2)₂-derivative, m.p. 173.5—174.5° (80.6% yield), hydrolysed to 2 : 4-(NO_2)₂ $\text{C}_6\text{H}_3\cdot\text{NH}_2$. *Dimethanesulphonanilide*, m.p. 201—202°, from (I) and MeSO_2Cl in C_6H_6 , is nitrated to 61% of the $p\text{-}$, m.p. 225—228°, 13% of the $m\text{-}$, and 6% of the $o\text{-NO}_2$ -derivative; the structure of the $p\text{-NO}_2$ -compound is established by synthesis and by hydrolysis. The % of isomerides are determined by hydrolysis and identification of the nitro-aniline.

C. J. W. (b)

Reduction of arylsulphonic acid salts and derivatives. Phosphorus pentabromide as a reducing agent. A. H. KOHLHASE (J. Amer. Chem. Soc., 1932, 54, 2441—2448).—Arylsulphonic acid salts, heated with PBr_5 , are converted into the corresponding arylsulphonyl bromides and diaryl disulphides. The relative yields depend on the nature of the aryl radical; in some cases the disulphide is the only product, whilst in other cases it is formed in very small amounts. The sulphonyl bromide is formed first and is subsequently reduced by the PBr_3 simultaneously formed by the dissociation of PBr_5 . The sulphonates are unaffected by PBr_3 alone. Arylsulphonyl bromides are readily reduced by PBr_3 ; sulphonyl chlorides are reduced with much greater difficulty, whilst neither chloride nor bromide is reduced by PCl_3 . Na 2 : 4 : 6-tribromobenzenesulphonate (+1.5 H_2O), heated for 5—10 min. with crude PBr_5 , gives 86.5% of 2 : 4 : 6 : 2' : 4' : 6'-hexabromodiphenyl

disulphide; with pure PBr_5 , the yield is 13—38%. The disulphide is obtained in 34% yield from 2 : 4 : 6-tribromobenzenesulphonyl chloride and PBr_3 . 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\text{Cl}$ does not react with PBr_3 ; 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\text{Br}$ and PBr_3 , heated for 15 min., give 28.7% of the disulphide and 19.7% of $\alpha\text{-C}_{10}\text{H}_7\cdot\text{SH}$. 4-Nitro- $o\text{-toluenesulphonyl chloride}$ and PBr_3 , heated for 30 min., give 85.7% of 3 : 3'-dinitro-6 : 6'-dimethyldiphenyl disulphide, m.p. 147.3—148°, whilst PhSO_2Na and PBr_5 , heated for 30 min. at 85—90°, give 45% of PhSO_2Br and 3% of Ph_2S_2 (the yield is improved by using PBr_5 and PBr_3). $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ and PBr_5 , heated for 70 min., give about 25% of $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Br}$ and 27.4% of the disulphide; a mixture of PBr_5 and PBr_3 gives 57% of the disulphide, but no bromide. Na 3 : 5-dinitrobenzenesulphonate does not react with PBr_5 ; the Ba salt and PCl_5 give 84% of the sulphonyl chloride, which with PBr_3 affords about 60% of 3 : 5 : 3' : 5'-tetranitrodiphenyl disulphide (I), m.p. 175—177.5°. The chloride and PhSNa in C_6H_6 give *Ph* 3 : 5-dinitrobenzenethiosulphonate, m.p. 139—141°, converted by PBr_3 into (I) (85—95% yield). The reaction product from Na 2 : 4-dibromo-6-nitrobenzenesulphonate and PBr_5 at 150° could not be identified.

C. J. W. (b)

Nitration of $m\text{-diphenylbenzene}$ and derivatives of nitro- $m\text{-diphenylbenzene}$. C. A. WARDNER and A. LOWY (J. Amer. Chem. Soc., 1932, 54, 2510—2515).— $m\text{-C}_6\text{H}_4\text{Ph}_2$ and HNO_3 (d 1.5) in Ac_2O at 0—50° give a NO_2 -derivative (I), b.p. 197—198°/1 mm., which may be 4-nitro-1 : 3-diphenylbenzene or 2-nitro-5'-phenyldiphenyl; with HNO_3 (d 1.42) and H_2SO_4 , a (NO_2)₂-derivative (II), m.p. 214°, results. (I) and $m\text{-C}_6\text{H}_4\text{Ph}_2$ are both nitrated further to a (NO_2)₃-derivative (III), m.p. 204°. Oxidation of (I) with CrO_3 in AcOH gives a *nitrodiphenylcarboxylic acid*, m.p. 227°, whilst (II) gives $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$; (III) could not be oxidised. Catalytic reduction of (I) gives the NH_2 -compound, m.p. 64° (hydrochloride; *Ac*, m.p. 117°, and *Bz*, m.p. 152°; derivatives). $m\text{-Diphenylbenzeneazo-}\beta\text{-naphthol}$, red, and azo-dyes from the following compounds are prepared : 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, reddish-purple; $\alpha\text{-naphthol-4-sulphonic acid}$, bright red; 1 : 8-aminonaphthol-3 : 6-disulphonic acid, bluish-purple; $\beta\text{-naphthol-7-sulphonic acid}$, bright red; 1 : 8-aminonaphthol-2 : 4-disulphonic acid, purple; $\beta\text{-naphthol-3 : 6-disulphonic acid}$, light purple.

C. J. W. (b)

Action of sulphur on organic compounds. XI. Action of sulphur on dibenzyl. L. SZPERL and M. GRADSZTAJN (Rocz. Chem., 1932, 12, 478—481).—Tetraphenylthiophen and *s*-tetraphenylbutane are identified amongst the products of reaction of S with dibenzyl.

R. T.

Ultra-violet absorption of bismesitylenic hydrocarbons. J. SORDES (Compt. rend., 1932, 195, 247—249).—The ultra-violet absorption of hydrocarbons of the type $[\text{CH}_2]_n(\text{C}_6\text{H}_2\text{Me}_3)_2$, where $n=0, 1$, and 2, is independent of the no. of CH_2 groups separating the mesitylene residues. Mesitylacetonitrile affords on hydrolysis *mesitylacetamide*, m.p. 216°. This with Na and EtOH affords $\beta\text{-mesitylethyl alcohol}$, m.p. 79° (*Ph urethane*, m.p. 147°), which with PBr_3 yields $\beta\text{-mesitylethyl bromide}$, m.p. 74°, acted on

by Na to give *dimesitylbutane*, m.p. 124°. *Et γ-mesitylpropionate*, b.p. 163—164°/16 mm., is reduced by Na and EtOH to *γ-mesitylpropyl alcohol*, m.p. 54° (*Phurethane*, m.p. 102°), which with PBr₃ affords *γ-mesitylpropyl bromide*, b.p. 163°/18 mm. Na reacts with the bromide to yield *dimesitylhexane*, m.p. 74°.

J. L. D.

Isatogens. IX. Halogen derivatives of 4:6-dinitro-1:3-distyrylbenzene and their transformation into isatogens. P. RUGGLI and A. ZIMMERMANN (Helv. Chim. Acta, 1932, 15, 855—878; cf. this vol., 175).—Unless otherwise stated, the following reactions were carried out in pyridine solution. 4:6-Dinitro-1:3-distyrylbenzene (I) and Br (2 mols.) in CHCl₃ give the known 4:6-dinitro-1:3-di-(αβ-dibromo-β-phenylethyl)benzene (II), m.p. 206° (37% yield), and an *isomeride* (III), m.p. 164° (53% yield). (II), when boiled, gives 4:6-dinitro-3-styryl-1-[(?)*-bromostyryl*]benzene (IV), m.p. 196°. (III) similarly loses Br and HBr; the product (V), m.p. 174°, is impure, but contains a little (IV) (with, probably, a tolane derivative), and, in sunlight, gives 6-nitro-2-phenyl-5-styrylisatogen (VI), which is also obtained by illumination of (IV), or, less well, of (II) or (III). (I) and Br (1 mol.) in CHCl₃ give isomeric forms of 4:6-dinitro-1-(αβ-dibromo-β-phenylethyl)-3-styrylbenzene, m.p. 212° (VII), and 184° (VIII). (VII), when boiled, gives (I) and is largely or entirely unchanged by illumination. (VIII) yields (VI) when illuminated, and, when boiled, gives the mixture (V). The preps. of 4:6-dinitro-1:3-di-(αβ-dichloro-β-phenylethyl)benzene (IX) and 4:6-dinitro-1-(αβ-dichloro-β-phenylethyl)-3-styrylbenzene (X) are modified. Illumination of 4:6-dinitro-1:3-di[(?)*-chlorostyryl*]benzene gives 6-nitro-2-phenyl-5-[(?)*-chlorostyryl*]isatogen (XI). When boiled, (X) gives 4:6-dinitro-1-[(?)*-chlorostyryl*]benzene (XII), lemon-yellow, m.p. 191° (lit. 184°), changed into (V) by illumination. (X) passes in sunlight or, less well, in light from a Hg-lamp, into a copper-brown *isomeride* of (XII), m.p. 191°, transformed by further illumination in excellent yield into (V), which is obtained in poor yield directly from pure (X) in sunlight. Crude (X) in sunlight gives (V), (I), and a *substance*, probably 4:6-dinitro-3-styryltolane, m.p. 178—179°. (V) may be most conveniently prepared from (IV) or the crude mixture of (II) and (III). The Br-derivatives [except (VII)], in contrast to the Cl-derivatives, all give the halogen-free isatogen compound. R. S. C.

Orientation in substitution reactions of alkyl-naphthalenes. I. Side-chain nitration of 1:4-dimethylnaphthalene. R. ROBINSON and H. W. THOMPSON (J.C.S., 1932, 2015—2019).—1:4-C₁₀H₆Me₂, m.p. 5.5—6.5° (corr.) (from Mg 4-methyl-1-naphthyl bromide and Me₂SO₄), is nitrated in aq. suspension or in Ac₂O or MeNO₂ to ω-nitro-1:4-dimethylnaphthalene, m.p. 107°, oxidised by alkaline K₂Fe(CN)₆ or KMnO₄ to 1:4-C₁₀H₆(CO₂H)₂ and an ω-nitro(methylnaphthylidene)dimethylnaphthalene, C₁₀H₆Me·C(NO₂)₂·CH·C₁₀H₆Me, m.p. 203°, and reduced (H₂, PtO₂, EtOH) to ω-amino-1:4-dimethylnaphthalene [hydrochloride (I), m.p. 285°; Ac derivative, m.p. 142°]. 1:4-C₁₀H₆Me₂ and HNO₃, alone or in AcOH, give a small amount of a *mixture*, m.p. 150°, of

(NO₂)₂-compounds, much amorphous material, and an oil, whilst dinitration in Ac₂O affords a (NO₂)₂-derivative, m.p. 128°, and a *substance*, m.p. 174° (decomp.). Mg 4-methyl-1-naphthyl bromide and CH₂O give 4-methyl-1-naphthylcarbinol; the *bromide*, m.p. 80°, and o-C₆H₄(CO)₂NK at 180—200° afford ω-phthalimido-1:4-dimethylnaphthalene, m.p. 148° [corresponding *phthalamic acid*, m.p. 179° (decomp.)], also obtained when (I) is heated with o-C₆H₄(CO)₂O and NaOAc. 1-C₁₀H₆-Me, HCN, HCl, and AlCl₃ give a poor yield of 4-methyl-α-naphthaldehyde (*semicarbazone*, m.p. 237°). 4-Bromo-1-methylnaphthalene, prepared by bromination of 1-C₁₀H₆-Me, has b.p. 157—158°/10 mm., m.p. 5.5—6° (corr.). H. B.

Synthesis of eudalene. G. DARZENS and A. LÉVY (Compt. rend., 1932, 194, 2056—2059).—*p*-isopropylbenzyl chloride and Et sodioallylmalonate give Et *p*-isopropylbenzylallylmalonate, b.p. 172—173°/2 mm.; the free acid, m.p. 142—143°, heated at 180—190°, gives 80% of β-*p*-isopropylphenyl-α-allylpropionic acid (I) and 20% of lactone (II), b.p. 180°/17 mm. Treatment of (I) with cold 84% H₂SO₄ during 5 days gives 20% of (II) and 80% of 1-methyl-7-isopropyl-1:2:3:4-tetrahydro-3-naphthoic acid (III), m.p. 102°, dehydrogenated by S at 230—240° to 1-methyl-7-isopropyl-3-naphthoic acid, m.p. 198.5°, the Ca salt of which when heated with Ca(OH)₂ in vac. affords 1-methyl-7-isopropyl-naphthalene (eudalene), b.p. 152°/18 mm. [picrate, m.p. 92.8° (corr.); styphnate, m.p. 119.8° (corr.)]. (II) is a mixture of the lactones of β-*p*-isopropylphenyl-α-(β'- and γ'-hydroxypropyl)propionic acids; the former (γ-lactone) is converted by 84% H₂SO₄ into (III), whilst the latter (δ-lactone) is unaffected. H. B.

Preparation of 1-chloronaphthalene by direct chlorination of naphthalene. C. B. DE WITT and J. B. EKELEY (Univ. Colo. Stud., 1931, 18, 119—121).—Chlorination is effected at 140° in presence of I or FeCl₃ in an inert (N₂) atm. HCl was removed from the distillation residues by distillation over Al shavings. When FeCl₃ is used as catalyst a trace of H₂O must be present. CH. ABS.

Synthesis of alkyl aromatic hydrocarbons. G. HUGEL and M. LERER (Compt. rend., 1932, 195, 249—251; cf. A., 1914, i, 396).—Interaction of the Na₂ compound of anthracene with *isoamyl* chloride affords 1:4-di*isoamyl*-1:4-dihydroanthracene, b.p. 134—138°, and some di*isoamyl*anthracene. Similarly, C₁₀H₈ and Na in liquid NH₃ afford a Na derivative which with Bu³Cl affords 1:4-di*isobutyl*-1:2:3:4-tetrahydronaphthalene, b.p. 170—175°/16 mm. J. L. D.

Analysis of aromatic two-component systems by means of viscosity and density gradients. A. L. BERNOULLI and E. A. VEILLON (Helv. Chim. Acta, 1932, 15, 810—839).—From published data it is shown that variation of the ratios Δη/Δ composition and Δd/Δ composition (viscosity and density "gradients") for mixtures of C₁₀H₈ (I) with 1:3:5-trinitro-, *m*-dinitro-, and nitro-benzene indicate equimol. compounds in the first two cases and no compound in the last, in agreement with the results of thermal analysis. When *a* and *d* are substituted for the gradients, such agreement is not obtained in the

above or the following cases. The η and d gradients at several temp. for mixtures of the components indicate the existence of the following compounds, many of which are new and not shown by thermal analysis: *p*-NO-C₆H₄-NMe₂ (II) and PhOH (III), 1:10, 1:4, 1:3, and 2:1; (II) and *p*-toluidine, 1:2, 1:1, and 2:1; (II) and thymol, 1:2, 2:3, and 1:1; (I) and (III), 1:6, 1:4, 2:3, 1:1, and 2:1. No compounds are indicated for mixtures of 1-C₁₀H₇-NO₂ with (I) or NPhPh₂. Compounds indicated by thermal analysis are always shown by the above methods. A new thermostat is described, the temp. of which is controlled by the b.p. of a liquid under slightly reduced pressure, and details for measuring η and d are given. R. S. C.

Ditolyl series. IV. Resolution into optical antipodes of *dl*-2-chloro-2'-amino-6:6'-dimethyldiphenyl. A. ANGELETTI (Gazzetta, 1932, 62, 376—380).—The NO₂-compound (this vol., 152) is reduced by SnCl₂ to *dl*-2-chloro-2'-amino-6:6'-dimethyldiphenyl, m.p. 87—88°, from which the *d*-tartrates, each of m.p. 138—144° (partly hydrolysed), of l-, [α]_D²⁰ -4.62°, and *d*-2-chloro-2'-amino-6:6'-dimethyldiphenyl, [α]_D²⁰ +4.12°, are separated. The base does not easily racemise. E. W. W.

Stereochemistry of 2:2'-disubstituted diphenyls. I. Optical resolution of phenyl benzidine-2:2'-disulphonate. M. S. LESSLIE and E. E. TURNER (J.C.S., 1932, 2021—2026).—2-Chloro-5-nitrobenzenesulphonyl chloride, PhOH, and anhyd. Na₂CO₃ at 100° give *Ph* 2-chloro-5-nitrobenzenesulphonate (I), m.p. 92—93°, reduced to the NH₂-compound, m.p. 75—76°, by SnCl₄ in AcOH-HCl. *Na* 2-iodo-5-nitrobenzenesulphonate (from *p*-nitroaniline-2-sulphonic acid) (does not react with Cu in H₂O at 100°) and PCl₅ give 2-iodo-5-nitrobenzenesulphonyl chloride, m.p. 122—123°, yielding the *Ph* ester, m.p. 128—129°, which with Cu-bronze at 205° forms *Ph*₂ 4:4'-dinitrodiphenyl-2:2'-disulphonate, m.p. 149—150°, also obtained from (I) and Cu-bronze at 275°. Reduction (SnCl₄ in AcOH-HCl) affords the 4:4'-(NH₂)₂-compound (II), m.p. 226—227°, giving the following *d*-camphorsulphonates: *dl*-base, [α]_D²⁵ +24.3°, *l*-base, +15.2°, *d*-base, +38.1° (all in COMe₃). The *d*- and *l*-isomerides of (II) have m.p. 222—223°, and [α]_D²⁵ 28.0° and -24.6° in COMe₃. The existence of separable optically active forms of (II) is in agreement with spatial considerations. R. S. C.

Direction of the carbon valencies in benzene derivatives. D. VORLANDER and A. APEL [with W. GALKA] (Ber., 1932, 65, [B], 1101—1109).—*p*-Phenetoleazoxybenzoic acid is converted by SOCl₂ into the corresponding chloride, m.p. about 140°, which with pyrocatechol in boiling C₆H₆ in presence of pyridine affords *p*-phenetoleazoxybenzoylpyrocatechol, OEt-C₆H₄-N₂O-C₆H₄-CO₂-C₆H₄-OH, m.p. I 150°, II 171°, transformed by Ac₂O at 100° into the *Ac* derivative, m.p. I 126°, II 130° after softening at 121°, and by pyridine and BzCl into the *Bz* compound, m.p. I 140°, II 144° after softening at 135°. *Di*-*p*-phenetoleazoxybenzoylpyrocatechol has m.p. I 164°, II 213°. Similarly, resorcinol gives *p*-phenetoleazoxybenzoylresorcinol, m.p. I 169°, II 185° (*Ac* derivative, m.p. I 135°, II 138° after softening at 129°; *Bz* com-

pound, m.p. I 127°, II 129° after softening at 122°), and *di*-*p*-phenetoleazoxybenzoylresorcinol, m.p. I 184°, II 218° after softening at 179°. Quinol yields *p*-phenetoleazoxybenzoylquinol, m.p. I 172°, II 225° (decomp.) after softening at 165° (*Ac* derivative, m.p. I 180°, II 183°), and *di*-*p*-phenetoleazoxybenzoylquinol, m.p. I 231° after softening at about 220°, decomp. 240°. As expected, the liquid cryst. properties are most pronounced in the quinol derivatives.

H. W.

Interaction of acetonephenylhydrazone and phenylcarbimide. W. A. CALDWELL, J. CHAPMAN, H. W. GOODWIN, and F. J. WILSON (J.C.S., 1932, 2086—2087).—Acetonephenylhydrazone and PhNCO (I) under various conditions give a mixture of acetone-2:4-diphenylsemicarbazone, m.p. 141° (also formed from COMe₂ and 2:4-diphenylsemicarbazide), and $\alpha\beta$ -*di*(phenylcarbamyl)phenylhydrazine, NPh(CO-NHPh)-NH-CO-NHPh, m.p. 208° [also formed from NPh-NH₂ and (I) (2 mols.) at 100°, or hot (I) and 1:4- or 2:4-diphenylsemicarbazide] (cf. A., 1928, 516). Acetone-*p*-bromophenylhydrazone and (I) in hot C₆H₆ in CO₂ give a little CO(NHPh)₂ and $\alpha\beta$ -*di*(phenylcarbamyl)-*p*-bromophenylhydrazine, m.p. 206—207°, also formed from *p*-bromophenylhydrazine and (I). R. S. C.

β -Phenylethylhydrazine. E. VOTOCEK and O. LEMINGER (Coll. Czech. Chem. Comm., 1932, 4, 271—281).—CH₂Ph-CH₂Cl and N₂H₄·H₂O in EtOH at 100° (bath) give β -phenylethylhydrazine, b.p. 137—139°/12—13 mm. [hydrochloride, m.p. about 171° (sinters from 102—103°); oxalyl, m.p. 161—162° (from Et oxalate), *Bz*₂, m.p. 144—145°, phenylcarbamyl, m.p. 148°, and phenylthiocarbamyl, m.p. 133° (sinters at 123°), derivatives], which is readily oxidised by O₂; *di*- β -phenylethylhydrazine, m.p. 64—65° [hydrochloride, m.p. about 200° (sinters at 130°)], is a by-product. *d*-Galactose- β -phenylethylhydrazone, m.p. 125°, [α]_D²⁰ -13.76° in MeOH; *d*-mannose- β -phenylethylhydrazone, m.p. 147—148°, [α]_D²⁰ -4.47° \rightarrow 8.43° in MeOH, and fructose- β -phenylethylhydrazone, an oil, are prepared.

Diazo-resins. II. Z. JOLLES (Atti R. Accad. Lincei, 1932, [vi], 15, 395—397).—Phenylazoxycarbonamide, which is converted into the normal diazonium hydroxide by alkali, gives a resin identical with that obtained from diazotised NH₂Ph (this vol., 841) on prolonged contact with alkali. A resin of the same composition is obtained (1) from nitrosoacetanilide, the additive compound OH-NAr-NH-OH and the diazonium hydroxide forming intermediate stages, and (2) by the action of H₂O₂ on PhN₂Cl (cf. Bamberger, A., 1909, i, 977). T. H. P.

Styphnates of phenols. N. N. EFREMOV (Ann. Inst. Anal. Phys. Chim., Leningrad, 1931, 5, 75—141).—The following double compounds of styphnic acid and phenols are described: with 1 mol. PhOH, m.p. 115.1° (decomp.), *m*-nitrophenol, m.p. 113.8° (decomp.), *o*-, m.p. 113.5°, *m*-, m.p. 115.7°, and *p*-cresol, m.p. 111°, α -naphthol (unstable), β -naphthol, m.p. 166.3°, *o*-, m.p. 129°, *m*-, m.p. 125°, and *p*-di-hydroxybenzene (2 mols.), m.p. 142.6°. *o*- and *m*-Nitrophenol, picric acid, chloro-2:4:6-trinitrobenzene, 2:4:6-trinitrocresol, nitroquinol, 3- and 4-

nitropyrocatechol, 2- and 4-nitro-, and 2:4- and 4:6-dinitro-resorcinol do not form compounds.

R. T.

Molecular rearrangement in the hydrolysis of chlorotoluenes with alkali. V. E. MEHARG and I. ALLEN, jun. (J. Amer. Chem. Soc., 1932, 54, 2920—2922).—*o*- and *p*-C₆H₄Cl·Me undergo partial mol. rearrangement when hydrolysed with 15% NaOH in presence of Cu at 315—320°. Thus, *o*-C₆H₄Cl·Me gives 55.4% of mixed phenols, of which 25.3% is *m*-cresol, whilst *p*-C₆H₄Cl·Me affords 55.5% of phenols containing 38.2% of *m*-cresol. *m*-C₆H₄Et·OH is probably similarly produced from *o*-C₆H₄Cl·Et.

C. J. W. (b)

***p*-Alkylphenolsulphonic acids.** C. M. SUTER and E. W. MOFFETT (J. Amer. Chem. Soc., 1932, 54, 2983—2984).—*p*-C₆H₄Bu·OH and conc. H₂SO₄ at 100° (bath) give (after addition to saturated NaCl) 66% of Na *p*-butylphenol-2-sulphonate; Na *p*-propyl-, -amyl-, and -hexyl-phenol-2-sulphonates are similarly prepared in yields of 56, 72, and 83%, respectively. The m.p. of the corresponding *p*-toluidine salts are 149—150°, 141—143°, 147—149°, and 139—140°, respectively. Only the Pr and Bu derivatives have a detectable disinfectant action; the PhOH coeffs. are 1.8 and 2.4, respectively.

C. J. W. (b)

Preparation of 5-bromo-2-methoxybenzyl chloride. R. QUELET (Compt. rend., 1932, 195, 155—156).—*p*-Bromoanisole, (CH₂O)₃, and ZnCl₂ in ligroin (freed from aromatic and unsaturated compounds) at 15° yield 5-bromo-2-methoxybenzyl chloride, b.p. 152—153°/15 mm., in 50% yield, and 5:5'-dibromo-2:2'-dimethoxydiphenylmethane. Anisole reacts similarly.

R. S. C.

Some dichloro-anisidines and -phenetidines. F. MADESANI (Gazzetta, 1932, 62, 402—410).—2:5-Dichloro-*p*-nitroanisole is reduced by SnCl₂ to 2:5-dichloro-*p*-anisidine, m.p. 79—80° [hydrochloride, m.p. 225° (decomp.)]; Bz derivative, m.p. 139°; 2:5-dichloro-4-methoxy-diphenylthiocarbamide, m.p. 166°, of which the Ac derivative, m.p. 190°, is also prepared from *p*-acetanisidide with KClO₃ and HCl. 2:4:5-C₆H₂Cl₃·NO₂ treated with KOH and EtOH gives a mixture of 2:5-dichloro-4-nitrophenetole, m.p. 96°, reduced to the phenetidine (A., 1929, 552), and 4:5-dichloro-2-nitrophenetole, m.p. 65°, reduced to 4:5-dichloro-*o*-phenetidine [hydrochloride, m.p. 221° (decomp.)]; picrate, m.p. 139°; Ac derivative, m.p. 120°; Bz derivative, m.p. 120°; 3:4-dichloro-6-ethoxydiphenylcarbamide, m.p. 140°. If MeOH is used instead of EtOH, only 2:5-dichloro-4-nitrophenetole is formed.

E. W. W.

Action of sulphur on amines. III. Recognition of trithio-*o*-toluidine as 2:2'-diamino-5:5'-ditolyl trisulphide. H. H. HODGSON and H. V. FRANCE (J.C.S., 1932, 1987—1988; cf. *ibid.*, 1914, 105, 952).—5-Bromo-2-nitrotoluene, when boiled with aq. Na₂S₂ and then oxidised with air, gives 2:2'-diamino-5:5'-ditolyl disulphide, m.p. 112° [previously (*ibid.*, 1912, 101, 1693) called dithio-*o*-toluidine], and the trisulphide (previously called trithio-*o*-toluidine). The position of the S atom is confirmed by the ready coupling of the diazotised compounds with β-naphthol.

R. S. C.

Dihydrotetene. G. KOMPPA and H. P. FOGELBERG (J. Amer. Chem. Soc., 1932, 54, 2900—2908).—Dihydrotetene (I) and H₂SO₄ (*d* 1.84) at 66—68° give 69.1% of a monosulphonic acid (designated the A-acid) (+2H₂O), m.p. 147—148° [Me, m.p. 98—99°, and Et, m.p. 72.5—73.5°, esters; Na (+H₂O), K (+H₂O), NH₄, Ba, Ca, and Cu (+2H₂O) salts; chloride, m.p. 91—92° (in some cases a modification, m.p. 82—83°, was obtained); amide, m.p. 193—194°; anilide, m.p. 112—114°]. Reduction of the chloride gives A-dihydrotetenesulphinic acid, m.p. 123—130° (Na salt), and then A-thioldihydrotetene, m.p. 170—172°. Fusion of the acid with alkali gives A-retenol (A., 1931, 226). Sulphonation of (I) at 200° gives B-dihydrotetenesulphonic acid (+2H₂O), m.p. 106—107° [K (+H₂O), NH₄, Ba (+H₂O), Ca (+6H₂O), and Cu (+5.5H₂O) salts; Me, m.p. 85—86°, and Et, m.p. 78—79°, esters; chloride, m.p. 112—113°; amide, m.p. 189—190°; anilide, m.p. 196—197°], converted by alkali fusion into B-retenol (*loc. cit.*). Oxidation of the above Et esters gives Et A- (II), m.p. 183—184°, and B- (III), m.p. 169—171°, retenequinonesulphonates, also formed by oxidation of Et A-, m.p. 137.5—138.5°, and B-, m.p. 114—115°, retenesulphonates. A-Retene-sulphonyl chloride, m.p. 135—136°; A-methoxyretene, m.p. 147—148°; A-, m.p. 177—178°, and B-, m.p. 112°, benzoyloxyretenes are described. (II) boiled with 50% KOH for 3 hr. gives a K ketoretene-sulphonate and a product, which when fused with KOH affords a methylisopropylidiphenylmonocarboxylic acid, m.p. 160°. (III) and 50% KOH give a ketoretene, m.p. 88—89°, reduced to the corresponding alcohol, m.p. 132—133°. A small amount of a hydrocarbon, C₂₄H₂₀, m.p. 297—298°, occurs with retene in the highest boiling fractions of pine tar.

C. J. W. (b)

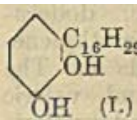
Nitrosites and nitrosates. II. L. MONTI and D. DINELLI (Gazzetta, 1932, 62, 368—376; cf. A., 1931, 194).—Nitrosites of isosafrole and anethole heated in CO₂ or N₂ evolve N₂ and NO, 37—38.8% of the total N being evolved. cycloHexene treated in AcOH with nitrous fumes (cf. A., 1921, i, 553) gives a stable nitrosite, m.p. 150—151°, and nitrosate, m.p. 153° (piperidine derivative, C₁₁H₂₀ON₂, m.p. 120°), which at 140—160° evolve respectively 10% and 38% of their total N. The stability of the above compounds is compared.

E. W. W.

Diphenyl and its derivatives. IX. Dipicric acid and its [attempted] optical resolution. L. MASCARELLI and B. VISINTIN (Gazzetta, 1932, 62, 358—368).—Dipicric acid [2:4:6:2':4':6'-hexanitro-3:3'-diphenol (A., 1917, i, 558); K₂ salt, m.p. 106°, resolidifies at 112°, decomp. 280°, explodes at 320°; (NH₄)₂ salt, decomp. 275—305°] does not give cryst. salts with alkaloids. 1-Menthylamine gives a neutral dipicrate, decomp. 258—259°, [α]_D²⁰ +1.23°, which cannot be resolved.

E. W. W.

Constitution of laccol. G. BERTRAND and G. BROOKS (Compt. rend., 1932, 195, 405—408).—Catalytic hydrogenation (Pt-black) of laccol (I), C₂₂H₃₄O₂ (lit. C₂₃H₃₆O₂), m.p. 23°, gives tetrahydro-laccol [Ac₂, m.p. 57.6° (corr.), and dipropionyl derivatives]. (I) has the annexed formula.



dipropionyl derivatives]. (I) has the annexed formula.

R. S. C.

Dehydrogenation of cholesterol and of cholic acid. H. RAUDNITZ, F. PETRU, and F. HAUROWITZ (Z. physiol. Chem., 1932, 209, 103—109).—Distillation of cholesterol with Zn dust followed by fractionation of the products afforded $C_{10}H_8$ and chrysene. Similar treatment of cholic acid gave hydrocarbons, $(C-H)_x$, m.p. 229—230° and C_{21} or ${}_{22}H_{14}$ (golden-yellow), m.p. 277°.

J. H. B.

Constitution of cholesterol. Bromo-derivatives of cholesterol. F. PIRRONE (L'Ind. Chimica, 1932, 7, 131—145; cf. this vol., 54).—Cholesterol dibromide (I), m.p. 106—107°, prepared by Windaus' method (A., 1906, i, 174), is shown, by the action of reducing and dehalogenating agents and of substituting agents, to be neither the 6:6- nor the 7:7-compound, but probably a Br_2 -additive product in the $\Delta^{6:7}$ -position. A dibromodihydrodicholesteryl obtained by the method of Cloez (A., 1897, i, 406) is shown similarly to be probably 7:7'-dibromo-6:6'-dihydrodicholesteryl. The Br-derivative, m.p. 74—76°, containing about 9% Br and already obtained by various authors, appears to be 7-bromo-6:6'-dihydrodicholesteryl. A second dibromodihydrodicholesteryl, m.p. 98—100°, isomeric with that obtained by the Cloez method from (I), was observed, but attempts to prepare from this an isomeric of cholesterol always yielded the original compound. The action of HCN on (I) yields dicyanocholesterol, m.p. 102—103°. Study of the action of Cu, Zn, KOH, etc. on the Br-derivatives confirms the presence of the double indene linking in the 6:7-position of nucleus II of cholesterol.

T. H. P.

Neoergosterol. H. H. INHOFFEN (Annalen, 1932, 497, 130—139).—Neoergosterol (I), $C_{27}H_{40}O$ (cf. Windaus and Borgeaud, A., 1928, 425; Bonstedt, A., 1930, 84) [3:5-dinitrobenzoate, m.p. 218—220° (corr.), $[\alpha]_D^{25}$ —13° in $CHCl_3$; acetate dibromide, m.p. 179—181° (corr.)], is oxidised by HNO_3 (d 1.4) to 1:2:3:4- $C_6H_2(CO_2H)_4$, whilst ergopinacol (*loc. cit.*) is similarly oxidised to toluenetetracarboxylic acid (II) (this vol., 611). When the pinacol is heated in decahydronaphthalene (or Ac_2O), CH_4 is eliminated and (I) (or its acetate) results; the formation of (I) from ergosterol (III) involves the loss of 1 C. Ozonolysis of (I) gives α -methylisovaleraldehyde, showing that the change (III) \rightarrow (I) does not involve the unsaturated side-chain. The production of (II) from (III) (*loc. cit.*) appears to involve migration of Me. H. B.

Choleic acids. H. SOBOTKA and A. GOLDBERG (Biochem. J., 1932, 26, 555—568).—Choleic acids have been synthesised from deoxycholic acid with aliphatic acids and their co-ordinative valencies established by the determination of their acid equivs. and by the study of their m.p. and thawing point diagrams. The co-ordination no. of succinic acid is 2, of adipic acid 3, of pimelic, suberic, azelaic, sebacic, and enneamethylenedicarboxylic acids 4, and that of decamethylenedicarboxylic, brassylic, dodecamethylenedicarboxylic, thapsic, hexadecamethylene- and octadecamethylene-dicarboxylic acids 6. The co-ordination no. of isomeric butyric and valeric acids is 2 with the exception of *n*-butyric and *n*-valeric acids, which display a max. co-ordinative valency of 4. Crotonic acid combines with deoxycholic acid in

the mol. ratio of 3:1. Butyric acid and Et butyrate form two choleic acids each depending on the method of synthesis with mol. ratios 4:1 and 2:1. A second EtOH-choleic acid of mol. ratio 2:1 is formed at elevated temp.

S. S. Z.

Choleic acids. IV. Keto-enol tautomerism and co-ordination compounds. H. SOBOTKA and J. KAHN (Biochem. J., 1932, 26, 898—904).—Co-ordination compounds consisting of 3 mols. of deoxycholic acid and 1 mol. of a tautomeric substance (benzoylacetone, Et acetoacetate, acetylacetone, or anthrone) were prepared and analysed. Whilst the tautomeric compounds in the free state contain varying proportions of keto-form, they are completely enolised when bound in choleic acids. Anthrone-tetracholeic acid contains the acholic component in the keto-form. There is evidence of rapid and complete mol. dissociation when these choleic acids are dissolved.

S. S. Z.

Mechanism of chemical reactions. III. Hydrogenation and specific hydrogenation with combined hydrogen. K. KINDLER and W. PESCHKE (Annalen, 1932, 497, 193—200).—Cinnamic acid is reduced by Pd-black and boiling tetrahydronaphthalene (I) to $CH_2Ph\cdot CH_2\cdot CO_2H$; *p*- $C_6H_4Cl\cdot CH_2\cdot CH_2\cdot CO_2H$, $CH_2Ph\cdot CH_2\cdot CN$, and furylpropionic acid are similarly obtained from *p*-chlorocinnamic acid, cinnamionitrile, and furylacrylic acid, respectively. Reduction (H_2 , Pd-black, EtOH) of β -phenylethylidene- β -phenylethylamine gives di-(β -phenylethyl)amine (II); the use of Pd-black and (I) affords PhEt (about 60%), also formed similarly from (II) and $CH_2Ph\cdot CH_2\cdot NH_2$. Benzylidene- β -phenylethylamine and *N*-benzyl- β -phenylethylamine are reduced by Pd-black and (I) to PhEt and PhMe, whilst $CH_2Ph\cdot NH_2$ and $N(CH_2Ph)_3$ give PhMe. H. B.

Derivatives of 2-methylantracene prepared by means of oxalyl chloride. D. BUTTESCU (Bul. Chim. Soc. Romane Stiin., 1929, 31, 103—107)—2-Methylantracene-10-carboxylic acid, m.p. 197°, 9-chloro-2-methylantracene-10-carboxylic acid, yellow, m.p. 198° (I), and 9:10-dichloro-2-methylantracene, golden-yellow, m.p. 211° (II), are formed when a mixture of 2-methylantracene, $AlCl_3$, and CS_2 is run into a mixture of $H_2C_2O_4$ and PCl_5 which has been kept in ice for 5—6 days. (I) and (II) are oxidised by CrO_3 in AcOH to 2-methylantraquinone.

Constitution of Stadeler's tyrosinesulphonic acid. F. R. CONKLIN and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 2914—2917).—Sulphonation of tyrosine with 6 mols. of conc. H_2SO_4 at 95—100° gives 90% of the 3-sulphonic acid, chars and decomp. rapidly above 280° (cf. Stadeler, Annalen, 1860, 116, 91) (amorphous Ba, Na, and K salts), which does not react with $KCNO$ or $PhNCO$. The structure of the acid is established by the formation of 3:5-dinitrotyrosine by the action of HNO_3 . Deamination of the acid by MeI and KOH causes degradation of the greater part; a small quantity of the *K* salt of 4-hydroxy-3-sulphocinnamic acid was isolated.

C. J. W. (b)

Preparation of benzoylacetate ester and its homologues. J. B. DORSCH and S. M. McELVAIN

J. Amer. Chem. Soc., 1932, 54, 2960—2964).— α -Benzoylalkyl cyanides are prepared by heating 1 mol. each of BzOEt and NaOEt at 80° until the mixture is homogeneous, slowly adding 1.25 mols. of the alkyl cyanide during 2 hr., and then heating at 110—120° (Me or Et) or 140—160° (Pr or Bu) for 10 hr. Benzoylacetonitrile, α -benzoylpropionitrile, b.p. 128—130°/3 mm., α -benzoylbutyronitrile, b.p. 134—135°/3 mm., and α -benzoylvaleronitrile, b.p. 139—140°/3 mm., are thus prepared in approx. 60% yield. The cyanides with EtOH-HCl give the corresponding imino-ether hydrochlorides, hydrolysed to the corresponding esters in 64—74% yield. Hydrolysis of the imino-ethers with EtOH containing the theoretical amount of H₂O gives (except with CH₃Bz-CN) considerable quantities of the amides; α -benzoyl-propionamide, m.p. 145—146°, -butyramide, m.p. 148—149°, and -valeramide, m.p. 157—158°, are new. Details are given of the direct condensation of BzOEt and EtOAc to CH₃Bz-CO₂Et in 37% yield; EtCO₂Et and PrCO₂Et give 19 and 4%, respectively, of the corresponding keto-ester. C. J. W. (b)

Mechanism of the condensation of phthalic anhydride and glycerol. J. SAVARD and S. DINER (Bull. Soc. chim., 1932, [iv], 51, 597—615).—The above substances react rapidly at 160° to give glyceryl H₂ diphthalate. This with excess of glycerol forms a neutral diglyceryl diphthalate, with excess of phthalic anhydride gives glyceryl H₃ triphthalate, and with neither reagent in excess undergoes internal esterification. Velocity coeffs. valid for the first 50 hr. are given for the three last reactions. A. A. L.

Stereochemistry of diphenyl. XXIII. Optically active 2'-nitro-2:5-dimethoxydiphenyl-6'-carboxylic acid and the mutarotation of its salts. H. C. YUAN and R. ADAMS. XXIV. Preparation and properties of 2:2'-difluoro-6:6'-dimethoxydiphenyl-3:3'-dicarboxylic acid. B. C. BECKER and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 2966—2973, 2973—2982).—XXIII. 1-Iodo-2:5-dimethoxybenzene, Me 2-bromo-3-nitrobenzoate, and Cu at 260—300° give (after hydrolysis) a little 2'-nitro-2:5-dimethoxydiphenyl-6'-carboxylic acid, m.p. 141—142°, which gives *brucine* (+H₂O), m.p. 158—160°, $[\alpha]_D^{25}$ -167° \rightarrow +3.2° in CHCl₃, *cinchonine*, m.p. 198—204°, $[\alpha]_D^{25}$ -135° \rightarrow +57° in CHCl₃, and *strychnine*, m.p. 220—223°, $[\alpha]_D^{25}$ -23.1° in CHCl₃, salts. Decomp. of the *brucine* salt with dil. HCl at 0° affords the *l*-acid, m.p. 141—142°, which racemises extremely readily (the half-val. period is 10.8 min. at 28° and 274 min. at 0°). The above final rotations are identical with those of equiv. quantities of the *dl*-acid and the alkaloid. The Na salt of the *l*-acid racemises less readily in H₂O (but more readily in EtOH) than the acid in org. solvents.

XXIV. 2-Iodo-3-fluoroanisole (prep. of intermediates described) and Cu at 180—200° give 2:2'-difluoro-6:6'-dimethoxydiphenyl, m.p. 135—136°, which with AcCl and AlCl₃ in CS₂ affords the 3:3'-Ac₂ derivative, m.p. 138—139.5°, oxidised by NaOCl to 2:2'-difluoro-6:6'-dimethoxydiphenyl-3:3'-dicarboxylic acid, m.p. 285—289° (decomp.) (*brucine*, *morphine*, *quinine*, *strychnine*, and *cinchonine* salts, none of which shows mutarotation or gives an optically active acid

on decomp.). 3-Fluoroanisole, b.p. 158°/743 mm., from *m*-anisidine, could not be converted into the 2-NO₂-derivative by sulphonation and nitration. 6-Methoxy-*m*-4-xylidine and Br in AcOH give the *hydrobromide*, m.p. 187° (decomp.), of *o*-bromo-6-methoxy-*m*-4-xylidine (*Ac* derivative, m.p. 147—148°), convertible into 5-bromo-4-fluoro-6-methoxy-*m*-xylene, b.p. 125°/15 mm., which does not form a Grignard reagent, does not undergo the Ullmann reaction, and could not be nitrated. 4-Fluoro-6-nitro-*m*-xylene, b.p. 133°/30 mm., 234°/750 mm., from the nitroxylidine, is reduced to the 6-NH₂-derivative, m.p. 57—58° (*Ac* derivative, m.p. 133—134°), which is brominated to 5-bromo-6-fluoro-*m*-4-xylidine (I), m.p. 56° (*Ac* derivative, m.p. 170—171°; *hydrobromide*, decomp. 220°), and is nitrated to 6-fluoro-2- (II), m.p. 88—89° (*Ac* derivative, m.p. 148—149°), and 6-fluoro-5-, m.p. 72—74° (*Ac* derivative, m.p. 193—194°), -nitro-*m*-4-xylidines. Nitration of (I) gives 5-bromo-6-fluoro-2-nitro-*m*-4-xylidine, m.p. 105.5—106°, also prepared by brominating (II), convertible into 4-chloro-5-bromo-6-fluoro-2-nitro-*m*-xylene, m.p. 113.5—114°. 6-Fluoro-*m*-4-xylene, m.p. 44—45°, and its 5-Br-derivative, m.p. 75—76°, are described.

C. J. W. (b)

Quinovic acid. IV. H. WIELAND and K. KRAUS (Annalen, 1932, 497, 140—159; cf. A., 1931, 1158).—Pyroquinovic acid (I) is converted by ZnCl₂ in AcOH at 130° into a *lactone*, C₂₉H₄₄O₂, m.p. 262°, decomp. slightly at 280°, also formed similarly from pyroanhydroquinovic acid, m.p. 188°. The bromohydroxylactone, C₂₉H₄₅O₃Br, previously obtained (A., 1930, 600) from (I), is reduced by Zn dust and AcOH to (I) and oxidised by CrO₃ in cold AcOH to a *bromo-ketolactone* (II), C₂₉H₄₃O₃Br, m.p. 172° (decomp.), and a *bromolactonedicarboxylic acid* (III), C₂₉H₄₃O₆Br, m.p. 205° (decomp.) [also produced by further oxidation of (II)]. Oxidation in more conc. solution gives (III) and a neutral compound, C₂₉H₃₉O₆Br or C₂₅H₃₅O₄Br, m.p. 188°, which is reduced by Zn dust and AcOH to a neutral substance, C₂₉H₄₂O₅ or C₂₅H₃₆O₄, or an acid, C₂₉H₄₂O₅ or C₂₅H₃₈O₄, m.p. 255—258° (with darkening), or an acid, C₂₉H₄₄O₆ or C₂₅H₄₀O₅, m.p. 256—258°. Boiling pyridine converts (II) into a doubly-unsaturated *keto-acid*, C₂₉H₄₂O₃, dimorphous, m.p. 193° (sinters at 187°), whilst (III) similarly gives a *tricarboxylic acid*, C₂₉H₄₂O₆, m.p. 288° (decomp.) (*Me*₃ ester, m.p. 146—147°), which passes at 300°/12 mm. into (mainly) a *cycloketocarboxylic acid* (IV), C₂₈H₄₀O₃ (+COMe₂), m.p. 178°, (+ $\frac{1}{3}$ AcOH), m.p. 165° (decomp.) (*Me* ester, m.p. 161°), a *ketolactone*, C₂₈H₄₀O₃, m.p. 254—256°, and a *dilactone*, C₂₈H₄₂O₄, decomp. about 268°. (IV) is probably a *cyclopentanone* derivative and is oxidised (CrO₃-AcOH) to a *ketolactonemonocarboxylic acid* (V), C₂₈H₄₀O₅, decomp. 293° [*Me* ester, m.p. 213° (previous sintering)], prob-

ably thus $>\text{CH}\cdot\text{CO}\cdot\rightarrow>\text{CO}\cdot\text{CO}_2\text{H}$; by-products are a *lactone*, C₂₈H₃₈O₄, m.p. 232° (decomp.) (passes at 280° into a neutral substance, C₂₇H₃₈O₂, m.p. 193°), and a compound, C₂₅H₃₄O₄, m.p. 286—288° (decomp.). Clemmensen reduction of (V) gives a *lactonic acid*, C₂₈H₄₂O₄, m.p. 280—286° (decomp.), whilst thermal decomp. affords a *lactone*, C₂₇H₄₀O₃, m.p. 242°. (V) and Br in AcOH give a *Br₂*-derivative, m.p. 267°

(decomp.), reduced by Zn dust and AcOH to (V), decomp. 307° , converted by pyridine into a *dibromoketolactone*, $C_{27}H_{36}O_3Br_2$, m.p. 266° (decomp.), and transformed by MeOH-KOH into an unsaturated lactone, $C_{27}H_{34}O_3$, m.p. 278° (decomp.) (darkens at 258°) [*Br*-derivative, m.p. 238° (decomp.)]. This lactone is oxidised (CrO_3 -AcOH) to a compound, m.p. 232 – 233° . Dehydrogenation of (I) with Se at 200 – 350° gives a hydrocarbon, $C_{30}H_{16}$, m.p. 280 – 285° . Possible structures for (I) and quinovic acid are suggested. H. B.

Salts of phenolphthalein. W. M. DEHN (J. Amer. Chem. Soc., 1932, 54, 2947–2951).—Additive compounds (salts) (+2 or more mols. of H_2O) of phenolphthalein (I) and bases are prepared. Most of the hydrated salts are colourless but become coloured by loss of H_2O , which is effected by heat, pressure, friction, or certain solvents; such loss of H_2O is probably a dehydration of the carbinol to the quinonoid form. The colours of dehydrated salts, containing either chromogenic or non-chromogenic metals, differ widely. The probable cause of the colour of salts of (I) is the quinonoid chromophore. Hydration and dehydration are important influences effecting changes in colour. Isomerisation, neutralisation, addition, hydrolysis, and ionisation are concerned but precede, or are incidental to, the transformation of colourless carbinol forms into the coloured quinonoid form. (I) and NH_3 in COMeEt give the colourless NH_4 salt [(I). NH_4OH]; KOH in COMeEt gives the colourless K salt, whilst in 95% EtOH, there results the red K salt (+ H_2O). The red Na_2 , the red and colourless Ca, and the *piperidine* salts are also prepared. Analyses are given of the additive compounds of 2 mols. of (I) with 1 mol. of $Ba(OH)_2$ (+4 H_2O); $Sn(OH)_2$ (?) (+4 H_2O); $Cu(OH)_2$ (+3 H_2O); $Co(OH)_2$ (+3 H_2O); $Mn(OH)_2$ (+3 H_2O); $Cd(OH)_2$ (+3 H_2O), and $Zn(OH)_2$ (+3 H_2O). C. J. W. (b)

Reactions between hexamethylenetetramine and phenolic compounds. I. Preparation of 3- and 5-aldehydosalicyclic acids. J. C. DUFF and E. J. BILLS (J.C.S., 1932, 1987).—Salicylic acid and hexamethylenetetramine in boiling H_2O give 3- and 5-aldehydosalicyclic acids (improved method of separation). *m*- and *p*-Hydroxybenzoic acids give resins. R. S. C.

Reimer-Tiemann reaction. R. N. SEN and S. K. RAY (J. Indian Chem. Soc., 1932, 9, 173–179).—The use of a 1 : 3 mixture of $CHCl_3$ (CCl_4) and EtOH in the Reimer-Tiemann reaction increases the yield of aldehyde (acid). When the Na aryloxide is insol. addition of a little pyridine is often advantageous. Aq. pyridine can replace aq. NaOH in the reaction between PhOH and $CHCl_3$; *o*-OH- C_6H_4 -CHO (10% yield) is the sole product. The following preps. are reported: *o*- and *p*-OH- C_6H_4 -CHO from PhOH; *o*- and *p*-OH- C_6H_4 -CO $_2H$ from PhOH and CCl_4 ; 3- and 5-nitrosalicylaldehydes from *o*- and *p*-NO $_2$ - C_6H_4 -OH, respectively; 2-nitro-4-hydroxybenzaldehyde from *m*-NO $_2$ - C_6H_4 -OH; 3-bromo-2- and -4-hydroxybenzaldehyde (*semicarbazone*, m.p. 195 – 196°) from *o*- C_6H_4 Br-OH; 5-bromosalicylaldehyde (*semicarbazone*, decomp. 297°) from *p*- C_6H_4 Br-OH;

3- and 5-bromosalicyclic acids from *o*- and *p*- C_6H_4 Br-OH, respectively; 5-chloro-salicylaldehyde and -salicyclic acid from *p*- C_6H_4 Cl-OH; 6-aldehydophenol-2-sulphonic acid, not melted at 250° , from *o*-OH- C_6H_4 -SO $_3H$; 2-hydroxy-5-aldehydocinnamic acid [*Ag* salt; *phenylhydrazone*, m.p. 236° (decomp.)]; *semicarbazone*, m.p. 275°] (converted by warm conc. H_2SO_4 into 6-aldehydocoumarin) from *o*-coumaric acid; 2-hydroxy-5-carboxycinnamic acid, decomp. 186° and then m.p. 210° (*Ag* salt), from *o*-coumaric acid and CCl_4 ; 2-, b.p. 233° (*semicarbazone*, m.p. 242°), and 4-, m.p. 108 – 110° (*semicarbazone*, m.p. 191°), -hydroxy-6-methyl-3-isopropylbenzaldehydes from thymol; 5- and 7-aldehydo-8-hydroxyquinolines, both m.p. above 250° , from 8-hydroxyquinoline; 2-hydroxy-1-aldehydoanthraquinone, m.p. above 300° , from 2-hydroxyanthraquinone; thiosalicyclic acid from PhSH and CCl_4 . Reaction is inhibited by NO $_2$, Cl, Br, and SO $_3H$ groups. H. B.

Suppression of the ketonic function and theories held to interpret this phenomenon. R. CORNUBERT and G. SARKIS (Compt. rend., 1932, 195, 252–254).—The belief that steric effects suppress the ketonic reactions of $\alpha\alpha'$ -tetra-substituted cyclohexanones is shown to have little foundation. 2 : 2 : 6 : 6-Tetra-alkylcyclohexanones usually afford no oximes or Grignard compounds in Et $_2$ O, but react easily in Bu $_2$ O. They are reduced by Na in EtOH to sec. alcohols. 2 : 2 : 6 : 6-Tetramethylcyclohexanone slowly affords an oxime but no semicarbazone, whereas 2 : 2 : 6 : 6-dibenzylcyclohexanone affords a semicarbazone but no oxime. 2-Methylcyclohexanone immediately affords a H sulphite compound, whereas the 2 : 6-Me $_2$ derivative does not. J. L. D.

Phenacyl esters of oleic acid series. W. KIMURA (J. Soc. Chem. Ind. Japan, 1932, 35, 221–224B).—The following are prepared in almost quant. yield by interaction of the Na salt of the acid with the appropriate phenacyl bromide in aq. EtOH: *p*-phenylphenacyl oleate, m.p. 61° , erucate, m.p. 76° , and cetoleate, m.p. 72.5° ; *p*-chlorophenacyl oleate, m.p. 40° , erucate, m.p. 56° , and cetoleate, m.p. 54.5° ; and *p*-bromophenacyl oleate, m.p. 46° , erucate, m.p. 62.5° , and cetoleate, m.p. 60.5° . H. A. P.

Transposition of benzoyl group in phenols. A. PIERONI (Gazzetta, 1932, 62, 387–393).—By the action of BzCl and AlCl $_3$ the following are obtained: from *p*-chlorophenol (in CS $_2$), *p*-chlorophenyl benzoate and 5-chloro-2-hydroxybenzophenone; from PhOH (in CS $_2$), 4-hydroxybenzophenone and 4-benzoyloxybenzophenone, m.p. 112.5° ; from 4-hydroxybenzophenone (at 100 – 150°), 4-hydroxy-3-benzoylbenzophenone, m.p. 105° ; from resorcinol (in CS $_2$), its dibenzoate and 4-Bz derivative; from resorcinol dibenzoate (at 100 – 150°), 2 : 4 : 6-tribenzoylresorcinol, also obtained, with 6-benzoylresorcinol, when BzCl is omitted from the reaction mixture. E. W. W.

Condensation of benzotrichloride with phenols. R. N. SEN and S. K. RAY (J. Indian Chem. Soc., 1932, 9, 181–184).—CPhCl $_3$ (I) and PhOH in aq. EtOH-NaOH at 100° (bath) give about 5% of *o*-hydroxybenzophenone. α -C $_{10}$ H $_7$ -OH and (I) similarly give 16% of the 2-Bz, m.p. 114° , and 4-Bz, m.p. 162 – 164°

(lit. 164—165°), derivatives, whilst β -C₁₀H₇·OH affords 20% of its 1-Bz derivative, m.p. 174°. *o*-Coumaric acid and (I) give 30% of 2-hydroxy-5-benzoyl-cinnamic acid (?), m.p. 188° [Ag salt; phenylhydrazine, m.p. 120° (decomp.)]. Nitrophenols do not react with (I). H. B.

Isomeric deoxybenzanisoin. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1932, 54, 3012—3013).—Further details (cf. A., 1931, 732) are given for the prep. of anisyl benzyl and Ph *p*-methoxybenzyl ketones and the oximes of the latter, in view of Jenkins' criticism (this vol., 516). C. J. W. (b)

Constitution of benzils. A. BURAWOY (Ber., 1932, 65, [B], 1068—1071).—The introduction of positive groups has a similar chemical and optical effect on benzils (dicarbonyl compounds) and on aldehydes and ketones (monocarbonyl compounds). The existence of two forms of 4:4'-dibenzylxy-, 2:2'-dimethoxy-, and 4:4'-dihydroxy-benzil can be explained by the assumption of an isomerism between ketonic and peroxide forms, but the hypothesis is arbitrary (cf. Schönberg and Bleyberg, A., 1923, i, 116; Brass and others, A., 1930, 1589). H. W.

Optical method for the study of reversible organic oxidation-reduction systems. I. Benzoquinones. W. H. HUNTER and D. E. KVALNES (J. Amer. Chem. Soc., 1932, 54, 2869—2881).—The oxidising strength of a series of quinol-benzoquinone systems is determined by using an optically active system, viz., 2:5-dimethylquinol- and *p*-xyloquinone-*d*-camphorsulphones, as a standard. *Quinol-d-camphorsulphone* (2-*d*-camphorsulphonyl-quinol), m.p. 159—160°, [α]_D²⁵ +46.55° in C₆H₆ (diacetate, m.p. 119—122°, [α]_D²⁵ +17.5° in EtOH); 2:5-dichloroquinol-*d*-camphorsulphone, m.p. 169—173°, [α]_D²⁵ +29.99° in C₆H₆; 2:6-dichloroquinol-*d*-camphorsulphone, m.p. 104—106°, [α]_D²⁵ +35.4° in C₆H₆; 2:5-dibromoquinol-*d*-camphorsulphone, m.p. 172—173°, [α]_D²⁵ +19.6° in C₆H₆; 2:6-dibromoquinol-*d*-camphorsulphone, m.p. 108—112°, [α]_D²⁵ +37.9° in C₆H₆, and 2:5-dimethylquinol-*d*-camphorsulphone, m.p. 176—177°, [α]_D²⁵ +24.22° in C₆H₆ (diacetate, m.p. 103—106°, [α]_D²⁵ +21.7° in C₆H₆, are prepared by Hinsberg's method (A., 1896, i, 685). *p*-Benzoquinone-*d*-camphorsulphone, m.p. 135—136°, [α]_D²⁵ +305° in C₆H₆ (prepared by oxidation of the quinol with PbO₂ or Ag₂O in Et₂O); *p*-xyloquinone-*d*-camphorsulphone, m.p. 148—151°, [α]_D²⁵ +223° in C₆H₆; α -naphthoquinone-*d*-camphorsulphone, m.p. 144—148°, [α]_D²⁵ +237.3° in C₆H₆, are described. The optically active quinols show no change in rotation even after several days; the rotations of the active quinones fall slowly, but the error thereby introduced is small and does not affect the comparative results, since the observed equilibrium points, using various quinones, are reached in approx. the same length of time. The following vals. are the equilibrium consts., conversions, and benzoquinone equivs. (mols. of benzoquinone necessary to give the same conversion as is given by 1 mol. of the quinone in question), respectively: *p*-xyloquinone, 0.00059, 2.4, 0.03; toluquinone, 0.00437, 6.2, 0.10; benzoquinone, 0.114, 25.2, 1.00; chloro-, 0.669, 45.0, 3.7; bromo-, 0.853, 48.0, 4.4; 2:6-di-

chloro-, 1.09, 51.2, 5.2; 2:6-dibromo-, 1.43, 54.5, 6.3; tetrachloro-, 1.27, 53.0, 5.8; tetrabromo-, 1.69, 56.5, 7.0; 2:5-dichloro-, 1.73, 56.8, 7.1; 2:5-dibromo-benzoquinone, 9.04, 75.0, 20.5. Me lowers and a halogen group raises the conversion val. of the parent compound; a Me group is more effective than a halogen atom. The successive introduction of like groups causes the conversion vals. to change consistently in the same direction, the first group being the most effective. The position of the groups is also of importance. The results are compared with electrochemical data. C. J. W. (b)

Laboratory and technical preparation of chloranil. R. SCHULOFF and R. POLLAK (Chem.-Ztg., 1932, 56, 569—570).—Chloranil can be obtained from pentachlorophenol by methods and with yields as follows: with Cl₂ in ClSO₃H at 80° (90%); with Cl₂ in ClSO₃H and 10% oleum at 80° (10%), or at 120° (90%); with ClSO₃H and 65% oleum at 100° (almost 100%); with Cl₂ in 10% oleum alone (small); with Cl₂ in 65% oleum at 120° (60%); with 10—65% oleum and Cl₂ in presence of FeCl₃ or NaCl at 120° (50—75%); or with 10% oleum and HCl at 120°, followed by Cl₂ at 120—130° (90%). Trichlorophenol, 10% oleum, FeCl₃, and Cl₂ followed by ClSO₃H give 90% yield of chloranil, or followed by HCl and SO₃ a 75% yield. Benzoquinone dissolved in conc. HCl and treated with Cl₂ at room temp. gives tetrachloroquinol, but at the b.p. also chloranil, which is obtained almost quantitatively when the former is heated with conc. HCl and Cl₂. Benzoquinone or quinol in conc. HCl boiled under reflux with Cl₂ gives chloranil almost quantitatively. E. W. W.

Sulphonation of synthetic anthraquinone. Direct preparation of anthraquinone-2-sulphonic acid from *o*-benzoylbenzoic acid. A. BERETTA and M. GALLOTTI (Annali Chim. Appl., 1932, 22, 272—290).—*o*-Benzoylbenzoic acid dissolved in oleum (25% SO₃) and sulphonated with further oleum (67% SO₃) gives 32% of anthraquinone-2-sulphonic acid, 18% of a mixture of anthraquinone-2:6- and 2:7-disulphonic acids, and 50% of anthraquinone. These as isolated are sufficiently pure for most technical uses. E. W. W.

Basic character of α -methoxyanthraquinones. K. C. ROBERTS (J.C.S., 1932, 1982—1984).—1:2-Dimethoxyanthraquinone (I) gives a stannichloride, B₂SnCl₄, volatile at 150° in vac. The 1:4-isomeride (II) gives a red hydrochloride, a chloroplatinate, B₂H₂PtCl₆, retaining H₂O at 110° in vac., a chlorostannate, B₂H₂SnCl₆, and a diperchlorate, but a stannichloride, B₂SnCl₄. The 1:5-isomeride (III) gives similar salts, but the chloroplatinate is B₂H₂PtCl₆·8H₂O (after drying at room temp.). The 1:8-isomeride (IV) gives a chlorostannate, B₂H₂SnCl₆, chloroplatinate, B₂H₂PtCl₆·12H₂O (after drying in vac. at 110° over P₂O₅), and a perchlorate, B₂HClO₄ (also existing as trihydrate). Titration indicates the following order of basicity: (IV) > (II) > (III) > 1-methoxythioxanthone > 1-methoxyxanthone > (I), 1:3-dimethoxy- and 1-methoxy-anthraquinone. The salts described above are highly coloured and are assigned co-ordination formulæ. R. S. C.

Manufacture of 1:2:5:6-diphthaloylnaphthalene and halogen-substitution products thereof. I. G. FARBENIND. A.-G.—See B., 1932, 672.

Manufacture of condensation products of the anthraquinone series [amino-1:4-dianthraquinonylaminoanthraquinones]. A. CARPMAEL. From I. G. FARBENIND. A.-G.—See B., 1932, 672.

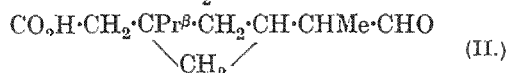
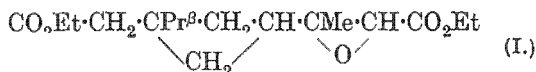
Strophanthin. XXVI. Dehydrogenation of strophanthidin. W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1932, 97, 57—61; cf. this vol., 748).—The hydrocarbon $C_{18}H_{16}$ (cf. A., 1931, 606) is shown to have the formula $C_{16}H_{14}$, and m.p. 125—126° [picrate, m.p. 138—140°; quinone, m.p. 208—210° (quinoxaline derivative, m.p. 187—188°)]. It is not identical with the known dimethylphenanthrenes.

A. A. L.

Determination of santonin. O. FERNANDEZ and L. SOCIAS (Anal. Fis. Quím., 1932, 30, 477—478).—To a stirred EtOH solution (0.5%) of santonin is added a 1% solution of 2:4-dinitrophenylhydrazine in 10% H_2SO_4 . After 48 hr. (in the dark) the pptd. *santonin-2:4-dinitrophenylhydrazone*, m.p. 267—268° (decomp.), is collected, washed with 45% EtOH, and dried at 106°.

H. F. G.

Partial synthesis of thujone (tanacetone). L. RUZICKA and D. R. KOOLHAAS (Helv. Chim. Acta, 1932, 15, 944—948).—Et α -thujaketone (from the Ag salt), $CH_2Cl \cdot CO_2Et$, and NaOEt give *Et, thujaketoglycid-dicarboxylate* (I), b.p. 129—139°/0.2 mm., which with cold aq. 1.48*N*-KOH (not NaOH-EtOH) yields a neutral oil, b.p. 105—110°/0.1 mm. and *homothujacamporphoraldehydecaboxylic acid* (II), b.p. 138—146°/0.16 mm. (semicarbazone, m.p. 178°), oxidised by cold,



alkaline $KMnO_4$ to the corresponding dicarboxylic acid, a resin. The Ag salt thereof with EtI gives *Et, homothujacamporate*, b.p. 103—107°/0.1 mm., which, when heated for 0.5 hr. (not longer) with Na in C_6H_6 (not xylene), yields the dicyclic keto-ester, converted by boiling aq. $Ba(OH)_2$ into β -thujone [identified as semicarbazone, *p*-nitro- (m.p. 148—150°) and 2:4-dinitro-phenylhydrazone, m.p. 114—115°] and other products.

R. S. C.

Attempted synthesis of Δ^4 -carene. L. RUZICKA [with J. ZEPER and P. NEBBELING] (Helv. Chim. Acta, 1932, 15, 957—959).—Carylamine, MeI, and NaOEt in boiling EtOH give an inactive, monocyclic hydrocarbon, $C_{10}H_{16}$, b.p. 65—67°/12 mm. With MeI and NaOMe in cold MeOH an oil is formed, which, when treated with Ag_2O in H_2O and then distilled in a high vac., yields a monocyclic hydrocarbon, $C_{10}H_{16}$, b.p. 178—182°/755 mm., reduced (PtO_2-H_2) to a hydrocarbon, $C_{10}H_{20}$. It is presumed that formation of unstable Δ^5 -carene precedes ring fission, the different result by the xanthate method (A., 1927, 882) being due to the intermediate alcohol undergoing Walden inversion in the present case.

R. S. C.

Action of Japanese camphor on the heart. IV. *allo-p*-Ketocamphor ("Vitacamphor"). K. TAMURA, G. KIHARA, and M. ISHIDATE (Proc. Imp. Acad. Tokyo, 1932, 8, 213—216).—Mild oxidation of *p*-hydroxycamphor with $Na_2Cr_2O_7$ gives *p*-ketocamphor (I) (Bredt, A., 1924, i, 408) (formed solely by more drastic oxidation) and *allo-p*-ketocamphor (II) (A., 1931, 358), m.p. 200—203°, $[\alpha]_D^{25} +70.6^\circ$ and $+92.1^\circ$ in EtOH (according to temp. of oxidation); (II) passes into (I) when heated with AcOH. (II) is an intermediate in the degradation of Japanese camphor in the animal body. (II) is readily absorbed from subcutaneous tissue; after absorption, it acts principally on the heart and central nervous system.

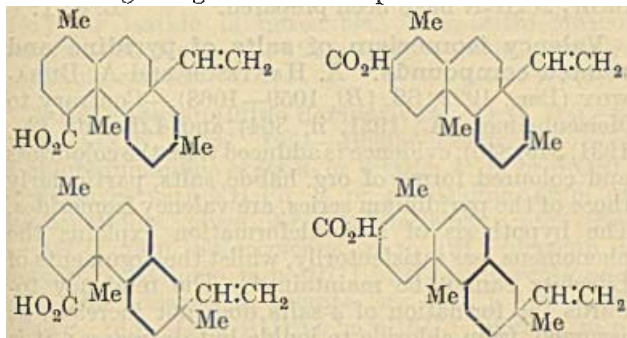
H. B.

Polyterpenes. LXX. Synthesis of pimanthrenequinone. LXXI. Oxidative degradation of *d*-pimaric acid. L. RUZICKA and H. WALDMANN (Helv. Chim. Acta, 1932, 15, 907—914, 915—923; cf. this vol., 749).—LXX. *p*-Tolualdehyde, Na succinate, and Ac_2O at 110° give a poor yield of γ -*p*-tolylisocrotonic acid, m.p. 111—112°, affording at 300° 7-methyl- α -naphthol (I). *p*-Tolualdehyde, Et_2 bromosuccinate, and activated Zn in hot C_6H_6 give a product, which, when treated with PBr_3 in C_6H_6 and then with $NPhMe_2$ at 190°, yields *Et, α -p-tolyl- Δ^4 -propene- β -y-dicarboxylate*, m.p. 195—196° (decomp.), which does not form (I) when distilled. γ -*p*-Tolyl-*n*-butyric acid (prepared by Clemmensen reduction of γ -keto- γ -*p*-tolyl-*n*-butyric acid) and $SOCl_2$ give the acid chloride, b.p. 130°/11 mm., which with $AlCl_3$ in CS_2 affords 1-keto-7-methyl-1:2:3:4-tetrahydronaphthalene, transformed into (I) in 45% yield by S and CuS at 190—200°, but only in poor yield by Se at 280—300°. (I) with Me_2SO_4 and NaOH gives the *Me ether*, m.p. 42—43.5°, b.p. 140°/10 mm., which with succinic anhydride and $AlCl_3$ in cold C_6H_6 affords γ -(4-methoxy-6-methylnaphthoyl)-propionic acid, m.p. 175—176°, reduced (Clemmensen) to γ -(1-methoxy-7-methyl-4-naphthyl)butyric acid (II), m.p. 142° (*Me ester*, m.p. 62—63°, b.p. about 165°/0.5 mm.). (II) and $SOCl_2$ give the acid chloride, which, when distilled, gives a 50% yield of 1-keto-9-methoxy-7-methyl-1:2:3:4-tetrahydropheanthrene, m.p. 118—119°, b.p. 190—193°/0.7 mm. (semicarbazone). This with $MgMeI$ affords a mixture of *tert*. alcohol and unsaturated hydrocarbon, which with Se at 290—300° and later at 260° forms 9-methoxy-1:1-dimethylphenanthrene (50% yield), m.p. 126—127°, b.p. about 165°/0.7 mm., oxidised by CrO_3 in hot AcOH to pimanthrenequinone (identified as quinoxaline derivative). 9-Methoxyphenanthrene is similarly oxidised to phenanthrenequinone. β -(2:5-Dimethylbenzoyl)propionic acid, m.p. 81—82°, is reduced (Clemmensen) to γ -(2:5-dimethylphenyl)butyric acid, b.p. 177—179°/11 mm. (90% yield), the acid chloride, b.p. 142—143°/11 mm., of which leads to 1-keto-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 145°/10 mm. (semicarbazone, m.p. 228°), giving with S 5:8-dimethyl- α -naphthol (*Me ether*, m.p. 68°, b.p. about 150°/11 mm.).

[With G. B. R. DE GRAAFF.] α -Naphthyl *Me ether*, succinic anhydride, and $AlCl_3$ in CS_2 give β -(4-methoxynaphthoyl)propionic acid, m.p. 171°, oxidised by NaOBr to 4-methoxynaphthoic acid. This proves

the constitution of the products of the above reactions.

LXXI. *d*-Pimaric acid (I) (modified prep.) with HNO_3 under certain conditions gives the acids $\text{C}_{11}\text{H}_{16}\text{O}_6$ (II) and $\text{C}_{12}\text{H}_{18}\text{O}_6$, previously (A., 1931, 736) obtained from abietic acid, and with O_3 in CCl_4 yields CH_2O . The amorphous by-products obtained in the prep. of dihydroxy-*d*-pimaric acid (III) with KMnO_4 (equiv. to 23 O atoms) give (II). (III) with CrO_3 (equiv. to 20) in AcOH at $50\text{--}60^\circ$ gives a dibasic acid, $\text{C}_{19}\text{H}_{28}\text{O}_4$, m.p. $260\text{--}261^\circ$ (with a product, m.p. $246\text{--}247^\circ$, possibly the same acid impure), reduced catalytically (PtO_2) to an acid, $\text{C}_{19}\text{H}_{30}\text{O}_4$, m.p. not sharp, $210\text{--}220^\circ$, and yielding pimanthrene with Se at 350° . These and previous results indicate that (I) has one of the annexed formulæ, the second ethylenic linking being at one of the positions indicated in



heavy type. The isoprene chains from which (I) and abietic acid are built up differ only in one respect, and both are unsymmetrical.

R. S. C.

Furan-3-aldehyde (3-furfuraldehyde). H. GILMAN and R. R. BURTNER (J. Amer. Chem. Soc., 1932, 54, 3014).—*Furan-3-aldehyde*, b.p. $144^\circ/732$ mm. (*phenylhydrazone*, m.p. $149\text{--}5^\circ$), prepared by way of 3-furoyl chloride, does not give a coloration with $\text{NH}_2\text{Ph}, \text{AcOH}$.

C. J. W. (b)

Amino-acids. II. *N*-Benzoylfurylalanine. V. DEULOFEU (Anal. Fis. Quím., 1932, 30, 456—459).—*N*-benzoylfurylalanine, m.p. $149\text{--}150^\circ$ (lit. 163°), identical with that obtained by reducing *N*-benzoylfurylaminoacrylic acid, has been prepared by direct benzoylation.

H. F. G.

Comparison of the directive powers of elements having consecutive atomic numbers. III. Nitration of halogeno-2-phenylbenzopyrylium salts. (MRS.) C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1932, 1988—1992).—*Salicylidene-p-chloroacetophenone*, m.p. 151° (decomp.), obtained from salicylaldehyde and *p*-chloroacetophenone, gives with HCl and HClO_4 4'-chloro-2-phenylbenzopyrylium perchlorate, m.p. 193° ; *salicylidene-p-bromoacetophenone*, m.p. 133° , 4'-bromo-2-phenylbenzopyrylium perchlorate, m.p. $243\text{--}245^\circ$; 5-chloro-, m.p. $170\text{--}171^\circ$, 5-bromo-, m.p. $162\text{--}163^\circ$, 3:5-dichloro-, m.p. $183\text{--}184^\circ$, and 3:5-dibromo-salicylideneacetophenone, m.p. 168° ; 6-chloro-, m.p. 240° , 6-bromo-, m.p. $248\text{--}250^\circ$, 6:8-dibromo-, m.p. $257\text{--}259^\circ$, and 6:8-dichloro-2-phenylbenzopyrylium, m.p. $249\text{--}250^\circ$, perchlorates are similarly prepared. Nitration of the benzopyrylium salts yields 90—100% of the corresponding *m*- NO_2 -derivatives, which have also been synthesised from

the corresponding *m*-nitroacetophenones: 4'-chloro- ($+\text{xH}_2\text{O}$), m.p. $180\text{--}190^\circ$ (nitration product, m.p. $225\text{--}226^\circ$, reacts almost 100% with $\text{C}_5\text{H}_{11}\text{N}$), 4'-bromo-3'-nitro-2-phenyl- ($+\text{xH}_2\text{O}$), m.p. $180\text{--}190^\circ$ (nitration product, m.p. $239\text{--}240^\circ$); 6-chloro-, m.p. $233\text{--}5^\circ$, and 6-bromo-2-*m*-nitrophenyl-benzopyrylium perchlorate, m.p. 228° . *p*-Chloro-acetophenone is nitrated to 4-chloro-, m.p. $99\text{--}101^\circ$, and *p*-bromo- to 4-bromo-3-nitroacetophenone, m.p. $117\text{--}118^\circ$. 6-Chloro-4'-nitro-, m.p. $252\text{--}253^\circ$, is different from the nitration product of 6-chloro-2-phenylbenzopyrylium perchlorate. 4'-Chloro-, m.p. $179\text{--}181^\circ$, 4'-bromo-, m.p. $173\text{--}176^\circ$, 6-chloro-, m.p. $160\text{--}161^\circ$, 6-bromo-, m.p. $158\text{--}159^\circ$, 6:8-dichloro-, m.p. $187\text{--}188^\circ$, and 6:8-dibromo-2-phenylbenzopyrylium ferrichlorides, m.p. 185° , have been prepared. 3:4':5-Trichlorosalicylideneacetophenone, m.p. $211\text{--}212^\circ$, is described.

F. R. S.

Developments in the chemistry of anthocyanins. G. M. ROBINSON and R. ROBINSON (Nature, 1932, 130, 21).—Mainly a summary of recent work. The anthocyanin, proposed name gesnerin, occurring in the orange-red flowers of *Gesnera fulgens* and *G. cardinalis*, is a 5-saccharide of 4':5:7-trihydroxyflavylium chloride. Hirsutin, malvin, and cyanin chlorides, which have been synthesised, and peonin and pelargonin chlorides all bear 2 glucose residues separately attached to the 3 and 5 O atoms.

L. S. T.

Preparation of di- and isomeric tetra-chloro-dioxans. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1932, 54, 2987—2992).—The work of Boeseken *et al.* (A., 1931, 1162) on the structure of dichlorodioxan (I) is confirmed; $(\text{CH}_2\text{OH})_2$ is identified as the dibenzoate amongst the hydrolysis products. Treatment of the hydrolysis product of (I) with $\text{CO}(\text{NH}_2)_2$ gives glycoluril (70% yield), from which hydantoin is prepared in 67% yield; dichlorodioxan is a practical source of glyoxal for reactions of this type. (I) and warm EtOH give 71% of diethoxydioxan. Dioxan could not be brominated. Four tetrachlorodioxans, b.p. $93\text{--}95^\circ/11\text{--}12$ mm., and m.p. $57\text{--}58^\circ$, $59\text{--}60^\circ$, and $143\text{--}144^\circ$, are prepared by chlorination of crude (I). The hydrolysis products indicate that the first two are *as*- and the last two (obtained in small yield) *s*- Cl_4 -derivatives.

C. J. W. (b)

1:3-Dioxins. II. 1:3-Benzdioxin and its derivatives. F. CALVET and M. C. CARNERO [with D. L. MOSQUERA] (Anal. Fis. Quím., 1932, 30, 445—455).—1:3-Benzdioxin (I) (A., 1929, 573), m.p. $12\text{--}13^\circ$, on nitration yields NO_2 - and $(\text{NO}_2)_2$ -derivatives and picric acid, the heterocyclic ring being therefore relatively stable. Oxidation with KMnO_4 in COMe_2 yields 4-keto-1:3-benzdioxin, which is readily hydrolysed to salicylic acid and CH_2O . Br in the cold gives 6-bromo:3-benzdioxin, excess of Br at higher temp. a compound, $\text{C}_8\text{H}_5\text{O}_3\text{Br}$; the former is oxidised to 6-bromo-4-keto-1:3-benzdioxin. Conc. acids rupture the heterocyclic ring of (I), yielding amorphous products, probably resulting from condensation between CH_2O and PhOH . 6-Amino-1:3-benzdioxin, m.p. 68° , has been isolated: *Ac* derivative, m.p. $123\text{--}130^\circ$; the Br- and Br_2 -derivatives have m.p. 124° and $130\text{--}132^\circ$, respectively.

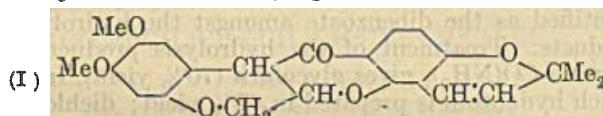
Condensation of *p*-nitrophenol with CH_2O yields, in addition to 6-nitro-1:3-benzodioxin, *di*-(6-nitro-1:3-benzodioxinyl)methane, m.p. 218—220°, which on oxidation yields the corresponding benzophenone derivative, m.p. above 310°.

H. F. G.

Rotenone. XXII. New data in confirmation of the structure of rotenone. L. E. SMITH and F. B. LaFORGE (J. Amer. Chem. Soc., 1932, 54, 2996—3000; cf. this vol., 401).—Anhydro-derivatives, m.p. 160°, 149°, and 164°, are obtained from derritol, isoderritol, and dihydroderritol, respectively, by the action of P_2O_5 in xylene. These are insol. in alkali but give colorations with FeCl_3 and afford the corresponding acetates, m.p. 146°, 158°, and 138°, respectively. Acetyldihydroderritol *Me ether* has m.p. 98°. Dihydrotrotenonic acid yields a Ac_2 derivative, m.p. 119°. The mechanism of the formation of the anhydrotrotenols proposed by Butenandt (A., 1928, 1017) is correct. These reactions afford confirmation of the derritol formula previously proposed (*loc. cit.*). Rotenone, isorotenone, and dihydrotrotenone give Ac derivatives, m.p. 135°, 144°, and 209—211°, respectively, which are enol acetates; one of the Ac groups in diacetyldihydrotrotenonic acid is of this type. Acetyldihydrotrotenone is reduced catalytically to dihydrodeoxyrotenone, m.p. 168°. The methyl-derritols do not yield anhydro-derivatives.

C. J. W. (b)

Deguelin. IV. Structure of deguelin and tephrosin. E. P. CLARK (J. Amer. Chem. Soc., 1932, 54, 3000—3008; cf. A., 1931, 1298).—Reactions are discussed which lead to a formula for deguelin (I). Catalytic reduction of (I) gives a *dihydro*-derivative,



m.p. 173—174°, oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ to dehydrodeguelin. The mother-liquor from the oxidation of dehydrodeguelin (II) with KMnO_4 (after removal of 2-hydroxy-4:5-dimethoxybenzoic acid) contains a small quantity of rissic acid and nicouic acid, $\text{C}_{12}\text{H}_{12}\text{O}_8$ [10.2 g. from 50 g. of (II)], m.p. 196° (decomp.) (Me_3 ester, m.p. 120—121°) (one of the products of decomp. at the m.p. is α -hydroxyisobutyric acid; decomp. in boiling NH_2Ph gives resorcinol). Nicouic acid is formulated as α -3-hydroxy-2:4-dicarboxyphenoxyisobutyric acid. Tephrosindicarboxylic acid when heated in boiling Ph_2O for 0.5 min. gives α -hydroxyisobutyric acid and tephrosinmonocarboxylic acid, m.p. 268—269° (decomp.) (Ac derivative, m.p. 230°, decomp. 250—255°), oxidised by alkaline H_2O_2 to rissic acid, and hydrolysed by 10% EtOH-KOH to tephrosic acid, m.p. 196°. Acetyltephrosin has m.p. 200°.

C. J. W. (b)

[Metallic derivatives of thiophen.] W. STEINKOPF (Ber., 1932, 65, [B], 1248).—In reply to Krause and Renwanz (this vol., 762) it is pointed out that 2-bromothiophen can be prepared in 45% yield from thiophen and CNBr .

H. W.

Preparation and properties of substituted 2-methylthiophens. A. F. SHEPARD (J. Amer. Chem.

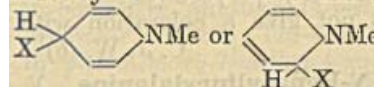
Soc., 1932, 54, 2951—2953).—2-Methyl-5-ethylthiophen, b.p. 159.8—160.4° (corr.)/760 mm., f.p. —68.6° to —68.4°, results in 40% yield when the semicarbazone of 2-methyl-5-acetothienone is heated with moist powdered KOH . α -Ethyl-lævulic acid and P_2S_5 (?) give 20% of 2-methyl-4-ethylthiophen, b.p. 162—164°/760 mm., f.p. —60° to —59°, whilst β -methyl-lævulic acid and P_2S_5 give 20% of 2:3-dimethylthiophen, b.p. 140.2—141.2°/760 mm., f.p. —49.1° to —48.9°, [5-chloromercuri-derivative, m.p. 218.5—219.5° (corr.)].

C. J. W. (b)

Preparation of tin methyl dipyridine iodide, tin diquinoline chloride, and tin diquinoline bromide. G. DIMITRIOU (Praktika, 1929, 4, 140—143; Chem. Zentr., 1932, i, 1375—1376).—The compounds $\text{MeSnI}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$, $\text{SnCl}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$, and $\text{SnBr}_4 \cdot 2\text{C}_9\text{H}_7\text{N}$ have been prepared.

L. S. T.

Valency isomerism of salts of pyridine and related compounds. A. HANTZSCH and A. BURAWOY (Ber., 1932, 65, [B], 1059—1068).—Contrary to Meisenheimer (A., 1921, ii, 364) and Lifschitz (A., 1931, 349, 840), evidence is adduced that the colourless and coloured forms of org. halide salts, particularly those of the pyridinium series, are valency isomerides. The hypothesis of ionic deformation explains the phenomena less satisfactorily, whilst the arguments of Lifschitz cannot be maintained. The tendency towards the formation of ψ -salts does not increase, as assumed, from chloride to iodide but decreases; it is also present in the nitrates and trichloroacetates. The intense colour of pyridinium ψ -iodides is not a characteristic property of ψ -salts but is attributable to the proper absorption of the homopolar united I atom. The ψ -salts of the pyridinium and quinolinium series are not constituted with the acid residue united directly to N but have the quinolide constitution,



in direct union with a C atom.

H. W.

Synthesis of isonipecotinic [piperidine-4-carboxylic] acid. V. HANOUSEK and V. PRELOG (Coll. Czech. Chem. Comm., 1932, 4, 259—270).— $\beta\beta'$ -Dichlorodiethyl ether and $\text{CHNa}(\text{CO}_2\text{Et})_2$ in EtOH give Et tetrahydropyran-4:4-dicarboxylate (45% yield) together with Et γ -(β -ethoxyethoxy)propane- $\alpha\alpha$ -dicarboxylate, b.p. 146—147°/high vac. [the free acid (*Ba* salt; *amide*, m.p. 138—139°) is decarboxylated to γ -(β -ethoxyethoxy)butyric acid, b.p. 151—153°/high vac.], and $\gamma\gamma'\gamma'$ -tetracarbethoxydiethyl ether, b.p. 187—192°/high vac. [converted by MeOH-NH_3 into the tetra-*amide*, m.p. 226° (decomp.)]. Tetrahydropyran-4-carboxylic acid and conc. HBr at 100° give $\alpha\alpha$ -dibromopentane- γ -carboxylic acid (I), m.p. 58—59° (unstable *amide*, m.p. 77—78°), the Et ester, b.p. 153°/7—8 mm., of which is converted by successive treatment with MeOH-NH_3 at 130°, aq. $\text{Ba}(\text{OH})_2$, CO_2 , dil. H_2SO_4 , Ag_2O , and H_2S into isonipecotinic acid [*hydrochloride* m.p. 293° (decomp.); *Me* ester *hydrochloride*, m.p. 169° (corr.)]. Vac. distillation of (I) gives α -(β -bromoethyl)butyrolactone, b.p. 151—153°/6—7 mm. $\alpha\alpha$ -Dichloropentane- γ -carboxylic acid has m.p. 54—55°.

H. B.

2:6-Dihydroxy-3- β -phenoxyethyl-4-methylpyridine. K. MATEJKA, R. ROBINSON, and J. S. WATT (J.C.S., 1932, 2019—2021).—The K derivative of Et α -cyano- β -methylglutamate reacts with β -phenoxyethyl bromide or iodide [the latter (improved prep.) gives better yield] to form mainly Et γ -cyano- γ -phenoxyethyl- β -methylcrotonate, b.p. 170—172°/0.2 mm., hydrolysed by HCl to 2:6-dihydroxy-4-methyl-3- β -phenoxyethylpyridine, m.p. 161°, and some (probably) anhydro-2:6-dihydroxy-4-methyl-3-(β -hydroxyethyl)-pyridine, m.p. 249—250°. F. R. S.

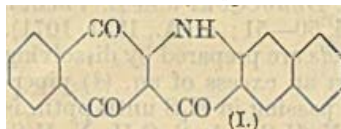
Structure of isatide. W. C. SUMPTER (J. Amer. Chem. Soc., 1932, 54, 2917—2918).—5-Methyldioxindole and isatin give the same 5-methylisatide as is obtained from 5-methylisatin and dioxindole (Wahl and Faivret, A., 1926, 960), indicating that the unsym. quinhydrone formula (Heller and Lauth, A., 1929, 451) for isatide is untenable. The isatin-pinacol formula (cf. Kohn, A., 1912, i, 800; 1916, i, 607) is probably correct. C. J. W. (b)

4-Anilinoquinaldine derivatives. O. G. BACKEBERG (J.C.S., 1932, 1984—1986).—Condensation of 4-chloroquinaldine or its 8- or 6-OMe- or 8- or 6-OEt-derivatives with NH_2Ph , *o*- or *p*-anisidine, or *o*- or *p*-phenetidine gives 4-chloro-8-methoxy-, m.p. 89° [$+1\text{H}_2\text{O}$, m.p. 83°; picrate, m.p. 191° (decomp.)], 4-hydroxy-8-ethoxy-, m.p. 197° [$+2\text{H}_2\text{O}$; hydrochloride, m.p. 264° (decomp.); picrate, m.p. 211°], 4-chloro-8-ethoxy-, m.p. 44° [$+1\text{H}_2\text{O}$, m.p. 61°; picrate, m.p. 193° (decomp.)]; 4-*o*-, m.p. 203° [hydrochloride, m.p. 252° (decomp.); picrate, chars 276°], 4-*p*-anisidino-, m.p. 209° [hydrochloride, m.p. 286° (decomp.); picrate, m.p. 223° (decomp.)]; 4-*o*-, m.p. 171° [hydrochloride, m.p. 143°; picrate, chars 274°], 4-*p*-phenetidino-, m.p. 182° [hydrochloride, m.p. 277° (decomp.); picrate, m.p. 223°]; 4-anilino-, m.p. 268° (picrate, m.p. 189°), 4-*o*-, m.p. 198° (picrate, m.p. 192°), and 4-*p*-anisidino-, m.p. 234° (picrate, m.p. 187°), 4-*o*-, m.p. 191° [hydrochloride, m.p. 210° (decomp.); picrate, m.p. 174°], and 4-*p*-phenetidino-8-methoxy-, m.p. 228° [hydrochloride, m.p. 245° (decomp.); picrate, m.p. 188°]; 4-*o*-, m.p. 193° [hydrochloride, m.p. 274° (decomp.); picrate, m.p. 233° (decomp.)], and 4-*p*-anisidino-, m.p. 203° [hydrochloride, m.p. 292° (decomp.); picrate, m.p. 274° (decomp.)], 4-*o*-, m.p. 172° [hydrochloride, m.p. 238° (decomp.); picrate, m.p. 229°], and 4-*p*-phenetidino-6-methoxy-, m.p. 223° [hydrochloride, m.p. 282° (decomp.); picrate, m.p. 251° (decomp.)]; 4-anilino-, m.p. 245° (picrate, m.p. 191°), 4-*o*-, m.p. 203° (picrate, m.p. 163°), and 4-*p*-anisidino-, m.p. 211° (picrate, m.p. 174°), 4-*o*-, m.p. 143° [hydrochloride, m.p. 147° (decomp.); picrate, m.p. 164°], and 4-*p*-phenetidino-8-ethoxy-, m.p. 209° [hydrochloride, m.p. 240° (decomp.)]; 4-anilino-, m.p. 223° [hydrochloride, m.p. 311° (decomp.); picrate, m.p. 227°], 4-*o*-, m.p. 158° [hydrochloride, m.p. 255° (decomp.); picrate, m.p. 200°], and 4-*p*-anisidino-, m.p. 194° [hydrochloride, m.p. 281° (decomp.); picrate, m.p. 221°], and 4-*o*-phenetidino-6-ethoxy-2-methylquinoline, m.p. 177° [hydrochloride, m.p. 279° (decomp.); picrate, m.p. 219°]. The picrates of the following have been prepared: 4-hydroxy-8-methoxy-, m.p. 217°, -6-methoxy-, m.p. 202°, and -6-ethoxy-, m.p. 205°; 4-chloro-6-methoxy-, m.p. 210° (decomp.), and -6-ethoxy-, m.p. 209°; 4-anilino-

6-methoxy-, m.p. 269° (decomp.); and 4-*p*-phenetidino-6-ethoxy-2-methylquinoline, m.p. 217°.

F. R. S.

Linear dinaphthacridone quinone. J. PAJAK (Rocz. Chem., 1932, 12, 507—517).—2-Amino- β -naphthoic acid condenses with 2-hydroxy-1:4-naphthaquinone to yield the corresponding naphthaquinoneaminonaphthoic acid, m.p. 272°, which when heated with H_3PO_4 at 170° gives dinaphthacridone-quinone (I), m.p. 410° (Ac and Ac_2 derivatives of the corresponding quinols, m.p. 305° and 160°). Sulphonic acids of (I) and of its NO_2 -derivatives are described.



R. T.

Creatine and creatinine. I. Acyl derivatives of creatinine. H. R. ING. Their electrometric titration. R. A. KEKWICK and G. M. RICHARDSON (J.C.S., 1932, 2047—2055).—Benzylideneacetylcreatine (I) forms a *K* salt, the slightly acidic properties being due to the lactam group; the *K* salt gives with MeI , benzylideneacetylmethylcreatine, m.p. 129—130°, hydrolysed by acid to benzylidenedimethylhydantoin, and (I) must be therefore CHPh

. Creatinine and Ac_2O , at 60—65°, yield acetyl-, m.p. 124—125° [hydrochloride, m.p. 185—186° (decomp.); picrate, m.p. 170—172° (decomp.); *K* salt], and at 100°, form diacetyl-, m.p. 164—165° (picrate, m.p. 139—140°), and triacetylcreatine, m.p. 63—65°. Benzoylation of creatinine gives only one monobenzoyl-, m.p. 193—194° (lit. m.p. 187°; *K* salt), and tribenzoyl-creatine. Creatinine and diphenoxyphosphoryl chloride when anhyd. yield diphenoxyphosphorylcreatine, m.p. 127—128° (*Na* salt), which exhibits phenolic properties, and when not completely dry, creatinine diphenoxyphosphate, m.p. 158—159°, results. Monoacyl derivatives of creatinine have been shown to exhibit phenolic properties due to enolisation of the $\cdot\text{CH}_2\cdot\text{CO}\cdot$ group. Electrometric titrations of mono- and di-acetyl-, benzoyl-, and benzylideneacetyl-creatine are recorded.

F. R. S.

N-Substituted derivatives of barbituric acid. B. HEPNER and S. FRENKENBERG (Rocz. Chem., 1932, 12, 500—506).—The following analgesics have been prepared by condensing *s*-phenylmethylcarbamide or *p*-ethoxyphenylcarbamide with the corresponding substituted malonic acid: 3-phenyl-1-methylbarbituric acid, m.p. 118—122° (5-Et, m.p. 81°, 5-Pr, m.p. 106°, 5-allyl-, m.p. 107—108°, 5-Pr², m.p. 91°, 5:5-Et₂, m.p. 87°, 5:5-Pr₂, m.p. 89°, 5:5-diallyl-, m.p. 96.5°, 5-phenyl-5-ethyl-, m.p. 104°, and 5-allyl-*o*-*n*-propyl derivative, m.p. 97°), 3-*p*-ethoxyphenylbarbituric acid, m.p. 211° (5-Pr, m.p. 208°, 5:5-Pr₂ derivative, m.p. 150°). Diethylmalonyl-N-phenyl-N'-methylthiocarbamide, m.p. 110°, is obtained from *s*-phenylmethylthiocarbamide and diethylmalonyl chloride.

R. T.

Reactions of alloxan. G. ROSSI and G. SCANDELARI (Gazzetta, 1932, 62, 351—357).—Alloxan after prolonged heating with *p*-toluidine yields a compound, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_4$, decomp. above 150°; with

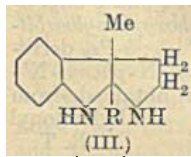
m-phenylenediamine a compound, $C_{10}H_{10}O_4N_4$, and with anthranilic acid a compound, $C_{11}H_7O_5N_3$, are formed; each of these contains $\cdot NH_2$. A compound, $C_{10}H_5O_5N_4$, decomp. 245° , with *p*-nitroaniline does not diazotise. With either carbamide or biuret a compound, $C_8H_{11}O_8N_8$, m.p. 146 – 147° (cf. A., 1912, i, 589), is formed. E. W. W.

Organic derivatives of tellurium, arsenic, and tin sulphides. L. DEBUCQUET and L. VELLUZ (Compt. rend., 1932, 195, 50–51; cf. A., 1931, 1071).—The following compounds are prepared by dissolving the appropriate oxide in an excess of aq. (?) piperazine or piperidine, and passing in H_2S until pptn. is complete: $TeS_2 \cdot C_4H_{10}N_2 \cdot H_2S$, $As_2S_3 \cdot C_4H_{10}N_2 \cdot H_2S$, $As_2S_5 \cdot 3(C_4H_{10}N_2) \cdot 3H_2S$, and $SnS_2 \cdot C_4H_{10}N_2 \cdot H_2S$ (from piperazine), and $As_2S_3 \cdot 2(C_5H_{11}N) \cdot H_2S$ (from piperidine). They are decomposed by dil. acids with formation of H_2S and the metallic (or metalloid) sulphide, and are regarded as salts of the thio-acids H_2TeS_3 , $H_2As_2S_4$, $H_2As_2S_5$, and H_2SnS_3 . H. A. P.

Pyrimidines. CXXIX. Synthesis of 2-thio-rotic acid. T. B. JOHNSON and E. F. SCHROEDER (J. Amer. Chem. Soc., 1932, 54, 2941–2945).—2-Thiouracil-4-aldehyde and aq. KOH give 4-hydroxy-methyl-2-thiouracil (I), m.p. 259° (decomp.), and 2-thio-rotic acid (II), decomp. 338 – 339° . (II) is desulphurised by CrO_3 or alkaline H_2O_2 (but not by $CH_2Cl \cdot CO_2H$) to rotic acid (III), whilst (I) and aq. $CH_2Cl \cdot CO_2H$ give 4-hydroxymethyluracil (IV). Uracil-4-aldehyde and aq. KOH give (III) and (IV). The Na salt of (I) with EtI and CH_2PhCl give 2-ethyl-, m.p. 168° , and 2-benzyl-, m.p. 156° , -thiol-4-hydroxymethyluracils, respectively. Similarly, (II) yields 2-ethyl- and 2-methyl-thiolrotic acids, m.p. 248° and 255° , respectively. The prep. of the 2- CH_2Ph derivative (cf. Bachstetz, A., 1931, 495) is also described. C. J. W. (b)

Preparation of indolenines and synthesis of [a substance with] the so-called eserine structure. T. HOSHINO (Proc. Imp. Acad. Tokyo, 1932, 8, 171–174).—Mg 3-methylindolyl iodide and MeI give about 40% of 3:3-dimethylindolenine and small amounts of 1:3-dimethylindole and an I-containing substance. Mg 2-methylindolyl iodide and MeI afford 2:3:3-trimethylindolenine (I) and 2:3-dimethylindole; with CH_2PhCl , 3:3-dibenzyl-2-methylindolenine (II), m.p. 59° , and 3-benzyl-2-methylindole result. (I) and (II) (accompanied by 1:3-dibenzyl-2-methylindole) are also prepared from MeI and Mg 2:3-dimethyl- and CH_2PhCl and Mg 3-benzyl-2-methyl-indolyl iodides, respectively.

[With K. TAMURA.] The product from β -3-indolylethylamine (1 mol.) and $MgMe(Et)I$ (4 mols.) with MeI in C_6H_6 gives about 30% of dinordeoxyeseroline (III; $R=H$), m.p. 72 – 73° (Ac_2 derivative, m.p. 142 – 143°); cryst. (m.p. 142°) and non-cryst. by-products are also formed. Similarly, β -2-methyl-3-indolylethylamine is converted into 9-methyldinordeoxyeseroline (III; $R=Me$) (70% yield), m.p. 78 – 79° (Ac_2 derivative, m.p. 148 – 149°), which with MeI gives the hydriodide, m.p. 181° , of 9-methyldeoxyeseroline, m.p. 85 – 86° . H. B.



Action of acetoacetic ester on benzeneazo- β -naphthylamine. G. B. CRIPPA and M. LONG [with U. MOLIGNONI] (Gazzetta, 1932, 62, 394–401).—These when heated with conc. HCl at 180° and further heated with C_5H_5N give the Et ester, m.p. 96° , of a substance which is (I) 3-methyl- $\alpha\beta$ -naphthoquinoxaline-2-carboxylic acid or (II) $\alpha\beta$ -naphthoquinoxaline-3-acetic acid, m.p. 206° . Of these (II) is preferred, since oxidation by alkaline $KMnO_4$ yields a substance, m.p. 146° , which is apparently 6-carboxy-5-o-carboxyphenylpyrazine-2-acetic acid. By-products of the condensation are, in the Et_2O extract, *N*-phenyl-lutidonecarboxylic acid, m.p. 268 – 269° (converted by heat into phenyl-lutidone), a substance, m.p. 218° , which is not *N*-anilino-*C*-methyl-1:2-naphthoglyoxaline (new m.p. 236°), and products of m.p. 320° and 230° . E. W. W.

Electrometry of cyanines. E. CALZAVARA (Bull. Soc. Franç. Phot., 1932, 19, 15–16).—The alkyl iodides of the cyanines can be electrometrically titrated with $AgNO_3$. Intermediate complexes of cyanine and $AgNO_3$ are formed, but are quickly decomposed by further $AgNO_3$. The method is tedious. J. L.

Alkaloids of Anabasis aphylla. V. *N*-Aminoanabesine and racemic anabesine. A. OREKHOV and S. NORKINA (Ber., 1932, 65, [B], 1126–1130; cf. this vol., 405).—*l*-Anabesine is slowly racemised when neutralised with H_2SO_4 and heated with H_2O at 200° , thereby becoming partly resinified and yielding *dl*-anabesine [picrate, m.p. 212 – 213° ; picrolonate, m.p. 237 – 239° ; Bz derivative, m.p. 94 – 95° ; *NO*-derivative, b.p. 186 – $192^\circ/9$ mm., and its picrate, m.p. 129 – 130° , and picrolonate, m.p. 173 – 174° (decomp.)]. *dl*-*N*-Aminoanabesine, b.p. 145 – $146^\circ/7$ mm., yields a picrate, m.p. 214 – 215° , picrolonate, m.p. 238 – 239° , and Bz derivative, m.p. 170 – 171° . Reduction of *l*-*N*-nitrosoanabesine with Zn dust and dil. AcOH and subsequent distillation of the product affords a mixture of *dl*-*N*-amino- and *l*-*N*-amino-anabesine, b.p. 146 – $147^\circ/9$ mm. [picrate, m.p. 186 – 187° ; picrolonate, m.p. 189 – 190° ; Bz derivative, m.p. 150 – 151° , $[\alpha]_D^{25}$ -31.1° in EtOH (also $+0.5C_6H_5$)]. *l*-*N*-Aminoanabesine does not suffer marked diminution in $[\alpha]_D$ when distilled in vac. After 9 distillations under atm. pressure [b.p. about 280° (partial decomp.)] $[\alpha]_D$ decreases from -103° to -37° . H. W.

Rotatory power of quinine in alcoholic solution. C. LAPP (Compt. rend., 1932, 195, 243–245).—The variation of $[\alpha]_D$ for quinine with the concn. depends on the loose union of quinine with solvent mols. From viscosity measurements, the approx. no. of EtOH mols. associated with 1 mol. of quinine is determined. J. L. D.

Dimethylmorphine (methylcodeine). E. CHERBULIEZ and A. RILLIETT (Helv. Chim. Acta, 1932, 15, 857–862).—Anhyd. codeine (I) and CH_2PhCl at 50° give codeine benzylchloride, $+4H_2O$ (giving with 5% Na–Hg a 40% yield of codeine), which with Me_2SO_4 and cold NaOH, followed by aq. KI, yields *O*-methylcodeine benzyl iodide, m.p. 181° , unstable when dried (corresponding picrate, stable), affording with 5% Na–Hg (not Al–Hg) *O*-methylcodeine (II) in 40%

over-all yield. (II) is unchanged by $\text{H}_2\text{C}_2\text{O}_4$ at 150° . With Pd-black at 165° in vac. (I) is entirely decomposed, but (II) is unaffected.

R. S. C.

7-Aminodihydrothebainone. New method of oxygen ring closure of alkaloids of the thebainone type. H. KONDO and S. IKAWA (Ber., 1932, 65, [B], 1214—1217).—Dihydrocodeinone and amyl nitrite in CHCl_3 at -15° are converted by conc. HCl into 7-oximinodihydrocodeinone, decomp. about 230 — 240° after softening at 200 — 210° , reduced (Pd- H_2) to 7-aminodihydrothebainone, decomp. about 235 — 245° after softening at 206° [oxime, m.p. about 215 — 220° (decomp.) after softening at 199°]. 7-Amino-4-benzylidihydrothebainone (I), m.p. 183 — 185° (decomp.) after softening at 180° , from the base, CH_2PhCl , and KOH in EtOH , is transformed by NaNO_2 and $\text{N-H}_2\text{SO}_4$ into 7-hydroxydihydrocodeinone, m.p. 195 — 197° (decomp.) after softening at about 180° [oxime, m.p. 178 — 180° (decomp.) after softening at 172°], also obtained from (I), AgNO_2 , and HCl-MeOH .

H. W.

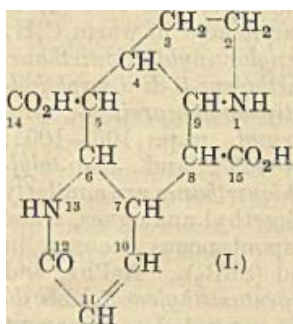
Strychnos alkaloids. LXVII. Relationship of the brucine- to the strychnine-sulphonic acids. Oxidation of quaternary brucinium salts. H. LEUCHS, G. SCHLEMPF, and W. BAUR (Ber., 1932, 65, [B], 1121—1125).—Direct oxidation of brucinesulphonic acid I with CrO_3 ($=310$) or conversion of strychninesulphonic acid I into the NO_2 - and NH_2 -derivative and oxidation of the latter with CrO_3 ($=240$) affords diketonucinesulphonic acid I hydrate, $\text{C}_{17}\text{H}_{19}\text{O}_5\text{N}_2\cdot\text{SO}_3\text{H}$, $[\alpha]_D^{25} -82.3^\circ/d$, and carboxyapocucinesulphonic acid I, $\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}_2\cdot\text{SO}_3\text{H}$, $[\alpha]_D^{25} -185^\circ/d$. The C_{17} is converted into the C_{16} acid by H_2O_2 . It is thus shown that the SO_3H group cannot be attached to the benzenoid nucleus and the structural and steric relationship of the strychnine- and brucine-sulphonic acid I is established.

The substance $\text{C}_{21}\text{H}_{21}\text{O}_7\text{N}_3\cdot\text{Me}\cdot\text{SO}_3\text{H}$, obtained from *N*-methylcacotheline and Na_2SO_4 , is converted by successive treatment with CrO_3 and HClO_4 into the *N*-methoperchlorates of the Wieland and Hanssen acid $\text{C}_{17}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{Me}\cdot\text{ClO}_4$ and $\text{C}_{16}\text{H}_{20}\text{O}_4\text{N}_2\cdot\text{Me}\cdot\text{ClO}_4$, respectively. They are also obtained by oxidation of brucine dimethosulphate, from carboxyapocucine through the methylbetaine, and from the Ag salt of the Wieland acid and MeI .

H. W.

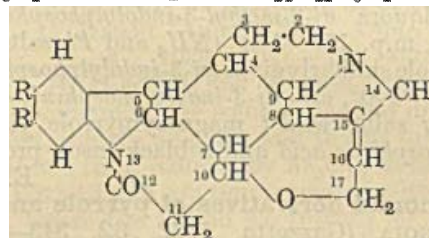
Strychnos alkaloids. LXVIII. Non-acidic products of the oxidation of brucine with permanganate and oxidation of brucinonic acid by chromic acid to the amino-acid, $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$. Structural formulæ of brucine and strychnine. H. LEUCHS [with, in part, W. BAUR] (Ber., 1932, 65, [B], 1230—1239).—The following substances have been isolated in small amount as by-products of the oxidation of brucine with KMnO_4 : $\text{C}_{23}\text{H}_{21}\text{O}_7\text{N}_2$, from which is derived the semicarbazone $\text{C}_{23}\text{H}_{20}\text{O}_6\text{N}_3$, m.p. 228° (decomp.); $\text{C}_{23}\text{H}_{26}\text{O}_7\text{N}_2$ ($+4\text{H}_2\text{O}$), m.p. 240° [Ac derivative, m.p. 290° (decomp.)]; $\text{C}_{21}\text{H}_{22}\text{O}_6\text{N}_2$; $-\text{C}_{21}\text{H}_{20}\text{O}_6\text{N}_2$, m.p. 289 — 292° after softening, $[\alpha]_D^{25} +30.7^\circ/d$ in AcOH ; $\text{C}_{23}\text{H}_{24}\text{O}_7\text{N}_2$, m.p. 265 — 282° (decomp.), $[\alpha]_D^{25} -28^\circ/d$ in AcOH . Oxidation of the non-cryst. resin remaining after isolation of the products described above with CrO_3 affords the NH_2 -acid (I), not molten below 305° , $[\alpha]_D^{25} -210.5^\circ/d$ in 0.1N-

HCl . Brucinonic acid with CrO_3 and $5\text{N-H}_2\text{SO}_4$ affords



(I.)

darkening at about 220°), reduced by SO_2 to the quinol, $\text{C}_{21}\text{H}_{20}\text{O}_8\text{N}_2$ ($+2\text{H}_2\text{O}$), which yields an *Et* ether, $\text{C}_{23}\text{H}_{21}\text{O}_8\text{N}_2$, m.p. about 285° (decomp.) after softening at 270° . Similarly, brucinolic acid affords the quinone, $\text{C}_{21}\text{H}_{20}\text{O}_8\text{N}_2$, m.p. 230 — 235° (decomp.) when rapidly heated [monosemicarbazone, m.p. 185 — 190° (decomp.)], and the quinol $\text{C}_{21}\text{H}_{22}\text{O}_8\text{N}_2$, m.p. 267° (decomp.) after softening (Ac_3 derivative, m.p. 259°). Likewise, dihydrobrucinonic acid gives the quinone, $\text{C}_{21}\text{H}_{20}\text{O}_8\text{N}_2$, and the quinol, $\text{C}_{21}\text{H}_{22}\text{O}_8\text{N}_2$. The acid



(II.)

(I) as accompanied by a second NH_2 -acid, $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_2$, $[\alpha]_D -23^\circ$ ($\text{R}=\text{H}$ or OMe), which is neutral in reaction, stable to KMnO_4 , and resistant to hydrogenation. It is derived only from the resin, not from homogeneous brucinonic acid. 2:3-Diketonecucine in H_2O at 5 — 20° is converted by Br into bromodiketonecucine hydrate isolated as the perchlorate $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}_2\cdot\text{Br}\cdot\text{HClO}_4$, $[\alpha]_D^{25} +98^\circ/d$. The constitution (II) is assigned to strychnine and brucine for reasons explained fully in the original.

H. W.

Substituted dihalogenophenylarsines. F. F. BLICKE, L. D. POWERS, and G. L. WEBSTER (J. Amer. Chem. Soc., 1932, 54, 2945—2947).—The following arsines are prepared from the halogen acid and the arylarsine oxides: *m*-nitro-, m.p. 53 — 54° (lit. 46 — 47°); *p*-benzoyl-, m.p. 118 — 120° , and 4-*p*-phenoxybenzoyl-, m.p. 83 — 85° , -phenyldichloroarsines; *o*-, m.p. 52 — 54° , and *m*-nitro-, m.p. 63 — 64° ; *o*-iodo-, m.p. 71 — 72° ; *o*-, m.p. 84 — 85° , and *p*-methoxy-, m.p. 40 — 41° ; *p*-carboxy-, m.p. 161 — 162° ; *p*-benzoyl-, m.p. 116 — 118° , and 4-*p*-phenoxybenzoyl-, m.p. 105 — 106° , -phenyldibromoarsines; *o*-, m.p. 83 — 84° , and *m*-, m.p. 64 — 65° , -nitro-; *o*-iodo-, m.p. 97 — 98° ; *o*-, m.p. 74 — 76° , and *p*-, m.p. 38 — 40° , -methoxy-; *o*-, m.p. 115 — 117° , and *p*-, m.p. 92 — 93° , -benzoyl-, and 4-*p*-phenoxybenzoyl-, m.p. 127 — 128° , -phenyldi-iodoarsines.

C. J. W. (b)

Interaction of diarylarsinyl iodides, diarylstibinyl iodides, and dihalogenophenylarsines with the piperidine salt of *N*-pentamethylenedithiocarbamic acid. F. F. BLICKE and U. O. OAKDALE

(J. Amer. Chem. Soc., 1932, 54, 2993—2996).—Equiv. quantities of AsPh_2I and the piperidine salt (I) of *N*-pentamethylenedithiocarbamic acid in warm C_6H_6 give *N*-pentamethylene-*S*-diphenylarsinyldithiourethane, m.p. 114—115°; *N*-pentamethylene-*S*-di- α -naphthylarsinyl-, m.p. 214—215°; -diphenylenearsinyl-, m.p. 155—158°; -6-iodophenoxarsinyl-, m.p. 105—106°; -diphenylstibinyl-, m.p. 124—127°, and -di-*p*-tolylstibinyl-, m.p. 123—124°, dithiourethanes are similarly prepared. Unlike the triarylmethyl analogues, these substances do not undergo spontaneous decomp. in solution, to form $(\text{AsR}_2)_2$ and $(\text{SbR}_2)_2$. AsPhI_2 and (I) give phenylarsinylene *N*-pentamethylenedithiocarbamate, m.p. 173—174°. (I) is suggested as a reagent for the identification of small quantities of alkyl- and aryl-dihalogenoarsines. C. J. W. (b)

New phosphine oxides and phosphinic acids with pyrrole and indole nuclei. Q. MINGOIA (Gazzetta, 1932, 62, 333—342).—Magnesylmethylindole treated with POCl_3 in Et_2O , followed by addition of ice and extraction with Et_2O , gives a small residue of tri- α -methyl-*N*-indolylphosphine oxide, PR_2O , m.p. 140—142°, in the Et_2O extract tri-2-methyl-3-indolylphosphine oxide, m.p. 170°, and in the mother-liquors di-2-methyl-3-indolylphosphinic acid, $\text{PR}_2\text{O}_2\text{H}$, m.p. 159—160° (NH_4 and *Pb* salts). Magnesylindole similarly gives tri-3-indolylphosphine oxide, m.p. 138—140°, and di-3-indolylphosphinic acid, m.p. 190° (*Ag* salt), whilst magnesylpyrrole yields di-2-pyrrolylphosphinic acid and a black insol. product.

E. W. W.

Antimonial derivatives of pyrrole and indole. Q. MINGOIA (Gazzetta, 1932, 62, 343—350).—*p*-Aminophenylstibinic acid (A., 1928, 80; prep. improved) is diazotised and coupled with pyrrole etc. to give the following azo-*p*-phenylstibinic acids: 2-pyrrole-, black and insol. in most solvents (NH_4 and *Pb* salts); 3-indole- (NH_4 and *Ag* salts); 2-methyl-3-indole- (*Ag* salt); 3-methyl-2-indole- (*Pb* salt).

E. W. W.

Lipins and substances analogous to lecithin. G. SOLAZZO (L'Ind. Chimica, 1932, 7, 704—714, 865—873).—A summary of the literature on: classification of lipins; synthesis of lecithin; composition, prep., physiological importance, and content in animal tissues and organs, of cephalin, sphingomyelin, cuorin, phrenosin, cerasin, and protagon. T. H. P.

Identification of norvaline in the fission products of proteins. E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1932, 209, 27—32).— NMe_3 with α -bromo-*n*-valeric acid gives *N*-trimethyl-norvaline (I), m.p. 219° (chloroaurate, m.p. 173—174°), and with α -bromoisovaleric acid, *N*-trimethyl-valine (II), m.p. 125° (chloroaurate, m.p. 239°). Since (I) is formed more rapidly than (II) the reaction may be used for isolating and identifying norvaline in mixtures of NH_2 -acids. J. H. B.

Clupein. IV. K. DIRR and K. FELIX (Z. physiol. Chem., 1932, 209, 5—11; cf. this vol., 529).—The partial hydrolysate of clupein Me ester hydrochloride gave a cryst. *dipicrate*, decomp. 185°, then 275°, probably of arginylarginine. The hydrochloride of the latter formed non-cryst. *Me* and *Et* esters.

J. H. B.

Physico-chemical behaviour of polypeptides of various structures. E. ABDERHALDEN and E. HAASE (Helv. Chim. Acta, 1932, 15, 717—721).—Partly a lecture. The following observations appear to be new. The particle size of penta-*l*- α -aminobutyryl-*l*- α -aminobutyric acid, which is entirely, and of the pentapeptide, which is partly, colloidal in H_2O , increases with time. The colloidal particles are negatively charged. Higher peptides retain H_2O of crystallisation tenaciously, which may vitiate analyses of proteins. The di-, tri-, and tetra-peptides from *l*- α -aminobutyric acid have $[\alpha]^{20}_D$ —7.03°, —46.04°, and —86.3°, respectively, and the nearly const. differences may be significant. R. S. C.

Determination of carbon and hydrogen in organic substances by a dry method. D. BUTRESCU (Bul. Chim. Soc. Romane Stiin., 1929, 31, 109—117).—The combustion is conducted in the ordinary way, except that oxidation is effected by passing the vapour, mixed with air or O_2 , over heated Pt-asbestos. Combustion is complete in <1 hr.

D. R. D.

Detection of oxygen in liquid organic compounds. T. ESTREICHER (Z. anal. Chem., 1932, 89, 126—128).—Wüstner's method (this vol., 762) is stated to be untrustworthy.

O. J. W.

Analysis of complex gaseous mixtures. M. BUSI (Annali Chim. Appl., 1932, 22, 352—380).—Analysis of complex gaseous hydrocarbon mixtures, particularly unsaturated hydrocarbons, by ordinary methods and by condensation and fractional distillation, is discussed, and apparatus described. Velocity of absorption and solubility of gases in absorbents is studied.

E. W. W.

Raman effect as basis of an organic spectrum analysis. I. L. BIRCKENBACH and J. GOUBEAU (Ber., 1932, 65, [B], 1140—1148).—The possibilities of the application of the Raman effect to org. analysis are examined in the cases of the following mixtures; $\text{C}_6\text{H}_6\text{--CCl}_4$; $\text{C}_6\text{H}_6\text{--MeOH}$; C_6H_6 , CCl_4 , and MeOH ; $\text{C}_6\text{H}_6\text{--PhMe}$; *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}_2$. The apparatus is described. Constancy in the conditions of exposure and use of freshly-distilled specimens are essential. Exposures are made over a range of periods and the intensities of the lines are judged according to the length of exposure after which they first appear. For analytical purposes the strongest and sharpest lines are selected. The spectra of the individual components of the mixture are recorded and selection is made from the lines not common to both substances. The relationship of the intensity of the various lines to the concn. of the components is plotted and the graph is employed in the analysis of the mixtures. Under the most favourable conditions <1% of impurity can be measured.

H. W.

Apparatus for determination of methoxyl groups. W. G. CAMPBELL (Chem. and Ind., 1932, 590—591).—A simple all-glass apparatus is described and illustrated.

E. W. W.

Detection of hydroxy-acids. C. H. LIBERALLI (Bol. assoc. brasil. pharm., 1931, 12, No. 10, 24).—A solution of FeCl_3 (10%, 32.4 c.c.) and KCNS (10%, 58.2 c.c.) in H_2O (to 100 c.c.) becomes yellow on

addition of a neutral solution of a OH-acid. AcOH and $\text{H}_2\text{C}_2\text{O}_4$ give the same colour, but unlike OH-acids do not permit the return of the original colour on addition of 1 drop of HNO_3 .
CH. ABS.

Potentiometric determination of benzidine by diazotisation. J. A. ATANASIU and A. I. VELCULESCU (Ber., 1932, 65, [B], 1080—1082).—Benzidine is determined potentiometrically by titration in 10% HCl at 60° with 0.1*M*- KNO_2 using a Pt and Ni electrode. KNO_2 must be added slowly at first, but the change is more rapid towards the close of the reaction. The method is applicable to benzidine sulphate.

H. W.

Polarimetric analysis of ternary systems. A mixture of three sterols. E. KAHANE and J. RABATE (Bull. Soc. Chim. biol., 1932, 14, 808—821).—A ternary system containing ergosterol, cholesterol, and zymosterol may be analysed by the application of two equations based on polarimetric determinations combined with one based on a gravimetric determination.

H. D.

Determination of 2-phenylquinoline-4-carboxylic acid and salicylic or acetylsalicylic acid in the presence of one another. E. SCHULEK and B. KERENYI (Z. anal. Chem., 1932, 88, 401—414).—The mixture is dissolved in the min. of NaOH and any org. base removed by extraction with CHCl_3 . The aq. layer is treated dropwise with twice its vol. of H_2SO_4 to convert the phenylcinchoninic acid (I) into its sulphuric acid compound, and the salicylic acid is then extracted with Et_2O . The acid layer is treated with an excess of NaOH to decompose the sulphate and, after acidifying with H_2SO_4 , (I) is extracted with Et_2O , the solution evaporated to dryness, the residue heated at 130° to expel any AcOH, and the acid titrated with NaOH. The ethereal salicylic acid solution is neutralised with NaOH, the Et_2O removed, and the acid determined by titration with KBrO_3 . For accurate results the details given in the original must be closely followed.

A. R. P.

Microchemistry of atophan (2-phenylquinoline-4-carboxylic acid). G. DENIGES (Bull. Soc.

Pharm. Bordeaux, 1931, 3, 163—168; Chem. Zentr., 1932, i, 1375).—Crystals of atophan obtained by various means are described. Alkali hypochlorite, hypobromite, or I-KI solution gives an amorphous ppt. of halogen derivative.

L. S. T.

Volumetric determination of strophanthin. I. E. NOVAK (Pharm. Ztg., 1932, 77, 774—775).—*g*- and *k*-Strophanthin can be determined by oxidation with an excess of 0.1*N*- KMnO_4 in hot dil. H_2SO_4 , followed by back-titration. Both substances use the same quantity of KMnO_4 .

R. S. C.

Detection and determination of arsenic in organic substances after perchloric acid treatment. E. KAHANE (Compt. rend., 1932, 195, 48—50).—As is freed from org. matter by treatment with 2 vols. of HClO_4 : 1 vol. of HNO_3 in place of HClO_4 alone (cf. this vol., 71), and is finally obtained as a solution of H_3AsO_4 in H_2SO_4 in which the As may be determined by standard methods. It is claimed that the method is applicable to small quantities of As in org. matter (toxicology) and to organo-As compounds.

H. A. P.

Simultaneous determination of mercury and halogens [or arsenic or sulphur] in organic substances. G. ILLARI (Annali Chim. Appl., 1932, 22, 261—272; cf. A., 1930, 101).—The substance is mixed with HNO_3 (*d* 1.4) and oxidised electrolytically. With Br compounds, the solution is then diluted and electrolysed, the Hg weighed, and the Br (in the main vessel and in a trap) reduced by As_2O_3 and determined as Br'. With Cl, the solution is treated with $\text{Na}_4\text{P}_2\text{O}_7$ and NH_3 before the second electrolysis (cf. A., 1893, ii, 93). With I, either of these methods may be used. In compounds containing Hg and As, after oxidation and dilution the Hg is removed at 0.05 amp./1.7—1.8 volts, and the As determined as H_3AsO_4 . When Hg and S (but not Cl) are present they may similarly be determined, the latter as H_2SO_4 .

E. W. W.

Determination of copper, cobalt, and nickel in organic substances. A. OKAC.—See this vol., 922, 924.

Biochemistry.

Graphical registration of the oxygen consumption and the carbon dioxide production by men and animals. G. MANSFELD (Arch. exp. Path. Pharm., 1932, 167, 111).—Suitable apparatus has been devised.

W. O. K.

Oxygen affinity of chlorocruorin. H. M. FOX (Nature, 1932, 130, 92).— O_2 pressure curves for chlorocruorin, the respiratory pigment of *Spirographis spallanzanii*, show that $[\text{H}^+]$ and temp. affect the O_2 affinity in a manner similar to that of mammalian haemoglobin. The O_2 affinity between 10° and 26° is of the same order of magnitude as that of haemoglobin in the human body.

L. S. T.

Haemoglobin content of the blood of dairy cattle. H. J. BROOKS and J. S. HUGHES (J. Nutrition, 1932, 5, 35—38).—In 335 determinations the

average val. was 10.96 ± 0.064 g. of haemoglobin per 100 c.c. of blood. No significant variations were observed in cattle of various ages and breeds, or in day-to-day observations or as a result of prolonged fasting.

A. G. P.

Effect of oral administration of amino-acids and intraperitoneal injection of various elements and hydrochloric acid on regeneration of haemoglobin. H. L. KEIL and V. E. NELSON (J. Biol. Chem., 1932, 97, 115—126).—The following treatments failed to stimulate haemoglobin regeneration in rats suffering from anaemia on a milk diet: oral administration of 10 mg. of pure Fe daily as FeCl_3 ; feeding 100 mg. daily of tyrosine, tryptophan, glutamic acid, aspartic acid, or arginine; and intraperitoneal injection of salts of Ni, Zn, Ge, Mn, V, As, Ti,

Se, Hg, Rb, and Cr. Injection of 0.005 mg. of Cu daily is sp. in causing hæmoglobin regeneration. A temporary improvement is caused by injection of HCl in rats maintained on milk and FeCl_3 . Hæmoglobin formation is also stimulated by intraperitoneal injection of FeCl_3 or ferric citrate and of $\text{Fe}(\text{OH})_3$ with Cu added. A. C.

Renal thresholds for hæmoglobin in dogs. Depression of threshold due to frequent hæmoglobin injections and recovery during rest periods. J. A. LIGHTY, jun., W. H. HAVILL, and G. H. WHIPPLE (J. Exp. Med., 1932, 55, 603—615).—The renal threshold for hæmoglobin (the smallest intravenous dose which causes its appearance in the urine) for dogs is 155 mg. per kg. (max. 210, min. 124); repeated daily injections depress the initial level by 46%, and rest periods produce a recovery threshold level. CH. ABS.

α -Lipase and amylase in the blood of Crustaceæ. Z. GRUZEWSKA (Compt. rend., 1932, 195, 278—280).—The serum-lipase of the crayfish is the most active of the group, whilst the enzyme is absent from the serum of the lobster and turtle. The sera of all the Crustaceæ contain amylase. P. G. M.

Enzymes of leucocytes. VIII. Maltases. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem. 1932, 209, 33—37; cf. this vol., 292).—After glycerol treatment, leucocyte residues contain maltase but the extract is inactive, whereas after phosphate elution of the residues the activity is increased although the eluate contains maltase. Grinding the cells with quartz sand renders a part of the maltase sol. Cell residues after glycerol and phosphate treatment lose some of their activity on papain treatment, the solution becoming active. Glycerol inhibits the enzyme, both in sol. and in insol. form; hence the apparent inactivity of the glycerol extract. J. H. B.

F. p. of serum and corpuscles. D. A. COLLINS and F. H. SCOTT (J. Biol. Chem., 1932, 97, 189—213).—In the determination of the f.p. of serum and corpuscles the main sources of error are evaporation during centrifuging and undercooling; loss of CO_2 and the temp. during centrifuging are less important. Elimination of these errors gives results indicating equality of the f.p. and therefore of the osmotic pressures of serum and corpuscles of dog- and ox-blood. F. O. H.

Effect of electrolytes on serum-proteins. M. PIETTRE and A. GULBERT (Compt. rend., 1932, 195, 282—284).—The κ of NaCl solutions is unaffected by the presence of mixed serum-proteins, within the limits 0.1—0.001M. P. G. M.

Dilution of horse-serum in electrolytic solutions. C. ACHARD, A. BOUTARIC, and M. DOLADILHE (Compt. rend., 1932, 195, 196—198).—With the same cation the product of the diluted vol. (*l*) of 1 c.c. of serum and the opacity (*h*) of the solution varies inversely as the valency of the anion. In dil. solution the reverse holds good for multivalent cations (H_2O , 5; AlCl_3 , 18; ThCl_4 , 33). P. G. M.

Phosphorus distribution in chicken blood as affected by the diet. V. G. HELLER, K. R. HUNTER,

and R. B. THOMPSON (J. Biol. Chem., 1932, 97, 127—132).—Vals. of 108.5 and 114.6 mg. per 100 c.c. have been found for the total blood-P of chickens on diets containing 0.483 and 1.16% P, respectively. These are 3—4 times as great as those of mammals. In contrast to Ca, the P content of the cells is greater than that of the plasma. Inorg. plasma-P represents a very small fraction of the total P. A. C.

Normal relationships of blood- and urine-phosphorus. B. S. WALKER (J. Lab. Clin. Med., 1932, 17, 347—353).—The urinary inorg. P in young adults after fasting is normally 0.0256—2.10 mg. per c.c., and the org. P 0—0.195 mg. The correlation coeff. between the blood-inorg. P and the rate of elimination of inorg. PO_4 is 0.416 ± 0.071 . No correlation was observed between the blood-org. P and the rate of excretion of inorg. or org. P. CH. ABS.

Hexosephosphoric acids and blood glycolysis. A. ROCHE and J. ROCHE (Compt. rend., 1932, 195, 340—342).—Erythrocytes, centrifuged with iced H_2O , when added to Na glucose- and fructose-phosphates, lower the reducing power of the hexosephosphates with the production of H_3PO_4 . It is probable that the formation of hexosephosphoric acids is a step in the process of glycolysis in erythrocytes. H. D.

Distribution of sugar between blood-cells and plasma. II. M. JACOBY and H. FRIEDEL (Biochem. Z., 1932, 249, 308—311; cf. this vol., 413).—Blood from rabbits suffering from experimental hyperglycæmia does not differ in the respect concerned from normal blood or from blood to which sugar has been added *in vitro*. W. McC.

Reducing power of glomerular urine and blood-plasma from the frog. A. M. WALKER and E. H. ELLINWOOD (Amer. J. Med. Sci., 1932, 183, 298).—The mean difference in reducing substance content is 2.1 mg. per 100 c.c.; the cerebrospinal fluid contains 13 mg. per 100 c.c. less than the plasma. The glomeruli play no part in phloridzin glycosuria. CH. ABS.

Fructose content of blood. M. H. POWER (Proc. Staff Meetings Mayo Clinic, 1931, 6, 690).—Blood contains only traces of ketose-like substances, probably not fructose. CH. ABS.

Filtration of protein tungstate precipitates from unclaked blood. H. S. H. WARDLAW (Austral. J. Exp. Biol., 1932, 10, 61—63).—Protein is pptd. from unclaked blood by treatment with 8 vols. of 0.6% aq. Na_2WO_4 in 1.5% aq. Na_2SO_4 and 1 vol. of 1.5% aq. Na_2SO_4 in $N/3\text{-H}_2\text{SO}_4$. Clear filtrates are obtained. A. C.

Diurnal variations of the cholesterol content of the blood. M. BRUGER and I. SOMACH (J. Biol. Chem., 1932, 97, 23—30).—The mean standard deviation in the cholesterol content of whole blood in 9 patients in the absorptive state was $\pm 8.0\%$ for 24 hr. and $\pm 3.5\%$ during the morning. In a fasting group, 5 normal subjects showed variations in plasma-cholesterol similar to those of 4 patients, the mean standard deviation during 4 hr. in the morning being $\pm 3.9\%$. Ingestion of food has little effect on blood-cholesterol. A. C.

Determination of ammonia in blood and other biological fluids. O. FOLIN (J. Biol. Chem., 1932, 97, 141—154).—The blood sample, after treatment with K_2CO_3 - $K_2C_2O_4$ solution, is aerated by an impinging air stream, and NH_3 is collected in a specially designed absorption tube, and determined by nesslerisation. This method removes the defects of that of Folin and Denis (A., 1912, ii, 703). Vals. of blood- NH_3 below 0.05 mg. of NH_3 -N per 100 c.c. have not been observed with this method. A. C.

Physics of blood coagulation. H. LAMPERT (Kolloid-Z., 1932, 60, 3—13).—Blood coagulation depends on the material of the containing vessel, particularly on the degree of adherence of the blood clots to the solid wall. The influence of this surface is less in the case of blood rich in fibrin, such as that of the horse. The separation of serum is due to adhesion at the wall of the vessel and to the retraction of the fibrin coagulum; the amount of serum separating varies with these factors. Amber and certain artificial resins retard the coagulation of blood, in consequence of the wall effect, and are therefore preferable to glass in instruments and apparatus for experiments on blood. E. S. H.

Substances involved in the coagulation of the blood of the newborn. H. N. SANFORD, T. H. GASTEYER, and L. WYAT (Amer. J. Dis. Children, 1932, 43, 58—61).—The blood-prothrombin, -fibrinogen, and -antithrombin are higher than for adults. CH. ABS.

Influence of the base-binding power of hæmoglobin on osmotic hæmolysis. M. H. JACOBS and A. K. PARPART (Amer. J. Med. Sci., 1931, 181, 450—451).—Fragility tests made without control of temp. and p_H are of doubtful val. CH. ABS.

Is osmotic hæmolysis an all-or-none phenomenon? A. K. PARPART (Amer. J. Med. Sci., 1931, 182, 153).—Osmotic hæmolysis produced by hypotonic NaCl solutions is accompanied by complete liberation of hæmoglobin from the cell, both during hæmolysis and at equilibrium. When induced by a penetrating substance of small mol. vol. (e.g., ethylene glycol) it is an "all-or-none" phenomenon; with substances of large mol. vol. (e.g., glycerol) this is so at equilibrium. CH. ABS.

Serological specificity of peptides. K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1932, 55, 781—796).—Glycylglycine [*p*-nitro-, m.p. 217—218°, and *p*-amino-benzoyl, darkens at 220° (decomp.), derivatives], glycyl-*dl*-leucine (*p*-nitro-, m.p. 179—180°, and *p*-amino-benzoyl, m.p. 83—86°, derivatives), *dl*-leucineglycine (*p*-nitro-, m.p. 205—206°, and *p*-amino-benzoyl, m.p. 123—125°, derivatives), and *dl*-leucyl-*dl*-leucine (*p*-nitro-, m.p. 209—210°, and *p*-amino-benzoyl, m.p. 122—125°, derivatives) differ serologically, their specificity depending chiefly on the structure of the terminal NH_2 group carrying the free CO_2H group. *p*-Aminobenzoyl-glycine, m.p. 198—199°; *p*-nitrobenzoyl-*dl*-leucine, m.p. 229—230°; *p*-aminobenzoyl-*dl*-leucine, m.p. 182—183°; *chloroacetyl*glycine, m.p. 92—93°; *dl*-leucyl-*dl*- α -aminobutyric acid, m.p. 245—246° (*p*-nitrobenzoyl derivative, m.p. 220—221°); and *dl*- α -aminobutyryl-*dl*-leucine, m.p. 241—242° (*p*-nitrobenzoyl derivative, m.p. 182—184°), are described. CH. ABS.

Chemo-immunological studies on conjugated carbohydrate proteins. VI. Synthesis of *p*-aminophenol α -glucoside and its coupling with protein. W. F. GOEBEL, F. H. BABERS, and O. T. AVERY. VII. Immunological specificity of antigens prepared by combining α - and β -glucosides of glucose with proteins. O. T. AVERY, W. F. GOEBEL, and F. H. BABERS (J. Exp. Med., 1932, 55, 761—767, 769—780).—VI. 3:4:6-Triacetyl- β -glucosyl chloride and Ag *p*-nitrophenoxide in dry $CHCl_3$ give 3:4:6-triacetyl-*p*-nitrophenol α -glucoside, m.p. 148—149°, which with NH_3 in MeOH at 0° affords *p*-nitrophenol α -glucoside, m.p. 216—217°, and the corresponding β -glucoside, m.p. 164—165°. The α -glucoside is unstable in the presence of OH^- . *p*-Aminophenol α -glucoside has m.p. 185—186°.

VII. Further evidence is adduced in support of the view that the immunological specificity of carbohydrates is determined by their chemical constitution. It is possible to differentiate selectively between the two isomeric glucosides of the same sugar.

CH. ABS.

Iron content of blood-free tissues and viscera. Variations due to diet, anæmia, and hæmoglobin injections. R. P. BOGNIARD and G. H. WHIPPLE (J. Exp. Med., 1932, 55, 653—665).—When the renal threshold is not exceeded by the blood-hæmoglobin little excess Fe is deposited in the kidneys, but with superthreshold doses of blood the Fe content of the epithelium of the convoluted tubules is increased 5-fold. The normal dog has a large reserve store of Fe in the liver, spleen, and marrow. The tissue-Fe (1—2 mg. per 100 g.) is lowest in the pancreas, stomach, jejunum, colon, and urinary bladder. Striated muscle (heart, psoas) contains about 4 mg.; lungs (6—7 mg.) show low vals. (3.7 mg.) in anæmia, corresponding vals. for spleen being 25—50 and 7—15 mg., and for liver 25 mg. and 4—5 mg. CH. ABS.

Composition of rabbit carcasses. I. White Angoras. W. K. WILSON and S. MORRIS (J. Agric. Sci., 1932, 22, 453—459).—The H_2O , protein, fat, ash, and carbohydrate contents of male and female rabbits are recorded. Females have a notably larger proportion of fat. A. G. P.

Egg-yolk proteins. T. H. JUKES and H. D. KAY (J. Nutrition, 1932, 8, 81—101).—A review with extensive bibliography. A. G. P.

Isolated cell and tissue constituents. I. Isolation of cell nuclei from calf's heart-muscle. M. BEHRENS (Z. physiol. Chem., 1932, 209, 59—74).—The tissue is frozen in liquid air, dried in vac. below 0°, ground, and the constituents are separated by centrifuging after suspension in liquids of suitable sp. gr. In this manner cell nuclei of calf's heart-muscle are obtained free from protoplasm. From the P content (2.5%) of the purified nuclei, they contain about 30% of thymus-nucleic acid. J. H. B.

Highly unsaturated fatty acids of ox-brains. J. B. BROWN (J. Biol. Chem., 1932, 97, 183—187; cf. A., 1929, 1329; 1930, 249).—Ox-brains were hydrolysed by aq. NaOH, the hydrolysates extracted by BuOH, and the extracted fatty acids brominated. The Et_2O -insol. fraction of the brominated acids was

reduced, esterified (Me), and fractionated. The greater part of the distillate, b.p. 200—210°, consisted principally of acids belonging to the C_{22} series, docosapentenoic acid predominating. Arachidonic acid could not be detected.

F. O. H.

Phosphatides of human brain. I. Separation of α - and β -series of lecithins. Y. YOKOYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1932, 8, 183—185).—The α - and β -series of lecithins from human brain (and herring roe) are separable by the method previously used (A., 1931, 401) for soya-bean lecithins.

H. B.

Phosphatides. V. Fatty acids of phosphatides and of neutral fat of ox-liver. E. KLENK and O. VON SCHOENEBECK (Z. physiol. Chem., 1932, 209, 112—133; cf. this vol., 636).—The fatty acids of liver-phosphatides are in general similar to those of brain-phosphatides but differ in that the amount of C_{22} acids is less than that of the C_{20} acids (with the brain acids the reverse holds), and the C_{18} acids contain, in addition to oleic acid, more highly unsaturated acids, principally linoleic acid. The neutral liver-fat also contains unsaturated acids of the C_{20} and C_{22} groups, but in smaller amount than the phosphatides, and the stearic exceeds the palmitic acid. In these respects liver-fat is more closely allied to depot-fat. Since the unsaturated acids of liver-lipins consist principally of the C_{20} and C_{22} acids they cannot arise by dehydrogenation of depot-fat, which contains chiefly C_{16} and C_{18} groups.

J. H. B.

Bromine content of testicles, epididymis, and Plexus pampiniformis. I. L. KRIVSKY (Biochem. Z., 1932, 249, 288—295).—Administration of NaBr to castrated dogs restores conditioned reflex activity lost on castration but, since testicles, epididymis, and Plexus pampiniformis (I) (horse, ox) do not contain appreciably more than the average amount, for the body, of Br, no relationship between sex hormones and Br has been demonstrated. The Br content of (I) is somewhat greater than that of the other two organs, possibly because of richer blood supply.

W. McC.

Isolation, identification, and determination of ethyl alcohol normally present in human and animal tissues. A. O. GETTLER, J. B. NIEDERL, and A. A. BENEDETTI-PICHLER (Mikrochem., 1932, 11, 167—199).—A detailed account of work already noted (this vol., 637).

Rate of penetration of fixatives. B. M. L. UNDERHILL (J. Roy. Micros. Soc., 1932, 52, 113—120).—The following fixatives are arranged in decreasing order of rate of penetration into guinea-pig's liver at the concns. indicated; AcOH 5, $HgCl_2$ 5, EtOH (abs.), OsO_4 0.5, picric acid 0.7, CrO_3 0.5, CH_2O 4, and $K_2Cr_2O_7$ 1.5%.

A. C.

Increase of dry matter and water content in the silk gland and some properties of the aqueous solution of liquid silk. H. KANEKO and F. KURASAWA (Bull. Sericult., Japan, 1932, 4, 12—16).—The growth curves of dry matter and H_2O content, respectively, are represented by the equations $\log [x-w/0.31-(x-w)]=1.03(t-5.3)$ and $\log [x-w/0.9-(x-w)]=1.01(t-4.6)$, where t is in days and x in g.

The H_2O content of the silk gland of the fully grown larva is about 76%. The sp. conductivity of an aq. solution of liquid silk decreases, and the p_H and relative viscosity increase, with increasing age, while there is an increase of aggregation of the protein mols. and slight gelatinisation.

B. P. R.

Blood-sugar and digestive secretion. L. BUGNARD and C. SOULA (Compt. rend., 1932, 194, 2330—2332).—The psychic gastric secretion produced by sham feeding in dogs is accompanied by a hyperglycæmia, but normal feeding does not cause a similar change in blood-sugar. In the latter case the loss of acid from the system is presumably quickly counterbalanced by the secretion of alkali through pancreas, liver, and intestinal mucous membrane.

W. O. K.

Effect of administration of fat on the sebum of the skin. B. LUSTIG and A. PERUTZ (Biochem. Z., 1932, 249, 370—372).—Subcutaneous administration of olive oil to rabbits results first in an increase in the cholesterol content of the sebum of the skin and then in an increase in its content of unsaturated substances.

W. McC.

Lactation. I. Production of milk in the dog as influenced by different kinds of food proteins. R. G. DAGGS (J. Nutrition, 1931, 4, 443—467).—Liver was a better source of protein than eggs or steak and produced greater milk yields of higher fat content.

A. G. P.

Human milk. VIII. Comparison of composition of milk from the two breasts. M. BROWN, I. C. MACY, B. NIMS, and H. A. HUNSCHER (Amer. J. Dis. Children, 1932, 43, 40—51).—The composition is uniform, but the total vols. may vary considerably.

CH. ABS.

Determination of the hydrogen-ion concentration of urine. F. MAINZER and W. EDEN (Biochem. Z., 1932, 249, 296—307).—Three methods (H electrode, quinhydrone electrode, and colorimetric) have been compared and a table showing the best as well as other methods applicable, within various p_H ranges, to each case is given, the influence of protein content and colour being considered.

W. McC.

Determination of free organic acids in urine. M. LAFARGUE (Bull. Soc. Pharm. Bordeaux, 1931, 3, 202—207; Chem. Zentr., 1932, i, 1275).—Determination of the p_H and P_2O_5 content gives (by formula and tables) the H_2PO_4' ; the remainder of the titratable acidity (phenolphthalein) is due to free org. acids.

A. A. E.

Urinary albumin and pseudo-albumin. V. ZOTIER (Bull. Sci. pharmacol., 1931, 38, 337—346; Chem. Zentr., 1932, i, 1275).—Only the reaction with HNO_3 in the cold is sp. for albumin; AcOH, $CCl_3 \cdot CO_2H$, HCl, and boiling always co-ppt. pseudo-albumin. Pseudo-albumin is a normal constituent of urine (0.05 g. per litre).

A. A. E.

Renal threshold of bilirubin. I. M. RABINOWITCH (J. Biol. Chem., 1932, 97, 163—175).—Bilirubin may be found in urine when the blood concn. of this substance is as low as 0.12 mg. per 100 c.c. If there is a renal threshold val. for bilirubin, it is therefore much lower than that generally accepted. It is suggested that a more sensitive analytical

method may show that bilirubin is a normal constituent of urine. A. C.

Regular occurrence of pyridine derivatives in normal urine. II. W. LINNEWIEH and H. REINWEIN (*Z. physiol. Chem.*, 1932, 209, 110—111; cf. this vol., 767).—Trigonelline is present in human urine during abstinence from coffee, tea, cocoa, and nicotine and is therefore probably a normal constituent. J. H. B.

Vitamin-B in anaemia. S. DAVIDSON (*Lancet*, 1931, 221, 1395—1398).—Clinical evidence suggests that the anti-anaemic factor contained in liver or liver extracts is not vitamin-B. L. S. T.

Value of the oyster in nutritional anaemia. H. LEVINE, R. E. REMINGTON and F. B. CULP [with C. B. ANDERSON] (*J. Nutrition*, 1931, 4, 469—481).—The anti-anaemic potency of the oyster shell is ascribed to its Fe, Cu, and Mn contents. Similar rates of blood regeneration in rats were produced by the ingestion of solutions of Fe, Cu, and Mn salts in proportions corresponding with those in shell. A. G. P.

Effects of radiant energy on milk anaemia in rats. P. C. FOSTER (*J. Nutrition*, 1931, 4, 517—524).—The haemoglobin content and the no., size, and saturation of the red cells of the blood of rats rendered anaemic by a milk diet were increased by exposure to a quartz-Hg arc. A. G. P.

Antianæmic substance in the blood activated by ultra-violet irradiation. R. SEYDERHELM (*Arch. exp. Path. Pharm.*, 1932, 167, 106—107).—The anaemia produced by the intravenous administration of saponin to a dog is inhibited when the blood of the animal is subjected to ultra-violet irradiation. Irradiated blood from a normal dog injected into an animal suffering from saponin anaemia brings about an increase in the no. of red blood-corpuscles in the anaemic dog. The serum of the irradiated blood is inactive and the active substance exists in the stroma of the corpuscle. Normal irradiated blood contains some active material, but the greater bulk of the substance exists in an inactive form which is activated by ultra-violet light and for which the name "cytagenin" is proposed. W. O. K.

Bush sickness. I. H. O. ASKEW and T. RIGG. II. L. J. GRANGE, N. H. TAYLOR, T. RIGG, and L. HODGSON. III. **Soil-iron in relation to the incidence of bush sickness.** T. RIGG and H. O. ASKEW (*New Zealand Dept. Sci. Ind. Res. Bull.*, 1932, No. 32, 62 pp.).—I. Pasture soils in affected areas are not notably deficient in the principal nutrients, but have sufficiently coarse textures to facilitate leaching and low Fe and Ti contents. The mineral content (including Fe) of the herbage is not unduly low.

II. Soil profiles in affected areas are described. Sickness is more acute on soils having high SiO₂ contents and low proportions of Ca, Ti, and more especially of total and available Fe.

III. A considerable proportion of the Fe required by animals is obtained from soil contaminating the herbage. Extraction of soil with 5% H₂C₂O₄ gives a measure of the available Fe, and vals. so obtained

are closely correlated with the incidence of sickness. Addition of Fe oxides or carbonate to salt licks reduces sickness. A. G. P.

Glutathione content and autolysis of malignant growths. H. HEINLEIN (*Z. Krebsforsch.*, 1932, 35, 161—163; *Chem. Zentr.*, 1932, i, 1265).—The glutathione content of tumours (Ehrlich mouse carcinoma, Rous sarcoma, and human carcinoma) is lower than that of normal organs. Hence the degree of activity of the cathepsin in malignant tumours cannot be higher than in other organs. There appears to be no simple relationship between the growth of tumours and proteolysis. A. A. E.

Composition of lipins of normal and pathological organs. I. Lipins of lymph glands of cattle. II. Lipins of normal and of carcinomatous or sarcomatous liver. III. Lipins of normal and of sarcomatous horse-spleen. B. LUSTIG and E. MANDLER (*Biochem. Z.*, 1932, 249, 344—351, 352—365, 366—369).—I. The lipins from the mesenteric and axillary lymph glands of cattle occur partly free (directly extractable) and partly combined (extractable after peptic digestion). In the free portion the P is completely pptd. as phosphatide (chiefly monoaminophosphatide) by COMe₂. Digitonin ppts. one third of the unsaponifiable matter as cholesterol. The solid fatty acids consist chiefly of palmitic and stearic acids and the liquid acids have mol. wt. corresponding with >16—18 C. The combined portion contains much more unsaponifiable matter than does the free. A smaller proportion of it is pptd. by digitonin and it contains only traces of phosphatide precipitable by COMe₂. The fatty acids of the combined portion have moderately high mol. wt. Solid fatty acids (largely unsaturated) preponderate in the material from the axillary glands, and liquid in that from the mesenteric.

II. In the lipins from normal human liver the P is completely precipitable by COMe₂ and most of the unsaponifiable portion consists of cholesterol, which is accompanied by highly unsaturated hydrocarbons, including (in one case) squalene. The solid fatty acids consist chiefly of palmitic and stearic acids and the liquid acids include oleic. The combined lipins differ in several respects from the free. Lipins from hepatic carcinoma differ in various ways (particularly in their low P content) from normal hepatic lipins and so also do lipins from melanotic sarcoma.

III. The lipins of the normal horse spleen have low sap. vals. and high contents of unsaponifiable matter and of material pptd. by COMe₂. The fatty acids, especially the liquid fatty acids, are highly unsaturated and have high mol. wt. Low P and high N contents characterise the phosphatides pptd. by COMe₂. In the lipins from melanotic sarcoma the amount of free fatty acids is higher than in the case of the normal organ, whilst only part of the P can be pptd. with COMe₂. In comparison with the phosphatides of the lipins from the normal organ those of the melanotic sarcoma have high P contents. W. McC.

Cholesterol content of the blood of female rats suffering from tumours and of pregnant rats. C. KAUFMANN and R. ERDMANN (*Biochem. Z.*, 1932,

249, 438—442).—In female rats pregnancy or the presence of tumours does not affect the cholesterol (free or esterified) content of the blood. W. McC.

Sex hormones in cancerous tissue. S. LOEWE, W. RAUDENBUSCH, and H. E. VOSS (Biochem. Z., 1932, 249, 443—445).—Cancerous tissue from men (tissue from genital organs excluded) contains, per kg. of fresh material, at least 125 mouse units of thylykinin and 1—2 mouse units of androkinin.

W. McC.

Purified (protein-free) virus of chicken tumour. I. M. R. LEWIS and W. MENDELSON (Amer. J. Hyg., 1931, 13, 639—642).—The (Berkefeld) protein-free filtrate of tumour extract retains tumour-producing activity. The association of the active principle with the globulin is physical.

CH. ABS.

Influence of magnesium on cancer mortality. A. SARTORY, R. SARTORY, J. MEYER, and E. KELLER (Compt. rend., 1932, 195, 400—403).—Analyses show that there is no correlation between cancer mortality, and the Mg in the essential foods and H₂O of different villages in Alsace-Lorraine.

H. D.

Total nitrogen and non-protein-nitrogen partition of gastric juice obtained after histamine stimulation. L. MARTIN (Bull. Johns Hopkins Hosp., 1931, 49, 286—301).—During normal gastric secretion the non-protein-N excreted is within fairly definite limits; higher concns. are found in benign achylia, gastric cancer, and nephritis.

CH. ABS.

Specific gravity of cholesterol from human gall-stones. R. ZEYNEK (Z. physiol. Chem., 1932, 209, 97—102).—Cholesterol from human gall-stones has d_{40}^{19} 1.052—1.053, d_{40}^{160} (i.e., melted) 0.907, d_{20}^{160} 0.915. The heat expansion of solid cholesterol is little greater than that of H₂O.

J. H. B.

Hypochloræmia and intravenous supply of chlorides. A. PIERINI (Semana Med., 1932, i, 378—386).

CH. ABS.

Significance of cholesterol in cellular oxidation and its bearing on mental disorder. B. H. SEAW and J. S. SHARPE (J. Mental Sci., 1931, 77, 53).—Lecithin is almost completely protected from oxidation by combination with small quantities of cholesterol. Blood-cholesterol in dementia præcox and mania was determined.

CH. ABS.

Non-glucose reduction present in normal and increased in nephritic blood. R. J. PICKARD, L. F. PIERCE, C. S. MARSDEN, jun., R. K. TANAKA, and H. A. TOWNSEND (J. Lab. Clin. Med., 1932, 17, 471—480).—The (average) non-glucose reducing substance present in the blood, as determined by the difference in vals. obtained by Benedict's modification of Lewis and Benedict's method and by Folin and Wu's method, is normally 40.4 mg., and in nephritis 108.7 mg., per 100 c.c.

CH. ABS.

Variations in the antigen content of serum in disease. A. Q. WELLS (Lancet, 1931, 221, 1348—1349).—When titrated against the appropriate antisera, sera from different normal animals and from man show const. antigen contents. Serum from nephritic patients differs from normal human sera in antigen content. Antisera against any one serum

do not always contain the same antibody; two anti-human sera probably contained anti-albumin bodies in the one case and anti-globulin in the other. After severe hæmorrhage the antigen content of a horse agreed with the total protein content.

L. S. T.

Biuret reaction in urinary pus-detection. JUSTIN-MUELLER (Chem.-Ztg., 1932, 56, 604).

H. D.

Globulin and albumin fractions of serum. V. Distribution of the substances responsible for the Wassermann-Meinicke and Muller-Ballung reactions amongst the fractions of syphilitic serum. VI. Distribution of agglutinins of paratyphus-B in paratyphus antiserum and in normal human serum. E. FREUND and B. LUSTIG (Biochem. Z., 1932, 249, 373—377, 378—380).—V. In syphilis, sera which react either positively or negatively to the Wassermann test (I) contain increased amounts of globulin belonging to the fraction sol. in NaCl solution. It is this fraction, and to a smaller extent that sol. in Na₂CO₃ solution, with which the substances responsible for (I) are associated. The albumins and H₂O-sol. globulins react negatively to (I). The globulins sol. in H₂O and those sol. in NaCl solution (as well as the H₂O-sol. euglobulins in high concn.) react positively to the Meinicke tests. Almost all the globulins give the Muller and Ballung reaction.

VI. Paratyphus-B anti-sera (horse) contain more H₂O-sol. pseudoglobulin and much less H₂O-insol. globulin than do normal sera and it is almost entirely with the H₂O-sol. pseudo- and eu-globulin that agglutinating power is associated. In normal human sera the agglutinins are associated with other fractions.

W. McC.

Effect of administration of iodine on the total iodine, inorganic iodine, and thyroxine content of the pathological thyroid gland. A. B. GUTMAN, E. M. BENEDICT, B. BAXTER, and W. W. PALMER (J. Biol. Chem., 1932, 97, 303—324).—Normal and pathological human thyroid glands were desiccated and defatted. The total I was then directly determined by a modified method of Kendall (A., 1930, 1060), inorg. I by analysis of the aq. extract (*ibid.*, 504), and, after hydrolysis, thyroxine by the method of Leland and Foster (this vol., 432). The vals. for exophthalmic goitre indicate that on treatment with I there occurs an increase in both inorg.- and thyroglobulin-I, a change in the chemical nature of the thyroglobulin, and increases in the relative and abs. thyroxine and di-iodotyrosine contents of the gland. Thus treatment with I converts the exophthalmic gland into a normal gland except for the increased relative inorg. I content and for the increased abs. content of I compounds due to its enlarged size.

F. O. H.

Pharmacology of urea; problem of uræmia. M. BAUR (Arch. exp. Path. Pharm., 1932, 167, 104—106).—Various dyes in different degrees have their permeability through the animal organism increased by the presence of urea in the tissue. The toxicity of strychnine to frogs is increased by the presence of urea, presumably as the result of increased permeability of the tissues to the poison. The rate of diffusion of certain dyes in gelatin gel is altered by 1%.

urica, the acid dyes tending to move more rapidly and the basic dyes more slowly. The high urea concn. in the tissues in uræmia may result in the development of toxic symptoms in consequence of the increased permeability of the tissues. W. O. K.

Bismuth diuresis and the blood and urinary changes under clinical conditions. A. B. STOCKTON (Arch. Int. Med., 1932, 50, 142—149).—Intramuscular injection of BiNa tartrate caused an increase in diuresis in 11 of the 15 cases observed, and the increase in the amount of urine correlated with the losses of œdema fluid in œdematous patients. The blood-urea showed no change, whilst the urinary urea, blood- and urine-Cl increased with increasing diuresis. A. L.

Sodium dehydrocholate diuresis. L. KAUFFHEIL and E. NEUBAUER (Arch. exp. Path. Pharm., 1932, 166, 675—692).—Generally in diseased humans and without exception in dogs intravenous injection of the bile salt leads to the rapid onset of a diuresis accompanied by a lowering of the abs. and relative urinary Cl'. In dogs the serum-proteins and -Cl' also decrease, whilst the abs. but not the relative bile-Cl' increases. The diuresis, unless very great, is inhibited by posterior pituitary extract. F. O. H.

Renal glycosuria. Calcium and glucose in blood. I. MORTADA (J. Egypt. Med. Assoc., 1932, 15, 522—544).—A discussion of the lowering of the renal threshold for glucose by pathological conditions of endocrine glands, and of the rôle of Ca in carbohydrate metabolism. A. C.

Iron retention by women during pregnancy. C. M. COONS (J. Biol. Chem., 1932, 97, 215—226).—In practically all the cases examined the Fe content of the food ingested exceeded that of the excreta, the retention being sufficiently great to supply the fetal need and the Fe reserves of the new-born infant. F. O. H.

Changes in the composition of the blood and in the tonus of the vegetative nervous system of cows during pregnancy and delivery. L. SEEKLES, B. SJOLLEMA, and F. C. VAN DER KAAJ (Biochem. Z., 1932, 249, 424—437; cf. A., 1931, 383).—Until the fourth day before delivery the mineral composition of the blood-serum of pregnant cows varies only slightly. Then decrease in Ca and inorg. P begins, the lowest vals. being reached just before or just after delivery, but alternate increases and decreases may occur during the period of birth. During the same period the Mg content of the serum increases and the K decreases, the min. val. for K being reached a few days *post partum*. The diffusible Ca, inorg. P, Mg, and total ionic Ca may vary during the period either in parallel with the total content of these mineral constituents or very irregularly, whilst the blood-sugar increases and the residual N remains unchanged. For a few days before and after delivery the ketonic compounds increase largely and then vary greatly *post partum*; as a rule high vals. accompany low sugar vals. and *vice versa*. When parturient paresis occurs it is not when the serum-Ca is at its lowest but after considerable increase has occurred. Injection of parathyroid extract cures the paresis within 1.5 hr. and reduces the total Ca. As pregnancy advances a

relative increase occurs in the vagus tonus of the heart: this increase, which disappears after delivery, is related to the increased K : Ca ratio in the serum and to other factors. W. McC.

Respiration and fermentation of the surviving human placenta; influence of hormones and the lactic acid metabolism of the living placenta in pregnant animals. A. LOESER (Arch. Gynakol., 1932, 148, 118—148; Chem. Zentr., 1932, 1, 1389).—The metabolism of the placenta is similar to that of a benign tumour. The younger is the placenta the greater is the anaerobic lactic acid fermentation; in the first two months of pregnancy there exists a measurable aerobic lactic fermentation. Insulin raises the anaerobic lactic acid formation slightly and the respiration markedly. Folliculin is without effect. The blood-lactic acid is increased during pregnancy. L. S. T.

Total blood-lipin in alimentary lipæmia. H. F. WECHSLER (Arch. Int. Med., 1932, 50, 37—45).—Curves showing change with time in the total amount of blood-lipin after the ingestion of 100 c.c. of olive oil by persons free from pancreatic or hepatic disease are flat and ascending as age increases and descending in cases where arteriosclerosis is present. A. L.

Fatty acids essential in nutrition. III. G. O. BURR, M. M. BURR, and E. S. MILLER (J. Biol. Chem., 1932, 97, 1—9; cf. A., 1930, 810).—Linolenic and linoleic acids (given as Me esters) are effective and oleic acid is ineffective in curing rats suffering from fat deficiency. Although tung oil is curative, α -elaeostearic acid prepared from it is inactive. Me arachidonate depresses the action of a mixture of Me linoleate and linolenate. A. C.

Influence on carbohydrate metabolism of experimentally induced hepatic changes. I. Fasting and administration of thyroxine. II. Phosphorus poisoning. T. L. ALTHAUSEN and E. THOENES (Arch. Int. Med., 1932, 50, 46—57, 58—75).—I. Glucose, H₂O, and insulin were administered to fasting rabbits and to normal animals treated with thyroxine, this being followed by injections of adrenaline. The fasting animals showed a diminished sugar tolerance and a smaller rise in blood-sugar after adrenaline compared with normal animals, this being probably due to the lowered liver-glycogen. With the rabbits receiving small doses of thyroxine, the sugar tolerance was unchanged and the adrenaline response greater than that for normal animals. No hypoglycæmia was observed in either of these two groups after the modified sugar-tolerance test, and all rabbits showed an increase in hepatic glycogen at this point.

II. In rabbits receiving small daily doses of P, the normal blood-sugar level was not maintained. After administration of glucose, H₂O, and insulin to such animals, there was a progressive decrease in sugar tolerance, and in the last stages of poisoning blood-sugar curves ending in hypoglycæmia were obtained. When the administration of glucose, H₂O, and insulin was followed by injections of adrenaline the resulting hyperglycæmia increased, then decreased to zero as the P poisoning was continued. In the late stages of poisoning the liver could still convert

lactic acid into glucose. Experiments on acute P poisoning gave parallel results. A. L.

Variations in blood-sugar values of normal and vagotomised dogs following glucose administration. J. P. QUIGLEY, W. R. HALLARAN, and B. O. BARNES (*J. Nutrition*, 1932, 5, 77—80).—Glucose administered 20 hr. prior to the test caused an increased ability to metabolise sugar in vagotomised, but not in normal, animals. A. G. P.

Influence of cholic acid on sugar in intestinal resorption and on its behaviour in the liver. H. YUUKI (*Z. physiol. Chem.*, 1932, 209, 1—4).—Administration of cholic acid promotes resorption of sugar in the intestine of the rabbit, and the fixation of the resorbed sugar in the liver. J. H. B.

Basal metabolic rates of vegetarians. G. WAKEHAM and L. O. HANSEN (*J. Biol. Chem.*, 1932, 97, 155—162; cf. A., 1931, 1084).—The mean basal metabolic rate of 20 life-long vegetarians was 11% below Du Bois normals. A period of 6—8 years' vegetarianism is necessary to produce the decrease. A. C.

Protein intake and basal metabolism of college women. R. A. HETTLER (*J. Nutrition*, 1932, 5, 69—75).—The average daily intake of protein was slightly lower than for men (0.94 g. per kg. live-wt.) and the daily urinary excretion of N was 7.69 g. The average basal metabolism showed a deviation of -7.1% from the Harris-Benedict standard. No definite relationship was observed between protein intake and basal metabolic rate. A. G. P.

Growth-promoting values of dried buttermilk, dried skim milk, and dried whey for chicks. F. E. MUSSEHL and C. W. ACKERSON (*Poultry Sci.*, 1932, 11, 69—73).—When fed at the same protein level, dried buttermilk was more efficient than dried skim milk, apparently owing to the presence of lactic acid (approx. 6%). CH. ABS.

Question of the formation of citrulline in the animal body. D. ACKERMANN (*Z. physiol. Chem.*, 1932, 209, 12—19).—The fission of arginine into citrulline and NH_3 (by arginine deimidase) was not observed on subcutaneous injection of arginine into a dog, nor was it produced by ox liver, kidney, muscle, spleen, goose liver, or liver and muscle of the crayfish. After prolonged action, ox kidney, spleen, and muscle but not liver of goose and crayfish show a weak arginase effect. J. H. B.

Endogenous uric acid and hæmatopoiesis. III. Uric acid outputs and reticulocyte counts as affected by glycine, caffeine, urea, bilirubin, atophan, and xylose. J. KRAFKA, jun. (*J. Lab. Clin. Med.*, 1932, 17, 428—436).—Increased rate of excretion of uric acid which follows the oral administration to dogs of caffeine, glycine, urea, NaHCO_3 , and NH_4Cl appears to be due to diuresis. The increase is more marked when the bone marrow is in an active state. Bilirubin, xylose, atophan, and adenosine are not hæmatopoietic agents. CH. ABS.

Liver and elimination of phenols from the blood. A. D. MARENZI (*Rev. soc. argentina biol.*, 1931, 7, 27—35).—In hepatectomised animals con-

jugation of phenols is normal; disappearance from the blood is retarded. CH. ABS.

Kidney and elimination of phenols from blood. A. D. MARENZI (*Rev. soc. argentina biol.*, 1931, 7, 36—57).—Phenols are retained in the (dog's) kidney before being excreted. In severe experimental nephritis phenols are not excreted. CH. ABS.

Is some organ especially adapted for the conjugation of phenols? A. D. MARENZI (*Rev. soc. argentina biol.*, 1931, 7, 58—68).—Tying off dogs' abdominal viscera or extirpation of the intestines retards, but does not suppress, conjugation of phenols after injection of phenol. Hepatectomy, nephrectomy, or extirpation of the spleen, stomach, or colon has no effect on conjugation. CH. ABS.

Factors which determine the concentration of calcium and of inorganic phosphorus in the blood-serum of rats. II. B. KRAMER and J. HOWLAND (*J. Nutrition*, 1932, 5, 39—60).—The serum-Ca and -inorg. P varied with the amounts of these elements and of vitamin-D in the diet, and with min. quantities of vitamin-D the proportionality was direct. An increase of Ca in the diet raised the serum-Ca and lowered the -P. Increased P in the diet produced the reverse effect. Variations due to dietary changes became less marked as the vitamin-D content was increased. A Ca : P ratio of 1.5 (1.2 g. Ca and 0.8 g. P) in the diet produced a similar (normal) ratio in the serum irrespective of the vitamin-D supplied. Under these conditions the effect of vitamin-D was apparent in the live-wt. increases. Cod-liver oil regulated the Ca and P metabolism. A. G. P.

Mineral balance studies on poultry. R. H. COMMON (*J. Agric. Sci.*, 1932, 22, 576—594).—Pullets showed an increased retention of Ca and P during the 2—3 weeks prior to laying. During laying much P was voided in the droppings, involving a temporary negative P balance. A. G. P.

Effect of lime and cod-liver oil on sheep fed on a calcium-deficient ration. D. W. AUCHINACHIE and A. H. H. FRASER (*J. Agric. Sci.*, 1932, 22, 560—575).—Live-wt. increases in indoor sheep were raised to the same level as those of outdoor sheep by additions of cod-liver oil (but not by additions of CaO) to the diet. The effect is ascribed to vitamin-D in the oil and to its action in increasing the utilisation of P and maintaining a suitable Ca \times P product. A low level of serum-Ca is not incompatible with rapid growth. A. G. P.

Mineral exchanges of man. II. Effect of excess of potassium and of calcium on two normal men and an oedematous nephritic. S. H. BASSETT, C. A. ELLEN, and W. S. McCAHN (*J. Nutrition*, 1932, 5, 1—27).—Ingestion of K citrate did not alter the Ca, Mg, or P metabolism in normal or nephritic cases. Addition of CaCl_2 to the diet increased Ca excretion and led to a positive Ca balance in normal but not in nephritic patients. Administration of large proportions of K did not produce negative balances of Na or Cl in normal cases, but in the nephritic, caused increased urinary excretion of both elements, resulting in negative balances. During

the feeding of CaCl_2 to normal patients, the Na and K balances were negative. The N metabolism was not affected by administration of K citrate or CaCl_2 . Fe storage occurred in normal subjects with an average daily intake of 21 mg. and in the nephritic case, 12 mg. of Fe. The proportion of Ca and Na in the urine of the nephritic was abnormally low.

A. G. P.

Calcium content of common dietaries in India. D. R. N. SAHU and A. N. BOSE (Indian Med. Gaz., 1932, 67, 140—141).

CH. ABS.

Phosphorus metabolism in infants fed [with] breast milk or cow's milk. D. B. WITT (Amer. J. Dis. Children, 1932, 43, 306—316).—Of the P ingested, 51—63.8 or 29.2—44.2% was retained for human or cow's milk, respectively.

CH. ABS.

Effect of [administration of] magnesium salts on the growth of rats receiving constant amounts of carotene. H. VON EULER and E. VIRGIN (Biochem. Z., 1932, 249, 393—403).—Mg (as MgCl_2) when given in a diet containing excess of vitamins-B and -D and sufficient carotene and vitamin-A in const. amount, exerts its max. effect on growth when the dose is 150—350 mg. per 100 g. of dry food. Greater doses have less pronounced effects. It is possible that the effect is greatest when just the necessary amount of carotene is given.

W. McC.

Utilisation of the iron of protein foods by the albino rat. I. Comparison of growth and iron assimilation as affected by different protein foods. II. Comparison of protein foods supplementary to milk as sources of iron in nutrition. R. C. MILLER and E. B. FORBES (J. Nutrition, 1931, 4, 483—505).—Examination of numerous protein foods is recorded. The dry wt. of rats is not a significant basis of reference for their Fe contents.

A. G. P.

Design and use of a glass [metabolism] cage [for rats]. J. T. SKINNER, H. STEENBOCK, and W. H. PETERSON (J. Biol. Chem., 1932, 97, 227—234).

Relations between chemical constitution and pharmacological action. J. SCHÜLLER (Arch. exp. Path. Pharm., 1932, 167, 70—71).—Certain radicals may be arranged in a series which represents the order in which they affect the physico-chemical properties of ions or mols. of which they form a part, as well as the pharmacological properties of chemical compounds into which they are introduced.

W. O. K.

Oxygen consumption of the insufficient dog's heart. A. RÜHL (Arch. exp. Path. Pharm., 1932, 167, 100—101).—When in a heart-lung prep. heart-insufficiency is produced by histamine, "unmal" or "sommifen," the O_2 consumption falls and the R.Q. is raised. Strophanthin tends to make the insufficient heart nearly like the normal.

W. O. K.

Carbon monoxide affinity for hæmoglobin. Acute and chronic poisoning. Effect of automobile exhaust gas on guinea-pigs. T. L. RAMSEY and H. J. EILMANN (J. Lab. Clin. Med., 1932, 17, 415—427).—Guinea-pigs, when maintained in an atm. completely or 50% saturated with CO, do not survive after the blood has become >70% saturated

with CO. When maintained at lower concns. for longer periods they are able to survive 60% saturation. Blood-CO may be detected after 28—31 days. *Post mortem* indications of CO poisoning are described.

CH. ABS.

Detoxicating action of colloidal sulphur in carbon monoxide poisoning. N. VITA and E. SALMOIRAGHI (Arch. exp. Path. Pharm., 1932, 166, 519—528).—The absorption spectrum of blood containing CO is markedly changed on treatment with colloidal S. The min. lethal dose of CO for guinea-pigs is increased threefold when the animals are injected with colloidal S. This detoxicating action, however, is very transient, lasting < 1 hr.

F. O. H.

Antagonism of carbohydrate and hydrogen cyanide. A. W. FORST (Arch. exp. Path. Pharm., 1932, 167, 108—111).—The inhibiting action of glucose and other carbohydrates on HCN poisoning is probably dependent on the addition of HCN to the carbonyl group with formation of cyanohydrin. Curative as opposed to inhibiting effects are obtained only with trioses and appear to be a sp. action of these on the central nervous system.

W. O. K.

Comparative pharmacology. I. Toxic and lethal doses of various substances for the mouse and frog. H. FUHNER (Arch. exp. Path. Pharm., 1932, 166, 437—471).—The toxic and lethal doses of the following substances were determined for the grass frog and the white mouse: NaCN, chloral hydrate, camphor, PhOH, *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$, adrenaline, sympatol, acetylcholine, histamine, methylguanidine (I), caffeine, picrotoxin, colchicine (II), pyramidone, novocaine, and percaine. The ratio of the toxicities for each substance in the two animals gives the "frog-mouse index," the vals. for which, in the case of the above substances, lie between 0.3 [for (I)] and approx. 400 [for (II)]. The importance of such an index for the characterisation of toxic substances is indicated.

F. O. H.

Stimulation by the salts of the normal aliphatic acids in the rock barnacle *Balanus balanoides*. W. H. COLE (J. Gen. Physiol., 1932, 15, 611—620).—The efficiency of stimulation in *B. balanoides* of the Na salts of normal aliphatic acids increases with concn. and in the order, NaOAc , propionate, formate, butyrate, valerate, hexoate.

A. L.

Stimulation by hydrochloric acid and by the normal aliphatic acids in the sunfish *Eupomotis*. J. B. ALLISON (J. Gen. Physiol., 1932, 15, 621—628).—The stimulating efficiency of HCl and normal aliphatic acids in *E. gibbosus* increases with concn. and with increasing length of the C chain, HCO_2H being an exception.

A. L.

Influence of boric acid on the [toxic] action of arsenious acid. G. TAUBMANN and J. MUCKE (Arch. exp. Path. Pharm., 1932, 166, 545—554).—The toxicity due to local and absorptive action of solid As_2O_3 is considerably decreased by H_3BO_3 , whilst with dissolved As_2O_3 there occurs only a delay unaccompanied by alleviation of the toxic action. These findings are explained by As_2O_3 being less sol. in aq. H_3BO_3 than in H_2O to an extent dependent on the $[\text{H}^+]$ of the solution.

F. O. H.

Determination, localisation, and elimination of bismuth in the organism. PAGET, LANGERON, and DEVRIENDT (J. Pharm. Chim., 1932, [viii], 15, 600—608).—The determination of Bi in body-fluids, tissues, and faeces is described. After Bi injections, the metal appears in the urine and faeces within 24 hr., but elimination is prolonged over a considerable period, max. elimination occurring after 3—4 days. Elimination also occurs through the saliva and Bi is found in all the body-fluids; it is localised especially in the liver and kidneys, and, to a smaller extent, in the brain. J. W. B.

Local irritation effect of calcium salts in relation to their chemical constitution. F. WEILGUNY (Arch. exp. Path. Pharm., 1932, 167, 71—72).—When injected subcutaneously solutions of Ca salts at the same p_H produce irritation which is greater with increase in the hydrophobic character of the anion and less with increase of its hydrophilic character. W. O. K.

Role of unantagonised cations in protecting the membrane-forming function in the eggs of the sea-urchin. A. R. MOORE (Protoplasma, 1932, 15, 268—275).—The addition of alkali metal and alkaline earth cations preserves the membrane-forming function of eggs exposed to non-electrolyte (e.g., urea, glycerol) solutions. Univalent (Na, K, Li, Rb, Cs) cations are almost equally potent, having an effective concn. of 0.14M. Similarly Ca^{++} , Sr^{++} , and Mg^{++} are equally effective in 0.002M solution, but Ba^{++} is uniformly more active. Ca^{++} and Na^+ are not antagonistic but additive in their action. A. G. P.

Importance of atmospheric moisture in the growth of organisms. E. JANISCH (Naturwiss., 1932, 20, 589—591).—The H_2O v.p. in % of relative humidity at various temp. is discussed. W. R. A.

Variation in physiological activity of alcohols among isomerides and homologues. R. W. HUFFERD (J. Amer. Pharm. Assoc., 1932, 21, 549—556).—The toxicity of purified alcohols to guinea-pigs (as measured by inability to walk) is in the following order: *tert.*-hexyl > *sec.*-heptyl > *sec.*-hexyl > *tert.*-amyl > *sec.*-amyl > *iso*-amyl > *n*-amyl > *n*-hexyl > Bu^a > *sec.*-Bu > *n*-heptyl > Bu^b > *tert.*-Bu > Pr^a > Pr^b > 96% Et > 100% Et > Me. R. S. C.

Toxicity of methyl alcohol. R. W. HUFFERD (J. Amer. Pharm. Assoc., 1932, 21, 548).—Very pure MeOH is slightly less toxic to rats than EtOH even in repeated doses. R. S. C.

Pharmacological methods for determination of nitro-compounds (glyceryl nitrate) in pharmaceutical preparations. F. A. LEHMANN (Arch. exp. Path. Pharm., 1932, 167, 87).—Glyceryl nitrate is determined by observation of the lowering of the blood-pressure on intravenous injection into a narcotised rabbit. W. O. K.

Oxidative poisoning and detoxication with respect to habituation. H. VOLLMER (Arch. exp. Path. Pharm., 1932, 166, 405—431).—Mice continuously injected with EtOH become habituated to the narcotic. Continuous injection of quinol, however, results in an increasing sensitivity to this substance.

Mice habituated or hyposensitive to EtOH are hypersensitive to quinol, colchicine, or NH_2Ph ; those hypersensitive to quinol are hyposensitive to EtOH. These facts are explicable only on the ground of an increase in the vital oxidative processes accompanying habituation (positive or negative) to quinol or EtOH. Thus the increase in metabolism is the cause of habituation to EtOH and is connected with the relationship between age and metabolic rate on the one hand and sensitivity towards poisons on the other. F. O. H.

Influence of ethylthiocarbimide, ethyl thiocyanate, and allylthiocarbimide on sulphur metabolism in rabbits. M. SANDBERG and O. M. HOLLY (J. Biol. Chem., 1932, 97, 31—35).—The urinary S excretion (% of intake) of rabbits decreases when EtSCN or EtNCS is added to the diet, and slowly returns to normal after the experimental period. Allylthiocarbimide exerts a similar effect, but the excretion rises above the normal in the after-period. A. C.

Toxicity to goldfish of organic thiocyanates and thiocarbimides. N. L. DRAKE and R. L. BUSBEY (J. Amer. Chem. Soc., 1932, 54, 2930—2935).—Data are given, as survival time curves, regarding the toxicity to goldfish of *n*- and *iso*-amylthiocarbimides, BzNCS, PhCNS, and *p*- $NMe_2 \cdot C_6H_4 \cdot CNS$. Except in very low concns. the amyl compounds are the least toxic. The other three substances possess almost the same toxicity at high concns.; BzNCS is the least toxic in low concns. *tert.*-Amylthiocarbimide has no effect at a concn. of 3.48×10^{-5} mol./litre; $CH_2Ph \cdot CNS$ has little or no action at concns. of 3.36 to 7.38×10^{-5} mol./litre. BzNCS is much more toxic than the amyl compounds in high concn.

C. J. W. (b)
Biological assay of strophanthus (kombe) in comparison with ouabain. J. H. GADDUM (Quart. J. Pharm., 1932, 5, 274—300).—A comparison of the potencies of five different tinctures with the International Standard ouabain by nine different observers using seven different methods has revealed that the U.S.P. X method gives higher results than any of the other methods, and that such discrepancies are due, to some extent, to the use of ouabain, instead of a standard tincture of strophanthus, as a standard of comparison. W. S.

Assay of tinctures of digitalis by colorimetric and biological methods. F. J. DYER (Quart. J. Pharm., 1932, 5, 172—179).—The assay of tinctures of digitalis by the chemical (colorimetric) method of Knudson and Dresbach (A., 1922, ii, 882) furnishes results which deviate so profoundly and irregularly from those obtained by the biological (frog) method of Trevan and Boock (B., 1929, 112) as to render the former method useless, even as an approx. index of biological potency. W. S.

Xenopus in digitalis standardisation. J. W. C. GUNN and D. EPSTEIN (Quart. J. Pharm., 1932, 5, 180—182).—*Xenopus laevis* is preferable for use in the assay and standardisation of digitalis preps. to *Rana temporaria*, employed for this purpose by Trevan (A., 1927, 792; B., 1929, 112). Tinctures of digitalis deteriorate by 10—15% in two years, but

thereafter retain 80% of their original strength, even after 11 years. W. S.

Action of digitalis on metabolism. H. FREUND (Arch. exp. Path. Pharm., 1932, 167, 73—76).—Small therapeutic doses of digitalis preps. increase the quantity of glucose utilised by finely-divided tissue, but the proportion of glucose converted into lactic acid is decreased whilst in presence of larger toxic doses much less glucose is utilised, but it is all converted into lactic acid. The amount of glycogen converted into lactic acid and reducing sugar is increased by therapeutic, but decreased by toxic, doses. Therapeutic doses increase the amount of lactic acid which disappears anaerobically (in presence of bromoacetate) whilst toxic doses have the opposite effect. Insulin and thyroxine have sp. and opposed actions on the system. W. O. K.

Action of Japanese camphor on the heart. IV. *Allo-p-ketocamphor* ("vitacamphor"). K. TAMURA, G. KIHARA, and M. ISHIDATE.—See this vol., 948.

Antiseptic value and toxicity of menthol isomerides. F. WOKES (Quart. J. Pharm., 1932, 5, 233—244).—*l*-, *d*-, *dl*-, and *dl-iso*-Menthol, and *dl-neo*-menthol exert a toxic action on mice (average oral dose for 50% mortality 3—4 mg. per g. of body-wt.). These substances are 5—12 times as lethal as PhOH towards *B. coli* and *Staph. pyogenes aureus*. *l*-Menthol has a lower activity than its *d*-enantiomorph. W. S.

Action of a soluble derivative of hexylresorcinol. K. S. GREWAL (J. Pharm. Exp. Ther., 1932, 45, 283—290).—Sodium hexylresorcinol disulphate gives a yellow ppt. with aq. Br which dissolves in aq. NH_3 to form a yellow solution. It is practically devoid of antiseptic power and has no effect on paramecia. H. D.

Absorption of salicylic acid in the mouth. W. BLUME and G. BUCHHOLZ (Arch. exp. Path. Pharm., 1932, 166, 472—492).—Absorption of Na salicylate from the rabbit's mouth is slow, the first traces of the acid appearing in the urine 25 min. after injection into the mucous membrane. The total excretion is dependent on the type of food. With rabbits fed on turnips 80% of the acid injected is excreted, the first appearance in the blood occurring 15—30 min. after injection. The acid appears in the urine 2 min. after intravenous injection. The detailed changes in the urinary and blood levels following injection of Na salicylate by various routes are described. F. O. H.

Amphibian poisons. O. GESSNER (Arch. exp. Path. Pharm., 1932, 167, 92—93).—In the gland secretion of *Molge marmorata*, 3 poisons are found: (a) a volatile substance with local irritating action, (b) a non-volatile substance agglutinating red blood-cells, and (c) a saponin. The alkaloids of the salamander (samandarine, m.p. 325°, and salamander alkaloid II) have been investigated pharmacologically. On mammals they act as convulsive poisons. W. O. K.

Poisons in edible fungi. H. STEIDLE (Arch. exp. Path. Pharm., 1932, 167, 91—92).—Poisons may be extracted from many edible fungi. *e.g.*, a muscarine-

like substance from *Cantharellus cibarius*, blood poisons from *Boletus edulis* and *Agaricus campestris*, and poisons attacking the blood vessels from many fungi. W. O. K.

Pharmacological actions of benzoyl-*N*-methylhomogranatoline. G. K. ELPHICK and J. A. GUNN (Quart. J. Pharm., 1932, 5, 220—232).—Several pharmacological actions of benzoyl-*N*-methylhomogranatoline (I) are qualitatively similar to those of tropacocaine (II). Quantitatively, (I) stands approx. between (II) and benzoyl-*N*-methylgranatoline (cf. Tanret, A., 1923, i, 832). W. S.

[Pharmacology of] morphine, codeine, and derivatives. I. General methods. II. Isomerides of codeine. N. B. EDDY (J. Pharm. Exp. Ther., 1932, 45, 339—359, 361—381).—I. Methods of comparing the physiological action of morphine and its derivatives on mice and rabbits are described.

II. The effects of the isomerides codeine, ψ -codeine, isocodeine, and *allo-ψ*-codeine as regards depression of respiration, toxic, analgesic, and constipating effects are compared. H. D.

Influence of atropine on sugar metabolism. A. CASANEGRA (Semana Méd., 1932, i, 803—809).—Normally atropine does not affect blood-sugar. In diabetes it is slightly lowered by administration of atropine before meals; the tolerance curves are not influenced. In the dog large doses produce hyperglycaemia; small doses slightly reduce the sugar. The hypoglycaemic curve after injection of insulin is unchanged. CH. ABS.

Determination of atropine in human urine. P. PULEWKA (Arch. exp. Path. Pharm., 1932, 167, 96).—The method involving the pupil of the mouse's eye is used. During several months' treatment with atropine, the amount excreted in the urine falls slowly from the normal fraction ($\frac{1}{3}$ to $\frac{1}{2}$ of that administered) to sometimes $< \frac{1}{4}$. W. O. K.

Hyperglycaemic action of hordenine sulphate. G. TANRET (Compt. rend., 1932, 195, 271—273).—The substance exerts a hyperglycaemic action in rabbits and dogs, the effect being approx. twice as great by intravenous as by subcutaneous injection.

P. G. M.
Effects on the circulation of tissue-constituents. H. H. DALE (Arch. exp. Path. Pharm., 1932, 167, 21—32).—A review of present knowledge of vaso-pressor and vasodilator substances. W. O. K.

Effects on the circulation of tissue-constituents. G. EMBDEN (Arch. exp. Path. Pharm., 1932, 167, 50—52).—A review of the pharmacological action of adenylic acids and related substances. The action on the heart which decreases with increased phosphorylation is apparently associated with deamination, whilst the uterus action which increases with increased phosphorylation would appear to be produced by undeaminised adenylic acid.

W. O. K.
Tissue-constituents with effects on the circulation. F. VOLHARD (Arch. exp. Path. Pharm., 1932, 167, 32—50).—A review of the mechanism of skin reactions and blood-pressure disturbances, especially

in pathological conditions with vasomotor symptoms. W. O. K.

Influence of histamine on the gaseous metabolism of the isolated perfused dog's limbs. A. BERGWALL (Arch. exp. Path. Pharm., 1932, 167, 101).—Histamine reduces the difference in O_2 content between arterial and venous blood but no change in the corresponding CO_2 contents. W. O. K.

Action of histamine on the gaseous metabolism of isolated perfused dog's limbs. A. BERGWALL and A. RÜHL (Arch. exp. Path. Pharm., 1931, 166, 529—535).—Large doses (3 mg.) of histamine result in a marked decrease of O_2 -consumption accompanied by an increase in the R.Q. due to a disturbance of O_2 -diffusion resulting from an oedema produced by the histamine. F. O. H.

Liberation of a histamine-like substance during anaphylaxis in the guinea-pig. R. BARTOSCH, W. FELDBERG, and E. NAGEL (Arch. exp. Path. Pharm., 1932, 167, 81—82).—When the lung of a guinea-pig which has been previously sensitised with ovalbumin is perfused with Ringer solution containing a small amount of ovalbumin it develops anaphylactic rigidity and the perfusate contains a histamine-like substance or histamine itself in quantities which may be detected biologically. The perfusate is able to induce anaphylaxis when perfused through the lung of a fresh unsensitised guinea-pig. W. O. K.

Determination of acetylcholine in the presence of choline, histamine, and adrenaline by means of leech preparations. B. MINZ (Arch. exp. Path. Pharm., 1932, 167, 85—87).—The action of acetylcholine on preps. of leech muscle sensitised with eserine may be used as a sp. quant. test for acetylcholine. W. O. K.

Pharmacology of sauerkraut-juice. W. GEHLEN (Arch. exp. Path. Pharm., 1932, 166, 703—710).—Parenteral introduction of the juice into animals is followed by a local reaction due to its acidity. Oral administration is followed by diarrhoea. The action of the juice on the isolated heart and its stimulating power on the parasympathetic nervous system and the fact that the latter property is destroyed by alkalis indicate the presence of lactyl- or acetyl-choline in a concn. of approx. 1 : 20,000. F. O. H.

Biological efficacy of various kinds of light. II. E. KEESER (Arch. exp. Path. Pharm., 1932, 166, 624—633).—With respect to their action on the blood-sugar of fasting rabbits, red light activates adrenaline and inactivates insulin, blue light activates insulin and inactivates adrenaline, whilst green light activates both hormones. The rise in blood-sugar following intravenous injection of glucose into fasting rabbits irradiated with blue light is less and the recovery more rapid than in rabbits with red light, whilst with green light there are only slight variations from the normal. The changes occurring in the sugar content of the skin and in the reduced glutathione contents of the skin and blood exhibit a similar dependence on the type of light. The possible relation of these phenomena to a primary action on the autonomic nervous system is discussed. F. O. H.

Chemistry of mitogenetic radiation. I. Oxidation reactions as a source of the radiation. A. E. BRAUNSTEIN and A. POTOZKY. II. Mitogenetic spectra of oxidation reactions. A. POTOZKY (Biochem. Z., 1932, 249, 270—281, 282—287).—I. Mitogenetic radiation is probably a special case of ultra-violet chemiluminescence of very low intensity and probably accompanies all oxidation and reduction reactions whether biological or not. It is independent of all other factors in these reactions. No such radiation has been detected in other types of reaction. If illumination conditions are the same in both cases, the order of intensity of the radiation is the same for biological and non-biological reactions. When yeast is used as detector great variations are observed in the times required to produce max. effect in the various reactions. In many cases, after an optimum time has elapsed the effect diminishes rapidly and may even be reversed.

II. The λ of the mitogenetic radiation from inorg. oxidation reactions lie in the range specified by Gurwitsch (1900—2500 Å.) and mainly between 2150 and 2350 Å., although radiations of other λ may also be emitted. Illumination of the source with visible light increases the intensity of the radiation in some cases. The radiations from the erythrocytes of pigeon's blood have λ in the same region (2150—2350 Å.). The spectra of the inorg. reactions differ slightly in the distribution and intensity of the lines, but they are to a great extent sp. W. McC.

Mitogenetic radiation from muscle and from oxidation reactions. G. FRANK and S. RODIONOV (Biochem. Z., 1932, 249, 323—343).—By means of a modification of the apparatus of Schreiber and Friedrich (A., 1931, 125) in which an Al cathode is used, the intensity of the mitogenetic radiation from working frog muscle and isolated heart as well as from muscle extract and from chemical oxidation reactions (oxidation of alkaline pyrogallol, $SnCl_2 + 2HgCl_2$, $K_2Cr_2O_7 + FeSO_4$) *in vitro* has been measured by entirely physical means without the aid of biological detectors. In the case of the last-named reaction the intensity of the radiation depends on the extent of the illumination with visible light. W. McC.

Enzymes and their action. (SIR) F. G. HOPKINS (Proc. Roy. Soc., 1932, B, 111, 280—297).—A discussion. A. L.

Chain reactions in enzymic catalysis. J. B. S. HALDANE; D. RICHTER.—See this vol., 917.

The enzyme model of Bredig and Fajans. P. RONA and F. REUTER (Biochem. Z., 1932, 249, 455—469; cf. A., 1908, ii, 268; 1924, ii, 842).—The unimol. decomp. of bromocamphorcarboxylic acid in $COPhMe$ is changed by addition of increasing amounts of quinine into a type of reaction resembling the autocatalytic, the time-% decomp. curve becoming S-shaped. During that part of the process to which the S-shaped portion of the curve corresponds the max. rate of decomp. is proportional to the concn. of quinine. If the max. rates of decomp. of the three forms (*d*, *l*, *dl*) of the acid be plotted against the corresponding concns. of quinine, the curves for the *d*- and *dl*-acids coincide. The slope of the curve for the

d-acid is less steep. If the concn. of quinine is kept const. and the amount of substrate varied the max. rates of decomp. tend towards a limit. W. McC.

Asymmetric synthesis with the aid of catalysts. II. G. BREDIG and M. MINAEFF (Biochem. Z., 1932, 249, 241—244; cf. A., 1912, i, 983; Rosenthaler, A., 1909, i, 622).—Optically active (*d* or *l* at will according to the alkaloid used) hydroxynitriles are produced from HCN and the following aldehydes by the action of quinine or quinidine which, in this respect, behave exactly as do appropriate enzymes: cinnamaldehyde, anisaldehyde, citral, piperonal, MeCHO. The alkaloids, in proportion to their concn., also greatly accelerate the reaction. As regards optical activity the reaction exhibits a max. attained after an optimum time. W. McC.

Amylosynthase. T. MINAGAWA (Proc. Imp. Acad. Tokyo, 1932, 8, 244—246).—The fractional pptn. of amylosynthase and amylase from autolysed yeast extract by $(\text{NH}_4)_2\text{SO}_4$ or $\text{Pb}(\text{OAc})_2$ is described. Further separation is effected by glycerol in which only amylase is sol. Amylosynthase is also obtained from potato and rice seeds. Its activity in polymerising achroodextrin is max. at 20° at p_{H} 6.2, and is destroyed in 10 min. at 50°. The synthase polymerises trihexosan and hexahexosan. A. C.

The lipoxidases of *Glycine soja* and *Phaseolus vulgaris*. E. ANDRE and K. HOU (Compt. rend., 1932, 195, 172—174).—The grains of different varieties of soya have no effect on guaiacol preps. *G. soja* and *P. vulgaris* oxidise the oils obtained from the former; this oxidation is produced by sp. oxidases. H. D.

Hydrolysis of acetylcholine and related substances. A. SIMONART (Amer. J. Med. Sci., 1931, 181, 879—880).—Acetyl- (I), propionyl- (II), and butyryl-choline (III) have equal rates of hydrolysis; (I) is destroyed twice as quickly as acetyl- γ -homocholine, and nearly 6 times as quickly as acetyl- β -methylcholine. Eserine strongly inhibits the hydrolysis of (II) and (III), and, less markedly, of triacetin. Probably the enzyme causing fission of (I) is not sp. CH. ABS.

Enzymic hydrolysis and synthesis of esters. P. RONA and R. AMMON (Biochem. Z., 1932, 249, 446—454; cf. this vol., 92).—In the presence of H_2O dry powder from the pig pancreas induces synthesis of ester from Bu^nOH and $\text{Pr}^n\text{CO}_2\text{H}$ or hydrolysis of PrCO_2Bu^n , the same equilibrium point being reached in both cases. The synthesis is greatly and the hydrolysis to a smaller extent inhibited by Ca (as CaCl_2) but both are unaffected by quinine hydrochloride, strychnine sulphate or Na taurocholate. When a buffer is present it undergoes vol. changes during the hydrolysis, which therefore cannot be followed dilatometrically. During the autohydrolysis (buffer absent) of the Et ester of *dl*-alanine a vol. decrease of 15.0 c.c. per mol. of alanine liberated is observed. W. McC.

Asymmetric hydrolysis by esterase (human liver) of racemic mandelic esters. R. AMMON and W. GEISLER (Biochem. Z., 1932, 249, 470—475; cf. this vol., 648).—Esterase from human liver asymmetrically hydrolyses Me, Et, Pr^n , and Bu^n

dl-mandelates and except in the case of the Bu^n ester (concn. 0.012—0.120*M*) reversal of the direction of optical rotation ("inversion") occurs when the concn. of the substrate is sufficiently high. The concn. of the substrate at which symmetrical hydrolysis occurs decreases as the no. of C atoms in the alcohol residue of the ester increases and, since the solubility of the esters in H_2O decreases with the increase in the no. of C atoms which they contain, the "inversion concn." may depend on solubility. If the ester is present in excess the specificity of the esterase is independent of the concn. of the substrate. *Bu}^n* *dl*-mandelate has b.p. 127—128°/0.3—0.4 mm., 161°/14 mm. W. McC.

Muscle-phosphatase. I. H. HARA (J. Agric. Chem. Soc. Japan, 1931, 7, 1053—1060).—The activity of muscle-phosphatase is greatest at p_{H} 6.4 for the female (fowl, horse, rabbit) and at p_{H} 7.94 for the male. CH. ABS.

Liberation of invertase from yeast. III. Condition of the sugar-hydrolysing enzymes in the yeast cell. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1932, 209, 38—48; cf. this vol., 305).—Invertase and other yeast carbohydrases are endo-enzymes; they are protected by the cell-membrane, a carbohydrate-protein complex on which they are loosely adsorbed. They are liberated only after enzymic hydrolysis or mechanical destruction of the cell-membrane. The enzymes attacking the membrane are of two kinds, malt amylase and plant proteinase. The desmo-enzymes of leucocytes differ from endo-enzymes in their inhibition by glycerol and non-dependence of their action on $\text{PO}_4^{''}$. They are chemically bound to the protoplasm and are liberated by enzymes which hydrolyse the colloidal carrier. J. H. B.

Coccarboxylase. II. E. AUHAGEN (Z. physiol. Chem., 1932, 209, 20—26; cf. this vol., 305).—Coccarboxylase is removed from yeast juice with difficulty by dialysis against H_2O , but more readily against aq. Na_2HPO_4 . In the latter case juices are obtained which are activated 25—50 times in fermentation of AcCO_2H by addition of coccarboxylase. Mg also stimulates the fermentation. J. H. B.

Fermentation activator Z and growth-promoting substances. H. VON EULER and T. PHILIPSON (Biochem. Z., 1932, 249, 245—256; cf. A., 1931, 263).—A method of determining the amount of the Z-complex and of its two components in extracts obtained from plants by boiling with H_2O and in other materials (egg, urine) is described. The complex or one of its components can be pptd. from solution by Zn, Fe, or Al hydroxide after preliminary treatment of the solution with Pb and Hg salts. $\text{Hg}(\text{NO}_3)_2$ is also a useful pptg. agent. W. McC.

Action of volatile substances and gases on the growth of moulds. R. G. TOMKINS (Proc. Roy. Soc., 1932, B, 111, 210—226).—In the presence of vapour of such substances as COMe_2 , CHCl_3 , and Et_2O , the latent period of germination of fungi is the same as that in air, the colony spreads at a const. but reduced rate, and the concns. of the substances necessary to inhibit growth check germination. Such

substances as MeCHO, HCN, H₂S, and NH₃ cause an increased latent period of germination and a reduced rate of growth which increases with the size of the colony, the concns. necessary to inhibit growth being greater than those required to inhibit germination.

A. L.

Influence of iron on the citric fermentation of *Aspergillus niger*. A. QUILICO and A. DI CAPUA (Giorn. Chim. Ind. Appl., 1932, 14, 289—293).—The contradictory statements of the literature are discussed, and two strains of the mould, both capable of forming citric acid from sugar, were tested. One strain (S) gives virtually no acid in presence of traces of Fe, whereas the other (A) gives a yield of acid increasing with the proportion of Fe (as FeCl₃).

T. H. P.

Influence of heavy metal salts on *Penicillium glaucum* with special reference to the action of anions. J. TALTS (Protoplasma, 1932, 15, 188—238).—Two phases in the growth of *P. glaucum* are observed, the first being characterised by a rapid increase in the dry wt. of the fungus and in the [H⁺] of the nutrient, the second by a decrease in the [H⁺] and a smaller increase in dry wt. These changes in [H⁺] are markedly affected by the presence of Zn, Co, Ni, and Cd salts in 0.005*M* solutions. The effect of the cations predominates, and causes delayed germination of spores and an actual decrease in the % germination. The relative toxicity of the anions Cl⁻, Br⁻, I⁻, NO₃⁻, SO₄⁻, and OAc⁻ varied with the cation associated with them and with the concn. of solutions containing the same cation. The order of toxicity of the cations was Ni < Zn < Co < Cd. The toxicity of these salts is due not to the coagulation of the plasma colloids, but to the retarded absorption of essential nutrients.

A. G. P.

Production of organic acids from carbohydrates by fermentation. O. E. MAY and H. T. HERRICK (Chem. News, 1932, 145, 81—92).—A survey of recent research on the production of acetic, butyric, citric, formic, fumaric, gallic, gluconic, kojic, lactic, malic, oxalic, propionic, and succinic acids.

E. S. H.

Biological purification in nature and industry. J. SMIT (Chem. Weekblad, 1932, 29, 486—490).—A lecture, dealing with the bacteriological processes occurring in rivers and the sea, and in sewage-disposal plants.

H. F. G.

Stability of physiological characters of bacteria. E. B. FRED (Proc. Nat. Acad. Sci., 1932, 18, 465—460).—N-fixing, lactic acid, and tubercle bacteria all show a remarkable constancy of properties when cultured over a long period of years.

H. D.

Mechanism of cellulose digestion in the ruminant organism. III. Action of cellulose-splitting bacteria on the fibre of certain typical feeding stuffs. H. E. WOODMAN and J. STEWART (J. Agric. Sci., 1932, 22, 527—547; cf. A., 1928, 1402).—The % fermentability by thermophilic bacteria of the crude fibre from a no. of feeding stuffs was higher than the digestion coeff. determined by feeding trials, and the order of magnitude of the two vals. was not the same. The fermentation coeff. of the fibre

of untreated feeding stuffs was much lower than that of the chemically separated fibre. Differences are ascribed to the manner of deposition of the resistant lignocellulose in the cells rather than to the actual amount present. During fermentation there was an apparent increase in fibrous material, probably due to the formation, from the oil fraction, of new and resistant substances. The fermentation coeff. of separated fibre is not a trustworthy index of its digestibility in the untreated feeding stuff, but gives information as to the partition of cellulose and lignocellulose in the material. The process of lignification and the corresponding reduction in fibre digestibility in growing rye grass is associated with the formation of relatively small amounts of lignocellulose. Cultural details and the adaptation of the fermentation method for the examination of faeces are described.

A. G. P.

Celluloses of *Acetobacter xylinum* and Tunicates. R. SUTRA (Compt. rend., 1932, 195, 181—182).—The membranes of *A. xylinum* after extraction with EtOH, CHCl₃, and Et₂O contain 1.8% N. By subsequently treating with NaOH until decolorised, 0.5% aq. NaOCl, EtOH, and Et₂O, all the N is removed, showing that the latter must be present as protein and not as chitin. The celluloses of *Acetobacter* and Tunicates as regards chemical and physical properties are identical with those of cotton.

H. D.

Formation of methylglyoxal by *Clostridium acetobutylicum*. L. B. PETT and A. M. WYNNE (J. Biol. Chem., 1932, 97, 177—182).—The bacterium, incubated at 37° for 48 hr. in solutions containing Mg hexosephosphate (mainly diphosphate) at *p*_H 6.0, produces methylglyoxal and possibly also AcCO₂H.

F. O. H.

Coagulation of milk by *B. typhosus* and other bacteria. C. GORINI (Compt. rend., 1932, 195, 187—188).—Sterilised milk is coagulated by various streptococci by adding it to a culture on gelatin; *B. typhosus* also produces a clot when treated in the same manner. The same stock of *typhosus*, if inoculated into milk alone, will not coagulate it. The proteolytic activity of the bacteria is independent of their action on caseinogen.

H. D.

Decomposition of proteins by micro-organisms with particular reference to purified vegetable proteins. S. A. WAKSMAN and R. L. STARKEY (J. Bact., 1932, 23, 405—428).—Purified proteins are readily decomposed in liquid media by bacteria, actinomyces, and fungi. The rate and extent of decomp. of various plant and animal proteins showed considerable variation, but no characteristic differences between the two classes of substances in this respect were observed. Where proteins were used as sole sources of C for the organisms, media rapidly became alkaline and much NH₃ was lost. The ratio of protein decomposed to protein synthesised by the organisms was greatest for bacteria and least for fungi. The resistance to decomp. shown by proteins contained in plant tissue is due not to sp. differences in chemical structure between these and animal proteins, but to their ability to form resistant complexes with non-nitrogenous compounds.

Porphyryn compounds derived from bacteria. F. M. STONE and C. B. COULTER (J. Gen. Physiol., 1932, 15, 629—639).—Extraction of *B. phosphorescens*, yeast, and *C. diphtheriae* with *N*-alkali gives hæmochromogens similar to cytochrome-*C*, those from the first two being identical and that from the last-named differing from them in the position of the main absorption bands. These extracts treated with AcOH and Et₂O give α -hæmatin and a porphyrin with a characteristic absorption spectrum, the latter yielding coproporphyrin and the Cu compound of coproporphyrin with 5% HCl. Lycopene occurs in the AcOH-Et₂O extract of *C. diphtheriae*. A. L.

Purification and concentration of diphtheria toxin. A. WADSWORTH, J. J. QUIGLEY, and G. R. SICKLES (J. Exp. Med., 1932, 55, 815—828).—A stable toxoid was obtained by pptn. with COMe₂ at 4°; its flocculating val. was studied. CH. ABS.

Effect of carbon monoxide on the biological reduction of nitrate. J. H. QUASTEL (Nature, 1932, 130, 207).—CO has a small inhibitory effect on the reduction of NO₃' by *B. coli*; the inhibition is the greater the smaller is the quantity of NO₃' present. In the presence of a suitable donator NO₃' reduction by *B. coli* is also inhibited, and to a greater extent, by O₂. The ClO₃'-oxidase of *B. coli* appears to be inhibited by O₂ and CO. L. S. T.

Oxygen consumption of *Escherichia coli* during the lag and logarithmic phases of growth. D. S. MARTIN (J. Gen. Physiol., 1932, 15, 691—708).—The rate of O₂ consumption of a growing culture of *E. coli* increases logarithmically before the growth curve becomes logarithmic. The rate of O₂ consumption per cell reaches a max. near the end of the lag phase of growth curve, and then gradually decreases, the time of max. respiration coinciding with that of max. surface area of the average cell. Results based on O₂ consumption, CO₂ output, and heat production agree within fairly close limits. A. L.

Correlation of the cellobiose test for the colon-aerogenes groups. C. F. POE (J. Amer. Water Works' Assoc., 1932, 24, 891—894).—The correlation of the cellobiose fermentation test with Me-red and Voges-Proskauer tests is almost perfect for the aerogenes group, but unsatisfactory for the colon organisms. C. J.

Physico-chemical studies of acid-resistant strains of tubercle and timothy-grass bacilli. A. MACHEBGEUF, G. SANDOR, and C. NINI (Compt. rend., 1932, 195, 275—277).—Emulsions of the bacilli in saline were kept at 0° for several days and filtered. The filtrates contained 0.05—0.08% of protein when 5% saline was used, but less with isotonic saline. A lipin extract of the filtrates, made by means of boiling EtOH followed by Et₂O, was evaporated and extracted successively with Et₂O, H₂O, and EtOH, the last solvent containing all the antigen. P. G. M.

Fission of tubercle fat by lipases. I. H. KRAUT and H. BURGER (Z. physiol. Chem., 1932, 209, 49—58).—The lipase of serum and liver produces a slow and incomplete hydrolysis of the COMe₂-sol. portion of tubercle fat. The presence of tubercle

fat retards the fission of Me butyrate and tributyrin by horse-serum. Human, guinea-pig, and rabbit sera are more, rat-serum is less, inhibited. The liver-lipases show similar inhibition. This phenomenon indicates the formation of a relatively stable tubercle fat-lipase complex. J. H. B.

Structures produced in blood-sugar cultures by hydrogen peroxide and mercury. J. IDZERDA and W. A. G. VAN EVERDINGEN (Biochem. Z., 1932, 249, 381—392).—Ring structures identical with those produced by streptococci are formed in the cultures by H₂O₂ or Hg. Decrease in the concn. of the agent due to distance from the centre of application is not an explanation of the phenomenon, which depends on the ratio of this concn. to the number of erythrocytes. The resistance of the erythrocytes to the influence of temp., [H'], and other factors is also involved. On the assumption that the agent diffuses outwards from a centre in all directions, consideration of the distribution of the erythrocytes and of the changes of concn. of the agent leads to a satisfactory explanation of the process. W. McC.

Viruses. T. M. RIVERS (Science, 1932, 75, 654—656).—An address. L. S. T.

Twort-d'Herelle phenomenon (bacteriophagy). E. WOLLMAN and E. WOLLMAN (Ann. Inst. Pasteur, 1932, 49, 41—74).—Spontaneous formation of bacteriophage was observed in a culture of a "mucous" variety of *B. subtilis*. Heating the culture at 85° prevented the formation; despite this, sufficient evidence exists to refute the parasite hypothesis of the bacteriophage. Bacteriophages are more resistant than bacteria to the oligodynamic action of Ag salts. Their function as group- or type-sp. antigens compared with the lytic power of lipins indicates the latter as probable constituents of bacteriophages. Liberation of a bacteriophage which has been neutralised by the appropriate serum is not effected by acids, bases, trypsin, or heat. F. O. H.

Measurement of p_H of solid media in bacteriology. W. VAN DAM and A. VEDDER (Rec. trav. chim., 1932, 51, 312—314).—A special type of electrode is described, whereby the p_H may be determined within 2 min. to an accuracy of 0.1. D. R. D.

Adrenal cortex hormone. S. LOEWE, L. MARX, F. ROTHSCHILD, H. E. VOSS, and A. BURESCH (Klin. Woch., 1932, 11, 281—284; Chem. Zentr., 1932, i, 1391).—The extracts, prepared by the authors' androkinin procedure, were readily sol. in H₂O; the hormone is fairly stable towards hydrolysis. Experiments on rats, cats, and on the treatment of Addison's disease are described. A. A. E.

Metabolic study of an adrenal cortex hormone. G. A. HARROP, H. WIDENHORN, and A. WEINSTEIN (Münch. med. Woch., 1932, 79, 171—172; Chem. Zentr., 1932, i, 1390).—The hormone prep. (Swingle-Pfiffner) diminishes the O₂ demand in hyperthyroidism. The substance is of general metabolic importance and has a special influence on kidney function, relating particularly to H₂O excretion and urinary N.

Apparent prepotent function of the adrenal glands. S. W. BRITTON and H. SILVETTE (Science,

1932, 75, 644—646).—Evidence showing the essential importance of the adrenal cortex in regulating carbohydrate metabolism is presented. L. S. T.

Power of adrenaline to influence the condition in which calcium exists in the organism. S. HERMANN (Arch. exp. Path. Pharm., 1932, 167, 82—84).—In rabbits the Ca quotient (cf. this vol., 81) is increased by intravenous injection of adrenaline and also by administration of vitamin-D. W. O. K.

Formation of adrenaline. J. E. ABELOUS and R. ARGAUD (Compt. rend., 1932, 195, 338—340).—The cortex and medulla of the suprarenal gland of a horse are separated and pulped. A suspension of the cortical pulp in 3% aq. Na_2CO_3 at 24—27° contained more adrenaline after 5 hr. than initially, whilst the medulla and mixtures of medulla and cortex under the same conditions contained none after 5 hr. Aq. extracts behaved in the same way. The medulla appears to be merely a depository for the adrenaline produced in the cortex. H. D.

Effect of thymocrescin on growth. V. W. NOWINSKI (Biochem. Z., 1932, 249, 421—423).—From thymus preps. from which growth-promoting material has been extracted there is obtained, by repetition of the extraction, a second, more active, growth-promoting fraction (cf. A., 1930, 1615; Stotzer, A., 1931, 878). W. McC.

Sulphur and water content of liver and brain in hyperthyroidised or thyroxine-injected animals. C. I. PARHON and M. CAHANE (Compt. rend. Soc. Biol., 1931, 108, 1004—1006; Chem. Zentr., 1932, i, 1259).—The mean liver-S was 0.189% (normal, 0.2058%); the brain-S showed smaller differences. The liver- H_2O was slightly high. A. A. E.

Action of antithyreoidin on the gaseous metabolism of the rat. K. OBERDISSE and S. THADDEA (Arch. exp. Path. Pharm., 1932, 167, 79—80).—Antithyreoidin reduces the metabolism of normal and hyperthyroidised rats. W. O. K.

Influence of altitude on the effect of thyroid gland administration in dogs. IV. Hyperthyroidism in animals on a nitrogen-free diet. R. E. MARK (Arch. exp. Path. Pharm., 1932, 166, 493—518).—The metabolic and physiological characteristics of dogs kept at altitudes of 63, 1000, and 2000 m. are described. At 2000 m. the effects of thyroid administration as indicated by loss in body-wt., N-excretion, H_2O metabolism, and pulse-frequency are comparable with those at sea-level, whilst at 1000 m. such symptoms of hyperthyroidism are greatly diminished and, in addition, the increase in body-temp. and the degree of alimentary glycosuria are also somewhat less evident. F. O. H.

Standardisation of thyroid preparations. G. ROTTER and M. MECZ (Arch. exp. Path. Pharm., 1932, 166, 649—674).—The total, thyroxine-, and inorg. I and the biological response of various commercial preps. were determined. The thyroxine-I vals. were parallel with the biological vals. Fresh or dried pigs' thyroid glands had a much lower content of throxine-I than those of horses or oxen. Albino

guinea-pigs were much more sensitive to thyroxine poisoning than pigmented guinea-pigs. F. O. H.

Thyroid gland and the ovary. I. ABELIN and E. WIEDMER (Arch. exp. Path. Pharm., 1932, 166, 584—591).—Subcutaneous injection of thyroxine or oral administration of thyroid gland preps. to rats partly or totally suppresses the oestrous cycle. This action of the thyroid is antagonised by extracts of anterior pituitary lobe and, to a smaller extent, by cestrin. Any appreciable disturbance of the oestrous cycle due to the continuous influence of thyroxine may also be eliminated by means of suitable diets. This counteraction to hyperthyroidism is of importance for the correct functioning of the genitalia. F. O. H.

Specificity of the substance in anterior pituitary extracts having an excito-secretory action on the thyroid. M. ARON (Compt. rend. Soc. Biol., 1931, 105, 974—975; Chem. Zentr., 1932, i, 1258).—The effects produced on guinea-pigs by minute (0.001 mg.) quantities of anterior pituitary are not produced by Schockaert's substances, which are stated to be active with ducks. A. A. E.

Thyreotropic extracts from anterior pituitary lobe. A. LOESER (Arch. exp. Path. Pharm., 1932, 166, 693—702; cf. this vol., 199).—The lobes are dried with COMe_2 and extracted with aq. pyridine, NH_4Et , or aq. NH_3 . The extract is deproteinised by means of $\text{CCl}_3\text{CO}_2\text{H}$ and pptd. by excess of COMe_2 , yielding a crude prep. (yield 1.5%) which may be further purified by extraction with MeOH. The product is insol. in org. solvents, sol. in aq.-EtOH, $-\text{COMe}_2$, or $-\text{pyridine}$, is thermolabile, inactivated by BzCl (when it is no longer diazotisable), and gives ppts. with alkaloid reagents. Its activity on the thyroid gland is demonstrable histologically. F. O. H.

Anterior pituitary hormone. K. EHRHARDT (Arch. Gynakol., 1932, 148, 235—264; Chem. Zentr., 1932, i, 1390).—Clinical. The hormones from mammals appear different from those from birds and cold-blooded animals. A. A. E.

Is an active posterior pituitary hormone present in the blood during pregnancy? K. FEKETE (Endokrinol., 1932, 10, 16—23; Chem. Zentr., 1932, i, 1257).—Blood-pituitrin is decomposed by a substance which, towards the end of pregnancy, is present in excess. A. A. E.

Melanophoric agent of the posterior pituitary lobe. K. EHRHARDT (Arch. Gynakol., 1932, 148, 265—270; Chem. Zentr., 1932, i, 1390).—Parenterally administered melanophoric agent is excreted in the urine in 24—48 hr. In pregnancy the melanophore hormone content of the pituitary is not increased; the hormone is present in the pituitary of foetuses. The substance having uterine activity is to be distinguished from melanogens. A. A. E.

Malignant testicular tumours and anterior pituitary hormone. B. ZONDEK (Klin. Woch., 1932, 11, 274—279; Chem. Zentr., 1932, i, 1390).—In normal male human urine the anterior pituitary reaction is negative. Reaction I seldom occurs, the appearance of II and III indicates a malignant testicular tumour. The urine of a man with such a

tumour gives the same anterior pituitary reactions as that of a pregnant woman. The excretion of follicular-ripening hormone in testicular tumour is at least 5 times as great as in female genital carcinoma. The anterior hormone could not be found in the pituitary after death resulting from malignant testicular tumour. A. A. E.

Changes in the pituitary after castration as a test for a testicular hormone. T. MARTINS (Compt. rend. Soc. Biol., 1931, 108, 1080—1082; Chem. Zentr., 1932, i, 1257).—The appearance of castration cells in the pituitary is avoided by injection of testicular extracts or by testicular implantation; testicles of infantile animals are active. The pituitary of male reacts more readily than that of female animals. The testicles probably produce two or more hormones, one of which has a direct or indirect action on the pituitary. A. A. E.

Dual endocrine activity of the testes. D. R. McCULLAGH (Science, 1932, 76, 19—20).—Testicular extracts prepared with fat solvents prevent atrophy or bring about regeneration of secondary sex glands (prostate and seminal vesicles) if administered to rats after castration. The comb growth-promoting hormone from male urine appears to be identical with that extracted from the testes. The hormone from urine or blood is derived from the testes, and when given in doses large enough to regenerate atrophic secondary sex glands in castrated rats neither prevents nor corrects the hypertrophy of the pituitary or adrenals after castration. Aq. testicular extracts, which must contain a new hormone ("inhibin"), prevent cellular changes appearing in the pituitary of rats after castration and completely inhibit the hyperfunction of this gland. The testes thus secrete two hormones, inhibin and "androtin," the name given to the C_6H_6 -sol. substance responsible for the development and maintenance of the secondary sex glands. Androtin is comparable both physiologically and chemically with theelin. L. S. T.

Chemical constitution of the follicular and testicular hormones. A. BUTENANDT (Nature, 1932, 130, 238).—New results have not substantiated the formula given (this vol., 781) for the follicle hormone, but indicate the presence of 3 aromatic double linkings (C_6H_6 ring) in the mol., making 4 rings in all. Catalytic hydrogenation saturates only 3 double linkings in the hormone and hormone hydrate mol. and gives hexahydrohormone hydrate $C_{18}H_{27}(OH)_3$, m.p. 256°, hexahydrodeoxyhormone hydrate $C_{18}H_{28}(OH)_2$, m.p. 153°, and hexahydrodeoxyhormone, $C_{18}H_{29}OH$, m.p. 105°. These products react as completely saturated compounds, the first-named being stable towards $KMnO_4$, O_3 , BzO_2H , and $C(NO_2)_4$. Mol. refraction vals. for the deoxy-follicle hormone $C_{18}H_{23}OH$, m.p. 133°, the hormone hydrate, its acetate, and Me ether are compatible only with a hormone formula containing 3 isolated double linkings or 1 C_6H_6 ring. Dehydrogenation with Zn dust produced an aromatic hydrocarbon, probably $C_{18}H_{14}$ or $C_{17}H_{14}$, m.p. 234°, stable to $KMnO_4$; this also supports the view of a 4-ringed structure. Tentative results for the 4 cryst. products isolated from the oily, physiologically active fraction of human

male urine are as follows: (i) $C_{18}H_{28}(OH)_2$, m.p. 232°, $[\alpha]_D +16.6^\circ$, isomeric with hexahydrodeoxy-follicle hormone hydrate; acetate, m.p. 112°, (ii) hydroxy-ketone, $C_{18}H_{30}O$, or $C_{17}H_{28}O_2$, m.p. 163°, $[\alpha]_D +76^\circ$; oxime, m.p. 216°, (iii) hydroxy-ketone, $C_{18}H_{26}O_2$ (?), m.p. 176.5°, $[\alpha]_D +89.9^\circ$; acetate, m.p. 158°, oxime, m.p. 215°, and (iv) hydroxy-ketone, $C_{16}H_{26}O_2$ (?), m.p. 178°; acetate, m.p. 160°. Only (iv) produces high physiological activity in the smallest doses in the capon test, and is to be regarded as the hormone producing comb-growth. The remainder appear to be completely inactive when pure.

L. S. T.

Effect of gonadectomy and subsequent parathyroidectomy on the calcium exchange in dogs. J. CHEYMOL and A. QUINQUAUD (Compt. rend., 1932, 195, 287—288).—Gonadectomy does not affect the serum-Ca nor does it modify the effects of parathyroidectomy. P. G. M.

Further purification of gonadotropic hormones. (ρ -factors). P. G. MARSHALL (Nature, 1930, 130, 170).—The process described gives a very active product containing 9.1% of N (ash-free basis), and no S, P, or halogen. The ninhydrin reaction for α - NH_2 -acids is obtained only after hydrolysis by dil. mineral acids. The active principles appear to be N compounds, probably polypeptide in character.

L. S. T.

Active principle of the corpus luteum. E. ENGELHART (Arch. Gynakol., 1932, 148, 76—80; Chem. Zentr., 1932, i, 1389).—Oral administration (12 rabbit units) has no action on the uterus of the rabbit. The corpus luteum hormone is probably destroyed in the intestine, since lipase-containing pancreatic extracts *in vitro* quickly destroy the hormone. L. S. T.

Production of corpora lutea by ovarian transplants in male guinea-pigs. E. GUYENOT, W. BARTSCH, and K. PONSE (Compt. rend., 1932, 195, 198—200).—Injection of urine-extracts of ovariectomised women into male guinea-pigs which have previously had an ovarian transplant from immature females results in development of follicles without formation of corpora lutea. Similar injection of alkaline extract of the anterior lobe of the pituitary does not produce ovarian hypertrophy, whilst injection of both extracts leads to the formation of a large no. of true corpora lutea. Luteinisation depends on the degree of maturity of the follicles. P. G. M.

Standard of reference for oestrin, and the relation between the potency of ketohydroxy- and trihydroxy-oestrin (theelin and theelol). J. H. BURN and G. K. ELPICK (Quart. J. Pharm., 1932, 5, 192—204).—The relative potencies of ketohydroxy-oestrin (theelin) and trihydroxyoestrin (theelol) differ in aq. and in oily solutions; an aq. solution of theelin has 85% of the potency of a similar solution of theelol, but in oily solution the former is 4.5 times as potent as the latter. W. S.

Properties and bio-assay of oestrin. W. P. KENNEDY (Quart. J. Exp. Physiol., 1930, 20, 71—93).—The practical end-point for the vaginal smear reaction is furnished by a cell picture showing almost

complete disappearance of leucocytes with at least half the epithelial cells showing cornification. Two types of mucus are described. Very early oophorectomy diminishes sensitivity to oestrin. Subcutaneous injections are more potent than intraperitoneal injections. The growth test is useful; the Nissl test is most suitable for accurate work. CH. ABS.

Crystalline insulin. XIV. Isolation of glutamic acid. H. JENSEN and O. WINTERSTEINER (J. Biol. Chem., 1932, 97, 93—98; cf. A., 1928, 553).

A. A. L.

Crystalline insulin. XV. Action of acid and alkali on insulin. H. JENSEN and E. A. EVANS, jun. (Z. physiol. Chem., 1932, 209, 134—144).—Dil. alkali eliminates from insulin sulphide-S and NH_3 , the amount of the latter depending on reaction conditions. Some of the NH_3 appears to be essential to activity. The cystine is attacked to some extent, but not arginine. Hot dil. HCl likewise removes NH_3 , but without damaging the activity; this NH_3 probably arises from amide groups in the non-active portion of the mol. With acid and EtOH, the free NH_3 and CO_2H groups react with the formation of a diketopiperazine ring. The active group may be a glutamic acid-cystine complex. J. H. B.

Presence of a distinct insulin in depancreatized dogs after pancreatectomy. G. H. TUTTLE (Science, 1932, 76, 15—16).—A reply to criticism (cf. this vol., 655).

L. S. T.

Mechanism of the action of insulin. S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (Praktika, 1930, 5, 336—340; Chem. Zentr., 1932, i, 1392).—Insulin acts by means of substances found in intact blood vessels. The nature of these substances and the fate of the blood-sugar could not be determined.

L. S. T.

Effect of insulin on phosphorus compounds of muscle. S. E. KERR and M. E. BLISH (J. Biol. Chem., 1932, 97, 11—22).—Insulin injection causes a decrease in the sum of the phosphocreatine- and inorg.-P contents of rabbit muscle, and an increase in the hexosemonophosphate-P.

A. C.

Correlation between blood-sugar fall and initial blood-sugar in rabbits injected with insulin. A. M. HEMMINGSEN and H. P. MARKS (Quart. J. Pharm., 1932, 5, 245—254).—A statistical analysis of the results obtained in a large no. of experiments on the depression of blood-sugar in rabbits by insulin shows that this depression is related to the initial blood-sugar level, and that the latter should, therefore, be incorporated in the terms expressing unit insulin potency. W. S.

Comparison of the rabbit and mouse methods in the assay of highly active insulin preparations. H. P. MARKS (Quart. J. Pharm., 1932, 5, 255—273).—An exhaustive statistical treatment of results showed that the mouse method of assay of insulin preps. furnished results 15—30% higher than the "cross-over" rabbit test. W. S.

Callicrein (padutin). E. K. FREY (Arch. exp. Path. Pharm., 1932, 167, 64—66).—A review of present knowledge of callicrein, a vasodilator substance found in urine in a free condition and in blood

where it is combined with probably a polypeptide. It probably originates in the pancreas. W. O. K.

So-called tissue hormones. W. WEICHHARDT (Wien. med. Woch., 1932, 82, 139—142; Chem. Zentr., 1932, i, 1389).—The most diverse irritants influence metabolism in such a way that cleavage products are formed. These are stimulatory or inhibitory according to their amount. The term "activated cleavage product" is preferable to "hormone" in this connexion. L. S. T.

Dietary deficiency of fat-free diet for rats. U. TANGE (Proc. Imp. Acad. Tokyo, 1932, 8, 190—193).—Rats fed on a fat-free diet of caseinogen (21%), starch (75%), and McCollum's salt mixture (4%), supplemented by yeast extract, biosterol, and irradiated ergosterol, develop a pellagra-like disease. The further addition of linoleic (or linolenic) acid causes normal and healthy growth, whilst oleic acid causes normal growth but the rats show loss of hair around the nose and mouth, swelling of the front paws, and (later) slight scaling of the hind legs. H. B.

Vitamins and the growth of newly-born children. E. STRASSMANN (Med. Welt, 1932, 6, 158—160; Chem. Zentr., 1932, i, 1392).—The children of lactating mothers fed on cod-liver oil show accelerated growth. L. S. T.

Separation of vitamin-A, carotene, and xanthophylls. P. KARRER and K. SCHOPP (Helv. Chim. Acta, 1932, 15, 745—746).—Vitamin-A (I) can be separated from carotene by its more ready adsorption from ligroin by Al_2O_3 , and from xanthophyll and zeaxanthin by adsorption of these and similar compounds from ligroin or ligroin- C_6H_6 solution by pptd. CaCO_3 . No trace of (I) is adsorbed by CaCO_3 .

R. S. C.

Vitamin-A avitaminosis in the chick. C. A. ELVEHJEM and V. F. NEU (J. Biol. Chem., 1932, 97, 71—82).—A diet is described which, given to day-old chicks, causes fatal A-avitaminosis in 3—4 weeks marked by severe inco-ordination of movements but not by typical ophthalmia. Addition of 2% of cod-liver oil to the diet results in normal growth. The uric acid content of the blood of avitaminotic chicks varies from 5 (val. for normal chicks) to 44 mg. per 100 c.c., and depends on the extent of injury to the kidney. The degree of inco-ordination is not related to the uric acid content of the blood. A. C.

Carotene and xanthophyll as sources of vitamin-A for the growing chick. O. L. KLINE, M. O. SCHULTZE, and E. B. HART (J. Biol. Chem., 1932, 97, 83—91).—A daily dose of 0.03 mg. of carotene (m.p. 172.5°, from spinach) prevents symptoms of vitamin-A deficiency in chicks up to 7—8 weeks of age, but is inadequate above this age. In curative experiments more than 0.05 mg. of carotene per day is necessary. Xanthophyll (m.p. 174°, from spinach) does not act as a source of vitamin-A in doses of 0.25 mg. per day either in prophylactic or curative tests. No toxic effects of xanthophyll are observed. A. C.

Ferrous iodide as a substitute for vitamin-A in rats. H. C. CAMERON (Science, 1932, 76, 18—19).—Experiments on albino rats confirm the statement

that FeI, syrup is without effect on the xerophthalmia of rats deficient in vitamin-A. FeI₂ cannot replace vitamin-A in curing or preventing the terminal infections characteristic of this deficiency.

L. S. T.

Carotenoids and vitamin-A in animal and plant organs. H. VON EULER, U. GARD, and H. HELLSTROM (Svensk Kem. Tidskr., 1932, 44, 191—198).—Carotene occurs in all of the following fish roes in addition to the carotenoids mentioned. Sole; cod and *Lota vulgaris*, xanthophyll; *Hippoglossus*, xanthophyll and zeaxanthin; pike, xanthophyll and chlorophyll. Pike spermatozoa contain small amounts of carotene. A bone-marrow extract (ox) did not show absorption at 328 mμ. Rat suprarenals are very rich in carotene (56.9 blue units per g.). Carotene also occurs in calf thymus, ox spleen (a trace), and, with xanthophyll, in the anthers of tulips and narcissi, and narcissus pollen.

A. C.

Production of vitamin-A by a species of *Corynebacterium*. C. E. SKINNER and M. F. GUNDERSON (J. Biol. Chem., 1932, 97, 53—56).—Xerophthalmia in rats suffering from vitamin-A deficiency was cured and the rats increased slightly in wt. when fed 1 g. of dried bacteria daily from a culture of *Corynebacterium* made on a vitamin-A-free medium in the dark.

A. C.

Formation of vitamin-A from carotene in the animal organism. J. L. REA and J. C. DRUMMOND (Z. Vitaminforsch., 1932, 1, 177—183).—Contrary to Olecott and McCann (this vol., 97), the formation of vitamin-A is not observed when liver preps. from vitamin-A-deficient rats and cats are incubated with carotene. Attempts to prepare "carotenase" from the livers failed. The vitamin-A content of cat's liver does not increase after carotene administration either by injection of a colloidal suspension into the portal vein or orally. In the liver experiments considerable destruction of carotene occurs *in vitro* and *in vivo*. A carnivorous species appears to lack the function of converting carotene into vitamin-A.

A. C.

Vitamin-B in egg-yolk. K. SZYMANSKA (Poznan. Tow. Przy. Nauk. Prace Kom. Mat. Przyrod., 1931, VIb, 32 pp.).—The vitamin consists of 2 fractions, one (40%) being sol. in H₂O and exhibiting 40% of the total activity; the insol. fraction appears to be inactive.

CH. ABS.

Isolation of oryzanin (antineuritic vitamin) from rice polishings. II. S. OHDAKE (Proc. Imp. Acad. Tokyo, 1932, 8, 179—182).—Analyses of oryzanin hydrochloride (I), m.p. 249—250° (decomp.) (A., 1931, 881) [and the corresponding *picrolonate*, m.p. 226° (decomp.), *picrate*, m.p. 208° (decomp.), *chloroaurate*, m. p. 189° (decomp.), and *chloroplatinate*, blackens at 245—250° without melting], support the formula C₁₂H₁₆O₂N₄S₂·2HCl. Pigeons and rats fed on a vitamin-B-free diet are cured and protected by 0.0025—0.01 mg. of (I) per day.

H. B.

Effect of partial depletion of vitamin-B complex on the learning ability of rats. S. MAURER and L. S. TSAI (J. Nutrition, 1931, 4, 507—516).—Partial depletion of vitamin-B reduced the learning ability of rats in maze tests. Offspring of depleted

animals regained normal ability if fed on a diet rich in vitamin-B.

A. G. P.

Avitaminosis. XI. Specific effect of vitamin-B on growth as evidenced by the use of vitamin-B concentrates. B. SURE (J. Biol. Chem., 1932, 97, 133—139).—Experiments in which the plane of nutrition is controlled indicate that vitamin-B has a sp. influence on the growth of rats in addition to producing growth by stimulation of appetite. The sp. influence is shown by daily doses of 1—2 mg. of concentrates of vitamin-B complex, and 0.5—1 mg. of vitamin-B₁ concentrates.

A. C.

Isolation and identification of vitamin-C. W. A. WAUGH and C. G. KING (J. Biol. Chem., 1932, 97, 325—331; cf. this vol., 657).—A solution of the purified vitamin in PrOH-petrol (this vol., 201), from which the active material can be pptd. by addition of Pb(OAc)₂ in MeOH, was evaporated to dryness and the residue extracted with EtOAc. The extract was conc. to 5 c.c. and an equal vol. of petrol added at the temp. of solid CO₂, yielding a pale yellow cryst. material which on re-extraction with EtOAc gave a sol. cryst. solid identical with the hexuronic acid of Szent-Gyorgyi (A., 1929, 98; 1931, 533; this vol., 657) and an insol. fraction which, on drying, yielded crystals resembling the lactone form of the acid. The protective val. for guinea-pigs was approx. 0.5 mg. per day. That methylornarcotine functions as vitamin-C (this vol., 310) could not be confirmed.

F. O. H.

Value and limits of chemical vitamin reactions of cod-liver oil. II. Chemical examination of cod-liver oil for vitamin-D. W. BRANDRUP (Pharm. Ztg., 1932, 77, 728).—The violet colour reaction of cod-liver oil with P₂O₅ survives autoclaving at 135° and 3 atm. for 1 hr. It is not given by vigantol and is therefore not sp. for vitamin-D.

A. C.

Examination of special foods for antirachitic activity. L. WAMOSCHER and A. SCHMIEDEN (Munch. med. Woch., 1932, 79, 51—53; Chem. Zentr., 1932, i, 1261).—The Ca : P ratio in the total meal must be 4 : 1. Preps. rich in P should first be rendered low in P. Only preps. having a rat-protection dose under 0.05 g. daily are suitable for human prophylaxis and therapy.

A. A. E.

Accessory food factors. Fat-soluble vitamin requirements of cattle and pigs during growth. H. ISAACHSEN (J. Agric. Sci., 1932, 22, 460—484).—Trials with numerous commercial feeding stuffs indicate that pigs are much more likely to suffer from mineral deficiency (especially Ca, Na, and P or an unsuitable Ca : P ratio) than from shortage of fat-sol. vitamin. Mixtures of ground limestone and NaCl or of NaCl and bone meal are effective mineral supplements. A high-grade herring meal is a good source of vitamin-D for pigs on a deficient diet.

A. G. P.

Irradiated milk: the amount of energy required to prevent rickets in chickens. G. C. SUPPLEE, R. C. BENDER, and M. J. DORCAS (J. Biol. Chem., 1932, 97, 63—69; cf. this vol., 548).—The antirachitic activity of irradiated milk in dry form is determined in terms of the protection given to grow-

ing chickens against rickets. A min. of 1328×10^3 ergs of energy between 2000 and 3000 Å. must be applied per c.c. of milk to prevent rickets. The calc. vitamin-D content of this milk is 1.29×10^{-6} g. per litre. A daily intake of 0.0267×10^{-6} g. of vitamin-D per 100 g. of body-wt. did not prevent rickets completely, whilst 0.0341×10^{-6} g. daily prevented rickets up to 8 weeks of age. A higher dose was not superior in antirachitic effect. A. C.

Reaction of the chicken to irradiated ergosterol and irradiated yeast as contrasted with the natural vitamin-D of fish-liver oils. H. STEENBOCK, S. W. F. KLETZIEN, and J. G. HALPIN [with F. HANNING, J. T. LOWE, V. M. TEMPLIN, and R. W. HAMAN] (J. Biol. Chem., 1932, 97, 249–264).—Whereas normal bone production is produced in chickens by the inclusion of 1% of normal cod-liver oil in the diet, it requires 40–120% equivalence as cod-liver oil of irradiated ergosterol and 7.5–60% equivalence of irradiated yeast to produce the same result. Satisfactory results are also obtained with 4% egg meal and 1.6% of an irradiated *Penicillium*. Burbot-liver oil has an antirachitic potency equal to that of cod-liver oil. Excessive dosage of irradiated ergosterol gives rise to a toxicity manifested by anorexia, loss in body-wt., increase in serum-Ca, and decrease in serum-P. That the feeding of irradiated ergosterol in maize or cod-liver oil is accompanied by the same degrees of antirachitic efficiency and toxicity indicates that the vitamin-D of irradiated ergosterol is a different substance from that of cod-liver oil. Administration of carotene has no effect on the antirachitic activity of irradiated ergosterol.

F. O. H.

Vitamin-D and the conservation of calcium in the adult [rat]. I. S. W. F. KLETZIEN, V. M. TEMPLIN, H. STEENBOCK, and B. H. THOMAS (J. Biol. Chem., 1932, 97, 265–280).—The skeletons of adult rats fed on a rachitogenic diet of high Ca:P ratio yield a low ash. The decrease is reduced but not prevented by addition of vitamin-D to the diet. With rats on a stock diet two successive pregnancies, uncomplicated by lactation, do not significantly affect the ash content of the femur (cf. A., 1930, 808), whereas a marked reduction in the ash occurs on lactation despite ample provision of Ca, P, and vitamin-D in the diet. Thus the theory that factors other than vitamin-D are concerned with loss of Ca during lactation receives further support. F. O. H.

Immunological differentiation of normal and irradiated ergosterol. E. BERGER and H. SCHOLER (Klin. Woch., 1932, 11, 158; Chem. Zentr., 1932, i, 1260).—Treatment of rabbits with ergosterol (I) + pig serum affords immune serum towards (I). Such sera do not react with the purified irradiation product of (I). Anti-cholesterol sera give with (I) and particularly with the purified irradiation product a slighter complement fixation than that of anti-ergosterol sera with (I). A. A. E.

Distance- and contact-action of irradiated substances. O. RIED (Arch. exp. Path. Pharm., 1932, 166, 592–602).—The nature of the photo-active effect due to substances such as irradiated fat is discussed. The effect from irradiated fats is

increased by the presence of metals and their salts. Ultra-violet irradiation of aq. NaCl or KCl results in a marked change in the growth of bean roots immersed in (contact-action) or above (distance-action) such solutions. A distance-action on bean seedlings is also shown by irradiated earth, Al, and Sn. The influence of the emanation on bacterial growth, the growth of mice (both with distance-action and with feeding of irradiated salts), the inheritance of tail necrosis, and the growth of Ehrlich mouse carcinoma is described. F. O. H.

Effects of carbon monoxide on the oxygen consumption and carbon dioxide production of germinating seeds of *Lupinus albus*. P. S. TANG (J. Gen. Physiol., 1932, 15, 655–665).—CO reversibly inhibits the O₂ consumption of germinating seeds of *L. albus* to a max. extent of 36% with a mixture of 24% O₂ and 76% CO at 18° in darkness. Illumination prevents inhibition. On returning to air, O₂ consumption increases up to 68% above the original consumption in air. CO does not inhibit CO₂ production. A. L.

Fat and fatty acid contents of seeds of *Gramineae* in relation to light effects on germination. H. KUMMER (Ber. deut. bot. Ges., 1932, 50, 300–303).—Seeds of high fatty acid content germinate in darkness more readily than do those of lower acid contents. A. G. P.

Course of growth of agricultural plants. III. Maize, buckwheat, flax, tobacco, and poppy. H. WAGNER (Z. Pflanz. Düng., 1932, 26A, 8–57; cf. B., 1932, 696).—Variations in the % of N, P, K, Ca, and org. substances during the whole growth period are recorded and discussed. Relationships between the “relative vals.” of the nutrients taken up (i.e., % of max. content) to the relative vals. of dry matter produced in the same growth period offer a basis of plant classification from the point of view of nutritional physiology. A. G. P.

Distribution of some reserve substances in hard winter wheat plants at successive growth stages and their possible utilisation. R. C. MALHOTRA (J. Agric. Sci., 1932, 22, 485–496).—Plants contained lower proportions of H₂O in the early stage of winter growth and at maturity than during the major period of growth. Ash constituents are at a max. in seedlings, decreasing later and increasing again towards maturity. The oil content reached a max. at maturity. Sugar was low in seedlings, increasing later and declining again with the ripening of the grain. Starch occurred early in growth but disappeared later. The total N content was low in young plants but increased later. Hemicellulose reached a max. in spring but decreased later. A. G. P.

Physical and chemical changes in the ripening of deciduous fruits. F. W. ALLEN (Hilgardia, 1932, 6, No. 13, 381–441).—Changes in pigmentation and softening of fruits in storage are recorded. The proportion of sol. solids in plums, pears, and peaches increases during ripening on the tree and is approx. double that of total sugars. The increased sugar content during colouring on the tree consisted mainly of sucrose in stone fruits, sucrose and reducing sugars

in apples, and reducing sugars in pears. Apples and pears, normally harvested prior to full ripeness, show a decrease in starch and a considerable gain in sugar content after picking. During maturity on the tree there is a decrease in the acidity of apricots, apples, and most plums and peaches. Treatment of apples with C_2H_4 hastens the softening and yellowing of the fruit, the effect being most marked in early-picked apples and in those treated at 21° . Fruit treated at 10° showed marked changes in starch, sugar, and acid contents. The effects of C_2H_4 varied considerably with different fruits and with different varieties of the same fruit. A. G. P.

Hydrolysis in green plants by moonlight. E. S. SEMMENS (Nature, 1932, 130, 243).—Starch disappears in the leaves of the vine, spinach, and *Tropaeolum* exposed to moonlight at the time of max. polarisation. L. S. T.

Effects of tartaric acid and glucose on the metabolism of vine leaves. E. T. EVERINGHAM and W. H. PEARSALL (Proc. Leeds Phil. Soc., 1932, 2, 303—308).—The rate of hydrolysis of protein in vine leaves is reduced by both tartaric acid and glucose. The rate of deamination of NH_2 -acids and that of carbohydrate loss are reduced by addition of tartaric acid. Age of leaf and illumination also play a part in these effects, young leaves, or leaves illuminated by weak light, being affected most. The addition of glucose results in a tendency towards protein synthesis. A. J. M.

Pithecolobium saman. L. VAN ITALLIE (Pharm. Weekblad, 1932, 69, 941—963).—From the bark of *Pithecolobium saman* have been isolated gallic and tannic acids, glucose, sucrose, fatty materials, a *phytosterol*, two *alkaloids*, $C_8H_{17}ON$ (*hydrochloride*, $[\alpha]_D^{25}$ -13.90° ; *Au* salt, m.p. $184-185^\circ$) and $C_{17}H_{36}ON_3$ (*pithecolobine*; I) $[\alpha]_D^{25}$ -12.02° in EtOH (*dihydrochloride* $[\alpha]_D^{25}$ -19.27° ; *Au* salt, m.p. $178-181^\circ$), and a *saponin* (*samanin*; II), $[\alpha]_D^{25}$ -16.1° . (I) reacts with all alkaloid reagents except tannic acid, but contains no alkyl and probably no CO groups, does not form Ac or Bz derivatives, and does not reduce aq. NH_3 -Ag solution; it is alkaline, and distils in "abs. vac." at 224° . On distillation with Zn dust it yields piperidine and NH_2Me . (II) yields on hydrolysis the compound $C_{23}H_{36}O_4$ (37.27%), m.p. $215-216^\circ$, $[\alpha]_D^{25}$ -16° , probably $C_{21}H_{31}(OMe)(OH)(CO_2H)$, and arabinose (12.10%), rhamnose (15.84%), glucose (34.30%), and glycuronic acid (trace). The physiological actions of (I) and (II) are described. H. F. G.

X-Ray study of chitins of *Aspergillus niger*, *Psalliotia campestris*, and *Armillaria mellea*. V. KHOUVINE (Compt. rend., 1932, 195, 396—397).—Animal chitin has the same X-ray spectrum as that from *A. niger*, *P. campestris*, and *A. mellea*. The N contents are also identical. H. D.

Phytochemistry. I. Sugars of the gum of *Viscaria vulgaris* (*Lychnis viscaria*, L.). E. VOTOCEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1932, 4, 282—284).—Hydrolysis of the gum [obtained by extraction of the glutinous portions of the stems with boiling H_2O , evaporation of the aq. extract, clarification with $Pb(OAc)_2$, removal of Pb

with H_2S , further evaporation to a syrup, and pptn. with EtOH] with 1% H_2SO_4 at 100° (bath) gives glucose and *d*-xylose. H. B.

Two constituents of *Parosela barbata* (Oerst.), Rydb. J. R. SPIES and N. L. DRAKE (J. Amer. Chem. Soc., 1932, 54, 2935—2938).—Extraction of the ground plant with C_6H_6 gives 0.075% of montanyl alcohol, $C_{29}H_{60}O$, m.p. $84-84.5^\circ$ (*phenylurethane*, m.p. 96° ; *iodide*, m.p. $64-64.5^\circ$), and 0.6% of an oil, b.p. $95-110^\circ/4-5$ mm., which adds Br, decolorises neutral $KMnO_4$, does not reduce Fehling's solution, and is toxic (concn. of 1 : 10,000 at 27°) to goldfish. C. J. W. (b)

Coffee bean. I. Unsaponifiable matter of the coffee bean oil. Preparation and properties of kahweol. R. O. BENGIS and R. J. ANDERSON (J. Biol. Chem., 1932, 97, 99—113).—The unsaponifiable part of the oil extracted from roasted coffee beans with light petroleum contains *kahweol*, $C_{19}H_{36}O_3$, m.p. $143-143.5^\circ$ (softens 142°), $[\alpha]_D^{25}$ -161.06° (*Ac* derivative, m.p. $132-134^\circ$ (+ EtOH, $\frac{1}{2}H_2O$), m.p. $142-144^\circ$ (sinters 125° , softens $133-134^\circ$, remelts after solidifying $136-137^\circ$), reduced (H_2 -colloidal Pt) to a *substance*, $C_{19}H_{32}O_3$, m.p. $171-172^\circ$ (softens $165-166^\circ$, clears 175°) [*Ac*, derivative; *dinaphthylurethane*, m.p. 128° (softens 118°)] and an Et₂O-insol. *substance*. Kahweol is sensitive to light, air, and acid, but stable to alkali. A *sterol*, $C_{27}H_{46}OH.H_2O$, m.p. $138-139^\circ$ (resolidifies $127-126^\circ$, remelts 138°), was also isolated. A. A. L.

Catechin of the cacao bean. K. FREUDENBERG, R. F. B. COX, and E. BRAUN (J. Amer. Chem. Soc., 1932, 54, 1913—1917).—Contrary to Adam *et al.* (A., 1931, 535), *l*-epicatechin (and not *l*-acacatechin) is present in the cacao bean. Various papers of Nierenstein are criticised. C. J. W. (b)

Alkaloids of *Argemone mexicana*. A. C. SANTOS and P. ADKILEN (J. Amer. Chem. Soc., 1932, 54, 2923—2924).—Schlotterbeck's assumption (A., 1902, ii, 101) that *A. mexicana* contains berberine and protopine is correct. C. J. W. (b)

Croton-seed. III. Improbability of the existence of Tuson's alkaloid, and the presence of sucrose and glucose glucosides in croton-seed. E. CHERBULIEZ, K. BERNHARD, and E. EHNINGER (Helv. Chim. Acta, 1932, 15, 855—856; cf. this vol., 665).—Extraction of croton-seed (but not the oil therefrom) with H_2O gives sucrose. Neither the seed nor the oil contains an alkaloid (cf. J.C.S., 1864, 17, 195). The commercial oil contains 0.025% N. The MeOH extract of the seed, when freed from crotonoside and then hydrolysed, gives the aminohydroxy-purine and a mixture of reducing sugars, probably containing glucose. R. S. C.

Formation of betaines and of alkaloids in plants. I. Formation of stachydrine and trigonelline. G. KLEIN and H. LINSE (Z. physiol. Chem., 1932, 209, 75—96).—Stachydrine and trigonelline are determined by colorimetric determination of the Bi in the ppt. obtained with K Bi iodide. The greatest amount of these substances was found in the blossoms and roots of the plants examined. Etiolated shoots of *Trigonella fenum graecum* contained more

trigonelline after 6—15 days' germination than green shoots, later less. The effect of the injection of various NH_2 -acids into the hollow stems of plants was investigated. Proline, ornithine, and glutamic acid produced a marked increase in the betaine, glycine none. Addition of hexamethylenetetramine as source of CH_2O to proline gave a considerable increase. These findings agree with theoretical conceptions as to the origin of alkaloids in plants. J. H. B.

Occurrence and detection of choline in tobacco seeds and leaves. F. E. NOTTBOHM and F. MAYER (Z. Unters. Lebensm., 1932, 63, 620—623).—An extension of the authors' method (B., 1932, 367, 701) to the seeds or press-cake of tobacco after defatting with CHCl_3 . Fat-free *Nicotiana rustica* contained 0.0651 and 0.0575%, and *N. tabacum* 0.0689 and 0.0576% (press-cake and seeds, respectively), and the fatty portions only traces of choline. The determination of nicotine and choline in tobacco is described. J. G.

Plant dyes. XLI. Taraxanthin from *Tussilago farfara*. P. KARRER and R. MORF (Helv. Chim. Acta, 1932, 15, 863—864).—The dried petals of *Tussilago farfara* yield to ligroin an ester of taraxanthin and, possibly, some violaxanthin. The apparently incomplete reduction of dihydrolycopene (cf. Kuhn and Lederer, this vol., 782) is due to instability of the dihydro-compound. R. S. C.

Synthesis of carotenoids in plants. H. VON EULER and E. KLUSMANN (Svensk Kem. Tidskr., 1932, 44, 198—204).—The suggestion that polyenes and carotenoids are synthesised by a multiple aldol condensation of units of β -methylcrotonaldehyde is discussed. Carotenoids are probably not intermediates in the synthesis of sterols by yeast, but sterols may be directly synthesised from crotonaldehyde. A. C.

Spectrophotometric analyses of the colours and the content of pigments of autumnal foliage. C. SHEARD (Proc. Staff Mtg. Mayo Clinic, 1932, 7, 130—131).—As leaves of sumac, oak, and poplar change in colour the amount of chlorophyll *a* decreases, whilst that of chlorophyll *b* and of carotenoids changes little. The autumnal colours are ascribed chiefly to the diffusion of chlorophyll *a* at low temp. CH. ABS.

Juices of the leaves of *Monarda punctata* and *M. fistulosa*. A. A. HARWOOD (J. Amer. Pharm. Assoc., 1932, 21, 569—570).—The juice from the leaves of *M. punctata* and *M. fistulosa* contain 9.7 and 6.2% of bound H_2O , 1.41 and 1.48% of ash, 0.46 and 1.39% of reducing sugars, and 0.12 and 0.01% of invert sugar, respectively. R. S. C.

Fresh juice of the maguey plant (*Manso fino*, Karw.). M. D. JONES (J. Amer. Pharm. Assoc., 1932, 21, 574—575).—Dry maguey leaves yield to Et_2O an oil, from which an aldehyde, $(\text{C}_3\text{H}_5\text{O})_x$, m.p. 237—240° (decomp.), was obtained. R. S. C.

Chemical changes accompanying the fermentation of apple juice with and without the addition of sodium benzoate. C. F. POE, R. C. MEEHAN, and B. H. LINCOLN (Univ. Colorado Stud., 1929, 17, 1—16).—In apple juice containing NaOBz

there was only a slight decrease in 126 days in total solids and sugars; very little sucrose was hydrolysed. There was little increase in volatile acid and a rapid increase in fixed acid. In absence of NaOBz the EtOH was max. in 31 days and thereafter decreased. CH. ABS.

Mineral composition of dates. M. M. CLEVELAND and C. R. FELLERS (Ind. Eng. Chem. [Anal.], 1932, 4, 267—268).—The ash of the edible portion of dates contains about 40% K_2O , 4—7% CaO , and 7—10% P_2O_5 ; the alkalinity is high. E. S. H.

Degree of pigmentation and its probable relationship to the mineral constituents of honey. H. A. SCHUETTE and K. REMY (J. Amer. Chem. Soc., 1932, 54, 2909—2913).—The amounts of SiO_2 , Fe, Cu, and Mn in the ash from 22 samples of honey are determined. A relationship apparently exists between the degree of pigmentation and the mineral content (notably Mn and Cu). C. J. W. (b)

Accumulation of molybdenum in some aquatic plants. H. TER MEULEN (Rec. trav. chim., 1932, 51, 549—550).—*Azolla*, growing in H_2O containing only traces of Mo, contains 1.12 mg. of Mo per kg. of dry plant. Marine algæ contain Mo. R. S. C.

Concentration of potassium isotopes in plants. II. K. HELLER and C. L. WAGNER [with K. PEH and B. MENDLIK] (Z. anorg. Chem., 1932, 206, 152—160; cf. A., 1931, 1342).—Contrary to the results of Loring and Druce, at. wt. determinations of K in cabbage, sugar beet, and potatoes failed to show that any concn. in the isotope K^{41} had taken place. M. S. B.

Accidental occurrence of selenium in certain vegetation. TABOURY (Compt. rend., 1932, 195, 171).—By ashing plants of *Sium latifolium* and *Pastinaca sativa* which had grown near a Se-containing spring, adding HCl to the H_2O -sol. residue, evaporation nearly to dryness, and the addition of aq. NaHSO_3 a red ppt. of Se appears. H. D.

Germination of pollen and chemical stimulation. Microchemistry of pollen. A. NIETHAMMER (Biochem. Z., 1932, 249, 412—420; cf. A., 1929, 1112).—Pollen from many species of plants is not induced to germinate by treatment with 0.0001% solutions of inorg. (e.g., MnSO_4 , KI) or org. (e.g., peptone, malic acid) stimulants. In pollens which can be stimulated thus the extent of the action depends on the degree of ripeness, but the stimulants are not sp. in their action. Pollens which germinate with moderate ease are most stimulated. Thyroid has a surprisingly favourable effect on the germination, MnSO_4 is often favourable, and heavy metal compounds are only very slightly unfavourable. Digitonin is favourable and malic acid stimulates germination of pollen from apple blossom. Pollens which produce no sugar are usually incapable of germinating; changes in sugar content occur on keeping in some cases and small amounts of org. acids are always present in species which germinate well. Great variations are found in the constituents of the ash of pollens; these constituents may affect germination. Usually P and K are present, Fe, Na, and Mg rarely.

The nature of the envelope of the pollen grains has no effect on their capability to be stimulated to germination. W. McC.

Concentration-power of cytoplasm ; formation of crystals of neutral-red in pollen grains. L. PLANTEFOL (Compt. rend., 1932, 195, 264—266).—Crystal formation takes place in certain varieties of *Prunus* in the pollen grains after several hrs.' immersion in neutral-red solutions (5—75 in 100,000).

P. G. M.

Concentration of cell-sap of mulberry leaf. Y. IMAMURA and M. FURUYA (Bull. Sericult. Silk Ind., Japan, 1932, 4, 7).—The concn. of the sap increases for the various leaf cells in the following order: upper epidermis, lower epidermis, spongy parenchyma, and palisade parenchyma; it also varies with the part of the stem on which the leaf grows. In young leaves the concn. is lower, and in fully matured ones higher, whilst in over-matured leaves it is again lower.

B. P. R.

Physical and chemical properties of the cell-sap of *Halicystis ovalis* (Lyngb.), Aresch. G. J. HOLLENBERG (J. Gen. Physiol., 1932, 15, 651—653).—The cell-sap of *H. ovalis* has d_{25}^{25} 1.0257, v.p. same as sea-water (s), Cl' 1.926—1.978% (s, 1.851%), SO_4'' 0.013% (s, 0.279%), p_H 5.4 (s, 8.15), n_D 1.3384 (identical with that of s).

A. L.

Osmotic relationships between host plant and parasite. M. LILIENSTERN (Ber. deut. bot. Ges., 1932, 50, 337—340).—The osmotic concn. of the sap of *Oscula* is higher than that of *Cicer* but lower than that of *Melilotus albus*. Cryoscopic methods for such determinations are unsatisfactory and plasmolytic methods must be used. Certain data for saprophytic plants (Harris and Harrison) need reconsideration.

A. G. P.

Accumulation of electrolytes. V. Models showing accumulation and a steady state. W. J. V. OSTERHOUT and W. M. STANLEY (J. Gen. Physiol., 1932, 15, 667—689).—The accumulation of electrolytes in *Valonia* is investigated by means of a model consisting of a non-aq. layer (70% guaiacol and 30% *p*-cresol) placed between an alkaline aq. phase (0.05*M*-KOH or 0.05*M*-KOH and 0.05*M*-NaOH) and an acid aq. phase (CO_2). The order of penetration in the model is the same as in *Valonia*, viz., $K > Na > Ca > Mg > Cl > SO_4$, and salt formation in the acid phase causes an increase in K^+ Na^+ , and osmotic pressure. No equilibrium occurs, but a steady state is reached in which H_2O and salt enter at the same rate.

A. L.

Direct detection of the migration of materials in the sieve tubes of plants. W. SCHUMACHER (Naturwiss., 1932, 20, 364—365; cf. A., 1931, 1099).—Fluorescein, activated by ultra-violet light, can be used to show the direction and velocity of the translocation of materials in the sieve tubes of plants.

W. R. A.

Trustworthiness and limits of application of common methods of determining the osmotic concentration of plant cell-saps. H. R. OPPENHEIMER (Planta [Z. wiss. Biol.], 1932, 16, 467—517).—Results of cryoscopic and plasmolytic methods showed general agreement for leaf cell-saps of a no.

of plants. The cryoscopic method was the more trustworthy, since it is less affected by the condition of cell membranes at the time of examination.

A. G. P.

Determination of bound water in plant tissue. J. D. SAYRE (J. Agric. Res., 1932, 44, 669—688).—Comparison is made of the cryoscopic method (lowering of the f.p. by sucrose additions), the calorimeter method (heat required to thaw frozen H_2O), and the dilatometer method (expansion during freezing) for determining the "free" H_2O in tissues. The calorimeter method is recommended although both it and the dilatometer method are subject to changes in the free: bound H_2O ratio during freezing.

A. G. P.

Changes in the cells of *Spirogyra* associated with the presence of water polymerides. F. E. LLOYD and T. C. BARNES (Proc. Nat. Acad. Sci., 1932, 18, 422—427).—The cells of *Spirogyra*, cultured in pure melted ice, grow and divide more rapidly than when cultured in condensed steam. The difference is ascribed to the different states of polymerisation of the H_2O , the $(H_2O)_3$ form increasing growth.

H. D.

Nutritional aspects in mottle-leaf and other physiological diseases of citrus. A. R. C. HAAS (Hilgardia, 1932, 6, No. 15, 484—559).—In H_2O -cultures roots of lemon seedlings were injured by 5 p.p.m. of Zn in the nutrient. Mottled leaves were produced by 2—5 p.p.m. of B. Picric acid in the nutrient caused mottling of a different type. In soil cultures the excessive use of fertilisers containing urea produced yellowing and mottling of leaves. High proportions of NH_4 salts were also injurious, especially when the NO_3^- supply was low. $NaNO_3$ was non-injurious except in poorly-drained soils. Leaching of soil with very dil. H_2SO_4 or H_3PO_4 resulted in gum formation in orange leaves. Chromates, but not Cr salts, were very toxic. In soils treated to produce high K and low Ca contents premature leaf-fall occurred. Chlorotic leaves sprayed with Fe solutions showed darkening spots where each drop of solution dried. Addition of 20 p.p.m. of $CuSO_4$ to culture solutions induced a mosaic appearance in leaves. In sand cultures high $[Cl^-]$ was injurious even where Ca^{++} was the dominant cation. In the absence of sol. Ca^{++} (other than that derived from $CaCO_3$) K salts were more injurious than those of Na. Mottled leaves contained higher proportions of Na and K and less Ca than healthy leaves. The ratio insol. Ca: insol. ash is approx. the same in mottled and healthy leaves. The maintenance of an optimum % of sol. Ca in the nutrient is essential for healthy leaf growth. Excess of Mn produced varied conditions of mottling and gumming of leaves but no tip-burn.

A. G. P.

Filtration of plant viruses. D. MACCLEMENT and J. H. SMITH (Nature, 1932, 130, 129—130).—Difficulties in the prep. and use of graded collodion membranes are discussed. Plant viruses differ markedly in size. By the use of these membranes two viruses occurring in the same plant can be separated.

L. S. T.

Filtration of plant viruses. K. M. SMITH (Nature, 1932, 130, 243).—Results obtained with

potato mosaic viruses and collodion membranes are described. L. S. T.

Microchemical reactions in plant tissues. W. M. GLESEN (Pharm. Zentr., 1932, 73, 420—422).—Staining tests (which can be produced direct on tissue sections and observed under the microscope) with simple reagents (*e.g.*, H_2SO_4 , H_2SO_4 with EtOH vanillin solution, HNO_3 , furfuraldehyde, etc.) are described for *Semen colchici*, *S. sabadilla*, *S. hyoscyami*, *S. stramonii*, *S. strychni*, *Radix ipecacuanha*, and *Tubera aconiti*. E. L.

Use of basic fuchsin in plant anatomy. W. H. CAMP and F. G. LIMING (Stain Tech., 1932, 7, 91—93).—The cut ends of living plants are immersed in mixture of 1 part of 2.5% basic fuchsin in 95% EtOH to 2 parts of faintly alkaline H_2O until the dye has traversed the vascular bundles of herbaceous plants or the H_2O -conducting system of woody plants, which can then be studied. H. W. D.

Rapid digestion of biological material for analysis. A. BOLLIGER (Austral. J. Exp. Biol., 1932, 10, 57—60).—Dry or wet material is digested with 60% HClO_4 , HNO_3 , and H_2O_2 . On evaporation to dryness, any NH_4ClO_4 decomposes, leaving a N-free ash. A. C.

Destruction of organic substances for toxicological tests. M. DUYSTER (Z. Unters. Lebensm., 1932, 63, 501—503).—Complete destruction is obtained by heating at 125° for 30 min. under reflux with 30 pts. of conc. H_2SO_4 and 60 pts. of perhydrol. To avoid loss of Pb, Hg, etc. a tube is attached to the top of the condenser, dipping into more acid perhydrol mixture which is sucked back down the condenser on cooling. E. B. H.

Permanent nitroprusside solution for acetone tests. R. M. HILL (J. Lab. Clin. Med., 1932, 17, 375).—Na nitroprusside (2—10%) in 2% H_2SO_4 , when stored in brown glass bottles, does not deteriorate in 6 months. CH. ABS.

Determination of porphyrin with the step-photometer. R. FIKENTSCHER (Biochem. Z., 1932, 249, 257—269).—An accurate method for use with small amounts of biological fluids is described. W. McC.

Direct nesslerisation micro-Kjeldahl method for nitrogen. Determination in organic compounds and biological fluids. E. S. WEST and A. L. BRANDON (Ind. Eng. Chem. [Anal.], 1932, 4, 314—315).—Blood filtrates and urine are rapidly and completely digested by H_2SO_4 (1:1) containing approx. 0.2% Se. In the analysis of difficultly oxidisable substances, the digestion mixture is preferably saturated with K_2SO_4 . E. S. H.

Micro-determination of sulphate in biological material. S. MORGULIS and M. HEMPHILL (J. Biol. Chem., 1932, 96, 573—583).—The material, freed from PO_4 , is digested with fuming HNO_3 and H_2O_2 , the ash dissolved in H_2O and SO_4^{2-} in the solution pptd. as BaSO_4 by addition of an aq. HCl solution of BaCrO_4 . Excess of BaCrO_4 is pptd. by making

the liquid alkaline with NH_3 , BaSO_4 and BaCrO_4 are removed by centrifuging, and CrO_4^{2-} in the supernatant fluid is determined iodometrically. The method is applicable to urine from which uric acid and other interfering substances are removed by a mild preliminary oxidation with H_2O_2 , and a trace of FeCl_3 . F. O. H.

Triple acetate method for determination of sodium in biological material. P. W. SALIT (J. Biol. Chem., 1932, 96, 659—672).—The solution (2 c.c. containing 0.05—0.5 mg. Na) is pptd. with U Zn acetate reagent (6 c.c.) and EtOH (2.1 c.c.) added in aliquots of 0.3 c.c. with stirring between each addition. The ppt. is separated, washed with a saturated solution of Na U Zn acetate in AcOH, and the amount of ppt. determined either directly by weighing or colorimetrically with $\text{K}_4\text{Fe}(\text{CN})_6$ according to the quantity of ppt. The application of the method to serum, whole blood, urine, faeces, tissue, and ocular fluids is described. F. O. H.

Determination of phosphorus in calcium magnesium inositolphosphate. T. BODALSKI (Wiad. Farm., 1931, 58, 683—684, 697—699).—The ground seeds are treated for 6 hr. with excess of 5% AcOH; inositolphosphates are pptd. with NH_3 from the filtrate, and washed with Et_2O —EtOH followed by Et_2O . Fat-free seeds contained (wt.-%): *Sesamum indicum* 1.40, *Fagopyrum sagittatum* 0.53, *Lens esculenta* 0.52, *Avena sativa* 0.23, *Triticum vulgare* 0.73, *Panicum miliaceum* 0.20, *Zea mays* 0.81, *Hordeum vulgare* 0.61, *Vicia sativa* 0.11, *Phaseolus vulgaris* 0.20, *Pisum sativum* 0.12, *Lupinus luteus* 0.16, *Cannabis sativa* 4.37—8.20, rice bran 1.53, sunflower cake 0.92. The P content of the inositolphosphates depends on the plant, but is always < 22.8%. Vals. are: *C. sativa* 18.87, *S. indicum* 18.30, *F. sagittatum* 21.50, *H. vulgare* 21.87, *T. vulgare* 20.21, *Z. mays* 18.51, *L. esculenta* 21.49, *Helianthus annuus* 16.79, rice bran 20.35, 20.68%. Rice and *Cannabis* inositolphosphates are acidic; others are slightly alkaline. CH. ABS.

Determination of zinc in biological materials. W. R. TODD and C. A. ELVEHJEM (J. Biol. Chem., 1932, 96, 609—618).—The sample (equiv. to 0.1—2.0 mg. of Zn) is ashed, the ash dissolved in dil. HCl, Na citrate and CuSO_4 are added, and H_2S is passed through the hot solution at p_{H} 3.5. The $\text{CuS} + \text{ZnS}$ ppt. (cf. A., 1930, 563) is washed, oxidised by H_2O_2 , and the sulphide pptn. repeated. Oxidation of this ppt. with aq. $\text{HCl} + \text{H}_2\text{O}_2$ yields a solution of CuCl_2 and ZnCl_2 from which, after addition of HCl, Cu alone is pptd. by H_2S . Zn is then pptd. from the filtrate as ZnNH_4PO_4 and the P in the ppt. determined colorimetrically (A., 1926, 443). The Zn content of various biological substances is given. F. O. H.

Use of colour filters in colorimetric analysis. R. H. HAMILTON, jun. (Science, 1932, 75, 563—564).—A method for matching the colour of mixtures, such as blood or urine, with pure solutions is described. L. S. T.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1932.

General, Physical, and Inorganic Chemistry.

Stark effect for hydrogen lines. K. SJOOREN (Z. Physik, 1932, 77, 290—295). A. J. M.

Intensity relationships in the helium spectrum by superposition of canal-ray motion and an electric field. H. KIRSCHBAUM (Ann. Physik, 1932, [v], 14, 448—462). A. J. M.

Can neon lines be used as secondary standards of wave-length? H. NAGAOKA (Proc. Imp. Acad. Tokyo, 1932, 8, 231—232).—The Ne^{20} lines show broadening due to reversals; feeble Ne^{22} lines become more pronounced at low temp. N. M. B.

Second spark spectrum of neon, Ne III. T. L. DE BRUIN (Z. Physik, 1932, 77, 505—514). A. B. D. C.

Transition probabilities for $2P - 1S$ of sodium determined from absolute intensity measurements in flames. E. F. M. VAN DER HELD and L. S. ORNSTEIN (Z. Physik, 1932, 77, 459—477).—The transition probability is $0.62 \times 10^8 \text{ sec.}^{-1}$. A. B. D. C.

Stark effect in the argon spectrum. N. RYDE (Z. Physik, 1932, 77, 515—527). A. B. D. C.

Inverse Stark effect for the two members of the principal series of rubidium and caesium. Y. T. YAO (Z. Physik, 1932, 77, 307—316). A. J. M.

Hyperfine structure of arc and spark spectra of barium. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 304—314).—Data are recorded for 6 lines of Ba I and 13 lines of Ba II, giving the nuclear moments $3/2$ and 0 for Ba^{135} , 137 and Ba^{136} , 138 , respectively. No relative shift of even isotopes is found. N. M. B.

Nuclear moment of barium as determined from the hyperfine structure of the Ba II lines. P. G. KRUGER, R. C. GIBBS, and R. C. WILLIAMS (Physical Rev., 1932, [ii], 41, 322—326).—Hyperfine structure data for $\lambda 4934$ and $\lambda 4554$ are tabulated. The nuclear moment of Ba^{135} , 137 was determined as $5/2$. N. M. B.

Hyperfine structure of mercury spectrum. VI. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 299—303; cf. this vol., 787).—Data are recorded and interpreted for $\lambda 3650.15$, 2464.06 , and 6123.27 of Hg I, and for $\lambda 3983.96$, 2847.67 , and 6149.50 of Hg II. N. M. B.

Origin of the coronal lines. J. KAPLAN (Nature, 1932, 130, 241).—A criticism of de Bruin's conclusion (this vol., 441). L. S. T.

Theory of coupling width [of spectra]. V. WEISSKOPF (Z. Physik, 1932, 77, 398—400).—An extension of a previous paper (cf. this vol., 552). A. J. M.

Long wave-length portion of the visible spectrum of the night light of the sky. L. A. SOMMER (Z. Physik, 1932, 77, 374—390).—The spectrum consists of lines and bands showing the spectra of O , O_2 , and H_2O . The transitions giving rise to these spectra are obtained. Comparison of wave-lengths of the lines and bands with those of the aurora reveals agreement as regards structure, but quite different intensities. A. J. M.

Cosmic radiation. G. HOFFMANN (Physikal. Z., 1932, 33, 633—662).—A summary of methods used and results obtained during the last eight years. A. J. M.

New class of absorption series as a transition from the optical to the X-ray spectra. H. BEUTLER (Naturwiss., 1932, 20, 673).—The absorption spectra of Rb and Hg vapours have been obtained without change in quantum no. of the valency electron belonging to the fundamental state of the atom. A. J. M.

Diffuse scattering of X-rays from sodium fluoride. G. E. M. JAUNCEY and P. S. WILLIAMS (Physical Rev., 1932, [ii], 41, 127—135; cf. A., 1931, 896, 1205). N. M. B.

Very soft X-ray spectra of heavy elements. C. DEL ROSARIO (Physical Rev., 1932, [ii], 41, 136—140).—Measurements in the range 43.6 — 104.8 \AA . are recorded for Th, Pb, Ta, Hg, Au, Ir, and W. N. M. B.

Existence of K -absorption edge in phosphors, and a new sensitive method for high-frequency radiation spectral analysis. E. RUPP and F. SCHMIDT (Ann. Physik, 1932, [v], 14, 413—414). A. J. M.

Diffraction of cathode rays by single crystals. II. Mean inner potentials of some crystals. K. SHINOHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 315—322).—The vals. obtained for calcite, rock-salt, and mica were 10.5 , 6.3 , and 10.4 volts, respectively. N. M. B.

Grating type and fine structure of X-ray absorption edges. K. VELDKAMP (Z. Physik, 1932, 77, 250—256).—The fine structure of X-ray absorption edges is the same for crystals of the same type. A. B. D. C.

Shielding and the intensity of X-ray diagram lines. J. A. PRINS (Z. Physik, 1932, 77, 478—488).—The effect of a non-coulombian field on the intensity of X-ray lines is determined for ultra-soft radiation.

A. B. D. C.

Critical potential of helium. A. PLÜMER (Z. Physik, 1932, 77, 356—373).—The crit. potential of He was determined and compared with earlier vals.

A. J. M.

Dependence of high velocities and emission work of photo-electric electrons from broken zinc single-crystal surfaces on the orientation of the surfaces. A. NITZSCHE (Ann. Physik, 1932, [v], 14, 463—480).

A. J. M.

Surface ionisation of potassium by tungsten. P. B. MOON and M. L. E. OLIPHANT (Proc. Roy. Soc., 1932, A, 137, 463—480).—It is shown how surface ionisation may provide the source of a beam of positive ions which has great intensity, steadiness, and length of life. This source has been used for a detailed investigation of the drop in ionisation efficiency which occurs when fast K^+ ions strike a hot target.

L. L. B.

Dependence of luminosity due to electron collision with calcium tungstate on the energy of the colliding electrons. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 77, 528—533).—Potential falls of approx. 8200 volts are required to give the lumens per watt of the modern "Nitra" lamp.

A. B. D. C.

Elastic electron scattering in helium. A. L. HUGHES, J. H. McMILLEN, and G. M. WEBB (Physical Rev., 1932, [ii], 41, 154—163).

N. M. B.

Reciprocal action of two electrons. H. BETHE and E. FERMI (Z. Physik, 1932, 77, 296—306).—Mathematical.

A. J. M.

Wandering velocity of electrons. M. DIDLAUKIS (Z. Physik, 1932, 77, 352—355).—Theoretical. A simple method for calculating the migration velocity of electrons is described.

A. J. M.

Electrons, protons, and the so-called electromagnetism. E. KLEIN (Z. Physik, 1932, 77, 415—419).—An experimental method is described to discriminate qualitatively between the theory of Günther-Schulze (this vol., 442) and that of others.

A. J. M.

Theory of the passage of rapid electrons through matter. C. MÖLLER (Ann. Physik, 1932, [v], 14, 531—585).

Dirac electron in simple fields. M. S. PLESSER (Physical Rev., 1932, [ii], 41, 278—290).—Mathematical.

N. M. B.

Electron diffraction and inner potential of metals. R. FRISCH (Naturwiss., 1932, 20, 689).—It is contended that the inner potential of Ag given by Bühl (this vol., 893) is in error.

A. J. M.

Polarisation of a beam of electrons by crystal reflexion. J. THIBAUD, J. J. TRILLAT, and T. VON HIRSCH (J. Phys. Radium, 1932, [vii], 3, 314—319).—The diffraction rings of electrons regularly reflected from thin Au and Pt films show no irregularity in intensity, indicating no appreciable polarisation.

N. M. B.

Electron collision at crystal surfaces as a verification of optical energy levels. R. HILSCH (Z. Physik, 1932, 77, 427—436).—Study of electron reflexion at crystal surfaces of NaCl, KCl, KI, LiF, NaF, and CaF_2 showed that the reflexion intensity diminishes at energies corresponding with the frequencies of optical absorption bands.

A. B. D. C.

Investigation of finely crystalline powdered substances by electron diffraction. F. TRENDLENBURG (Naturwiss., 1932, 20, 655—656).—The powder is dusted very sparingly on to a metal foil, which is treated in the usual way.

A. J. M.

Physical constants of methyl fluoride and the at. wt. of fluorine. W. CAWOOD and H. S. PATTERSON (J.C.S., 1932, 2180—2188).—The mol. wt. and compressibility of MeF obtained by heating NMe_3F have been determined by the microbalance method (A., 1931, 890). The crit. data of MeF prepared by this method and also by the action of $KMeSO_4$ on KF , as well as the compressibility of the gas obtained by the latter method, have been measured. Both crit. and compressibility data are in close agreement in each case (cf. this vol., 106), but the compressibility and mol. wt. differ from the vals. found by Moles and Batuecas (A., 1921, ii, 389). The at. wt. of F is discussed.

J. W. S.

At. wt. of selenium and tellurium. O. HONIGSCHMID (Naturwiss., 1932, 20, 659).—The ratio $2Ag:Ag_2Se$ was found to be 0.732081 , giving for the at. wt. of Se 78.962 ± 0.002 . This agrees with Aston's figure obtained by mass-spectrograph determinations. The ratio $TeBr_4:4Ag$ was determined and gave for the at. wt. of Te 127.587 ± 0.019 , in agreement with the international val., but not with Aston's. Using other mass-spectrograph data, however, good agreement is obtained.

A. J. M.

Relative abundance of the nitrogen and oxygen isotopes. G. M. MURPHY and H. C. UREY (Physical Rev., 1932, [ii], 41, 141—148).— N_2 and O_2 from various sources were converted into NO , for which absorption spectra data gave $N^{15}O^{16}/N^{14}O^{18}$ as $0.549 \pm 0.007:1$, from which N^{14}/N^{15} is $346:1$.

N. M. B.

Reversibility of certain radioactive processes. H. ZANSTRA (Z. Physik, 1932, 77, 391—394).—Theoretical. The application of the law of mass action to the process of taking up an α -particle by a nucleus with the liberation of a proton or a neutron, and the reverse operation, enables the ratio of the effective collision cross-sections to be calc. in a simple manner.

A. J. M.

Atomic disintegration in aluminium and nitrogen. E. STEUDEL (Z. Physik, 1932, 77, 139—156).—The range of protons ejected from Al and N_2 was measured for disintegration of the nuclei by α -rays from Po; no resonance effect was observed on variation of the energy of the disintegrating rays.

A. B. D. C.

Collision of α -particles with atomic nuclei. H. S. W. MASSEY (Proc. Roy. Soc., 1932, A, 137, 447—463).—The collision of α -particles with at. nuclei is discussed, using a quantum theory of collisions which allows for the perturbation of the α -particle wave by the nuclear potential barrier.

The probability of α -particle exchange on impact is shown to be large when the energy of the incident α -particle coincides with that of a virtual level of the nucleus. The anomalous scattering of α -particles by light nuclei (Mg, Al, etc.) is also considered. The new theory should provide a means of determining the radii of light nuclei. L. L. B.

Search for evidence of the radioactive decomposition of barium. T. R. HOGNESS and (Miss) R. R. COMROE (Proc. Nat. Acad. Sci., 1932, 18, 528—531).—It is assumed that Xe and He could be formed from hypothetically radioactive Ba by α -particle disintegration. Five old Ba rocks were decomposed in a NaCl-KCl melt, all gases, except inert gases, were removed over heated Ca, and any residual gas was examined spectroscopically for Xe. Each of the specimens gave a small quantity of residual gas, but no Xe could be detected. W. R. A.

Artificial disintegration by neutrons. N. FEATHER (Nature, 1932, 130, 237).—Photographs of the tracks produced in an expansion chamber filled with O₂ (97 vol.-%) at approx. 1 atm. when a source of Po and Be is placed in the centre provide definite evidence of disintegration. The disintegration probability for neutron-O₂ encounters is smaller but of the same order of magnitude as that for similar encounters with N nuclei. Disintegration probably occurs with capture of the incident neutron, in which case the reaction may be $O^{16} + n^1 \rightarrow C^{13} + He^4$. Energy data show that the capture disintegration takes place with an absorption of energy in different amounts on different occasions. L. S. T.

Gamma radiation. A. BRAMLEY (Proc. Nat. Acad. Sci., 1932, 18, 543—550).—Theoretical. W. R. A.

Constitution and stability of atomic nuclei. A. SCHIDLÖF (Arch. Sci. phys. nat., 1932, 14, 125—148).—A survey is given of the theory of emission of β -rays from radioactive nuclei, isotopes and isobars, effect of nuclear mass and stability of the α -particle, and classifications of nuclei. Data on the constitution and stability of nuclei are deduced. N. M. B.

Mass defect and binding energy of neutrons. W. BRAUNBEK (Z. Physik, 1932, 77, 534—540).—Theoretical. The calc. mass defect of the neutron gives a binding energy of $1-1.5 \times 10^6$ volts. A. B. D. C.

Recombination of hydrogen atoms at metallic and oxidised nickel. L. S. ORNSTEIN and A. A. KRUTHOF (Z. Physik, 1932, 77, 287—289).—The mean free path of electrons in a discharge tube, determined by means of a Faraday cage, is somewhat smaller when a surface of metallic Ni is used than when oxidised Ni is employed. The superficial oxidation must diminish the recombination of H atoms at the Ni surface. A. J. M.

Evaporation of mercury particles and its influence on measurements of the ultimate quantum of electricity. R. NESTLE (Z. Physik, 1932, 77, 174—197).—Hg particles, without an impure surface layer, evaporate so that the mass of the particle diminishes linearly with time; this evaporation limits

the accuracy of measurements of charge by the Millikan method. A. B. D. C.

Evaporation of mercury droplets. K. SCHAFER (Z. Physik, 1932, 77, 198—215).—A theoretical and experimental study of evaporation of Hg particles of radii near 10^{-5} cm. Stable particles do not exist in chemically passive gases. A. B. D. C.

Cathode sputtering of beryllium and aluminium in helium. P. D. KUECK and A. K. BREWER (Rec. Sci. Instr., 1932, [ii], 3, 427—429).—The ratio of the relative nos. of Be and Al atoms sputtered in He under identical conditions is 1.5:1, the film thicknesses are in the ratio 2.45:1, and the light-absorbing power is 10:1. The results point to the suitability of Be as a cathode material. W. R. A.

Liquid currents and space charge around wire electrodes in water. M. KATALINIE (Z. Physik, 1932, 47, 257—270). A. B. D. C.

Constitution of atomic nuclei. D. IVANENKO (Compt. rend., 1932, 195, 439—441; cf. this vol., 672).—An elaboration of previously expressed views, the neutron being regarded as an elementary particle with spin 1/2 and obeying Fermi-Dirac statistics. C. A. S.

Band spectrum of sulphur monoxide. E. V. MARTIN (Physical Rev., 1932, [ii], 41, 167—193).—Wave nos., rotational and vibrational structure, and spin fine-structure data are recorded for the lines of 7 bands in the region 2400—4000 Å. N. M. B.

Absorption spectrum of sulphur trioxide and heat of dissociation of oxygen. A. K. DUTTA (Proc. Roy. Soc., 1932, A, 137, 366—372).—The absorption spectrum of SO₃ has been studied between 5000 and 2000 Å. Absorption is continuous, from 3300 to 2600 Å., where it disappears, and begins again at 2300 Å. It is assumed that in the first process of absorption SO₃ decomposes into SO₂ and normal O, and in the second process the O atom set free is in the excited state. The excitation energy of the O atom is 1.65 volts (cf. Henri's val. of 1.7 from predissociation spectra of NO₂). The heat of dissociation of O₂ calc. from the beginning of continuous absorption at 3300 Å. is 128 kg.-cal. L. L. B.

Post-dissociation radiation from sulphur trioxide. A. K. DUTTA (Nature, 1932, 130, 241).—Gaseous SO₃ at <1 mm. gives a weak line at 6364 Å. L. S. T.

Quantitative determination of absorption spectra of hydrogen bromide and hydrogen iodide. A. K. DUTTA (Z. Physik, 1932, 77, 404—411).—The determinations were made at various pressures. The extinction coeff. for HBr disappears at 3260 Å., and for HI at 4040 Å. The energies corresponding with the long-wave absorption limits are 87.7 kg.-cal. for HBr and 70.8 for HI. These compounds are definitely ionic. A. J. M.

Absorption and fluorescence spectra of the vapours of the mercury halides. II. HgBr₂ and HgCl₂. K. WIELAND (Z. Physik, 1932, 77, 157—165).—Absorption and fluorescence spectra to 1500 Å. were observed for HgBr₂ and HgCl₂. The longest wave-length region of continuous absorption

gives dissociation of HgX_2 into HgX and a metastable X ; the three shorter wave-length continuous absorption regions give dissociation of HgX_2 into $\text{HgX}^* + \text{X}$. HgX_2 is therefore an at. mol. (cf. this vol., 896). A. B. D. C.

Absorption spectrum of anhydrous ferric chloride. F. I. G. RAWLINS and C. P. SNOW (Z. Krist., 1932, 83, 41).—Besides general absorption from 5000 Å. there is a sharp absorption band of width 50–100 Å. at λ 6200. This discontinuous spectrum, the first case found elsewhere than among the rare earths, is attributed to the transition $^4X \rightarrow ^2Y$ in the Fe^{+++} ion. C. A. S.

Intensity change in the rotation oscillation spectrum of water vapour (ortho- and para-water). R. MECKE (Naturwiss., 1932, 20, 657).—The rotation-oscillation spectrum of H_2O has been analysed. An intensity change of 1 : 3 is noted in the series. The fundamental term must be a $^1\Sigma_g$ term. There are thus three dihydrides now known which exist in ortho- and para-forms, viz., H_2 , H_2O , and H_2O_2 . A. J. M.

Vibration-rotation spectrum of acetylene. K. HEDFELD and P. LUEG (Z. Physik, 1932, 77, 446–458).—Rotation lines were photographically measured in bands between 11,000 and 5000 Å. A. B. D. C.

Analysis of the (0,0) $^2\Pi \rightarrow ^2\Sigma$ CN band at 9168 Å. A. E. PARKER (Physical Rev., 1932, [ii], 41, 274–277).—Rotational analysis gives consts. in agreement with transitions involving higher vibrational levels of the $^2\Pi$ state (cf. Jenkins, this vol., 211). The band origin is at 10,905.12 cm^{-1} . N. M. B.

Ultra-violet spectrum of carbon disulphide and its apparent occurrence in the absorbing atmosphere of the sun. N. R. DHAR (Z. anorg. Chem., 1932, 207, 209–216).—Some unidentified lines in the solar spectrum appear to agree with ultra-violet absorption lines of CS_2 . E. S. H.

Effect of substitution on ultra-violet absorption and chemical properties of carbonyl compounds. W. HEROLD (Z. physikal. Chem., 1932, B, 18, 265–290; cf. this vol., 461).—With increase in the positive character of the substituents attached to the CO group in carbonyl compounds absorption is shifted towards the red. The positive character of substituents decreases in the order H, Me, Cl, NH_2 , OR. Since the carboxylic acids form semi-acetal compounds in hydroxylic solvents and their dissociation consts. increase with the positive character of the substituent, it seems that the formation of these compounds is a necessary preliminary to dissociation. In aq. solution AcOH is partly converted into the ortho-acid and in EtOH solution partly into the mono-ortho-ester. R. C.

Absorption spectrum of hexuronic acid. R. W. HERBERT and E. L. HIRST (Nature, 1932, 130, 205).—The single broad band at approx. 263 $\text{m}\mu$ reported by Bowden and Snow (this vol., 656) occurs with equal intensity in Szent-Györgyi's purified hexuronic acid. MeOH solutions do not obey Beer's law; they are unstable and, on keeping, show a gradual diminution in the intensity of the band. Aq. solutions show a single broad band at 260 $\text{m}\mu$ with a

rapid diminution in intensity. Tetramethyl- γ -fructose, glycuronic and galacturonic acids show no selective absorption. The keto-furanose structure previously suggested (this vol., 548) requires modification.

L. S. T.

Ultra-violet absorption of solutions containing two chromophoric groups. A. HILLMER and E. PAERSCH (Z. physikal. Chem., 1932, 161, 46–57).—The absorption of binary equimol. mixtures of C_6H_6 with MeI , EtI , or Pr^nI , and of PhPr with Pr^nI is additively constituted of the absorptions of the constituents. The absorption of $\text{Ph}[\text{CH}_2]_n\text{I}$ is additively constituted of the absorptions of the two chromophoric groups when $n=3$, but as n decreases the bands shift towards the red and there is exaltation of the extinction. PhI , however, does not continue this series, for the principal band is in practically the same position as in $\text{Ph}[\text{CH}_2]_3\text{I}$, and there is no exaltation. All the measurements have been made in hexane solution. R. C.

Ultra-violet absorption of substances with two chromophoric groups. A. HILLMER and E. PAERSCH (Z. physikal. Chem., 1932, 161, 58–60; cf. preceding abstract).—Existing data show that the absorption of a substance containing two chromophoric groups sufficiently far apart is additively constituted of the absorptions of the individual groups. As the groups approach there is displacement towards the red when they come very close, and independently of this there is exaltation of the extinction. The mode of variation of the extinction as the chromophores approach depends on the nature of the latter. R. C.

Muscular hæmoglobins. J. ROCHE (Compt. rend., 1932, 195, 501–503).—The absorption spectra of muscular hæmoglobin of the ox, horse, and dog obey the same laws as those of blood hæmoglobin.

F. R. S.

Infra-red photography. G. MÖNCH and H. WILLENBERG (Z. Physik, 1932, 77, 170–173).—Technical improvements have been made in the method previously described (cf. this vol., 444).

A. B. D. C.

Infra-red dispersion of carbon dioxide. H. M. SMALLWOOD (Physical Rev., 1932, [ii], 41, 164–166).—Mathematical. N. M. B.

Infra-red absorption spectrum of carbon dioxide. P. E. MARTIN and E. F. BARKER (Physical Rev., 1932, [ii], 41, 291–303).—The 15 μ band has been resolved into several constituent bands each consisting of a narrow, intense, zero branch with equally spaced rotation lines on each side. The 4.3 μ band shows similar line spacing, but no zero branch. The calc. moment of inertia is 70.8×10^{-40} g.- cm^2 . Harmonic and combination bands and a correlation with Raman spectra are discussed. N. M. B.

Vibrational levels of linear symmetrical triatomic molecules. D. M. DENNISON (Physical Rev., 1932, [ii], 41, 304–312).—Fermi's theory of energy levels of mols. of the CO_2 type is applied to the results of Martin (cf. preceding abstract) and to available data for CS_2 . N. M. B.

Two-minima problem and the ammonia molecule. D. M. DENNISON and G. E. UHLENBECK

(Physical Rev., 1932, [ii], 41, 313—321).—Formulae are deduced leading to the dimensions $H-H=1.64 \times 10^{-8}$ $H=1.02 \times 10^{-8}$ cm. for the NH_3 mol.

N. M. B.

Raman spectrum and molecular structure of ozone. G. B. B. SUTHERLAND and S. L. GERHARD (Nature, 1932, 130, 241).—A 30% solution of O_3 in liquid O_2 gives a very weak doublet corresponding with a mean shift of 1280 cm^{-1} when excited by the Hg arc. The O_3 mol. is concluded to be triangular but not equilateral.

L. S. T.

Raman effect in salt solutions. A. SILVEIRA and E. BAUER (Compt. rend., 1932, 195, 416—418; cf. this vol., 559).—Solutions of chlorides of Ca, Sr, Cd, Li, and H, and of $Ca(NO_3)_2$ have been examined. The line at or near 1650 cm^{-1} is due to H_2O , the position being slightly modified by the electrostatic field of the cations (cf. A., 1931, 1091). New lines are reported at 1762 for LiCl, and at 1811 for LiCl, $Mg(NO_3)_2$, and $Ca(NO_3)_2$.

C. A. S.

Investigation of intermediate compound formation by means of the Raman effect. J. A. HIBBEN (Proc. Nat. Acad. Sci., 1932, 18, 532—537).—The aldol-crotonaldehyde type of transformation has been studied, but results are inconclusive. There is evidence of possible compound formation in solution between $AlCl_3$ and EtOH and between $ZnCl_2$ and MeOH; of polymerisation of $AlCl_3$ in H_2O ; of no compound formation in solution between K_2SO_4 and $Al_2(SO_4)_3$; and of a stepwise ionisation of $ZnCl_2$ in H_2O . No Raman displacements were obtained with Al_2O_3 nor hydrated $AlCl_3$.

W. R. A.

Thermo-luminescence and photo-luminescence of fluorites. E. IWASE (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 910—933; cf. A., 1931, 1111).—A relation is found for the variation with temp. of photo- relative to thermo-luminescence.

N. M. B.

Significance of line emission and absorption spectra of chromium phosphors. O. DEUTSCHBEIN (Z. Physik, 1932, 77, 489—504).—Lines in the spectra of Cr phosphors are identified with lines in the Cr^{+++} spectra.

A. B. D. C.

Crystalloluminescence of barium bromate. E. A. ENGLE and L. SCHULTZ (J. Colo.-Wyo. Acad. Sci., 1931, 1, No. 3, 22).—No activating impurities are required. Luminescence is max. during slow crystallisation of a saturated solution from 72° to 55° .

CH. ABS.

Mass-spectrograph study of the ionisation and dissociation by electron impact of benzene and carbon disulphide. E. G. LINDER (Physical Rev., 1932, [ii], 41, 149—153).— C_6H_6 gave ions containing C in amounts from C_1 to C_6 with various amounts of H attached; the principal ion for electrons of 120 e-volt is $C_6H_6^+$; no negative ions and no H^+ ions were found. CS_2 at low pressure and impacts of 120 e-volts gave the ions CS_2^+ , CS^+ , S^+ , and C^+ .

N. M. B.

Photo-electric cells with thin layer alkali cathodes. P. SELENYI (Z. Physik, 1932, 77, 420).—A claim for priority over Sewig (this vol., 669).

A. J. M.

Photo-electric primary currents in non-conducting crystals. K. HECHT (Z. Physik, 1932, 77, 235—245).—The movement of electrons in AgCl on illumination was determined.

A. B. D. C.

Theory of the crystal photo-electric effect. H. T. WOLFF (Physikal. Z., 1932, 33, 621—624).—It is proved mathematically that crystals show a slight preferential photo-electron emission in the direction of the incident light, and that, owing to the strong light absorption of cuprite, more electrons are emitted from the front of an illuminated plane than from behind it.

J. W. S.

Electrical conductivity of metals at the lowest temperatures. J. C. McLENNAN (Proc. Roy. Inst., 1932, 27, 446—470).

Change of electrical resistance in iron crystals. W. GERLACH (Ann. Physik, 1932, [v], 14, 613—616; cf. Englert, this vol., 985).—All determinations on resistance change of Fe crystals with magnetisation agree with results obtained with polycryst. wires.

A. J. M.

Conductivity mechanism in dielectric liquids under intense electric fields. A. NIKURADSE (Z. Physik, 1932, 77, 216—234).—Saturation and breakdown potentials were measured for several dielectric liquids, e.g., PhMc, under fields of the order of 10^5 volts per cm. and increasing electrode separation. Results agree with Schumann's theory (*ibid.*, 76, 707).

A. B. D. C.

Electrical breakdown experiments with compressed gases and liquid carbon dioxide. O. ZEIER (Ann. Physik, 1932, [v], 14, 415—447).—Experiments were made with air, N_2 , and CO_2 at pressures of 1—120 kg. per sq. cm. Deviations from Paschen's law occurred at lower pressures as the spherical electrodes were increased in size. The deviations can be explained on the assumption of the existence of a positive space charge.

A. J. M.

Characteristic temperature for Rochelle salt crystals. R. D. SCHULWAS-SOROKIN (Z. Physik, 1932, 77, 541—546).—The temp. variations of the piezo- and di-electric consts. show a sharp max. at 22.5° .

A. B. D. C.

Dielectric properties of dipolar liquids. A. E. VAN ARKEL and J. L. SNOEK (Physikal. Z., 1932, 33, 662—664).—An improved formula connecting dielectric const. and dipole moment in place of that of Debye is put forward, and shown to agree with the experimental data.

A. J. M.

Polarisation measurements on basic beryllium acetate and acetylacetonate. J. W. SMITH and W. R. ANGUS (Proc. Roy. Soc., 1932, A, 137, 372—379).—Mol. polarisations have been calc. from dielectric const. and density measurements of two solutions of basic Be acetate in C_6H_6 and one in CCl_4 at 25° and 45° , and for a solution of Be acetylacetonate in CCl_4 at 20° , 25° , 35° , and 45° . Mol. refractivities were determined for each solution at 25° . The mol. polarisations do not vary with temp., but are considerably higher than the mol. refractivities. This difference is attributed to at. polarisation, and since this is more pronounced when atoms are linked by

electro-valencies than by co-valencies, it is considered that a structural formula in which all the atoms are electrically neutral is inadequate.

Measurement and interpretation of certain dipole moments. A. E. VAN ARKEL and J. L. SNOEK (Z. physikal. Chem., 1932, B, 18, 159—166).— C_2Cl_6 , CBr_3F , and CCl_3Br have zero dipole moment. The moments of all the Cl derivatives of C_2H_6 have been determined, some of these varying with the temp. and solvent. It is suggested that a solvent the dielectric const. of which shows no signs of polarity but which contains double linkings, e.g., C_6H_6 , may exhibit in respect of solutes some polarity, the mol. field in the immediate neighbourhood of the mol. being much greater than that near, say, a CCl_4 mol. Deviations of observed moments from the vals. calc. by vectorial addition are ascribed to valency angle distortion, a mechanism of which is suggested in the case of CH_3 derivatives. R. C.

Determination of configuration of certain geometrically isomeric cyclic dibromides by means of dipole moment measurements. H. L. DONLE (Z. physikal. Chem., 1932, B, 18, 146—152).—Configurations have been assigned to certain 1:2-dibromides of dihydro-dicyclopentadiene and -tricyclopentadiene by comparison of measured vals. of the dipole moments with vals. calc. from group moments by vector addition. Measurements of the ultra-violet absorption of hexane solutions show that the absorption of a *trans* form is displaced towards longer waves compared with the corresponding *cis* form. R. C.

Dipole moments of some aromatic compounds. W. BODENHEIMER and K. WEHAGE (Z. physikal. Chem., 1932, B, 18, 343—346).—The dipole moments of $\text{CH}_2\text{Ph}\cdot\text{OH}$, $\text{CHPhMe}\cdot\text{OH}$, and the three chlorobromobenzenes have been determined. R. C.

Dipole moments of benzene derivatives with freely rotatable substituents. H. L. DONLE and K. A. GEHRCKENS (Z. physikal. Chem., 1932, B, 18, 316—326).—The moments of various disubstituted C_6H_6 derivatives have been determined. The val. 1.56×10^{-18} e.s.u. has been obtained for the moment of PhOH , which gives $89 \pm 5^\circ$ for the angle between the group moment and the diameter of the ring passing through the O. Vals. of the moments of substituted phenols calc. by means of this angle agree with the observed vals. For NH_2Ph and PhOMe the angles are $40 \pm 10^\circ$ and $80 \pm 10^\circ$, respectively. R. C.

Dielectric polarisation measurements on some nitroso-compounds. R. J. W. LE FEVRE and J. W. SMITH (J.C.S., 1932, 2239—2245).—From measurements of the dielectric consts., refractive indices, and densities of dil. solutions the dipole moments of $p\text{-NMe}_2\text{C}_6\text{H}_4\cdot\text{NO}$ and $p\text{-NEt}_2\text{C}_6\text{H}_4\cdot\text{NO}$ have been calc. as 6.89 and 7.18, respectively, in C_6H_6 and 6.33 and 6.87 in CCl_4 and that of $p\text{-NHMeC}_6\text{H}_4\cdot\text{NO}$ in C_6H_6 as 7.38, all $\times 10^{-18}$ e.s.u. The results are discussed with reference to the behaviour of the NO-group in org. compounds. J. W. S.

Electric moment and molecular structure. IX. Oxygen and sulphur valency angles. C. P. SMYTH and W. S. WALLS (J. Amer. Chem. Soc., 1932,

54, 3230—3240; cf. this vol., 794).—The O valency angle is $121 \pm 5^\circ$ in *p*-substituted diphenyl ethers, about 135° in anisoles and phenetoles, and $65\text{--}140^\circ$ in heterocyclic compounds. The S valency angle is about 146° in the diphenyl sulphides. M. M. (c)

Ionisation of organic acids. H. M. SMALLWOOD (J. Amer. Chem. Soc., 1932, 54, 3048—3057).—The changes in ionisation of org. acids on substitution of polar groups are largely determined by the magnitude and orientation of the electric moments of the substituents. E. R. S. (c)

Effect of pressure on the index of refraction of paraffin oil and glycerol. T. C. POULTER, C. RITCHIE, and C. A. BENZ (Physical Rev., 1932, [ii], 41, 366—367).—Data for density, refractive index, and the Lorenz-Lorentz const. for the range 1—13,585 and 1—7212 atm., respectively, are tabulated. N. M. B.

Double refraction of α -thymonucleic acid in view of the double refraction of chromatin. W. J. SCHMIDT (Naturwiss., 1932, 20, 658).—It is to be expected that the chromatin form of the nucleic acid of nucleoproteins will show negative double refraction. Na α -thymonucleate shows this. A. J. M.

Photo-electric measurement of the rotatory dispersion of some sugars in the ultra-violet region. G. BRUHAT and P. CHATELAIN (Compt. rend., 1932, 195, 462—465).—Photo-electric measurement of $[\alpha]$ for ultra-violet light is as accurate as visual measurement in the visible region, and enables small differences in dispersion to be measured. It is less accurate than the photographic method, but much more rapid, so that the mutarotation of glucose can be followed. The dispersion of glucose and fructose (I) are represented by $A/(\lambda^2 - 0.0254)$ and $B/(\lambda^2 - 0.0210)$, respectively; that of (I) is very similar to that of sucrose. Lowry and Richards' formula (A., 1925, ii, 265) is confirmed. R. S. C.

Constitution of compounds and radicals consisting of sulphur and oxygen. G. HAGG (Z. physikal. Chem., 1932, B, 18, 199—218).—The electronic formulæ are discussed in the light of available physical and physico-chemical data. R. C.

Possibility of forming complex molecules. E. J. M. HONIGMANN (Naturwiss., 1932, 20, 635—638).—The formation of complex mols. is discussed. Application to association of water, $(\text{H}_2\text{O})_x$, is considered. W. R. A.

Constitution of certain cobaltammine bases. A. B. LAMB and R. G. STEVENS (J. Amer. Chem. Soc., 1932, 54, 2643—2653; cf. A., 1922, ii, 217; 1923, ii, 226).—Conductometric titration of several nominally tervalent ammine bases prepared from aquo-ammine bromides has shown the H_2O mols. in the complex to be completely displaced by an equiv. no. of OH' ions. The apparent ionisations of the OH groups remaining outside the complex are high and nearly identical, irrespective of the nature of the central atom, the co-ordinated groups, and the valency of the cation. The replacement of the H_2O mols. is not, however, always complete. Interaction between aquo- and OH' ions

is comparable with that between aquo-ions and anions generally, although the replacement of H_2O by OH^- is relatively extensive and the attainment of equilibrium is unusually rapid.

W. C. F. (c)

Internal structure of solid inorganic compounds at high temperatures. V. Electrical conductivity, diffusion, and reactivity of magnesium orthosilicate and magnesium orthogermanate in the solid state. W. JANDER and W. STAMM (Z. anorg. Chem., 1932, 207, 289—307; cf. A., 1931, 999, 1236, 1356).—The electrical conductivity of SiO_2 , GeO_2 , Mg_2SiO_4 , and Mg_2GeO_4 , and the rate of diffusion in the solid pairs Mg_2SiO_4 – Ni_2SiO_4 and Mg_2SiO_4 – Mg_2GeO_4 , have been measured at high temp. The reactions between $\text{MgO} + \text{Ni}_2\text{SiO}_4$, $\text{NiO} + \text{Mg}_2\text{SiO}_4$, and $\text{NiO} + \text{Mg}_2\text{GeO}_4$ in the solid state have been investigated at about 1100° . Mg_2SiO_4 has a low ionic conductivity and crystallises mainly as a double-oxide lattice; its constitution may be represented by the equilibrium $\text{Mg}^{2+}_2\text{SiO}_4^{4-} \rightleftharpoons 2\text{MgO} \cdot \text{SiO}_2$. The diffusion of Ge in Mg_2SiO_4 is very rapid at 1070 – 1200° , whilst the diffusion of Ni is relatively slow. Mg_2GeO_4 has a transformation point at 1065° ; at lower temp. it crystallises in a spinel type and at higher temp. it is isomorphous with olivine. The spinel type has a higher electrical conductivity, which is at least partly ionic, whilst the conductivity of the olivine type is electronic. The spinel type contains Mg^{2+} , Ge^{4+} , GeO_4^{4-} , and O^{2-} , but as the temp. is raised a part of the O is withdrawn from the GeO_4^{4-} to the Mg^{2+} . The spinel lattice thus becomes unstable and is transformed into the double-oxide olivine type.

E. S. H.

Connexion between ferromagnetism and structure of ferrites. S. HILPERT and A. WILLE [with A. LINDNER] (Z. physikal. Chem., 1932, B, 18, 291—315; cf. A., 1909, ii, 672).—The magnetisability is a max. for the mol. ratio $2\text{MO} : 3\text{Fe}_2\text{O}_3$. The ferromagnetism of the ferrites depends on the presence of Fe_2O_3 acting as an acid. Ferromagnetism seems to have no connexion with lattice structure and to be a purely mol. or at. property. Various ferrites have been prepared by interaction of the chloride with an alkali ferrite at a high temp.

R. C.

Variability of magnetic ionic moment of some elements of the iron series. H. FAHLENBRACH (Ann. Physik, 1932, [v], 14, 521—524).—Correction to previous work (this vol., 563).

A. J. M.

Ferromagnetism and electrical properties. VI. Longitudinal and transverse ferromagnetic resistance changes. E. ENGLERT (Ann. Physik, 1932, [v], 14, 589—612).—In high external longitudinal and transverse fields the resistance change is to be ascribed to increase in spontaneous magnetisation.

A. J. M.

Additivity law for diamagnetism. D. P. RAY-CHAUDHURI (Z. Physik, 1932, 77, 271—274).—Deviations from the additivity law for hydrated salts are proportional to the heat of hydration; this was established for many sulphates and other salts.

A. B. D. C.

Influence of crystalline fields on the susceptibilities of salts of paramagnetic ions. I. The

rare earths, especially Pr and Nd. W. G. PENNEY and R. SCHLAPP (Physical Rev., 1932, [ii], 41, 194—207).—Mathematical.

N. M. B.

Magnetic susceptibilities of α - and β -manganese. (Miss) M. A. WHEELER (Physical Rev., 1932, [ii], 41, 331—336).—Pure α -Mn prepared by distillation, and β -Mn prepared by melting α -Mn in a vac. and quenching in H_2O from about 1000° gave mass susceptibilities of 9.60×10^{-6} and 8.80×10^{-6} , respectively.

N. M. B.

Magnetic susceptibility of nitrogen dioxide. G. G. HAVENS (Physical Rev., 1932, [ii], 41, 337—344).—A method sensitive to 3×10^{-15} is described. Vals for mol. susceptibility are: NO_2 , $\chi = 0.375\chi(\text{O}_2)$; N_2O_4 , $\chi = -30 \times 10^{-6} \pm 20\%$.

N. M. B.

Variations in paramagnetic anisotropy among different salts of the iron group. J. H. VAN VLECK (Physical Rev., 1932, [ii], 41, 208—215).—Theoretical.

N. M. B.

Magnetochemical researches. VI. Compounds of gallium and indium. VI. Magnetic behaviour of gallium and indium halides. W. KLEMM and W. TILK (Z. anorg. Chem., 1932, 207, 175—176; cf. A., 1931, 547; this vol., 988).—The following vals. have been determined for mol. magnetic susceptibility ($\times 10^6$) at room temp.: GaCl_2 —63, GaI_3 —149, InCl —30, InCl_2 —56, InBr_3 —107, TlCl —55, AuCl —49, AuBr —61, AuI —91, AuCl_3 —112, KAuCl_4 —152.

E. S. H.

Chlorides of nickel and cobalt in solution. Magnetic varieties. Linear relations between Curie constants and Curie points. G. FOEX (J. Phys. Radium, 1932, [vii], 3, 337—344).—The results of Fahlenbrach (cf. this vol., 563) are discussed, and some deductions (particularly a linear relation between Curie const. and Curie point) are pointed out.

E. S. H.

Comparison of the primary photographic process in alkali and silver salts. R. HILSCH and R. W. POHL (Z. Physik, 1932, 77, 421—426).—The primary photographic process is transition of an electron from the anion to the cation, and the measurable transfer of electricity observed in Ag salts is a secondary phenomenon.

A. B. D. C.

Surface tension determinations of malonic esters, and the constitutive nature of the parachor. A. B. BECK, A. K. MACBETH, and S. W. PENNYCUICK (J.C.S., 1932, 2258—2262).—The surface tensions of a no. of esters of malonic acid have been measured by the max. bubble pressure method, and the parachors calc. The vals. obtained are generally lower than those calc. from the consts. of Sugden or Mumford and Phillips. With unsubstituted esters the non-additivity increases with the length of the alkyl chain and may be connected with the space packing of the ester group. With substituted malonic esters the discrepancies appear to depend on the deviation of the C valencies on substitution at the central C atom. This view is supported by the conductivities of the corresponding acids (cf. A., 1931, 1126).

J. W. S.

Oscillating crystal and its technical aspect. E. HABANN (Physikal. Z., 1932, 33, 615—621; cf.

A., 1931, 671).—The behaviour of various types of oscillator crystals and improved methods of arrangement are discussed. J. W. S.

X-Ray diffraction with liquids. H. MENKE (Physikal. Z., 1932, 33, 593–604).—The theory of the diffraction patterns obtained with liquids is discussed. Experimental data are given for Hg, Ga, and CCl_4 , and the results obtained compared with theoretical vals. J. W. S.

Uniform distribution of impurities in crystals after tempering. B. HOCHBERG (Z. Physik, 1932, 77, 547–552).—Tempered NaNO_3 crystals show a uniform space charge on passage of current, and therefore a uniform distribution of impurity.

A. B. D. C.
Kinetics of crystallisation processes. F. VON GOLER and G. SACHS (Z. Physik, 1932, 77, 281–286).—An expression for the kinetics of crystallisation processes including nucleus formation and growth of crystals is derived. A. J. M.

Electric strength and crystal structure. A. WALTHER (Z. Physik, 1932, 77, 275–276).—Criticism of von Hippel's theory (cf. this vol., 565).

A. B. D. C.
Electric strength and crystal structure. A. VON HIPPEL (Z. Physik, 1932, 77, 277–280).—A reply (cf. preceding abstract). A. B. D. C.

Equilibrium forms of homopolar crystals. I. N. STRANSKI and L. KRSTZNOV (Z. Krist., 1932, 83, 155–156; cf. A., 1931, 1115). C. A. S.

Stereochemistry of crystal compounds. IX. Geometrical derivation of structure types A_2B_3 . W. NOWACKI (Z. Krist., 1932, 83, 97–112; cf. this vol., 796). C. A. S.

Method of notation for the constants of the lattice types A_nB_m . P. NIGGLI (Z. Krist., 1932, 83, 111–112; cf. this vol., 564). C. A. S.

Crystal structure of mercury. C. HERMANN and M. RUHEMANN (Z. Krist., 1932, 83, 136–140).—Unoriented rotation photographs of Hg at -50° show it to be rhombohedral, the unit cell having a 3.05, α $72^\circ 32'$ (cf. A., 1923, ii, 864; 1929, 16). C. A. S.

X-Ray investigation on the change of direction of crystal axes during an allotropic change of a substance. H. SHÔJI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 895–900).—Results for the changes $\alpha\text{-Fe} \rightarrow \gamma\text{-Fe}$, Zn blende \rightarrow wurtzite, and aragonite \rightarrow calcite are discussed. N. M. B.

Crystal structure of AuCd. A. OLANDER (Z. Krist., 1932, 83, 145–148).—A Au–Cd alloy containing 47.5 at.-% Cd, d 14.5, at room temp., has a 3.144, b 4.851, c 4.745 Å., with 4 atoms in the unit cell, space-group V_2^1 , each atom being surrounded by 8 of the other kind at slightly varying distances (2.89 and 2.91 Å.), indicating a deformed CsCl structure. At about 400° the lattice is of CsCl type, a 3.34 and distances between atoms 2.89 Å. This supports the inference from electrode potential measurements that the β -phase existing around 50 at.-% Cd has a transition point at 267° with mol. heat of transition about 240 g.-cal. C. A. S.

Crystal structure of red manganese sulphide. H. SCHNAASE (Naturwiss., 1932, 20, 640–641).—Red MnS exists in two cryst. modifications, one having a ZnS structure with a 5.60 Å., the other having a wurtzite structure with a 3.976, c 6.432 Å., and $c:a=1.617$. The at. separation is 2.425 Å. Both modifications form mixed crystals with ZnS and CdS. A disulphide, MnS_2 , is formed under certain conditions; it has a hauerite structure with a 6.10 Å.

W. R. A.
Molecular rotation in solid state. Variation of crystal structure of ammonium nitrate with temperature. S. B. HENDRICKS, E. POSNJAK, and F. C. KRACEK (J. Amer. Chem. Soc., 1932, 54, 2766–2786).—The unit cell of tetragonal NH_4NO_3 ($84.2-125.2^\circ$) has a 5.75, b 5.75, c 5.00 Å., and n , the no. of mols. in the unit cell, is 2. The orthorhombic form ($32.3-84.2^\circ$) has a 7.06, b 7.66, c 5.80 Å., and n 4, and the space-group $Pbnm$ (V_2^{16}). The orthorhombic form (-18° to 32.3°) has a 5.75, b 5.45, c 4.96 Å., n 2, and the space-group $Pmmn$ (V_2^{10}). The form stable below -18° has possibly a hexagonal structure and a 5.75, c 15.9 Å., and n 6. Diffraction diagrams of specimens at -33° and -78° do not differ materially.

L. W. (c)
Crystal structure of caesium dithionate. G. HAGG (Z. physikal. Chem., 1932, B, 18, 327–342).—The hexagonal unit cell has a 6.326, c 11.535 Å., and contains two $\text{Cs}_2\text{S}_2\text{O}_6$ mols. In the S_2O_6 radical the O atoms lie at the corners of two equilateral triangles with a common trigonal axis, on which, between the triangles, are the S atoms. R. C.

Crystal structure of nickel sulphate hexahydrate. C. A. BEEVERS and H. LIPSON (Z. Krist., 1932, 83, 123–135).—Tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ has a 9.61, c 18.3 Å., with 4 mols. in the unit cell, space-group D_2^1 or D_2^2 . The structure consists of alternate tetrahedral SO_4 and octahedral $\text{Ni}(\text{H}_2\text{O})_6$ groups (cf. this vol., 681) arranged along the dyad axes. The crystals are dextro-rotatory for red, lævo- for blue light, approx. $+2^\circ$ and -1° , respectively.

C. A. S.
Crystal structure of ferric chloride. N. WOOSTER (Z. Krist., 1932, 83, 35–41).—Ferric chloride has a rhombohedral or hexagonal unit cell, the former with a 6.69 Å., α $52^\circ 30'$, and 2 mols. FeCl_3 ; the latter with a 5.92, c 17.26, and 6 mols. Space-group C_3^2 ($R\bar{3}$), perhaps C_3^4 ($R3$); Cl parameter 0.077. The structure is a layer lattice isomorphous with BiI_3 (cf. A., 1931, 549); at. distances are Fe–Cl 2.38, Cl–Cl 3.31, 3.42, and 3.67; the atoms are in the ionic state. Double refraction approx. 0.34; The recorded density, 2.898 (cf. A., 1924, ii, 489), is probably too low, d_{calc} being 3.04. C. A. S.

Crystal structure of lithium orthophosphate and its relation to the olivine type. F. ZAMBONINI and F. LAVES (Z. Krist., 1932, 83, 26–28; cf. this vol., 39).—The unit cell of Li_3PO_4 has a 4.86, b 10.26, c 6.07 Å., thus showing close similarity to chrysoberyl and olivine (cf. A., 1926, 227, 995). This similarity is attributed to the small Li cations occupying $3/4$ ths of the octahedral vacancies between the hexagonally close-packed O atoms which form the skeleton of the

olivine type of structure, just as in olivine itself the Mg cations occupy 2/4ths of these vacancies.

C. A. S.

Structure of covellite. I. OFTEDAL (Z. Krist., 1932, 83, 9—25).—The hexagonal unit cell has a 3.80, c 16.4 Å., and contains 6CuS, space-group D_{6h}^{14} ($C6/mmc$). The structure is that of Roberts and Ksanda (cf. A., 1929, 870), but with U_{Cu} 0.107 and U_S 0.125. At. distances are S-S 2.05, Cu-S 2.20—2.35, Cu-Cu 3.2 Å.

C. A. S.

X-Ray determination of crystal structure of epsomite. G. M. CARDOSO (Trab. Mus. Nac. Cienc. Nat., 1930, Geol., No. 37, 130 pp.; Chem. Zentr., 1932, i, 1626).—Epsomite, rhombic, pseudotetragonal, has a 11.91, b 12.02, c 6.87 Å.; space-group V_4 . The unit cell contains 4 mols. of $MgSO_4 \cdot 7H_2O$.

A. A. E.

Space-group of bournonite. I. OFTEDAL (Z. Krist., 1932, 83, 157—158).—Bournonite, $CuPbSbS_3$, is rhombic, a 8.10, b 8.65, c 7.75 Å., with 4 mols. in the unit cell, space-group V_4^3 ($Pmmn$).

C. A. S.

Space lattice of natrolite. F. HALLA and E. MEHL (Z. Krist., 1932, 83, 140).—Further consideration of the authors' results (cf. A., 1931, 550), and of those of others (cf. A., 1930, 1240; this vol., 715), and of the fact that natrolite is pyroelectric, show the space-group to be C^{19} .

C. A. S.

Crystal structure of kaolinite. J. W. GRUNER (Z. Krist., 1932, 83, 75—88).—Kaolinite, SiO_2 45.73, Al_2O_3 38.37, TiO_2 1.35, Fe_2O_3 0.40, CaO 0.56, SO_3 0.16, H_2O +110° 13.19, -110° 0.50, total 100.26, n_a 1.556, n_γ — n_a 0.008, has a 5.14, b 8.90, c 14.51 Å., β 100° 12'—101° 30', with 4 mols. $Al_2Si_2(OH)_4O_5$ in the unit cell; space-group C_4^1 . Pauling's structure (cf. A., 1930, 1396) is confirmed. Anauxite (cf. A., 1930, 569) is kaolinite in which Al replaces Si, compensation for different valency being effected by a corresponding replacement of OH by O.

C. A. S.

Structure of hemimorphite. T. ITO and J. WEST (Z. Krist., 1932, 83, 1—8).—Hemimorphite, $Zn_4Si_2(OH)_2O_7 \cdot H_2O$, is pyramidal orthorhombic, with a 8.38, b 10.70, c 5.11 Å., and 2 mols. in the unit cell; the $(OH)_2$ form an integral part of the mol., whilst the H_2O occupies a definite position between mols., thus explaining its removability without perceptible effect on the crystals (cf. A., 1909, ii, 154). The Si and O atoms form Si_2O_7 groups; each Zn is surrounded tetrahedrally by 3 O and one OH.

C. A. S.

X-Ray diffraction with molecules containing two carbon atoms. F. EHRHARDT (Physikal. Z., 1932, 33, 605—614).—Liquid Cl_2 -derivatives of C_2H_4 and C_2H_6 have been investigated by the Debye method and the distances of separation of the Cl atoms deduced. In $C_2H_4Cl_2$ the Cl atoms show a preferential tendency to maintain a *trans*-configuration.

J. W. S.

Determination of structure of the aromatic disulphides and diselenides $RS(Se) \cdot S(Se)R$ ($R = Ph, CH_2Ph, Bz$). L. EGARTNER, F. HALLA, and R. SCHACHERL (Z. physikal. Chem., 1932, B, 18, 189—198).—Determination of the lattice structure and consts. has shown that in these compounds the dis-

tance between the S or Se atoms > the interat. distance in the lattices of these elements, this effect being much more pronounced with the S than with the Se compounds.

R. C.

Rotation of carbon chains. J. D. BERNAL (Z. Krist., 1932, 83, 153—155; cf. A., 1930, 1097; this vol., 451).—Dodecylol shows both rotating and fixed forms, with transition point at 16°; octadecylammonium chloride a new fixed form in which the chains in alternate double layers slope in opposite directions. The following data are given (in this order), a , b , c (in Å.), β , d , mols. in unit cell, space-group (h denotes the high- and l the low-temp. form): $C_{29}H_{60}$ (h) 8.40, 4.85, 77.2, 90°, 0.86, 2, $C6/mcm$ (cf. A., 1928, 1176); $C_{12}H_{25}OH$ (h) 8.25, 4.76, 34.0, 90°, 0.905, 2, $C3m$; $C_{16}H_{33}OH$ (l) 8.80, 4.90, 44.2, 56° 40', 0.99, 4, $P2/a$; $C_{15}H_{31}CO_2H$ (h) 9.36, 4.95, —, —, 1.28°, 4, $P2/a$?; $C_7H_{15}NH_2 \cdot HCl$ (h) 4.96, 4.96, 21.1, 90°, 1.14, 2, $P4/nmm$; and $C_{18}H_{37}NH_2 \cdot HCl$ (l) 5.45, 5.40, 69.4, 90°, 0.97, 4, $P2_12_12_1$.

C. A. S.

Crystalline structure of hexuronic acid. E. G. COX (Nature, 1932, 130, 205—206).—Hexuronic acid (d 1.65) has a 17.71, b 6.32, c 6.38 Å., β 102.5°; space-group C_2^2 ($P2_1$) with 4 mols. of $C_6H_8O_6$ per unit cell. X-Ray and optical results indicate that the hexuronic acid mol. has a ring structure with fewer groups projecting out of the plane of the ring than a normal carbohydrate.

L. S. T.

Crystal structure of dihydrocinchonine dihydrobromide. F. SPAENHAUER (Z. Krist., 1932, 83, 112—116).— $C_{19}H_{24}ON_2 \cdot 2HBr$ (cf. this vol., 759) is rhombic sphenoidal, $a:b:c = 0.0793:1:0.8486$, n_a 1.601, n_β 1.632, n_γ — n_a 0.132. It is isomorphous with cinchonine dihydrobromide, and not pyroelectric.

C. A. S.

Retentivity and hysteresis of magnetostriktion for nickel. F. LICHTENBERGER (Z. Physik, 1932, 77, 395—397).

A. J. M.

Barkhausen effect. III. Nature of change of magnetisation in elementary domains. R. M. BOZORTH and (Miss) J. F. DILLINGER (Physical Rev., 1932, [ii], 41, 345—355; cf. A., 1930, 673; this vol., 327).—From an examination of annealed Fe, hard-worked Fe, and perminvar the longitudinal and transverse changes in magnetic moment with magnetisation were investigated, and interpreted in terms of the domain theory.

N. M. B.

Plastic limit properties of natural rock-salt deposited under water. L. PIATTI (Z. Physik, 1932, 77, 401—403).

A. J. M.

Thermo- and galvano-magnetic properties of a bismuth crystal. H. E. BANTA (Physical Rev., 1932, [ii], 41, 239—250).

N. M. B.

Variation with temperature of the thermo-electric power of nickel and some copper-nickel alloys. K. E. GREW (Physical Rev., 1932, [ii], 41, 356—363).—The thermoelectric power against Pt was measured for pure Ni, a 94% Ni-Cu, and a 79% Ni-Cu alloy. Results are discussed in relation to Stoner's theory.

N. M. B.

Determination of true specific heats of certain gases at high temperatures by the Lummer-Pringsheim method. A. EUCKEN and O. MÜCKE (Z. physikal. Chem., 1932, B, 18, 167—188).—By means of an apparatus permitting the measurement of sp. heat under pressures of several atm. sp. heats at const. pressure of O_2 , N_2 , H_2 , and CO_2 have been determined at 100—600°. Within the limits of experimental error (about 0.3%) the results can be represented by the Planck-Einstein formula, using characteristic temp. derived from band spectroscopic data. Sp. heat vals. obtained by the velocity of sound method, particularly for O_2 and N_2 , are too low because the sound frequency is so high that the oscillational degrees of freedom are unable to absorb their full share of energy. R. C.

Heat capacities of some hydrogen halides at high temperatures as calculated from Raman spectra. J. B. AUSTIN (J. Amer. Chem. Soc., 1932, 54, 3459—3460).—Vals. for HCl, HBr, and HI are compared with the vals. selected by Eastman (U.S. Bur. Mines, Tech. Paper 445). C. J. W. (c)

Heat capacity of selenium from 100° to 300° abs. T. DE VRIES and L. F. DOBRY (J. Amer. Chem. Soc., 1932, 54, 3258—3261).— C_p for metallic Se varies from 6.08 at 100° to 7.25 at 300° abs. L. P. H. (c)

Heat capacity and free energy of formation of ethylene gas. M. E. HAAS and G. STEGEMAN (J. Physical Chem., 1932, 36, 2127—2132).—The sp. heat of gaseous C_2H_4 at 2.5—66.8°, measured with an error of $\pm 1\%$, may be represented by $C_p = 4.064 + 0.02022T$. Using these and previously published data, the free energy of formation at 0—1000° has been calc. G. M. M. (c)

Active oxides. LIII. Natural constants of stable zinc oxide. G. F. HÜTTIG and K. TOISCHER (Z. anorg. Chem., 1932, 207, 273—288).—A compilation and crit. review of data recorded in recent literature for the following properties of ZnO: m.p., v.-p. curve, heat of sublimation, triple point, sp. heats, crystal lattice consts., d , infra-red spectrum, compressibility, thermal expansion, nature of lattice, atom and ion radii, existence of modifications, κ . E. S. H.

Affinity. LVIII. Compounds of gallium and indium. VIII. Ammoniates of gallium halides. W. KLEMM, W. TILK, and H. JACOBI (Z. anorg. Chem., 1932, 207, 187—203; cf. this vol., 998).—The following data have been determined: $GaCl_3 \cdot NH_3$, d_4^{25} 2.189, m.p. 124°, mol. heat of formation 33 kg.-cal.; $GaBr_3 \cdot NH_3$, d_4^{25} 3.112, m.p. 124°, mol. heat of formation 30 kg.-cal.; $GaI_3 \cdot NH_3$, d_4^{25} 3.635, m.p. 140°, mol. heat of formation 27 kg.-cal. The results are discussed in relation to the corresponding vals. for compounds of Al and In. $GaCl_3$ does not form ammoniates; at low temp. it reacts with NH_3 , forming Ga and $GaCl_3 \cdot 3NH_3$; above 100° the products of interaction of Ga powder and NH_3 are GaN and H_2 . Notes are given on the use of the diphenyl oxide calorimeter. E. S. H.

Compounds of gallium and indium. V. Properties of gallium trihalides. W. KLEMM and W. TILK (Z. anorg. Chem., 1932, 207, 161—174; cf. A., 1927, 812, 831).—The following data have been

determined: $GaCl_3$ has m.p. $78.0 \pm 0.3^\circ$, b.p. $205 \pm 1^\circ$ (759 mm.), d (solid) 2.47, d (liquid) $2.06_3 - 0.0020_5(t - 78^\circ)$, expansion coeff. (liquid) 100×10^{-5} , equiv. conductivity at m.p. $< 10^{-7}$; $GaBr_3$ has m.p. $124.5 \pm 0.5^\circ$, b.p. $284 \pm 1^\circ$ (750 mm.), d (solid) 3.69, d (liquid) $3.13_8 - 0.0029_5(t - 125^\circ)$, expansion coeff. (liquid) 94×10^{-5} , equiv. conductivity at m.p. 5×10^{-6} ; GaI_3 has m.p. $210 \pm 1^\circ$, b.p. $337 \pm 5^\circ$, d (solid) 4.15, d (liquid) $3.60_0 - 0.0022_4(t - 211^\circ)$, expansion coeff. (liquid) 62×10^{-5} , equiv. conductivity at m.p. 2×10^{-2} ; $SnCl_4$ has d (liquid) $2.35_5 - 0.0025_5(t + 33^\circ)$; SnI_4 has d (liquid) $3.73_0 - 0.0024_6(t - 143^\circ)$, equiv. conductivity at m.p. 10^{-6} ; TiI_4 has d (liquid) $3.42_6 - 0.0021_5(t - 150^\circ)$, equiv. conductivity at m.p. 10^{-6} . E. S. H.

Vapour pressures, evaporation, condensation, and adsorption. I. LANGMUIR (J. Amer. Chem. Soc., 1932, 54, 2798—2832).—The v.p., p , of liquids and solids may be represented by $p = AT^{\gamma e^{-b/T}}$, where p is in bars, and A , b , and γ are consts. Trouton's rule is equiv. to putting $\gamma = 0$ and $A = a$ universal const. Published v.-p. data for 20 elements give the val. 10.65 ± 1.19 for $\log A$. Hildebrand's rule is obtained with $\gamma = 1$ and $\log A = 7.83 \pm 0.52$. Better results are obtained with $\gamma = 1.5$ and $\log A = 6.37 \pm 0.22$. For solids with rigid mols. the experimental data may be represented by putting $\gamma = 1.5$ and $\log A = 6.9$, but if the vapour mols. have internal degrees of freedom much larger vals. of A are required. Application of the v.-p. equation to adsorption shows the rate of evaporation, r , of atoms or mols. from monat. adsorbed surface films to be given by $r = A(2\pi mk)^{-1/2} e^{-\theta T e^{-b/T}}$, where θ is the fraction of the surface covered by the adsorbed mols., of mass m . This agrees with experimental data for Th, O, and Cs films on W. Monat. and polyat. adsorbed films are treated by applying Clausius' virial to the repulsion of mol. dipoles, and by means of Gibbs' adsorption equation r can be obtained in terms of θ , T , and M , the dipole moment. By combining these equations with those of Boltzmann and Saha, equations are obtained for the rate of evaporation of ions and electrons. With W, apparently, the surface is homogeneous except for about 0.5%, on which adsorbed Cs atoms are held more firmly than on the remainder of the surface. P. H. E. (c)

Condition of water in the region 10—500° and from saturation pressure to 300 atmospheres. M. TRAUTZ and H. STEYER (Forsch. Gebiet Ingenieurwesens, 1931, A, 2, 45—52; Chem. Zentr., 1932, i, 1501).—Vals. for sp. vol. and the compressibility factor are tabulated for 50—300 atm. from 0° to 290°. The Joule-Thomson effect decreases markedly with rising temp. and between 50 and 300 atm. the inversion curve is linear. At low temp. the second differential coeff. of the heat content with respect to pressure is negative, at 50—55° it is zero, and then increases. C_p is a max. (10.7) at 250 atm., and at approx. 375° and 260 atm. the val. is 6.0. L. S. T.

Physical properties of pure ricinoleic acid; refractive index, specific gravity, and viscosity. E. ANDRE and C. VERNIER (J. Rheology, 1932, 3, 336—340).—The prep. of very pure ricinoleic acid is described. The Na salt crystallises readily from

EtOH, and it is suggested that pure soaps may not be colloidal. For the pure acid the variation of n with temp. (15–53°) is given by $n_D = 1.4732 - 0.000035(t-15)$, d (23.6–99.7°) is given by $0.2496 - 6.53 \times 10^{-4}(t-15) - 2.2 \times 10^{-4}(t-15)^2$, viscosity (23.6–100°) is given by $\log \eta = 1.044 + 1.19(1-t/100) + 1.08(1-t/100)^2$. E. S. H.

Theory of flow of very rarified gases. R. DARBORD (J. Phys. Radium, 1932, [vii], 3, 345–354).—Theoretical. E. S. H.

Inter-diffusion of metals. E. A. OWEN and L. PICKUP (Nature, 1932, 130, 201–202).—X-Ray diagrams showing the inter-diffusion of Zn and Cu particles heated in a vac. are reproduced and discussed. Inter-diffusion is controlled by the thermal equilibrium diagram, the rate of diffusion in the various phases being different. The rate at a given temp. is independent of particle size. The fundamental law of inter-diffusion is, apparently, $c_0 - c = \Sigma K e^{-mt}$, where c is the composition at time t , c_0 the final composition, and K and m are consts. depending on temp. of inter-diffusion and are sp. for each phase. L. S. T.

Changes in the solid phase of the system copper-gold. M. LE BLANC and G. WEHNER (Ann. Physik, 1932, [v], 14, 481–509).—An apparatus for the determination of conductivity in the system Au-Cu is described. For Cu there is a secondary dependence of conductivity on nuclear size which is not observed for Au. The data for alloys tempered below 450° give a curve with three max. corresponding with the existence of the compounds Cu_3Au , Cu_9Au_{10} , and $CuAu$, all of which form mixed crystals with excess of Cu or Au. The results were confirmed by thermo-electric force, micrographic, and X-ray determinations. A. J. M.

Constitution of the copper-silver series of alloys examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1932, 28, 705–707).—The liquid solution consists of monat. mols. of Cu and Ag; the solid solutions consist of monat. Ag dissolved in monat. Cu, and of monat. Cu dissolved in monat. Ag. E. S. H.

Solid cadmium amalgams. X-Ray proof of compound $Cd.Hg$. N. W. TAYLOR (J. Amer. Chem. Soc., 1932, 54, 2713–2720).—X-Ray examination of solid Cd amalgams, annealed in a vac. at 147° for 72 hr., shows the existence of a new crystal phase, body-centred tetragonal, with a 16.53, c 12.09 Å. Its range of existence is about 70–75 at.-% Cd. It may be regarded as Cd_3Hg or as a solid solution of Hg in Cd_3Hg . H. F. J. (c)

Crystal structures of electro-deposited alloys. X-Ray diffraction study of silver-cadmium deposits. C. W. STILLWELL and L. E. STOUT (J. Amer. Chem. Soc., 1932, 54, 2583–2592).—Electro-deposited Ag-Cd alloys from 96.0% to 31.0% Cd are either solid solutions or compounds. For any given composition the phase stable in the thermal alloy is the predominant phase in the electro-deposited alloy. Because of the presence of appreciable amounts of phases not found in a thermal alloy of the same composition, the complete composition of the electro-deposited alloy cannot be predicted. L. W. (c)

Recrystallisation and crystal recovery of pure aluminium and some hardenable aluminium alloys containing copper after cold deformation. H. BOHNER and R. VOGEL (Z. Metallk., 1932, 24, 169–178).—The primary and secondary recrystallisation structures of Al and its light alloys depend, not only on the composition of the alloy and the temp. and time of annealing, but also on thermal and mechanical treatment the metal has undergone, i.e., on the temp., nature, rate, and degree of deformation, and on the size and orientation of the original structure. Under certain conditions the surface layers of rolled sheets present a greater resistance to recrystallisation than does the core, and the time required to obtain a coarse-grained secondary structure is much longer than that required to obtain a fine-grained recrystallisation structure. The crit. region of deformation is greater for Al than for hardenable Cu-Al alloys; in the latter case increase in Si content lowers the crit. degree of deformation and the recrystallisation temp., whereas addition of Mn increases the crit. degree of deformation. After secondary recrystallisation of Cu-Al alloys containing Si, Mg, Mn, Cr, or Ti a regular, chess-board-like structure appears in the Lüder lines which are formed in stretching specimens quenched from 500°. The period of crystal recovery of deformed Al and its alloys depends on the thermal and mechanical treatment of the metal before deformation and is generally considerably influenced by small variations in the composition. It follows, therefore, that in the construction of recrystallisation diagrams for deformed metals and alloys the composition must be kept rigidly const. during all the tests and the thermal and mechanical treatment between casting and final deformation before recrystallisation must be standardised. A. R. P.

Time-potential curves on iron and steel and their significance. T. P. HOAR and U. R. EVANS (Iron and Steel Inst., Sept. 1932. Advance copy, 12 pp.).—Time-potential curves may be obtained by touching the metal with a filter-paper strip containing the electrolyte and connected with a $N-HgCl$ electrode in the usual way; rising curves show repair and falling curves a breakdown of the oxide film. Curves for iron and steel show rapidly falling potentials in chloride and sulphate solutions, whereas in phosphate and chromate solutions there is a rise in potential indicating a tendency to self-repair of the film. Repair is more readily effected in SO_4^{2-} than in Cl^- solutions, with pure Fe than with steel, and with smooth surfaces than with rough. Pure Fe treated with CrO_4^{2-} shows a rise in potential when first placed in SO_4^{2-} solutions, but a sudden breakdown occurs; a similar effect occurs in Cl^- solutions, but the breakdown is more rapid. Fe alloys containing Cr give rising, falling, or level potential curves in plain Cl^- solutions according to the conditions. A. R. P.

System Mg-Al-Cu. A. PORTEVIN and P. BASTIEN (Compt. rend., 1932, 195, 441–443; cf. A., 1919, ii, 414; 1931, 1224; B., 1932, 429).—Within the limits represented by $Mg-Mg_4Al_3-Mg_2Cu$ the thermal equilibrium data afford evidence of the solid phases Mg , Mg_4Al_3 , Mg_2Cu , and $Mg_2Al_3Cu_2$, and two eutectic points at 412° and 484°. The resistivity decreases

with increase in the Al content, but increases with the Cu content unless the Al > 10%, when the opposite effect is produced. C. A. S.

Constitution of the Fe-C-Si system. A. KRÍZ and F. POBORIL (Iron and Steel Inst., Sept., 1932. Advance copy, 27 pp.).—The equilibria for sections through the 3-dimensional diagram have been plotted at 4, 6, 8, 10, and 16% Si parallel with the plane of the binary system Fe-C and at 0.1, 0.22, 0.52, and 2.54% C parallel with the plane of the binary system Fe-Si, and based on these pseudo-binary sections isothermal sections have been constructed through the space diagram at 1000°, 1160°, 1170°, and 1300°. In the metastable system the non-variant equilibrium $\alpha + \gamma + \text{carbide} + \text{liquid}$ occurs at 1155°; the compositions represented by the edge points of the 4-phase plane are $\alpha = 10.2\%$ Si, 0.26% C, $\gamma = 8.2\%$ Si, 0.54% C, and $L = 6.9\%$ Si, 2.61% C. In the stable system the non-variant 4-phase equilibrium occurs at 1165°, and the edge points of the plane are $\alpha' = 9.7\%$ Si, 0.22% C, $\gamma' = 7.7\%$ Si, 0.52% C, $L' = 6.4\%$ Si, 2.54% C, and $C = 100\%$ C. (Cf. B., 1930, 1031.) A. R. P.

X-Ray study of phase boundaries in thermal diagrams of alloy systems. Cu-Zn system. E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1932, A, 137, 397—417).—An X-ray precision camera has been used to determine parameter vals. of the lattices of various phases in the Cu-Zn system with an accuracy of 1 in 4000; the data are employed to ascertain the phase boundary compositions. The increase in parameter with composition in a pure phase is independent of temp.; for mixed phases the parameter vals. of both phase lattices are independent of the composition in this region, but these values vary with temp. At a fixed temp. the const. parameters of a phase depend on the nature of the admixed phase. The X-ray method of phase boundary determination appears to give data as accurate as those given by other methods previously employed. L. L. B.

Thermal behaviour of certain solid solutions. E. L. NICHOLS and (Miss) M. A. EWER (J. Opt. Soc. Amer., 1932, 22, 456—465; cf. this vol., 793).—When ThO containing Tb, Pr, or U as activator is heated from above by a Bunsen flame to luminescence, one or more of the following effects may be observed after removal of the flame. (a) An evanescent glow may appear a fraction of a sec. to 2 sec. afterwards, characterised by an abrupt rise of temp. of 10—128°. (b) The temp. may rise steadily to a max. and then fall more slowly than normally, but with no abrupt disturbance. (c) A second disturbance may be observed in the cooling curve some sec. after the subsidence of effect (b). (d) With Th₂O₃ activated by Tb a succession of abrupt perturbations occur at 400—150° and at about 5-sec. intervals. (e) Contact with cold H₂ when at a temp. above 200° causes a rise in temp. (a) is explained as due to oxidation of the reduced material or of occluded H₂, (b) to the gradual oxidation of suboxides or occluded H₂, (c) to belated release and oxidation of H₂, (d) to crystallographic changes in the cooling substance, and (e) to storage and subsequent oxidation of the H₂. J. W. S.

Diffusion of sodium chloride in aqueous solutions. L. J. BURRAGE (J. Physical Chem., 1932, 36, 2166—2174).—The diffusion coeff. has been measured at 0—6M, and is a min. at about 1.5M. The coeff. for 0.1M-HCl has also been measured.

R. H. C. (c)

System water-phenol. I. Densities. O. R. HOWELL (Proc. Roy. Soc., 1932, A, 137, 418—433).—The d -concn. curve is complex for each temp., and there is no apparent continuity between the H₂O-rich and PhOH-rich portions. The d -temp. curve for each concn. can be represented by $d_t = d_{20} + \alpha(t-20) + \beta(t-20)^2$. The curves representing the mean d and mean concn. of the conjugate solutions are parabolic and can be expressed by $d_t^{\text{mean}} = d_{20}^{\text{mean}} - 5.75 \times 10^{-4}(t-20) - 2.50 \times 10^{-6}(t-20)^2$ and $wt C_t^{\text{mean}} = 9.0 \times 10^{-2}(t-20) - 5.5 \times 10^{-4}(t-20)^2$, respectively. Pure PhOH melts at 40.85+0.05° and the crit. solution temp. is 66.4°. L. L. B.

Solubility of nitrogen in water at 25° from 25 to 1000 atmospheres. R. WIEBE, V. L. GADDY, and C. HEINS, jun. (Ind. Eng. Chem., 1932, 24, 927).—The absorption coeff. at 1 atm. is about 20% less than that of H₂, but at 1000 atm. N₂ is less than half as soluble as H₂. J. W. S.

Solubility of gold in mercury. V. J. T. ANDERSON (J. Physical Chem., 1932, 36, 2145—2165).—The solubility of Au in Hg at 280—400°, and the composition of the solid and liquid phases in the system Pb-Au-Hg at 295—360° have been determined. The Au-Hg solubility curve shows a break at 310°. R. H. C. (c)

Determination of solubility in liquefied gases. I. Solubility of potassium nitrate in liquid ammonia. A. J. SCHATTENSTEIN and A. MONOS-SON (Z. anorg. Chem., 1932, 207, 204—208).—Apparatus is described for determining the solubility of substances in liquefied gases and the d of the solution. The solubility of KNO₃ in liquid NH₃ is 9.7 g. per 100 g. of solution at 0° and 10.6 at 25°. E. S. H.

Solubility of calcium sulphate and calcium carbonate at 182—316°. F. G. STRAUB (Ind. Eng. Chem., 1932, 24, 914—917).—The solubilities of both CaSO₄ and CaCO₃ decrease with rise of temp. over the range 182—316°. The influence of Na₂SO₄ on the solubility of these compounds has also been investigated, and from the data the activities of CaSO₄ for ionic strengths up to 0.05 have been calc. J. W. S.

Waters containing calcium sulphate and their use in cooling [plant]. [Solubility of calcium sulphate in presence of sodium chloride.] P. LEONE and S. VINTI (Annali Chim. Appl., 1932, 22, 393—394).—The solubility of CaSO₄ in H₂O containing NaCl in varying amounts from 0 to 15% at 15°, 20°, 40°, and 70° is tabulated. In 10% and 15% NaCl the solubility is considerably less at 70° than at 15°, and CaSO₄ may therefore separate out if natural (e.g., Sicilian) waters containing much NaCl and CaSO₄ are used in cooling plant.

E. W. W.

Solubilities of the phosphates of lead. M. JOWETT and H. I. PRICE (Trans. Faraday Soc.,

1932, 28, 668—681).—The solubilities of PbHPO_4 , $\text{Pb}_3(\text{PO}_4)_2$, and $\text{Pb}_5\text{Cl}(\text{PO}_4)_3$ in aq. solutions at 37.5° have been determined and the solubility products calc. PbHPO_4 and $\text{Pb}_3(\text{PO}_4)_2$ are in equilibrium when $[\text{PO}_4^{4-}]$ is $3 \times 10^{-6} M$; in presence of even very low $[\text{Cl}^-]$, $\text{Pb}_5\text{Cl}(\text{PO}_4)_3$ is the stable compound. A rocking electrode vessel for use with fluid Pb amalgams is described and a val. for E_0 of cells containing a Pb electrode and a liquid junction (saturated KCl) has been obtained. The first ionisation const. of H_3PO_4 at 37.5° has been determined. E. S. H.

Solubility of uric acid and the primary urates in water and salt solutions at 37° , with special reference to the formation of sediments in the urinary passages. G. HAMMARSTEN (Compt. rend. Lab. Carlsberg, 1932, 19, No. 7, 1—66).—Solubilities and solubility products for Li and K urates and for the stable and unstable forms of the Na and NH_4 salts are given, corrected for the free acid present. Li and K urates give true solutions at 37° , whilst saturated Na and NH_4 urates are partly colloidal. The presence of salts with a common ion causes increased solubility product. Data are also given for Na urate in presence of KCl and LiCl and for K urate with LiCl and CaCl_2 . The solubilities of NH_4 and Na urates in $0.02N$ -KCl are less than in pure H_2O , but increase at higher KCl concn. Salt effects cannot account for the large solubilities of uric acid and urates in urine, which are attributed to the tendency of urates to form stable supersaturated solutions. The solubility of Na urate is slightly raised by creatinine, but unaffected by hippuric acid. J. B. B.

Aqueous solutions of quinine hydrochloride and ethylurethane. G. MALQUORI (Annali Chim. Appl., 1932, 22, 440—448).—The solubility of quinine hydrochloride is increased in presence of ethylurethane. The n and d vals. for solutions of varying concn. and temp. are recorded; there is no indication of complex formation. E. W. W.

Solubility of cholesterol in mixed solvents. J. WEICHERTZ and H. MARSHIK (Biochem. Z., 1932, 249, 312—322).—The solubility in various binary mixtures of EtOH, H_2O , dioxan, C_6H_6 , and C_6H_{14} has been determined. It is in no case additive; certain mixtures exhibit a very steep max., whilst if both the solvents are polar the solubility rises or falls continuously. The solubility curves closely resemble the mol. polarisation curves of the mixed solvents and may be largely interpreted in terms of the interaction between the dipoles of the component solvent mols., but in the case of mixtures of non-polar solvents (C_6H_6 — C_6H_{14}) the max. may be attributed to solvation at different parts of the cholesterol mol. The solubility of cholesterol in the various simple solvents increases regularly as the dielectric const. of the solvent decreases (C_6H_{14} is anomalous). With Bu°OH and $n\text{-C}_5\text{H}_{11}\text{OH}$ cholesterol forms compounds and the (supersaturated) solutions readily form a cryst. mass. Solutions in Pr°OH form transparent gels which are stable for several weeks; on crystallisation they yield intermol. compounds. A similar compound is formed with furfuraldehyde. H. F. G.

Langmuir's adsorption theory and the adsorption isotherm. A. GANGULI (Kolloid-Z., 1932, 60, 180—184).—Theoretical. Formulae are derived by independent methods, expressing the relation between concn. of adsorbed substance and its concn. in the gaseous phase. A modified exponential equation for polar adsorption is derived. E. S. H.

Argon and amorphous carbon, 10 — 710° . M. W. TRAVERS (Proc. Roy. Soc., 1932, A, 137, 294—297).—The val. of $d \log V_{760}/d(1/T)$ is 0.98×10^3 , from which it follows that the energy change in the adsorption process between 300° and 700° is 4500 g.-cal./mol. The initial rate of adsorption is rapid, but the establishment of equilibrium is a relatively slow process. L. L. B.

Anomalous adsorption on active charcoal. C. OCKRENT (Nature, 1932, 130, 206—207; cf. this vol., 568, 689).—The 25° isotherm for the adsorption of PhOH by sugar-C is represented by 3 distinct curves, each of which appears to extrapolate to the origin and conforms to Langmuir's theory. L. S. T.

Molecular and activated adsorption of carbon monoxide on manganous oxide surfaces. A. T. WILLIAMSON (J. Amer. Chem. Soc., 1932, 54, 3159—3164; cf. A., 1931, 902).—The adsorption on MnO and MnO— Cr_2O_3 mixtures has been measured from -190° to 444° . The adsorption is mol. at low temp., with a heat effect = 1000—2000 g.-cal., but activated adsorption becomes noticeable above 0° . The activated adsorbate partly reduces the catalyst. The reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ possibly occurs on MnO at 444° , but is not measurable below 300° . G. M. P. (c)

Absorption of oxygen by sheets of rubber. G. A. LINHART (J. Physical Chem., 1932, 36, 1908—1911).—Kohman's results (B., 1929, 334) may be represented by $C = C_\infty bt^a/(1 + bt^a)$, where c is the absorption at time t and a and b are consts. S. L. (c)

Adsorption from solutions and its relation to the nature of the solvent and the adsorbed material. N. SATA and K. KURANO (Kolloid-Z., 1932, 60, 137—141).—The degree of adsorption of o -, m -, and p - $\text{C}_6\text{H}_4(\text{NO}_2)_2$, $-\text{NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$, and $-\text{NO}_2\text{-C}_6\text{H}_4\text{-OH}$ from solutions in CO_2 , CCl_4 , and C_6H_6 by C varies antipathetically with the solvent power of the medium, and increases with the polar character of the solvent. Adsorption and solubility of the solute do not always vary in opposite directions. The polar properties of the solvent appear to have a greater influence than those of the solute. E. S. H.

Inner adsorption in crystalline salts. A. KOLUSCHEWA and P. SEWRUGOWA (Kolloid-Z., 1932, 60, 141—145).—Experiments on the inclusion of K^+ , Na^+ , Ca^{++} , Cl^- , NO_3^- , KMnO_4 , NaMnO_4 , and $\text{Ba}(\text{MnO}_4)_2$ by BaSO_4 ppts. have given results in agreement with the views of Balarev (A., 1931, 795, 1121). E. S. H.

Adsorption of certain alkaloids on inorganic adsorbents. G. MALQUORI (Annali Chim. Appl., 1932, 22, 448—455).—The adsorption of nicotine, caffeine, and quinine hydrochloride on gels of SiO_2 and of the hydroxides of Al, Cr, and Fe is consider-

able, and follows Freundlich's law. The SiO_2 gel is much more active towards nicotine than towards quinine hydrochloride; hydrolytic adsorption of the latter is not observed. E. W. W.

Absorption of organic solvents by active charcoal, silica gel, and wash-liquids. E. BERL and L. WILL (*Angew. Chem.*, 1932, 45, 557—559).—The v.p.-composition curves for a no. of org. liquid binary mixtures are compared with the adsorption isotherms for C and SiO_2 gel. Excepting tetralin- CCl_4 and tetralin- C_6H_6 , all the mixtures examined deviate from the requirements of true solutions. Comparison of the v.p. curves with the heat changes on mixing suggests that the degree of mol. association is reduced in mixtures of (a) tetralin with EtOH, Et_2O , COMe_2 , EtOAc, and hexane, (b) AcOH with Et_2O , hexane, CCl_4 , C_6H_6 , and COMe_2 , and (c) cyclohexanol with EtOAc, hexane, CCl_4 , C_6H_6 , and EtOH. In other mixtures adsorption or compound formation is indicated. It is emphasised, however, that it is not possible to differentiate strictly between dissolution, depolymerisation, and adsorption. E. S. H.

Action of charcoal on dissolved heavy-metal [salts], especially platonic chloride. E. HEYMANN (*Z. anorg. Chem.*, 1932, 207, 251—256; cf. A., 1928, 471; 1930, 435).—The Pt compound adsorbed from aq. PtCl_4 by highly-purified beechwood C at room temp. can be removed by washing with HCl; it probably consists of $\text{Pt}(\text{OH})_4$ or other hydrolytic product, although X-ray examination failed to reveal its composition. At 100° metallic Pt is adsorbed and has been identified by X-ray analysis. E. S. H.

Hysteresis loop in the vapour pressure-concentration isotherms of the system human hair-water and its disappearance by careful removal of foreign gases. R. FRICKE and H. MARQUARDT (*Kolloid-Z.*, 1932, 60, 124—129).—Hysteresis is observed in presence of air, but the curves representing absorption and loss of H_2O are coincident when gases are removed by high vac. (cf. A., 1930, 1118).

E. S. H.

Equilibrium-layer theory of the formation of liquid films. C. W. FOULK (*Kolloid-Z.*, 1932, 60, 115—124).—Mainly a summary of published work (A., 1929, 1232; this vol., 17). Further results are given for the difference between static and dynamic surface tension in solutions of H_2SO_4 and of sucrose.

E. S. H.

Absorption and classical diffusion. A. T. MCKAY (*Trans. Faraday Soc.*, 1932, 28, 721—730).—Mainly theoretical. Experimental data are given for the absorption of H_2O by fibre boards and by waxed upper leather. E. S. H.

Quantum mechanics of activated adsorption. A. SHERMAN and H. EYRING (*J. Amer. Chem. Soc.*, 1932, 54, 2661—2675).—The temp.-sp. reaction rate curve for bimol. surface reactions in general exhibits a max. The quantum mechanical calculation of the activation energies for the hydrogenation of C_2H_4 and C_2H_2 and the activated adsorption of H_2 on charcoal indicates a probable mechanism for the ortho-para- H_2 conversion. H. F. J. (c)

Mechanism of ionic exchange in colloidal aluminium silicates. H. JENNY (*J. Physical Chem.*, 1932, 36, 2217—2258; cf. A., 1927, 415).—Electrodialysed colloidal Al silicates behave like colloidal acids, the order of strength being permutite < Putnam clay < bentonite. The lyotropic series for the adsorption of cations is $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{H}$ for permutite, $\text{Li} = \text{Na} < \text{K} < \text{H}$ for Putnam clay, and $\text{Na} = \text{Li} < \text{K} < \text{H}$ for bentonite. The release of adsorbed cations takes place in the reverse order. An explanation of the specificity of the behaviour of the cations in the exchange process is based on the magnitude of the attraction between the negative O ions of the lattice and adsorbed cations. C. T. S. (c)

Adsorption at the surface of solutions. I. Surface composition of H_2O -EtOH solutions. J. A. V. BUTLER and A. WIGHTMAN. II. Effect of lithium chloride on the surface of H_2O -EtOH solutions. J. A. V. BUTLER and A. D. LEES (*J.C.S.*, 1932, 2089—2097, 2097—2104).—I. The vals. of surface tension of H_2O -EtOH solutions, determined at 25° by the max. bubble pressure method, agree with those obtained by Bircumshaw (*J.C.S.*, 1922, 121, 887) by the drop wt. method, and also with some by the capillary rise method. Vals. for the Gibbs adsorption have been calc. and the connexion between the Gibbs adsorption and the surface composition is derived for the case in which the adsorption affects the surface layer only. The results show that in certain concns. there is a small excess of EtOH mols. in the solution under the surface layer. Estimated compositions of the surface layer are given, and also of the adsorption below it.

II. The Gibbs equation is used to determine the adsorption of two components at the surface of a ternary solution with reference to the third as zero. Vals. of the surface tension for the system H_2O -EtOH-LiCl have been determined at 25° by the capillary rise method, and the adsorption of H_2O and EtOH with respect to LiCl is calc. At small concns. of LiCl, as for salt-free H_2O -EtOH mixtures, there is an approx. complete unimol. layer of EtOH at the surface of solutions which contain more than 6 mols.-% EtOH. The ions are separated from the under surface of this layer by a layer of solution, the thickness of which decreases as the EtOH concn. increases, and disappears in pure EtOH solution. This is attributed to the hydration of the ions. At high LiCl concns. the ions penetrate the surface to an increasing extent.

M. S. B.

Surface activity and orientation of polar molecules in relation to nature of interface. VII. Surface activity and adsorption of *p*-toluidine at liquid-liquid interfaces. VIII. Analysis by surface tension measurements. Determination of partition coefficients of surface-active substances by capillary-manometric titration. A. TAUBMANN (*Z. physikal. Chem.*, 1932, 161, 129—140, 141—146; cf. A., 1930, 687).—VII. Measurements of the interfacial tension between aq. solutions of *p*-toluidine and hexane or C_6H_6 have shown that the adsorption at the interface obeys Langmuir's adsorption isotherm. At an air-aq. toluidine interface, however, the isotherm is applicable only at the higher

concs. For all three interfaces the surface occupied by a mol. in the saturated adsorption layer is 25.8×10^{-16} sq. cm., and the axial length of an oriented mol. is 6.6×10^{-8} cm.

VIII. Since, in general, surface-active acid or basic substances lose their activity when converted into salts by strong inorg. bases or acids, the end-point in titration may be found by measurements of surface tension, γ , preferably by the max. bubble pressure method. As titration proceeds γ rises, and becomes const. at the equiv. point. This method may be used to determine the solubility of surface-active substances in H_2O and their distribution ratio between H_2O and org. solvents.

Surface activity and electrical properties of molecules. V. K. SEMENTSCHENKO (Kolloid-Z., 1932, 60, 177—180).—Theoretical. E. S. H.

Variation of surface tension of aqueous solutions of certain complex organic substances with time. J. C. GHOSH and M. C. NOTH (J. Physical Chem., 1932, 36, 1916—1927).—Measurements have been made with solutions of various dyes. With true solutions, e.g., fuchsin-red, the surface reaches equilibrium too rapidly for the variation of the surface tension, γ , with time, t , to be measured; with solutions containing mainly multimol. aggregates, e.g., benzopurpurin solutions, γ changes with t as equilibrium is being established, and with colloidal dispersions, e.g., fuchsin-red with KCl, γ varies with t in a rather irregular manner. These observations have been confirmed by dialysis experiments.

Capillarity. XVII. Behaviour of organic liquids between parallel plates. K. SCHULTZE (Kolloid-Z., 1932, 60, 132—136).—The anomalies reported (this vol., 112) in the capillary rise of H_2O between small, parallel glass plates have also been observed with several org. liquids. E. S. H.

Optical detection of removal of films from iron. W. J. MULLER and W. MACHU (Z. physikal. Chem., 1932, 161, 147—153).—Polemical against Tronstad (cf. this vol., 343). R. C.

[Optical detection of removal of films from iron.] L. TRONSTAD (Z. physikal. Chem., 1932, 161, 154—157).—A reply to criticism (cf. preceding abstract). R. C.

[Optical detection of removal of films from iron.] W. J. MULLER and W. MACHU (Z. physikal. Chem., 1932, 161, 158).—Final comments (cf. preceding abstracts). R. C.

Viscosity of potassium chlorate in aqueous solution. G. R. HOOD (J. Rheology, 1932, 3, 326—333).—Viscosities of $KClO_3$ solutions have been determined at 18° between 0.002 and 0.525M and at 25° between 0.01 and 0.525M. The fluidity ϕ at 18° is related to the concn. c by the expression $\phi = 1 - 0.0028\sqrt{c} + 0.049c - 0.0275c^2$. An increase of viscosity due to ionic forces tending to maintain a space lattice structure has been observed. E. S. H.

Dependence of magnetism of Cr^{+++} in aqueous violet chromium nitrate solutions on concentration. Relation between the constants C and

0 of Weiss' law. H. FAHLENBRACH (Ann. Physik, 1932, [v], 14, 524—530).—The behaviour of Cr^{+++} is similar to that observed with Co^{++} and Ni^{++} . At high concns. a complex anion is probably formed. The magnetic ionic moment is a little different from that given by Bose's theory. With increasing dilution the val. approximates to that derived from Hund's theory.

Demonstration of Tyndall effect. K. SCHWIRTH (Kolloid-Z., 1932, 60, 217).—A lecture experiment. E. S. H.

Electrical properties of dust and mist. H. SACHSSE (Ann. Physik, 1932, [v], 14, 396—412).—Aerosols formed by condensation of vapour (As_2O_3 , NH_4Cl , SO_3 , $TiCl_4$) and paraffin oil are uncharged, as are also the mists obtained by atomising liquids. The aerosols obtained by other methods are charged, half the particles being charged positively, and the rest negatively. Charges produced by friction are proportional to the square of the radius of the particle.

Deduction of particle shape and size from viscosity and flow double refraction. W. KUHN (Z. physikal. Chem., 1932, 161, 1—32; cf. this vol., 571).—Particles suspended in a streaming liquid have both translatory motion and rotational motion about their centres of gravity. For spherical particles the rotation is uniform, but elongated particles tend to assume a particular orientation in relation to the direction of flow, this tendency being opposed by the Brownian motion. If v , the rate of flow, is small, the particles tend to make an angle of 45° with the direction of flow, independently of whether they are almost spherical or are much greater in length than in thickness. With increase in v this angle diminishes, and from the change the length, l , of the particles may be deduced. Unless the particles are spherical, they increase the viscosity, η . With very long particles, the ratio of l to the thickness may be obtained from η . It is suggested that variation of η with v is due to the particles aggregating loosely to form chains or networks, which break up when v is greater. Calculation of the forces holding together these aggregates gives vals. which indicate that the ordinary forces of adhesion are adequate for the purpose. R. C.

Determination of the magnitude, form, and solvation of macro-molecules. G. V. SCHULZ (Naturwiss., 1932, 20, 592).—If the sp. solvation vol. of a lyophilic colloidal solution, as determined by osmotic pressure measurements, is introduced into the Eischschitz formula for the relative viscosity, a val. in good agreement with experiment is obtained.

Optics of colourless sols. I. Theoretical derivation of absorption coefficients. T. CASPERSON (Kolloid-Z., 1932, 60 151—159).—With the help of Mie's theory the absorption coeffs. of colourless sols are calc. for different vals. of n , wave-length, and particle size. E. S. H.

Mercury as a dispersing medium. N. M. TSCHUJKO (Ukrain. Chem. J., 1931, 6, [Sci.], 229—240).—Sols of Fe in Hg are flocculated by addition of Zn-Hg, and are stabilised by Sn-Hg. The viscosity of amalgams of Zn or of Sn differs little from that of

Hg, whilst that of Fe sols is higher. The particles of Fe are positively charged. R. T.

Constitution of colloidal gold. W. PAULI (Naturwiss., 1932, 20, 551—557, 573—576).—The prep., constitution, and stability of sols of Au, $[\text{AuCl}_4]\text{H}$, and $[\text{Au}(\text{OH})_4]\text{K}$ are discussed.

W. R. A.

Structure of Bredig silver sols. I. J. LÖFFLER and W. PAULI (Kolloid-Z., 1932, 60, 146—150).—Experiments on the prep., stability, and electrical conductivity of Ag sols prepared by electro-dispersion in aq. NH_3 , KCl , NH_4Cl , HCl , H_2SO_4 , Na_2SO_4 , and in H_2O show that these sols, like the reduced Ag sols, owe their properties to the dissociation of ionogenic Ag complexes at the surface of the particles. The sols stabilised by OH' are flocculated on electro-dialysis, whilst those stabilised by Cl' exchange their cation for H' . E. S. H.

Hydrogen-ion concentration of ferric hydroxide sols. W. L. McCLATCHIE (J. Physical Chem., 1932, 36, 2087—2094; cf. A., 1923, ii, 218).—With glass and quinhydrone electrodes, p_{H} vals. of 4.05—4.43 were obtained, depending on the kind of bridge solution and the age of the sol. The H electrode gave higher and more irregular vals. Conc. aq. KCl as bridge solution seemed to give the most nearly correct result, about 4.4. Flocculation of the sol has no effect so long as it does not occur near the electrode. C. T. S. (c)

Emulsions. IV. Systems of sodium oleate, phenol, and water. I. J. WEICHERZ and H. SÄECHTLING (Kolloid-Z., 1932, 60, 192—210; cf. A., 1929, 260, 1379).—The viscosity of the system Na oleate- H_2O increases at all temp. with increasing concn., at first slowly and later rapidly. Systems containing >30% Na oleate are heterogeneous. The curve connecting the viscosity of $\text{PhOH-H}_2\text{O}$ systems with composition shows two inflexion points, indicating two systems, PhOH in H_2O , and H_2O in PhOH . The viscosity-composition curves for Na oleate- PhOH systems indicate a low degree of solvation. Systems containing >20% Na oleate are heterogeneous at 80° . Complex relations are observed in the system Na oleate- $\text{PhOH-H}_2\text{O}$, especially in regard to the amount of H_2O . When the Na oleate content is const., the viscosity falls with increasing PhOH content. The observed behaviour is ascribed to the lower solvation and association of Na oleate in PhOH as compared with H_2O . At high concns. of H_2O the PhOH no longer acts as a solvent. The formation of acid soaps through the action of PhOH is also considered. The regions of heterogeneity in the ternary system have been determined.

E. S. H.

Von Weimarn's precipitation theory, and formation of colloidal gold. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1932, 36, 1950—1959).—Contrary to this theory, the particles of colloidal Au formed by reduction processes are the larger the higher is the concn., c , of Au salt reduced. This cannot be explained by supposing that the hydrolysis of the Au salt with formation of $\text{Au}(\text{OH})_3$ nuclei is the main factor determining the degree of dispersity, for the greater the hydrolysis of a Au

solution of given concn. before the addition of a reducing agent, the fewer and hence the larger are the particles; in the absence of hydrolysis the particles are the smaller the lower is c . Because of the low solubility of Au in H_2O , the percentage of supersaturation, s , is relatively high for all vals. of c . Hence the rate of formation of nuclei is not directly proportional to s , but is relatively greater at lower concns. At these concns. the growth of nuclei is comparatively slow, so that relatively more nuclei can be formed before the supply of Au is exhausted. For both reasons the primary particle size is smaller in the sols formed from more dil. solutions.

H. B. W. (c)

Fibrillograms of the lines of force of the crystallisation process. T. HUZELEA (Z. Krist., 1932, 83, 89—96).—A drop of collagen solution, prepared by soaking the tendon of a rat's tail in very dil. AcOH , and a dil. aq. NaCl solution are allowed to interdiffuse on a microscope slide; the resulting fibre formation assumes various regular arrangements which are said to indicate the direction of action of the forces which cause crystallisation. C. A. S.

Mechanism of coagulation of sols by electrolytes. III. Exchange adsorption during coagulation of hydrous oxide sols. H. B. WEISER and G. R. GRAY (J. Physical Chem., 1932, 36, 2178—2193; cf. this vol., 463).—The "super-equiv." displacement of Cl' from hydrous oxide sols during gradual addition of electrolyte (A., 1928, 586) is the result of a faulty procedure which produces localised coagulation below the pptn. val., and does not allow time for equilibrium to be approached. By Weiser's method SO_4'' at all concns. enters into exchange adsorption with Cl' present in the diffuse outer layer of the oxide particles. The SO_4'' adsorption curve follows a smooth course above the Cl' displacement curve over the entire concn. range. C. T. S. (c)

Static and kinetic study of Liesegang rings. (MLLE.) S. VEIL (J. Phys. Radium, 1932, [vii], 3, 302—313).—The distribution, opacity, and successive phases of formation of the rings have been investigated.

N. M. B.

Interfacially bound and structurally bound water in inorganic jellies. S. PRAKASH (Kolloid-Z., 1932, 60, 184—191).—By interfacial hydration is understood the H_2O which is bound when the charge on the colloid particles is neutralised. During neutralisation the viscosity of the sol varies with the time t in accordance with the expression where h is a hydration const., depending on the thickness of the adsorbed layer of H_2O mols. For ideal hydrophobic colloids $h=0$ and no increase of viscosity is observed during coagulation; for hydrophobic colloids h has high vals., which can be determined from viscosity-time measurements during gelation. The exponential rise of viscosity is observed only when the hydration is of the interfacial type; in the later stages of gelation the viscosity rises more rapidly, indicating structure hydration, or the enmeshing of H_2O by the units of structure. At all stages the total hydration can be calc. from Hatschek's equation and the interfacial hydration can be found by extrapolation of the exponential curve. Experiments on

jellies of $\text{Zr}(\text{OH})_4$, Ce borate, Fe^{+++} arsenate and phosphate, Sn arsenate and molybdate, and Th arsenate show that about 80% of the H_2O is in the state of interfacial hydration, in agreement with observations on syneresis and thixotropy. E. S. H.

Influence of temperature on the setting of inorganic jellies. S. PRAKASH (J. Indian Chem. Soc., 1932, 9, 193—203).—The time of setting of gels of Zr hydroxide, molybdate, and borate, Th molybdate and phosphate, Cr tungstate, Sn^{+++} arsenate, phosphate, tungstate, and molybdate decreases markedly with rising temp. Gels of Th arsenate, V_2O_5 , and mercurisulphosalicylic acid show the reverse behaviour, but do not set above 60° ; these resemble org. jellies in melting. Rise of temp. increases the rate of coagulation of the sols which do not undergo hydrolysis and thus aids setting. Gels of polybasic salts are hydrolysed at higher temp. and the hydroxides formed also form gels; the setting time then depends on the composition of the mixed phases. E. S. H.

Structure viscosity. I. Concentration function of structure viscosity of gelatin sols. Wo. OSTWALD [with R. AUERBACH, J. FELDMANN, W. STAUF, and V. TRAKAS] (Kolloid-Z., 1932, 60, 159—170).—Concordant determinations have been made with 3 types of viscosimeter over the pressure range 0.5—150 cm. H_2O . Under turbulent streaming, <1% gelatin sols behave as dil. mol. disperse systems, but at low rates of flow a very great increase of viscosity is observed, due to some attraction among the structural components of the sol; the val. then varies markedly with the concn. The general results are in good agreement with the de Waele-Ostwald equation. Gelatin sols also show structure turbulence. E. S. H.

Influence of temperature and previous history on the osmotic pressure and micellar weight of gelatin solutions. M. FRANKEL (Biochem. Z., 1932, 249, 476—477).—A reply to criticism (this vol., 807). H. F. G.

Structure of gelatin sols and gels. IV. Fluidity and hydrolysis. S. E. SHEPPARD and R. C. HOUCK (J. Physical Chem., 1932, 36, 2319—2324; cf. A., 1930, 1518).—From data for the change of the fluidity with temp. the heat of hydrolysis is calc. to be 19,900—26,500 g.-cal., depending on the p_{H} (cf. A., 1927, 213). Fluidity changes are attributed to the hydrolysis of large mols. Dilatometric experiments show that the high viscosity of gelatin sols is not due to solvation. C. T. S. (c)

Modified gelatinisation and the influence of electrolytes on the sedimentation of the particles thus produced. H. G. B. DE JONG and W. A. L. DEKKER (Biochem. Z., 1932, 251, 105—115; cf. von Buzágh, A., 1931, 36).—The normal gelatinisation of dil. agar sols can be modified by mechanical agitation so that a "liquid gel" which shows little tendency to change its state is produced. Observations on the sedimentation of this gel and on the vol. of sediment produced when low concn. of neutral salts [KCl , BaCl_2 , $\text{Co}(\text{NH}_3)_6\text{Cl}_2$] are present show that the vol. of the sediment and the vol. of the gel vary in

opposite directions. An explanation of this phenomenon is given. W. McC.

Lyophilic colloids. XIV. Capillary-electric charge and hydration as state-variables of hydrophilic gels; changes in volume and elastic modulus of agar and gelatin gels. H. G. B. DE JONG and J. P. HENNEMANN (Kolloid-Beih., 1932, 36, 123—177; cf. A., 1929, 1381).—The vol. of cylindrical agar gels does not vary in pure H_2O , but low concns. of neutral salts cause a decrease, the amount of which is determined by the cation. The vol. of isoelectric gelatin gels increases slightly in H_2O and the increase is greater for positively- or negatively-charged gels. The isoelectric gel is practically unchanged by low concns. of neutral salts, but the increase of vol. of the charged gels is strongly reduced thereby, the Schulze-Hardy rule again being observed. During these changes the elastic modulus of the gel does not alter. The decrease of vol. brought about by small quantities of electrolytes is due to discharge of the particles and is consistent with the view that the gel consists of an irregular network of micelles, which are in contact at certain unprotected or hydrophobic spots. Higher concns. of neutral salts may produce a considerable increase or decrease of vol., the Schulze-Hardy rule then being replaced by the lyotropic series; in these circumstances there is a corresponding change of elastic modulus, but in the opposite direction, the lyotropic series being thus reversed. These changes are almost completely reversible, especially when a vol. decrease and an elasticity increase are involved. The incomplete reversibility attending an increase of vol. is observed particularly with gelatin, especially under peptising conditions (with KI or KCNS), and is attributed to secondary changes in the gel structure. The changes brought about by the more conc. neutral salts are interpreted in terms of solvation and desolvation, and have also been observed with EtOH . Tannin reduces both the vol. and elasticity of agar gel and appears to have a different mechanism of dehydration. E. S. H.

Structure of cellulose acetate gels from studies of diffusion. K. KLEMM and L. FRIEDMAN (J. Amer. Chem. Soc., 1932, 54, 2637—2642).—The rates of diffusion of 2—20% cellulose acetate in benzyl alcohol when brought in contact with MeOH or EtOH have been measured, and the diffusion coeff., D , and effective pore radius, R , calc. by means of the equations previously developed (A., 1930, 693). The law of diffusion is valid for this system. R varies from 18 μ for 2% to almost zero for 23% gels. The high vals. of D are inconsistent with a solid solution. The entire behaviour is what would be predicted by the liquid-solid theory of gel structure. F. E. B. (c)

Electro-rheic effect of a thixotropic gel. E. KARRER (J. Rheology, 1932, 3, 334—335).—When a p.d. is applied to two parallel Pt plates, arranged vertically and holding between them a thin film of clay suspension, the suspension immediately flows off the plates. E. S. H.

Significance of capillary width for streaming potential. H. B. BULL (Kolloid-Z., 1930, 60,

130—132).—The electro-osmosis caused in very narrow capillaries during measurements of streaming potential sets up an opposing pressure, which leads to low vals. for the ζ potential. The magnitude of the effect is calc. For aq. solutions the effect becomes appreciable in capillaries of radius $<1\mu$ and is observable with org. liquids in wider capillaries. E. S. H.

Phase-rule studies on the proteins. VII. Non-aqueous solutions. W. D. BANCROFT and S. L. RIDGWAY (J. Physical Chem., 1932, 36, 2299—2305; cf. this vol., 694).—Gelatin dissolved in a little H_2O was poured into a large amount of EtOH containing acid or base. Titration of the excess of acid or base showed compound formation with HCl, but adsorption only with NaOH. C. T. S. (c)

Flocculation of suspensions of myxoprotein by electrolytes. C. ACHARD and HO-DAC-AN (Compt. rend., 1932, 195, 429—432).—Electrolytes containing a uni- or bi-valent cation have no flocculating action on a suspension of myxoprotein from ox serum (cf. A., 1930, 235). With increasing concn. of $AlCl_3$ or $ThCl_4$ there is at first increasing flocculation, then a steady condition, followed by further increase, indicating either the presence of two substances in myxoprotein, or a difference in the sign of the charge which it carries. C. A. S.

Colloid-colloid reactions. III. Proteins and pure gold sol. K. OGIU and W. PAULI (Biochem. Z., 1932, 250, 535—548).—With high concns. of serum- and ov-albumin (highly purified by electro-dialysis) Bredig's Au sol gives a voluminous red ppt. and with low concns. only a change of colour to violet. Addition of neutral salts in the first case gives a protective and in the second a sensitising action. Glycine never shows a sensitising action and in sufficiently high concn. shows a protective action. Carbamide in high concn. in the cold protects serum- but not ov-albumin against pptn. with Au sol. P. W. C.

Combination curves, buffering powers, and equivalent of serum-albumin. E. B. R. PRI-DEAUX and D. E. WOODS (Proc. Roy. Soc., 1932, B, 111, 201—209).—Results of electrometric titrations for 1.0 and 0.1% aq. solutions of serum-albumin give a curve similar to, but more regular than, that obtained for ovalbumin (this vol., 631). The equiv. as an alkali, deduced from a slight inflexion at p_H 2.2, is 1150, and as an acid it is 1430 at p_H 10—11. Serum-albumin has a higher buffering power than ovalbumin, although their behaviour is identical at p_H 6—8. Results of quick titration of serum-albumin with relatively large amounts of alkali indicate that a max. of 34.5% of arginine is present. Heat-denaturation affects both albumins in the opposite direction to alkali hydrolysis, the former causing a large loss in buffering power towards acid. A. L.

Steric hindrance and collision diameters. H. EYRING (J. Amer. Chem. Soc., 1932, 54, 3191—3203).—The method of calculating the potentials between saturated mols. or groups of atoms is outlined and applied to two colliding H_2 mols. The result agrees with experiment. The potential energy curve for the collision of two saturated H atoms is

used in constructing a potential for the rotation of the two Me groups about the C—C axis. The increase in reactivity of an H atom attached to C as the neighbouring H atoms are replaced by Me is explained by calculations which show that the potential of H is 3.1 kg.-cal. higher in C_2H_6 than in CH_4 . M. M. (c)

Transitions in solution of salts of tervalent metals. IV. Equilibrium between the violet and green forms in solutions of chromic sulphate and sodium chromic sulphate. C. MONTEMARTINI and E. VERNAZZA (L'Ind. Chimica, 1932, 7, 1001—1004).—At 32.5° a solution of $Cr_2(SO_4)_3$ contains 34.5% of the violet form between the concn. limits of 3.5% and 7%. Equilibrium is established within 28 days from either side. Practically the same result is obtained with solutions of K and Na Cr alums, and the equilibrium is thus not altered by addition of K and Na sulphates. H. F. G.

Polyhalides. I. Formation and dissociation of polyhalides of hydrogen. S. K. RAY (J. Indian Chem. Soc., 1932, 9, 259—269).—F.-p. measurements for aq. solutions lead to the following dissociation consts.: $HClH_2$ 0.544, $HClBr_2$ 0.578, HBr_3 0.049. Heats of formation derived from these and data relating to 25° (or 30°) are: $HClH_2$ 762, $HClBr_2$ 1044, HBr_3 1467 g.-cal. The f.p. is raised by the addition of Br to 0.5N- or N-HBr, and of I to HBr or HI. This is ascribed to the separation of H trihalides with the ice, and the presence of these compounds in the solid phase is confirmed by analysis. A. G.

The phase rule. P. VAN RYSELBERGHE (J. Physical Chem., 1932, 36, 1733—1737).—De Donder's form of the phase rule $v=C-r+2-\phi$, where v is the variance, C the total no. of constituents of the system, r the no. of distinct chemical reactions which can occur, and ϕ the no. of phases, is deduced and illustrated. The quantity $(C-r)$ is considered to be more intelligible than Gibbs' "no. of components." J. H. R. (c)

Cryoscopic examination of liquids for purity, and purification of cyclohexanol. J. LANGE (Z. physikal. Chem., 1932, 161, 77—82).—If two samples of a liquid contained in similar vessels are partly frozen, the proportion frozen being considerably greater with one sample than with the other, and are then placed in the same thermostat, the temp. difference established between them is a criterion of purity. A suitable apparatus is described. Pure cyclohexanol has m.p. 25.46°. R. C.

Conversion of easily-crystallising substances into the glass state. G. TAMMANN and A. ELBRÄCHTER (Z. anorg. Chem., 1932, 207, 268—272).—An apparatus is described in which a melt or crystallisable solution is resolved by means of an air current into droplets (0.001—0.3 mm. diameter), which fall on to a cooled plate. The nos. of undercooled, crystallised, and vitreous drops are then counted. Results are given for some org. melts and aq. inorg. salt solutions. E. S. H.

Dilatometric determination of the transition temperatures of hydrated salts. M. MATSUI and S. KAMBARA (J. Soc. Chem. Ind. Japan, 1932, 35,

308—312B).—The following transition temp. are recorded: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4$, 32·377°;

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, 31·97°;
 $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, 36·55°. The accuracy of the last two figures quoted is less than that of the first, owing to the relatively low rate of crystallisation of the salt.

H. F. G.

Dilatometric determination of the transition temperature of sodium carbonate decahydrate. M. MATSUI, S. KAMBARA, and H. YOSHINO (J. Soc. Chem. Ind. Japan, 1932, 35, 313—316B).—The transition temp. deca-penta-hydrate is 31·91°. The pasty mixture which is obtained by heating to above 32° crystallises slowly, and the dilatometric method is not very suitable under these conditions.

H. F. G.

Sodium aluminium sulphate. ASTRUC and MOUSSERON (Compt. rend., 1932, 195, 423—425; cf. A., 1890, 1059).—Dilatometric, density, viscosity, and solubility measurements indicate that $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ undergoes partial dissociation below 11° and above 39°.

C. A. S.

Osmotic (permutoid) binding of water in oxide hydrates and similar compounds. E. HEYMANN (Z. anorg. Chem., 1932, 207, 257—267).—A theoretical discussion (cf. this vol., 228).

E. S. H.

Compounds of carbamide with alkaline-earth bromides. F. DE CARLI (Atti R. Accad. Lincei, 1932, [vi], 15, 747—752).—Solubility data at 11° indicate the existence of the compounds $\text{MBr}_2 \cdot 4\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ (M=Ca or Sr); no evidence of these is afforded by density or fluidity measurements.

T. H. P.

System FeO-SiO₂. N. L. BOWEN and J. F. SCHAIER (Amer. J. Sci., 1932, [v], 24, 177—213).—Equilibria have been investigated in electrolytic Fe crucibles in vac. and in pure N₂ at temp. below 1523°. All the melts in equilibrium with Fe contain some Fe₂O₃, the wt.-% of which decreases rapidly from 11·5 as SiO₂ is added. Thus, synthetic and natural fayalite (Fe₂SiO₄) and all FeO-SiO₂ mixtures melt incongruently with the separation of Fe. However, by regarding the system as essentially binary, the following invariant points are obtained: FeO, m.p. 1380+5°, wüstite-fayalite eutectic at 76% FeO and 1177°, Fe₂SiO₄, m.p. 1205°, fayalite-tridymite eutectic at 62% FeO and 1178°. These results differ from those of others, but are consistent with those of Greig (A., 1928, 132). The separation of crystals of FeSiO₃ could not be induced from either the liquid or the glass at temp. as low as 660°. The bearing of these results on petrology and the problems of slag formation and furnace linings is discussed. FeO is a strong flux for SiO₂ at temp. above 1178°, but becomes relatively weak in comparison with CaO at 1450°.

J. G. A. G.

Equilibrium of certain non-metallic systems.
III. Systems MnSiO₃-Fe₂SiO₄ and FeS-Fe₂SiO₄. J. H. ANDREW and W. R. MADDOCKS (Iron and Steel Inst., Sept. 1932. Advance copy, 10 pp.).—The equilibrium diagram of the system MnSiO₃-Fe₂SiO₄ indicates that the compounds form a simple eutectiferous series with a limited solid solution range at

both ends; the eutectic occurs at about 40% MnSiO₃ and 1110°. Above 90% Fe₂SiO₄ there is evidence of the formation of knebelite. The system FeS-Fe₂SiO₄ is also eutectiferous, the eutectic occurring at about 48% FeS and 1000°; about 12% FeS is soluble in Fe₂SiO₄ and about 1% Fe₂SiO₄ in FeS. The *d* of mixtures in the systems MnS-MnO, MnS-MnSiO₃, MnS-Fe₂SiO₄, MnSiO₃-Fe₂SiO₄, and FeS-Fe₂SiO₄ are shown graphically.

A. R. P.

Ceramics of highly refractory substances. V. Ternary systems ZrO₂-ThO₂-CaO, ZrO₂-ThO₂-MgO, ZrO₂-BeO-CaO, ZrO₂-BeO-CeO₂. O. RUFF, F. EBERT, and W. LOERFABEL (Z. anorg. Chem., 1932, 207, 308—312; cf. B., 1929, 474; A., 1929, 650, 766).—The thermal equilibrium diagrams of these systems are compared with X-ray analyses of the products. Colourless glasses formed from the first three systems at 2450—2520° are described.

E. S. H.

Recommendation of certain thermodynamical symbols by the Deutsche Bunsen-Gesellschaft. A. EUCKEN and K. FAJANS (Z. Elektrochem., 1932, 38, 681).—The following symbols are recommended: *E*=energy (general), especially in at. and mol. processes, *U*=internal energy, *S*=entropy, *A*=work added to a system, *A*=work taken from a system, *Q*=heat added to a system, *Q*=heat taken from a system.

E. S. H.

Essential properties of a system of thermodynamics. M. RANDALL (Z. Elektrochem., 1932, 38, 676—680).—A discussion.

E. S. H.

Chlorine equilibria and absolute entropy of chlorine. A. R. GORDON and C. BARNES (J. Physical Chem., 1932, 36, 2292—2298; cf. this vol., 695).—The entropy of Cl at 300—1000° has been calc. from spectroscopic data. From the known entropies of HCl, O₂, and steam, the equilibrium const. for the reaction $2\text{Cl}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{HCl} + \text{O}_2$ has been calc. at 600—1000°. The calc. and observed vals. agree. General considerations indicate that the existence of isotopes does not affect the entropy of reaction except as a second order effect.

G. M. M. (c)

Calculation of partial molal quantities. T. F. YOUNG and O. G. VOGEL (J. Amer. Chem. Soc., 1932, 54, 3025—3029).—Formulae to facilitate change of variable in the calculation of partial mol. properties of the constituents of solutions are presented.

M. M. (c)

Ionic activity coefficient product and dissociation of water in barium chloride solutions at 25°. H. S. HARNED and C. M. MASON (J. Amer. Chem. Soc., 1932, 54, 3112—3120).—From e.m.f. data for $\text{H}_2|\text{Ba}(\text{OH})_2(m_1)|\text{BaCl}_2(m_2)|\text{Ba}_2\text{Hg}|\text{Ba}(\text{OH})_2(m_0)|\text{H}_2$ and $\text{H}_2|\text{Ba}(\text{OH})_2(m_0)|\text{BaCl}_2(m)|\text{AgCl}|\text{Ag}$ the activity coeff. of Ba(OH)₂ in aq. BaCl₂ has been calc. From these and previous results the ionic activity coeff. of H₂O in aq. BaCl₂ has been calc. The dissociation of H₂O in BaCl₂ solutions is a max. at the ionic strength 1·5.

E. R. S. (c)

Heats of dissociation and the periodic law. C. R. BAILEY (Nature, 1932, 130, 239—240).—Periodicity of physical properties extends to the heats

of dissociation of simple compounds not only in the same group but also in the same period. The experimental val. for CN lies 1.6 volts below the curve for N and C compounds suggesting decomp. into normal C and N atoms, and the val. of one-half the heat of formation of N_2O lies midway between NN and ON confirming the structure NNO and not NON for this gas. L. S. T.

Heat of formation of aluminium halides. W. KLEMM and H. JACOBI (Z. anorg. Chem., 1932, 207, 186).—A correction (cf. A., 1931, 1380). The correct heats of formation are $AlCl_3$ 167, $AlBr_3$ 121, AlI_3 71 kg.-cal. E. S. H.

Compounds of gallium and indium. VII. Heats of formation of gallium trihalides. W. KLEMM and H. JACOBI (Z. anorg. Chem., 1932, 207, 177—186; cf. this vol., 988).—The following heats of formation have been determined at 27° by direct interaction of Ga and the halogen in solution: $GaCl_3$ 125 ± 1 , $GaBr_3$ 92.4 ± 0.3 , GaI_3 51 kg.-cal. These vals. are compared with those of related compounds and the relation between heat of formation and energy of ionisation is discussed. E. S. H.

Heats of formation of indium trioxide and germanium dioxide. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1932, 161, 69—76).—The heats of formation of In_2O_3 and GeO_2 at 20° under const. pressure have been found to be $222.5 \text{ kg.-cal.} \pm 0.3\%$ and $128.1 \text{ kg.-cal.} \pm 0.5\%$, respectively, by combustion of the metals. The heat of formation of $GeCl_4$ is calc. to be 124 kg.-cal. It has d^{25}_4 $7.28_2 \pm 0.1\%$ under H_2O . R. C.

Heats of formation of nitrides. III. Heats of dissolution of metals and metal nitrides in acids. B. NEUMANN, C. KROGER, and H. KUNZ. IV. Uranium, thorium, and lanthanum nitrides. B. NEUMANN, C. KROGER, and H. HAEBLER (Z. anorg. Chem., 1932, 207, 133—144, 145—149; cf. A., 1931, 432).—III. The heats of dissolution of Mn_5N_2 in dil. H_2SO_4 and of Cr, Mg, Mg_3N_2 , Ce, CeN, La, and LaN in dil. HCl have been determined; heats of formation calc. from these data are: Mn_5N_2 , 56.82, Mg_3N_2 , 115.18, CeN 156.00, LaN 145.36 kg.-cal. (calc. for N_2).

IV. The heats of formation, determined by the direct method described (*loc. cit.*), are as follows: U_3N_4 68.460, Th_3N_4 77.100, LaN 71.055 kg.-cal. per g.-atom N. E. S. H.

Heat of formation and structure of the carbon-oxygen and carbon-sulphur linkings. W. LOCHTE-HOLTGREVEN and C. E. H. BAWN (Trans. Faraday Soc., 1932, 28, 698—704).—The abs. vals. of the heats of formation of C:O and C:S linkings in CO_2 and CS_2 have been calc. from the thermochemical data for the ideal dissociation process, i.e., complete dissociation in one stage. The wide variation in these heats of formation in different compounds is attributed to the influence of neighbouring atoms on the normal vibrations. The C:O linking energy in CH_3O is approx. equal to the abs. val. The val. of the force const. is not a characteristic of the type of linking, except in the elements of the first period. Force consts. of corresponding linkings decrease

markedly with increasing at. wt. of the constituent elements. Force consts. and heats of linking of C:O and C:S in CO_2 , COS, and CS_2 show that all the linkings in these mols. are double. E. S. H.

Relative heat contents of constituents of aqueous sodium chloride solutions. T. F. YOUNG and O. G. VOGEL (J. Amer. Chem. Soc., 1932, 54, 3030—3040).—New and old data have been used to calculate the partial mol. heat contents at 25°. The activity coeffs. derived from these vals. differ but slightly from those of Lewis and Randall.

M. M. (c)

Integral heats of dilution and relative partial molal heat contents of aqueous sodium bromide and potassium bromide solutions at 25°. H. HAMMERSCHMID and A. L. ROBINSON (J. Amer. Chem. Soc., 1932, 54, 3120—3125).—Heats of dilution of 0.1—0.0002M-NaBr and -KBr solutions have been measured. Up to 0.01M the integral heat of dilution of NaBr is represented by $\Delta H = -359m^{\frac{1}{2}}$, and that of KBr by $\Delta H = -350m^{\frac{1}{2}}$, where m is the molality.

L. P. H. (c)

Electrical conductivity of aqueous calcium hydroxide solutions. T. NODA and A. MIYOSHI (J. Soc. Chem. Ind. Japan, 1932, 35, 317—320b).—The conductivity of 0.002—0.02M- $Ca(OH)_2$ solutions has been determined at 5 temp. between 20° and 50°. A 0.02 mol. per kg. solution, although nearly saturated at 20°, does not crystallise at 50°. A nomogram relating temp., concn., and conductivity is given.

H. F. G.

Electrical conductivity of aqueous solutions of hydrogen sulphide and the state of the dissolved gas. R. H. WRIGHT and O. MAASS (Canad. J. Res., 1932, 6, 588—595; cf. this vol., 14, 457).—Measurements between 5° and 60° suggest that H_2S forms with H_2O a complex which undergoes electrolytic dissociation. Consequently the const. of the Ostwald dilution law is an apparent rather than a real dissociation const.

J. W. S.

Conductivity of germanic oxide solutions. C. E. GULEZIAN and J. H. MÜLLER (J. Amer. Chem. Soc., 1932, 54, 3142—3150).—Determination of the conductivity of solutions of GeO_2 from various sources has given vals. which are invariably much lower than those hitherto published, and are practically unaffected by temp. changes either during or after dissolution (cf. A., 1926, 350). The dissociation const. of H_2GeO_3 calc. from the conductivity data is $1.0—3.0 \times 10^{-9}$ (cf. A., 1929, 997).

E. R. S. (c)

Conductivity and degree of hydrolysis of sodium hydrogen germanate, and primary dissociation constant of germanic acid. C. E. GULEZIAN and J. H. MÜLLER (J. Amer. Chem. Soc., 1932, 54, 3151—3158).—Conductometric titration of H_2GeO_3 with NaOH indicates the existence in solution of $NaHGeO_3$. The degree of hydrolysis of this salt has been determined at different concns. At 25° the dissociation const. of H_2GeO_3 is 1.5×10^{-9} , and the mobility of the $HGeO_3'$ ion 31.3.

E. R. S. (c)

Dispersion of conductivity of certain aqueous electrolytic mixtures. M. E. SPAGHT (Physikal.

Z., 1932, 33, 534—536).—The dispersion effect (cf. Gaertner, this vol., 126) of $\text{Ca}_2\text{Fe}(\text{CN})_6$ on solutions of KCl, HCl, and KOH is discussed in reference to the Debye-Falkenhagen theory. W. R. A.

Complex acids. VIII. Niobic acid. H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1932, 2265—2270).—Conductometric and potentiometric titrations of solutions of K niobate with KOH and HCl afford no evidence of the existence of "pyro-" or "ortho-niobates," the niobate in solution being $\text{K}_2\text{O} \cdot \text{Nb}_2\text{O}_5$, which ionises to form a colloidal anion $(\text{NbO}_3)_x$ in the presence of some stabilising free KOH. On addition of HCl very little change takes place at first in the conductivity of the NbO_3 . At a certain point there is, however, a rapid diminution probably due to aggregation which appears to be the first stage in pptn. Finally pptn. at a uniform rate occurs. M. S. B.

Electromotive force measurements with the aid of electron tubes. F. MÜLLER (Trans. Electrochem. Soc., 1932, 62, 117—124).—The use of electron tubes in measuring e.m.f. of voltaic cells, especially those which are readily polarised or have a very high internal resistance, is reviewed and discussed.

H. J. T. E.
Simple oscillators for electrochemical measurements. E. DENINA and G. SELLA (L'Ind. Chimica, 1932, 7, 986—992).—The advantages of thermionic valve oscillators are discussed, and details, including oscillograms, are given for a variety of circuits. H. F. G.

Absolute null-point of potential measurement. E. BAUR (Z. Elektrochem., 1932, 38, 665—666).—A discussion of the relations between the Lipmann boundary-potential, ϵ - and ζ -potentials leads to the conclusion that there is no occasion to depart from the accepted val. for the abs. potential of the $N\text{-Hg}_2\text{Cl}_2$ electrode. E. S. H.

Electrode potential of iron. II. Influence of occluded hydrogen and other factors on the electrode potential. K. MURATA (J. Soc. Chem. Ind. Japan, 1932, 35, 290—295b).—The potential of sintered Fe powder electrodes is not influenced by occluded H or by the degree of subdivision of the Fe. A film of $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OH})_2$ on the electrodes causes the initial e.m.f. to be abnormally high, but the effect diminishes within a few days; a somewhat similar effect is produced with electrodes reduced at 650° , i.e., in such a manner that a film of highly-dispersed FeO remains on the surface. Variation of the reduction temp. between 850° and 1050° , however, does not influence the e.m.f. Electrodes which have been exposed to the air and have become covered with an oxide film yield very low initial vals. of the e.m.f., but the normal val. is attained after several days; decrease of the p_{H} of the electrolyte produces a similar result. H. F. G.

Iron as a hydrogen electrode. E. LIEBREICH (Z. physikal. Chem., 1932, 161, 97—112).—The potential, E , of an Fe electrode in aq. HCl becomes more and more negative as the acid concn., c , increases up to a certain crit. concn., C . In air C is $0.0008N$, but in H_2 is smaller. When c rises above C the

potential becomes increasingly positive and although initially much more negative than the potential of a H electrode it approaches this val. as c rises; the cathodic overvoltage decreases at the same time. Current-voltage curves show that at C the separation of H_2 on the Fe becomes easier. These observations are explained by supposing at. H to dissolve in the Fe, saturation being attained at the crit. concn. C .

R. C.
Antimony electrode. S. BONFORSS and A. HOLMQUIST (Z. physikal. Chem., 1932, 161, 61—68).—Although Sb_2O_3 cannot exist as a solid phase in contact with a tartrate buffer or aq. HF, the potential, E , of an Sb electrode is a linear function of the p_{H} and much more negative than in an acetate buffer of the same p_{H} . It seems that E is not determined by the concn. of either Sb^{+++} or SbO^+ , but for a given p_{H} depends on the anion and probably also on its concn., e.g., E in $0.1N\text{-HCl}$ becomes more and more negative as increasing amounts of KCl are added. A cast electrode the surface of which is continually renewed by scraping or an electrode of electrolytic Sb exhibits a more negative potential than a cast or amalgamated electrode. R. C.

Chlorine-resistant silver-lead electrodes. I. M. A. RABINOVITSCH and A. S. RUBANTSCHIK. II. P. B. SHIVOTINSKI (Ukrain. Chem. J., 1931, 6, [Sci.], 245—251).—I. The electrolysis of aq. KCl or NaCl, using a Pt cathode and a Pb (39%)—Ag (61%) anode, is characterised by a series of breaks in the polarisation-voltage curve, corresponding with the decomp. potentials of PbCl_2 , PbO_2 , Ag_2O , and AgCl . Passivation of electrodes is due to formation of a film of AgCl , and the breaks due to PbCl_2 or PbO_2 are absent when such electrodes are used.

II. Pb—Ag anodes surrounded by PbO_2 can be used for the electrolysis of conc. aq. KCl or NaCl, without the necessity of isolating the anode electrolyte.

R. T.
Electromotive force of the combination $\text{Ag-AgCl}|N\text{-KCl}|\text{buffer substance}|\text{quinhydrone}|Pt$. A. UHL (Z. Elektrochem., 1932, 38, 673—676).—The combination gives a reproducible e.m.f., depending only on $[\text{Cl}^-]$, $[\text{H}^+]$, and temp. For a given p_{H} , the e.m.f. is proportional to the temp. At 18° the e.m.f. is proportional to p_{H} , but not at other temp. The e.m.f. is 0 at 18° and p_{H} 8.02. E. S. H.

Activity coefficient of zinc sulphate from electromotive force measurements. K. MASAKI and T. IKKATAI (Bull. Chem. Soc. Japan, 1932, 7, 238—246).—Data for Zn-Hg (saturated amalgam)| ZnSO_4 , Hg_2SO_4 (saturated)| Hg at 25° are recorded, the concn. of ZnSO_4 varying from 0.0004321 to $3M$. The solubility of Hg_2SO_4 leads to abnormal e.m.f. at high dilutions. The mean activity coeffs. of ZnSO_4 have been calc. for the more conc. solutions. When the ion activities for ZnSO_4 are $1M$, E_0 is 1.37475 volts at 25° . E. S. H.

Thermodynamic properties of fused salt solutions. V. Lead bromide in silver bromide. E. J. SALSTROM (J. Amer. Chem. Soc., 1932, 54, 2653—2661).—E.m.f. measurements have been made with the cell $\text{Ag}|\text{AgBr}(l)|\text{PbBr}_2(l)|\text{Br}(g)$ at $425\text{—}475^\circ$ for AgBr mol. fractions of $0.10\text{—}1.00$. At all temp.

the activities of solvent and solute agree with the vals. calc. by Raoult's law. P. H. E. (c)

Potential of $\text{Ag(s)}|\text{AgCl(s)}, \text{KCl(aq.)}, \text{AgCl(s)}|\text{Ag(s)}$ cell, showing effect of flowing electrolyte over one electrode only. J. Y. CANN and E. LA RUE (J. Amer. Chem. Soc., 1932, 54, 3456—3458).—The above cell was investigated, the electrolyte on one side being stationary and on the other side in motion. The KCl concn. was 0.025 or 0.05*M*. The results support Carmody's contention (this vol., 342) that there is a drop of potential when electrolyte is flowing over the $\text{Ag(s)}, \text{AgCl(s)}$ electrode.

C. J. W. (c)

Dependence of p_{H} on temperature in buffer solutions. S. V. BRUJEVICZ and N. P. KARPOVA (Biochem. Z., 1932, 251, 60—69).—Between 0° and 25° in the buffer solutions of McIlvaine (nitrate-phosphate) and in that of Sørensen (phosphate) the temp. coeff. of the changes in p_{H} depends on the temp., but is scarcely affected by changes in the acidity. In Palitzsch's solution (borate) the coeff. increases very considerably as the p_{H} increases, and the relation between p_{H} and temp. is linear between p_{H} 8.1 and 8.2. In more alkaline solutions the coeff. decreases with rise of temp., whilst in more acid solutions it increases.

W. McC.

Effect of potassium cyanide on the oxidation-reduction potential [ferricyanide-ferrocyanide]. K. MASAKI and T. IKKATAI (Bull. Chem. Soc. Japan, 1932, 7, 233—238).—The effect of KCN at 30° is represented by $E = 0.4660 + 0.0601 \log K^{0.59}$, where K is the concn. of KCN.

E. S. H.

Oxido-reduction system homogentisic acid-benzoquinoneacetic acid. G. BLIX (Z. physiol. Chem., 1932, 210, 87—93).—The electrode potential of the system is +0.25 to 0.26 volt (p_{H} 22—23) in the physiological p_{H} range, i.e., more positive than any of the biological oxidation-reduction systems hitherto examined. It appears probable that physiological homogentisic acid degradation does not proceed by way of quinoneacetic acid. The dissociation consts. of the acids are calc.

J. H. B.

Measurement of the electricity liberated during down-grade reactions of organic compounds. M. C. PORTER (Nature, 1932, 130, 242—243).—A reply to criticism (A., 1931, 915).

L. S. T.

Phase-boundary potentials and dielectric constants. P. FARKAS (Z. Elektrochem., 1932, 38, 654—665).—Dielectric consts. have been determined for the conjugate solutions of the liquid pairs: $\text{PhOH-H}_2\text{O}$, $\text{BuOH-H}_2\text{O}$, $\text{Et}_2\text{O-H}_2\text{O}$, $\text{guaiacol-H}_2\text{O}$, $\text{o-C}_6\text{H}_4\text{Me-NH}_2\text{-H}_2\text{O}$, $\text{furfuraldehyde-H}_2\text{O}$, $\text{EtOAc-H}_2\text{O}$, $\text{CH}_2\text{Ph-OH-H}_2\text{O}$, $\text{C}_5\text{H}_{11}\text{-OH-H}_2\text{O}$, $\text{cyclohexanol-H}_2\text{O}$, $\text{o-cresol-H}_2\text{O}$, $\text{PhCHO-H}_2\text{O}$, and for conc. solutions of dioxan in H_2O . The boundary potentials at the interfaces of these liquid pairs (excluding Et_2O and EtOAc) have been measured when in equilibrium with dissolved NH_4Cl , NaNO_3 , KOAc , and AgNO_3 . The conductivities of the org.-liquid phases in distribution equilibrium with aq. N-KCl and aq. 0.5*N*- NH_4NO_3 , respectively, have also been measured. The results are discussed in relation to Debye's formula. The determination of the metal/metal-ion potential

in the org.-liquid phase from the phase-boundary potential is discussed.

E. S. H.

Theory of concentration polarisation. B. BRUZS (Z. physikal. Chem., 1932, 161, 83—96).—By methods similar to those used previously (this vol., 123) equations containing only thermodynamic quantities, and no ionic concns. or similar magnitudes, have been obtained for the Hittorf coeff., χ , and the e.m.f. of cells with liquid junctions. These permit the calculation of entropies of dilution of ions and salts and heats of dilution from the vals. of χ and e.m.f. data. The theory accounts for the formation of anode mud. The existence of heats of transport is unlikely.

R. C.

Anodic behaviour of nickel. I. K. GEORGI (Z. Elektrochem., 1932, 38, 681—688).—The potential of air-passive Ni varies with the acid solution in which it is immersed and becomes more negative with time, the amount of change varying with the anion. Different vals. are assumed when air is replaced by O_2 , N_2 , or H_2 . The loss of wt. of a Ni electrode also varies with the acid solution and the nature of the atm., the loss being greater the more positive is the potential. The vals. are compared with the potentials assumed by a Ni electrode coated with Ni_2O_3 . C.d.-potential curves have been constructed for the dissolution of Ni anodes in acid and salt solutions. The potential at low c.d. is higher the greater is the size of the anion in the series Cl^- , Br^- , SO_4^{2-} , ClO_4^- . The curves are considerably affected by previously etching the Ni with 2*N*-HCl or by heat-treatment, but very little by polishing.

E. S. H.

Passivity phenomena. XV. Passivating action of oxide layers during the anodic passification of iron in neutral solutions of sodium sulphate. W. J. MULLER and W. MACHU (Monatsh., 1932, 60, 359—385).—Oscillographic records obtained with Fe electrodes coated with a natural or artificial oxide layer in $\text{N-Na}_2\text{SO}_4$ permit the separate determination of the resistance in the pores and the layer resistance. Increase in the thickness of the layer diminishes the size of the pores with consequent increase in resistance, whilst the layer resistance increases with the thickness. The free pore-surface can be calc. (1) from the amount of Fe salt deposited, the thickness of layer being deduced from the surface-covering rule, (2) from the i_0-t_p relationship which contains no assumption regarding the thickness of the layer, and (3) from the conductivity and initial current strength; with electrodes exposed to the air it is about 10^{-3} and with immersed electrodes about 10^{-4} of the total surface. The Fe in the pores is invariably active. Passivity is never observed under these conditions, since the current passing through the pores is never sufficiently large to cause chemical passivity of the underlying Fe. In this case, passivity depends essentially on the oxide layer over the Fe.

Reaction of chlorine with hydrogen. W. H. RODEBUSH and W. C. KLINGELHOEFER (Proc. Nat. Acad. Sci., 1932, 18, 531).—The reaction $\text{H}_2 + \text{Cl} = \text{HCl} + \text{H}$, which has been studied at low pressures, initiates chains producing 10 mols. of HCl at 1 mm.

pressure. If the reaction $\text{Cl}_2 + \text{H} = \text{HCl} + \text{Cl}$ is rapid, the reaction probability of the Cl atom is of the order of 10^{-5} per collision with the H_2 mol. The heat of activation is calc. as 5500 g.-cal. O_2 and H_2O do not affect the reaction at low pressures. W. R. A.

Kinetics of gas explosions. III. Influence of hydrogen on thermal decomposition of ozone sensitised by bromine vapour, and determination of explosion temperature. W. FEITKNECHT and B. LEWIS (J. Amer. Chem. Soc., 1932, 54, 3185—3191; cf. this vol., 701).— H_2 behaves as an inert gas in the non-explosive reaction, retarding it to about the same degree as other inert gases, but the explosion limit is about twice as high as when H_2 is replaced by He. In the explosive reaction H_2 is burned to H_2O , which with Br_2 establishes the equilibrium $2\text{H}_2\text{O} + 2\text{Br}_2 \rightleftharpoons 4\text{HBr} + \text{O}_2$, at a temp. which is calc. by comparing the measured equilibrium const. with known data to be $1600 \pm 100^\circ$ abs. This is probably below the max. explosion temp. in the mixtures. C. W. (c)

Mechanism of flame movement. I. Uniform movement of flame in mixtures of methane and air, in relation to tube diameter. H. F. COWARD and F. J. HARTWELL (J.C.S., 1932, 1996—2004).—The relation between the speed of uniform movement of flame in CH_4 -air mixtures and the diameter of the explosion tube (horizontal) has been studied. Photographs show that the results may be explained by the effect of convection currents on the area of the flame and hence on the amount of gas burnt in unit time. The definition of the term "uniform movement of flame" is revised. F. J. W.

Explosive gaseous reactions in a dynamic system. I. Reaction of oxygen and propane. S. P. BURKE, C. F. FRYLING, and T. E. W. SCHUMANN (Ind. Eng. Chem., 1932, 24, 804—811).—The reaction between O_2 and C_3H_8 has been investigated by passing the gases through a tube in a bath at known temp. and determining the O_2 in the product. Observed and calc. curves for the variation of reaction temp. with pressure, rate of flow, etc. are in close agreement. Similar results were obtained with other paraffins, but not with C_2H_4 and C_3H_6 , suggesting that oxidation of paraffins by O_2 does not involve initial formation of olefines. D. R. D.

Uniform movement of flame. J. TAUSZ and J. DRAXL (Petroleum, 1932, 28, 1—13).—The rates of downward uniform propagation of flame in vertical glass tubes of diam. 0.2—3.0 cm. have been determined for mixtures of air with H_2 , C_2H_2 , CO, and C_6H_6 vapour, and, in the 0.8 diam. tube only, for mixtures of air with CH_4 , C_2H_6 , hexane, *cyclo*-hexane and -hexene, and isoprene. It was considered that the statical method using a vertical tube gave more consistent results than could be obtained with a horizontal tube or by the dynamical method (cf. Bunte and Litterscheidt, B., 1930, 1053). The flame velocities in a const. mixture increased with increasing tube diam., and, in a tube of const. diam., increased, passed through a max., and fell again, with increasing concn. of the combustible gas. The so-called uniform movement could be exactly measured in general only

in mixtures of composition near the lower combustion limit. In the region of uniform flame movement the rate of increase of the velocity with tube diam. fell with increasing diam.; thus, when plotted, the results gave a curve convex upwards. In the other cases, e.g., when the velocity was proportional to the diam., and for high vals. of the velocity in general, a vibratory motion of the flame was observed. Chapman and Wheeler's formula relating the max. flame velocity with tube diam. ($V = CD^k$; cf. A., 1927, 211) is discussed. It is preferable to consider the velocities corresponding with the stoicheiometrical ratios of fuel to air; these velocities (V cm. per sec.) are related to the tube diam. (D cm.) by the formula $V = A(B + \log D)$, where A is an abs. const. and B is a const. which is characteristic of the combustible gas used. A. B. M.

Pressures developed in explosion waves. C. CAMPBELL, W. B. LITTLER, and C. WHITWORTH (Proc. Roy. Soc., 1932, A, 137, 380—396).—Experiments on the shearing of Cu foils of various thicknesses by explosion waves in a no. of gaseous mixtures are described. By calibration of the foils with static air pressures approx. vals. of the actual pressures developed in any one mixture are obtained. The experimental results are in fair agreement with the vals. calc. by Jonguet's method (J. Math. pur. appl., 1905, 1, 347), especially in the case of the more dil. mixtures. Photographs of the flame before and after collision with the Cu diaphragm give approx. vals. of the time required to break the diaphragm. In general, the distance over which the flame must travel before detonation is re-established increases with increasing thickness of the foil. The pressure near the point of detonation is much greater than that obtaining when the wave is fully established. L. L. B.

Combustion of hydrocarbons. W. A. BONE (Proc. Roy. Soc., 1932, A, 137, 243—274).—A historical survey of the subject is given, and the relative merits of the "hydroxylation" and "peroxidation" theories are discussed. Much evidence is adduced in support of the former theory, and it is considered that "peroxidation" can be regarded only as supplementary to "hydroxylation." L. L. B.

Propagation of explosion waves through a system of glass and rubber tubes. C. CAMPBELL, A. KING, and C. WHITWORTH (Trans. Faraday Soc., 1932, 28, 681—688).—Photographic records of explosion waves passing through a rubber section of a long explosion gallery show that in "non-striating" mixtures (e.g., $2\text{H}_2 + \text{O}_2 + \text{N}_2$, $\text{CH}_4 + 2\text{O}_2$, $2\text{CO} + \text{O}_2 + 7\% \text{H}_2$) the waves can pass through considerable lengths of even thin rubber tubing without appreciable alteration of velocity. In "striating" mixtures (e.g., $2\text{CO}_2 + \text{O}_2$, $2\text{H}_2 + \text{O}_2 + \text{CO}_2$, $\text{CH}_4 + 7\text{O}_2$) a marked reduction of flame velocity may occur on passing through the rubber. This change depends on the thickness and length of rubber and may be due to release of pressure behind the wave front. E. S. H.

Explosion limits. H. W. THOMPSON (Z. physikal. Chem., 1932, B, 18, 219—240).—The presence of MgO dust in binary mixtures of air with various combustible gases displaces the lower explosion limit

in the direction of richer mixtures. With C_2H_4 this effect is more marked than with H_2 and CO , with C_6H_6 and Et_2O it is barely perceptible, and with CH_4 it is absent. At the same time, the flame speed in mixtures having compositions near the limit is reduced. SiO_2 acts similarly to MgO . By means of Fe carbonyl vapour a much greater displacement of the lower limit can be effected than with MgO , and the upper limit is displaced more than the lower limit, but in the opposite direction. It is uncertain whether these effects are due to the undecomposed carbonyl mols. or to the Fe or oxide formed by their decomp. The above action of mineral dust is ascribed to its adsorbing the radicals or atoms propagating the reaction chains, such as OH and H , and converting them into stable mols. R. C.

Decomposition of ethyl bromide, alkyl halides, and acetal in the gas phase at 300–400°. E. T. LESSIG (J. Physical Chem., 1932, 36, 2325–2337).—The rate of decomp. in the gas phase of 13 org. compounds is determined at 300–400° by measuring the pressure increase in all-glass and all-quartz vessels totally immersed in a Pb thermostat. The dissociation of $EtBr$ is a homogeneous first order reaction: $EtBr \rightarrow C_2H_5 + HBr$. The energy of activation is approx. 50,000 g.-cal. The dissociations of n - and *iso*- $PrBr$ are of the first order and homogeneous, but complications cause a decrease of velocity coeff. with pressure; free Br is not found. The decomp. of EtI is complicated, since I is produced. The alkyl chlorides studied do not show simple first order reactions; the data for $CHCl_3$ are very irregular. The final pressure with acetal is nearly three times the original pressure, showing decomp. into 3 mols. This decomp. and those of methylal and Bu^{β} chloroformate are very complicated. E. J. R. (b)

Reduction of silver ions by ferrous ions. D. ROBERTS and F. G. SOPER (J.C.S., 1932, 2004–2008).—The reaction between Fe^{2+} and Ag^+ ions has an induction period during which Ag nuclei are formed. The rate of the reaction was profoundly affected by $[H^+]$ and the ionic strength of the medium, effects attributed to changes in the rate of deposition of $at. Ag$ on the Ag nuclei. The induction period could be eliminated by the addition of a colloidal solution of Ag . F. J. W.

Kinetics of reaction between potassium permanganate and oxalic acid. I. H. F. LAUNER (J. Amer. Chem. Soc., 1932, 54, 2597–2610).—In acid solution MnO_4^- reacts quickly with Mn^{2+} , forming Mn^{3+} , which, with $C_2O_4^{2-}$, enters into equilibrium with MnC_2O_4 by a reaction which is rapidly reversible. The rate of reaction of MnO_4^- with $C_2O_4^{2-}$ is proportional to the MnC_2O_4 concn. and inversely proportional to the $C_2O_4^{2-}$ concn. The influence of the ionic strength on the velocity agrees with Bronsted's hypothesis. A reaction mechanism involving the hypothetical CO_2^- ion is suggested. P. H. E. (c)

Effect of non-electrolytes on the velocity of reaction of ferric and iodide ions. P. VASS (Magyar Chem. Fol., 1931, 37, 217–229; Chem. Zentr., 1932, i, 1478).—The mechanism of the reaction is unchanged in aq. $MeOH$, $EtOH$, $PrOH$,

$COMe$, glycerol, sucrose, and carbamide. The velocity changes depend on ϵ , and the Grube-Schmid law is obeyed. Aq. carbamide forms complexes.

L. S. T.

Velocity of decomposition of diazo-compounds in aqueous solution. VIII. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 298–303B).—The decomp. velocities at various temp. and the temp. coeff. of the velocity are recorded for *o*-, *m*-, and *p*- $C_6H_4Cl-N_2Cl$. H. F. G.

Rate of esterification of methyl and ethyl alcohol in acetic acid. A. KAILAN and W. HAAS (Monatsh., 1932, 60, 386–413).—The rates of esterification of $MeOH$ and $EtOH$ in $AcOH$ containing various amounts of H_2O in presence and absence of HCl as catalyst at 25° have been determined by observation of the increases of depression of the m.p. and the unimol. consts. have been calc. The latter do not alter when the H_2O content is increased from 0.2 to 1.2 mols. per kg. $AcOH$. Addition of 0.0038 or 0.0237 mol. HCl per kg. causes an approx. proportional increase in the case of $MeOH$ to 31 or 240 times, in the cases of $EtOH$ to 21 or 108 times, the val. found in the absence of catalyst. The ratio of the coeffs. of $MeOH$ to those of $EtOH$ is 1.5, 2.2, or 3.3 in absence or presence of the smaller or larger amounts of catalyst. Almost complete esterification is invariably observed; this is verified by experiments starting with the esters. Between a content of 0.1 and 1.3 mols. of H_2O per kg. $AcOH$ the cryoscopic consts. for $MeOH$ (3.57) and $EtOH$ (3.64) are independent of the H_2O content within the limits of measurement and of the alcohol concn. between 0.15 and 0.3. For H_2O they fall from about 3.85 to 3.1 for a total H_2O content ($w=1.2$) and to 2.6 for a further H_2O increase of about 0.2 mol. For both esters $\kappa=3.9$. H. W.

Rate of chlorination of anilides and phenols as affected by association. R. E. ROBERTS and F. G. SOPER (J.C.S., 1932, 1979–1982).—The rate of chlorination of anilides and phenols dissolved in solvents such as CCl_4 is increased from 3 to 7 times by doubling the concn. It is suggested therefore that the associated mol. is more reactive than the unassociated, indicating that association causes one of the O or N atoms to become more negative. This is in agreement with the singly co-ordinated mode of association. F. J. W.

Thermal decomposition of dimethylamine. H. A. TAYLOR (J. Physical Chem., 1932, 36, 1960–1966).—In the thermal decomp. at 480–510° under 3.75–600 mm. the rate of pressure increase suggests that the reaction is homogeneous and unimol., with an activation energy of 44,300 g.-cal., but the reaction is so complex that this interpretation seems doubtful. S. L. (c)

Oxidation of colloiddally dissolved substances. S. VOSNESSENSKI [with I. M. ZINN] (Kolloid-Z., 1932, 60, 171–176).—The rates of oxidation of colloidal solutions and suspensions of S by Cl_2 , Br , and I have been measured. The presence of Na_2SO_4 or $NaHSO_3$ in concns. insufficient to cause pptn. of S stabilises the systems and reduces their rate of oxidation. The oxidation velocity is inversely proportional to the

concn. of Na_2SO_4 (at low concns.). Humus acts as a protective colloid to S and reduces the rate of oxidation, but in presence of humus Na_2SO_4 has the effect of increasing the rate of oxidation. E. S. H.

Conversion of metal ions into neutral atoms by interaction with metallic zinc. M. CENTNERSZWER and W. HELLER (Z. physikal. Chem., 1932, 161, 113—128).—The dissolution of a rotating Zn plate in aq. CuSO_4 follows the unimol. velocity law. With increasing speed of rotation, the velocity coeff., k , increases, but ultimately becomes const., which, adopting Nernst's theory of heterogeneous reaction, is assumed to correspond with equality of the rates of diffusion and chemical reaction. Between 0° and 50° k is a linear function of the temp., its temp. coeff. being equal to that of the diffusion coeff., indicating that the thickness of the diffusion layer is const. between these temp. The reaction is therefore regarded as a pure diffusion reaction. SO_4^{2-} , Cl^- , and CNS^- increase k , their effectiveness increasing in this order; NO_3^- , fatty acids, and various colloids reduce k , the colloids by mechanical action. Amalgamated Zn dissolves more rapidly than ordinary Zn. In solutions of Ni salts dissolution is extremely slow, in aq. Ag_2SO_4 it is more rapid than in aq. CuSO_4 , and in aq. AgNO_3 k diminishes as reaction proceeds. There seems to be no quant. relation between k and the position of the displacing metal in the electrochemical series. R. C.

Kinetics of dissociation of solid carbonates. P. AFANASIEV and S. ROGINSKI (Z. physikal. Chem., 1932, B, 18, 360).—The autocatalytic character of the thermal decomp. of CdCO_3 has been confirmed (A., 1929, 153). The oxide obtained by complete decomp. is, however, inactive. The active oxide is not an amorphous intermediate form. R. C.

Temperature increment of reaction velocity in heterogeneous reactions. III. Reactions of cadmium oxide. K. FISCHBECK and K. SCHNAIDT (Z. Elektrochem., 1932, 38, 649—653; cf. this vol., 475, 577).—The reactions (a) $\text{CdO} + \text{CO} = \text{Cd} + \text{CO}_2$, (b) $\text{CdO} + \text{H}_2 = \text{Cd} + \text{H}_2\text{O}$, and (c) $2\text{CdO} + 3\text{S} = 2\text{CdS} + \text{SO}_2$ have been investigated at 300 — 400° . The temp. increments E of these reactions, calc. from the formula $v = Ae^{-E/RT}$, are (a) 25.5, (b) 25.7, (c) 20.5 kg.-cal. Thus, the heats of activation of different reactions of CdO are of the same magnitude. E. S. H.

Kinetics of dissolution of dilute sodium amalgam. R. LIVINGSTON (J. Physical Chem., 1932, 36, 2099—2100).—The mechanism proposed assumes the existence of the equilibrium $\text{NaHg}_2 \rightleftharpoons \text{Na} + e + \text{Hg}_2$. S. L. (c)

Chemical inertia. LEMARCHANDS and JACOB (Compt. rend., 1932, 195, 380—382; cf. A., 1931, 1016).—The validity of previous assumptions is substantiated by showing that the temp. of commencement of interaction between Cl_2 and 15 elements and the products of the b.p. of the element and its resultant chloride follow approx. the same order. C. A. S.

Velocity of corrosion from the electrochemical viewpoint. II. U. R. EVANS and T. P. HOAR (Proc. Roy. Soc., 1932, A, 137, 343—365).—The

corrosion-time curves of Fe and steel in KCl, NaCl, Na_2SO_4 , and other salt solutions are linear and the temp. coeff. is low. Corrosion velocity-salt concn. curves show a max. velocity at $0.5N$, and the area of the corroded region is smallest in the region of most rapid corrosion. At high concn. corrosion is proportional to the O_2 solubility, but at low concn. it falls below the val. calc. therefrom. The potential at the anodic and cathodic areas has been measured in KCl solution. The corrosion rate is proportional to the current which the measured e.m.f. would force through the resistance of the circuit. L. L. B.

Film reactions and the problem of the corrosion of metals. L. TRONSTAD (Z. Metallk., 1932, 24, 185—188).—The use of viscous films containing gelatin or other colloid and the corrosive media in following the reactions which occur in the corrosion of metals is illustrated; the viscosity of the solution prevents diffusion of the corrosion products and the evolution of H_2 may readily be observed under the microscope. In the case of rolled Al sheet evolution of H_2 and dissolution of metal occur in spots which become sufficiently acid to attack the metal and at the same time show pits or fissures, whereas in the case of Fe with a low C content H_2 is evolved by corrosion with almost neutral media probably by the electrolytic action of local currents the origin of which cannot with certainty be traced. A. R. P.

Stability of bleaching powder and hypochlorite solutions. J. H. WALTON and C. S. R. AYYAR.—Sec B., 1932, 798.

Reactions between gas and solid. IV. Azotation of calcium carbide and the effect of temperature on its velocity. T. AONO (Bull. Chem. Soc. Japan, 1932, 7, 247—255; cf. this vol., 817).—At const. temp. below 950° the degree of azotation, n_t , of CaC_2 (containing 1% CaF_2) after a time t is represented by $n_t = n_\infty - \{n_\infty^{1/2} - \sqrt{k'_5(t-t')}\}$ where n_∞ is the final degree of azotation and k'_5 and t' are consts. At const. temp. between 1000° and 1060° the relation is $n_t - n_\infty = \{1 - e^{-k'_1(a+t')}\}$, where k'_1 is the velocity coeff. At each temp. there is a max. velocity, which varies with temp. according to the approx. relation $\log Y - A - B/T$, where Y is the degree of azotation at the max. velocity, T the abs. temp., and A and B are consts. From the temp. coeff. of the velocity coeff. the apparent heat of activation of powdered technical CaC_2 is calc. as 58.6 kg.-cal. per mol. at 1000 — 1060° , and about 33 kg.-cal. per mol. above 1080° . E. S. H.

Unimolecular decomposition of explosives. S. ROGINSKI (Z. physikal. Chem., 1932, B, 18, 364—366).—New and existing kinetic data show that spontaneous unimol. decomp. is a general characteristic of explosives. The heat of activation, A , is about 50 kg.-cal. and the val. of the const. B of Arrhenius' equation is 10^{19} — 10^{24} . Usually, the val. of $\log B$ is the higher the larger is A . No evidence of reaction chains has been observed. R. C.

Autoxidation of the double linking. P. RONA, R. ASMUS, and H. STENBECK (Biochem. Z., 1932, 250, 149—177).—The velocity of autoxidation of the Me

esters of linoleic, linolenic, and oleic acids is greatly increased by addition of pyridine and nicotine, the increase depending on the amount added and on the p_H of the medium. Of a no. of Fe compounds examined, only a few increased the rate of autoxidation. The reaction with linoleic acid is pseudo-unimol. The action of substances inhibiting the reaction has been investigated and the mechanism of the reaction is discussed. P. W. C.

Generalised theory of acid and base catalysis applied to ionic reactions. R. LIVINGSTON (J. Amer. Chem. Soc., 1932, 54, 2393—2394). P. H. (c)

Catalytic properties and the ageing of the mineral waters of Vrnjacka Banja, Arandelovac, and Mladenovac. G. SCHILDER (Liječnički Vjesnik [Croatian Med. J.], 1932, 54, 243—261).—The catalytic properties of natural mineral water with respect to Glenard's reaction appear to be associated with the Fe⁺⁺ concn. and their ageing to be due to oxidation by atm. O₂. J. W. S.

Catalytic effect of lignosulphonic acid. E. HAGGLUND and T. JOHNSON (Biochem. Z., 1932, 250, 321—325).—Lignosulphonic acid, in spite of its insolubility, possesses the characteristics of a strong acid and over a narrow range of p_H can catalyse the inversion of sucrose. P. W. C.

Ninth report of Committee on Contact Catalysis. J. N. PEARCE (J. Physical Chem., 1932, 36, 1969—2010).—A résumé of the recent papers on catalysis published prior to 1931. P. H. E. (c)

Theory of activity of contact catalysis. H. G. TANNER (J. Amer. Chem. Soc., 1932, 54, 2171—2176).—Catalytic activity is assumed to depend on the rate at which active spots act. The action of an active spot depends on its temp. fluctuations. The concept of average temp. and its possible relation to the action of promoters, supports, surface roughness, porosity, and thermionic emission are discussed. P. H. E. (c)

Basic magnesium carbonate as a promoter on a copper surface. T. HAGYARD (J.C.S., 1932, 2055—2062).—The adsorption isotherms of H₂, N₂, CO, CH₄, and NH₃ on surfaces of Cu, Cu promoted with basic Mg carbonate, and the promoter itself have been determined at 20°. The adsorbing areas have been calc. using a modified Langmuir equation. The initial surface consisted of areas of different activity and the promoter increased the extent of these areas, but not necessarily in the same ratio. The solubility of H₂ in the promoted and unpromoted Cu has been measured at 20°. The rate of dissolution is approx. proportional to the extent of the adsorption of the H₂. F. J. W.

Chain mechanism of catalytic oxidation of hydrogen. S. ROGINSKI and J. ZELDOVITSON (Z. physikal. Chem., 1932, B, 18, 361—363).—There seems no reason to believe that vol. chains play any significant part in heterogeneous catalysis at moderate temp. The effects observed by Kobosev and Anochin (A., 1931, 1017) are purely accidental, and have nothing to do with the presence of at. H. R. C.

Röntgenographic investigations on iron catalysts for ammonia synthesis. R. BRILL (Z. Elektrochem., 1932, 38, 669—673; cf. following abstract).

—X-Ray analysis shows that α - and γ -Al₂O₃ activate the Fe catalyst only when they form mixed crystals with the Fe₂O₃ present, independently of the general state of oxidation of the Fe. If the mixed crystals are very rich in Al₂O₃ the activating effect is poor; in general, activation ensues when the mixed crystals are readily reducible. In the case of reduced Fe-Al₂O₃ catalysts, the Al₂O₃ is distributed among the Fe crystallites, so preventing their destruction through recrystallisation. E. S. H.

Activation of iron by aluminium oxide in ammonia catalysis. A. MITTASCH and E. KEUNECKE (Z. Elektrochem., 1932, 38, 666—669; cf. A., 1931, 1247).—The relative efficiencies of Fe₂O₃-Al₂O₃ catalysts prepared in different ways for the catalytic NH₃ synthesis have been determined. Al₂O₃ exerts an activating effect under conditions such that it reduces the velocity of reduction of Fe₂O₃. Chemical and X-ray evidence agree in showing that both α - and γ -Al₂O₃ form mixed crystals with Fe₂O₃, to which the activating effect is due. E. S. H.

Poisoning and activation of zinc. K. JABLONZYNSKI and J. KULESZA (Z. anorg. Chem., 1932, 207, 157—160; cf. A., 1931, 692).—The reaction between chemically pure Zn and dil. HCl is strongly retarded by small quantities of HCN. HCNS (down to 0.000002*N*) accelerates the reaction markedly and CS₂ accelerates it appreciably. CS(NH₂)₂ and SO₂ have no influence. Under the action of poisons or of activating agents the etched surface of the Zn has a more finely-grained structure than is produced by HCl alone. Poisoning and activation cannot be attributed to an effect on impurities in the metal. E. S. H.

Catalytic partial oxidation of alcohols in the vapour phase. IV. W. L. FAITH, P. E. PETERS, and D. B. KEYES (Ind. Eng. Chem., 1932, 24, 924—926; cf. this vol., 28).—Four types of catalyst chamber, designed to improve heat transfer and temp. control in the catalytic oxidation of EtOH, are described. The effects of intermittent heating, of Cu and pyrex glass as materials for the catalyst chamber, and of the wall thickness of the latter have been investigated, as well as variation of the alcohol: air ratio. The yields of intermediate oxidation products under favourable conditions are max. J. W. S.

Hydrogenation of aromatic hydrocarbons at high pressure with nickel on kieselguhr as a catalyst. G. F. SCHOOREL, A. J. TULLENERS, and H. I. WATERMAN.—See B., 1932, 791.

Catalytic effect of acids on the rate of ester hydrolysis in relation to the ester concentration and the nature of the acid. H. M. DAWSON and W. LOWSON (Proc. Leeds Phil. Soc., 1932, 2, 331—335).—It is suggested that the process of ester hydrolysis involves a series of consecutive changes, e.g. EtOAc + H₂O \rightleftharpoons EtOAc.H₂O; EtOAc.H₂O + H⁺ \rightarrow EtOAc.H₂O.H \rightarrow AcOH + EtOH + H⁺. In such a case the rate of combination of the EtOAc.H₂O complex with the H⁺ may be the factor determining the observed rate of hydrolysis. Measurement of the rates of hydrolysis in presence of 0.01*N*-HCl, 0.1*N*-CH₂Cl-CO₂H, 0.1*N*-glycollic acid, and 0.1*N*-AcOH

support this view and show that the rate depends on the ester concn. J. W. S.

Catalytic action of silica gel in the reaction of camphene and oxalic acid. Synthesis of isoborneol. T. KUWATA and S. TATEGAI.—See this vol., 1037.

[Catalytic] reactions of phenol with hydrogen at high pressure. C. M. CAWLEY.—See B., 1932, 762.

Incomplete combustion of organic compounds in presence of catalysts. I—III. S. J. GREEN.—See B., 1932, 715.

Co-deposition of lead and bismuth. C. G. FINK and O. H. GRAY (Trans. Electrochem. Soc., 1932, 62, 189—194).—Solutions prepared by dissolving various amounts of PbO and Bi₂O₃ in aq. HClO₄, with addition of clove oil, were electrolysed at 20° or 40° and various c.d. at a brass cathode. At low c.d. smooth, adherent deposits ranging from pure Bi to 99% Pb were obtainable, but deposits became spongy above 0.58 amp. per sq. dm. With a solution of given composition raising the c.d. increases the proportion of Pb in the deposit. Deposits containing 75—85% Pb were most resistant to corrosion by 5% HCl or H₂SO₄. H. J. T. E.

Electrochemical production of formates from carbon dioxide. M. A. RABINOVITSCH and A. P. MASCHOVETZ (Ukrain. Chem. J., 1931, 6, [Sci.], 217—228).—Up to 90% yields of HCO₂Na are obtained by reduction of CO₂ by nascent H evolved by Na-Hg, prepared by electrolysis of NaOH, using a Hg cathode. The reaction is catalysed by Ni or Cu in the amalgam, but not by Fe. The cathode becomes foamy during the process, owing to formation of an emulsion of solution in Hg. R. T.

New method for electro-organic reductions. R. H. MCKEE and C. J. BROCKMAN (Trans. Electrochem. Soc., 1932, 62, 25—43).—Aromatic NO₂-compounds insol. in H₂O dissolve readily in saturated aq. solutions of Na cymenesulphonate or *p*-toluenesulphonate, and many are reduced to the corresponding azo-compounds by electrolysis of these solutions at 80—90°, using a phosphor-bronze gauze cathode in a diaphragm cell with aq. Na₂SO₄ solution as anolyte. Optimum c.d. usually lie between 0.6 and 2 amp. per sq. dm. and no stirring is required. With simple mononitro-compounds the current yields are excellent, but with compounds containing OMe or similar groups the yields are lower and tarry compounds are formed. The conductivity of the solutions is much higher than that of the corresponding alcoholic solutions, so that the energy consumption is lower. The products are readily pptd. by addition of H₂O, and the solvent can be used again after concn. The CO group in benzil is also reduced with high efficiency under the above conditions, but attempts to oxidise aromatic hydrocarbons to phenols were not successful. Conditions for the cathodic reduction of 10 NO₂-compounds are specified. H. J. T. E.

Electrochemical oxidation of paraffin and mineral oils. I. A. ATANASIU.—See B., 1932, 790.

Electrolytic reduction of aliphatic ketones to hydrocarbons. S. SWANN, jun. (Trans. Electrochem. Soc., 1932, 62, 153—158).—In the electrolytic reduction of COMePr, dissolved in aq.-alcoholic H₂SO₄, to *n*-pentane at a Cd cathode, the highest current efficiency (74.9%) was attained by using 20 g. of COMePr in 70 c.c. of 39% H₂SO₄ at 55—60° as catholyte and passing the theoretical quantity of electricity at 5 amp. per sq. dm. The cathode was previously activated by anodic oxidation.

H. J. T. E.

Electrolytic reduction of nitrobenzene to azoxybenzene. C. KERNS (Trans. Electrochem. Soc., 1932, 62, 125—144).—The influence of various factors on the current efficiency and yield of azoxybenzene in the electrolysis of PhNO₂ suspensions in aq. NaOH in a diaphragm cell with a Ni cathode has been studied. The reduction is favoured by high temp. and, in general, by low c.d., but the vol. of catholyte has little effect except on the time required for complete reduction. Max. yields were obtained by using 2.5% NaOH as electrolyte. Rates of stirring higher than that required to keep the PhNO₂ uniformly distributed throughout the electrolyte did not increase the yield. Under all conditions studied the current efficiency and yield were notably higher when the electrolysis cell was closed instead of being open to the air. H. J. T. E.

Electrochemical oxidation of naphthalene using a new type electrode. E. G. WHITE and A. LOWY (Trans. Electrochem. Soc., 1932, 62, 107—115).—A heated mixture of 60% of C₁₀H₈ and 40% C was pressed on to both sides of a Pt gauze, 7.62 cm. sq., and the resulting electrode used as anode in 1% H₂SO₄ solution. Max. yields of α -naphthoquinone were obtained at 25° with 0.5 amp. Notably lower current efficiencies were obtained at 55° or with currents <0.2 amp. Addition of Ce₂(SO₄)₃ or CrO₃ had no beneficial effect. Some CO₂ was formed and phthalic acid was detected. The previously described PbO₂ electrode (B., 1929, 886) was unsuitable because direct chemical oxidation occurs. H. J. T. E.

Temperature coefficients of photochemical reactions. N. R. DHAR and W. V. BHAGWAT (J. Indian Chem. Soc., 1932, 9, 225—232).—Theoretical. The temp. coeff. of a photochemical reaction can be calc. from the temp. coeff. of the dark reaction and its photo-acceleration at a definite temp. The increase of light absorption with rise of temp. leads to a decrease of the quantum yield, which can be explained by supposing that the no. of mols. available for activation by light absorption decreases with increased absorption. E. S. H.

Formation of carbon dioxide sensitised by chlorine in light. E. WARMING (Z. physikal. Chem., 1932, B, 18, 153—154).—Schumacher and Stieger's reaction scheme (A., 1931, 1137) is thermodynamically impossible. R. C.

[Formation of carbon dioxide sensitised by chlorine in light.] H. J. SCHUMACHER (Z. physikal. Chem., 1932, B, 18, 155).—The validity of Warming's observation (cf. preceding abstract) is conceded. R. C.

Photochemical reduction of carbon dioxide in aqueous solution. M. QURESHI and S. S. MOHAMMAD (J. Physical Chem., 1932, 36, 2205—2216).—The photochemical reduction of CO_2 in aq. solution is studied in presence of sensitizers, with Hg arcs, W-filament lamps, and the sun as light sources. No trace of CH_2O is found when CO_2 is passed through conductivity H_2O illuminated by mixed or monochromatic ultra-violet light (254 and 312 m μ). In sunlight and in presence of inorg. catalysts no CH_2O is found. With org. catalysts CH_2O is found in nearly the same amount in the solutions of CO_2 as in the CO_2 -free blanks. A trace of wax or cork (from a NaHCO_3 container) can cause formation of CH_2O , whilst pure NaHCO_3 does not. Repetition of Baly's work with basic carbonates of Ni and Co, using W lamps, gave negative results. Colloidal solutions of chlorophyll *a* and solutions of malachite-green, Me-orange, or $\text{Cu}(\text{OAc})_2$, when sealed in bulbs without CO_2 and exposed to sunlight, contain CH_2O . The results are compared with those of other workers.

E. J. R. (b)

Photochemical formation of carbonyl chloride under low pressure. E. WARMING (Z. physikal. Chem., 1932, B, 18, 156—158).—The mathematical difficulties of Bodenstein, Lenher, and Wagner's theory (A., 1929, 894) have been overcome, and the theory has been shown to agree with the experimental data.

R. C.

Photochemical oxidation of aqueous solutions of ammonia. L. GION (Compt. rend., 1932, 195, 421—423).—4% aq. NH_3 exposed to the light of a 220-volt Hg-vapour lamp in a quartz (but not pyrex or ordinary glass) vessel at 40° is oxidised to nitrite up to a max. of 34 mg. N_2O_3 per litre, the limit being due to photochemical decomp. of the nitrite. The oxidation is due to O_3 first formed, and its acceleration by ZnO or TiO_2 is due to these oxides accelerating the formation of O_3 (cf. A., 1921, ii, 670; B., 1931, 690).

C. A. S.

Reduction of ferric chloride by citric acid, malic acid, and sugars. R. M. PURKAYASTHA (J. Indian Chem. Soc., 1932, 9, 237—241).—The photochemical reduction (at 4350 and 3660 Å.) of FeCl_3 by citric acid, malic acid, glycerol, and sugars (except fructose) in presence of HCl gives a zero-mol. reaction coeff. The dark reaction is very small, except with fructose. With sugars, glycerol, lactic, tartaric, and malic acids as reductants about 2 quanta are required per mol. of FeCl_3 ; with mandelic and citric acids 1 quantum per FeCl_3 mol. is required for reduction.

E. S. H.

Autoxidation. VI. Action of light on sulphite solutions in absence and presence of oxygen. F. HABER and O. H. WANSBROUGH-JONES (Z. physikal. Chem., 1932, B, 18, 103—123; cf. this vol., 703).—In solutions free from O_2 the H and HSO_3 formed by the light reaction largely disappear by the reactions $\text{H} + \text{HSO}_3 = \text{H}' + \text{HSO}_3'$ and $\text{H} + \text{HOH} + \text{HSO}_3 = \text{H}_2 + \text{H}_2\text{SO}_4$. The former of these is the more important and the relative frequency of the latter diminishes as the p_{H} increases. The reaction $2\text{SO}_3' = \text{S}_2\text{O}_6''$ occurs very rarely. If the solution contains O_2 the autoxidation in light is affected in the same way by

variation of p_{H} as the H_2 evolution from O_2 -free solutions. The conditions for proportionality between autoxidation and O_2 pressure have been determined.

R. C.

Photochemical decomposition of some organic anions and free acids in ultra-violet light. L. FARKAS and O. H. WANSBROUGH-JONES (Z. physikal. Chem., 1932, B, 18, 124—145; cf. this vol., 480).—The decomp. in their electron affinity spectrum of the anions of HCO_2Na , NaOAc , and Na succinate in aq. solution follows the equation $\text{A}'\cdot\text{H}_2\text{O} + h\nu = \text{A} + \text{OH}' + \text{H}$ ($\text{A} = \text{anion}$), but owing to the subsequent reaction $\text{A} + \text{H} = \text{A}' + \text{H}'$ the yield of decomp. products is small. The reaction $\text{R}\cdot\text{CO}_2'(\text{H}_2\text{O}) + h\nu \rightarrow \text{RH} + \text{HCO}_3'$ occurs simultaneously. Addition of alkali favours the formation of acids of higher basicity and evolution of H_2 . HCO_2Na yields some CO . The undissociated acids in aq. solution undergo several photochemical reactions simultaneously, one of which is always $\text{R}\cdot\text{CO}_2\text{H} + h\nu \rightarrow \text{CO}_2 + \text{RH}$. With AcOH and EtCO_2H the reaction $\text{R}\cdot\text{CO}_2\text{H}(\text{H}_2\text{O}) + h\nu \rightarrow \text{ROH} + \text{HCO}_2\text{H}$ occurs, the yield being about 0.6 times that of the latter reaction. Other reactions are $\text{P}_1\text{CO}_2\text{H} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{AcOH}$ and $\text{CO}_2\text{H}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H} + h\nu \rightarrow 2\text{CO}_2 + \text{C}_2\text{H}_6$, and all the acids form some condensation products. The quantum yield of the decomp. sometimes approaches 1. Investigation of the decomp. of AcOH vapour has shown the primary reaction of the single mol. to be the spontaneous transformation of the excited mol. into $\text{CH}_4 + \text{CO}_2$ without collision. In solution the solvent mols. compete with this reaction for the excited mols. The double acid mols. undergo a more complex reaction. When AcOH decomposes in hexane solution the solvent is also attacked.

R. C.

New equation for rate of formation of photographic latent image. J. M. BLAIR and P. A. LEIGHTON (J. Physical Chem., 1932, 36, 1649—1654).—An equation has been derived and checked experimentally by development of coated emulsions containing very small amounts of Ag halide in order to eliminate effects of buried grains. The processes of latent image formation are postulated. The ideal max. d has been determined by analysis of developed Ag.

R. H. L. (c)

Photochemical oxidation of alcohols by potassium dichromate. IV. E. J. BOWEN and J. E. CHATWIN (J.C.S., 1932, 2081—2085).—The effect of changes in $[\text{H}']$ and $\text{K}_2\text{Cr}_2\text{O}_7$ concn. on the photo-oxidation of the lower aliphatic alcohols up to Bu has been studied. Measurements of the quantum efficiencies of a no. of acceptors have been made. The earlier work is summarised and possible reaction mechanisms are discussed.

F. J. W.

Photolysis of aliphatic aldehydes. I. Propionaldehyde. P. A. LEIGHTON and F. E. BLACET (J. Amer. Chem. Soc., 1932, 54, 3165—3178).—The photolysis of EtCHO is studied using monochromatic light (range 2537—3130 Å.). The polymerisation products could not be determined; the calc. quantum efficiency of apparent polymerisation increases steadily in the pressure range 13—200 mm. from 0.03 to 0.78. The quantum efficiency of decomp. does not vary with pressure; it increases with decreasing wave-

length from 0.51 at 3130 to 1.02 at 2537 Å. Decomp. seems to be a unimol. reaction, whilst polymerisation appears to be bimol. H_2 is found in the decomp. products, showing that two decomp. occur; in one case CO and C_2H_6 , whilst in the other CO, a higher hydrocarbon, and H_2 are formed. EtCHO shows fluorescence at wave-lengths longer than 2654 Å. Mechanisms for both photochemical reactions are discussed.
E. J. R. (b)

Quantum yield in the photo-decomposition of the alkyl halides in non-polar solvents. W. WEST and (Miss) B. PAUL (Trans. Faraday Soc., 1932, 28, 688—697).—Quantum efficiencies for the photo-decomp. of the lower alkyl iodides in hexane solution in absence of O_2 vary with the org. radical, being 0.05 for MeI and 1.15 for $Pr^{\beta}I$. The yield increases with diminishing wave-length (3130—2610 Å.), is uninfluenced by concn. of the iodide (0.005—1.0M), and within these limits is independent of temp. Oxidisability and readiness of photo-decomp. in absence of O_2 are not parallel. The yield is not markedly reduced in C_6H_6 as solvent. If the deviations of the quantum yield from vals. between 1 and 2 are ascribed mainly to recombination of free alkyl groups and I atoms, the efficacy of collisions in initiating chemical reaction between free radicals and I atoms is in the order $Me > allvl > vinyl > Et > Pr^{\alpha} > Pr^{\beta}$.
E. S. H.

Photochemistry of aromatic nitroaldehydes. C. JANSSEN (Z. physikal. Chem., 1932, B, 18, 241—264).—In the photochemical conversion of nitroterephthalaldehyde (I) into nitrosoterephthalaldehyde acid in $COMe_2$ solution in light of wave-length 3740—3251 and 3740—3345 Å. at various temp. the max. yield is 1 mol. for 10 quanta. With light of const. intensity, the rate of reaction, k , diminishes as exposure continues. k increases with the rate of supply of energy, but approaches a limit. This behaviour may be explained by assuming that before exposure the normal mols. of (I) are in equilibrium in solution with an intermediate substance, and that it is this substance, and not the normal mols., which undergoes photochemical reaction (cf. A., 1926, 1247). The absorption spectra of the vapours of (I) and *o*-nitrobenzaldehyde (II) are continuous, indicating primary photochemical dissociation. The absorption of (II) in solution diminishes with rise in temp., which is ascribed to the presence of an intermediate substance with a relatively small absorption coeff.
R. C.

Photochemistry of aromatic nitroaldehydes. F. WEIGERT (Z. physikal. Chem., 1932, B, 18, 367—368).—The theory that the photochemical decomp. of *o*-nitrobenzaldehyde occurs through a photo-sensitive [intermediate substance (cf. preceding abstract) is rejected.
R. C.

Chemical action of penetrating radium radiation. XIX. Action on isobutyl and benzyl alcohols. A. KAILAN (Monatsh., 1932, 60, 270—283; cf. A., 1929, 1406).—After the prolonged action of penetrating radiation from radium on $Bu^{\beta}OH$ and $CH_2Ph\cdot OH$, pure and in C_6H_6 solution, it is found that the no. of mols. of monobasic acid formed (m) is of the same order as the no. of ion pairs formed

(n), the ratios m/n being 0.7 and 1.73, respectively, for the pure liquids, but less for C_6H_6 solutions. The no. (m') of $PrCHO$ mols. formed from $Bu^{\beta}OH$ is also of the same order, the ratio m'/n being 0.26 for the pure liquid and 0.11 for a C_6H_6 solution. J. W. S.

Coloration of salts by radium radiation, and its application to research. K. PRZIBRAM (Arch. Hemiju, 1932, 6, 138—140).—A lecture. R. T.

Halogen compounds of the rare gases. A. VON ANTROPOFF, K. WEIL, and H. FRAUENHOF (Naturwiss., 1932, 20, 688—689).—The prep. of compounds of Kr with Cl_2 and Br is reported. The former is a dark red solid at the temp. of liquid air, and appears to be quite stable.
A. J. M.

Hydrogen from iron and water at room temperature. L. T. ALEXANDER and H. G. BYERS (J. Chem. Educ., 1932, 9, 916—918).—When 100 g. of sand or orthoclase were ground in a steel ball mill for 60 hr. at 20—28° with H_2O free from CO_2 , 816 c.c. of H_2 were liberated owing to chemical interaction following the removal of protective films. Contamination of materials in steel colloid mills probably results from the same action.
CH. ABS.

Preparation and purification of salts by the method of base-exchange. G. AUSTERWEIL (Bull. Soc. chim., 1932, [iv], 51, 729—747).—The conditions for base-exchange in zeolites are examined. A method is devised for preparing almost quant. yields of salts by double decomp., by leading the requisite solutions successively over zeolites. This process may be carried out even when the ordinary reaction between the solutions is incomplete. In this way, KCN has been obtained in almost quant. yield from KCl and NaCN, KOAc and NaOAc have been formed from KCl and NaCl with $Ca(OAc)_2$, and $BaCl_2$ and $Ca(NO_3)_2$ yield $Ba(NO_3)_2$. The method may be employed further for the purification of commercial salts; e.g., for removing traces of Fe^{+++} in $Al_2(SO_4)_3$, or Ni^{++} in Co^{++} salts.
E. S. H.

Optical investigation of the reaction of polyhydroxides with Schweitzer's reagent. F. ROSENBLATT (Z. anorg. Chem., 1932, 207, 217—224).—Absorption measurements in the visible region show that the reaction of mannitol or glycerol with $[Cu en_2(H_2O)_2](OH)_2$ or Schweitzer's reagent is of the type $[Cu en_2(H_2O)_2](OH)_2 + 2OH\cdot CH(CH_2OH)_2 \rightarrow [Cu en_2(H_2O)_2][O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH]_2 + 2H_2O$. Neither reagent gives anionic Cu with biuret.
E. S. H.

Silver thiosulphates of ammonium, potassium, and sodium. II. Potassium silver thiosulphate. G. SPACU and J. G. MURGULESCU (Z. anorg. Chem., 1932, 207, 150—156; cf. A., 1931, 1252).—By potentiometric titration of $K_2S_2O_3$ and $AgNO_3$ solutions at different concns. the following compounds have been recognised: $K_2[Ag_4(S_2O_3)_3]$, $K[Ag(S_2O_3)]$, $K_4[Ag_2(S_2O_3)_3]$, $K_3[Ag(S_2O_3)_2]\cdot H_2O$. The last compound does not correspond with that obtained when $(NH_4)_2S_2O_3$ is used.
E. S. H.

Hydrothermal synthesis of calcium aluminate hydrates. S. NAGAI (Z. anorg. Chem., 1932, 207, 313—318; cf. this vol., 822).—By heating CaO and Al_2O_3 (or $Al_2O_3\cdot xH_2O$) with steam at high temp. and

pressures the following compounds are formed: $3\text{CaO}, \text{Al}_2\text{O}_3, 6\text{H}_2\text{O}$, $2\text{CaO}, \text{Al}_2\text{O}_3, 7\text{H}_2\text{O}$, $2\text{CaO}, \text{Al}_2\text{O}_3, 6\text{H}_2\text{O}$, and $2\text{CaO}, \text{Al}_2\text{O}_3, 3\text{H}_2\text{O}$. E. S. H.

Hydrothermal synthesis of calcium silicates at ordinary pressure. IV, V. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 320—326B, 380—384B). —IV. Na_2CO_3 solution (10%) does not dissolve CaO, SiO_2 at 100° , and may therefore be employed to separate this silicate from those of higher SiO_2 content. The method has been employed, in conjunction with determinations of free and combined CaO and SiO_2 , for the examination of the products obtained by heating 1:1, 1.25:1, and 1.75:1 mixtures of CaO and SiO_2 (cf. this vol., 583) at temp. between 900° and 1200° . In the 1:1 mixtures, $3\text{CaO}, 2\text{SiO}_2$ is formed during heating at 900 — 1100° . When a 1.25:1 mixture is heated for 6 hr., the CaO, SiO_2 content increases with rise of temp. from 900° to 1200° and the $2\text{CaO}, \text{SiO}_2$ content decreases, whereas with the 1.75:1 mixtures the reverse is the case. Even after 6 hr. three silicates are present in the product. The experiments show also that the silicate sol. in 10% Na_2CO_3 solution is a mixture of $2\text{CaO}, \text{SiO}_2$, and $3\text{CaO}, 2\text{SiO}_2$.

V. In mixtures of CaO and SiO_2 (3:2) heated in H_2O vapour at temp. between 900° and 1200° the amount of $3\text{CaO}, 2\text{SiO}_2$ and $2\text{CaO}, \text{SiO}_2$ formed increases abruptly at the highest temps., whilst that of CaO, SiO_2 diminishes; at still higher temp. (1250 — 1300°) about 90% of $3\text{CaO}, 2\text{SiO}_2$ is present in the product. Part of the CaO remains uncombined after heating for 6 hr. at 900° . In absence of H_2O , $2\text{CaO}, \text{SiO}_2$ and $3\text{CaO}, 2\text{SiO}_2$ are formed in nearly equal quantities at 1420 — 1450° . H. F. G.

Preparation of pure zinc chloride. R. T. HAMILTON and J. A. V. BUTLER (J.C.S., 1932, 2283—2284).—Pure ZnCl_2 is prepared in quantity by passing dry HCl over pure Zn in anhyd. Et_2O and evaporating the solution in vac. E. E. J. M.

Active oxides. LI. Hydrates, methyl alcoholates, and pyridinates of zinc oxalate. G. F. HÜTTIG and B. KLAPHOLZ. LII. Characterisation of the thermal decomposition of zinc oxalate dihydrate by dispersoid-analytical investigations. G. F. HÜTTIG and T. MEYER (Z. anorg. Chem., 1932, 207, 225—233, 234—241).—LI. $\text{ZnC}_2\text{O}_4, 2\text{H}_2\text{O}$ is pptd. from aq. solutions. Previous analyses showing higher H_2O contents are due to sorbed H_2O . The crystals lose H_2O when heated, but when the composition $\text{ZnC}_2\text{O}_4, 0.03\text{H}_2\text{O}$ is reached, marked decomp. occurs with evolution of CO and CO_2 . There is no point of arrest corresponding with a monohydrate. The prep. of $\text{ZnC}_2\text{O}_4, 2\text{MeOH}$ from ZnCl_2 , MeOH , and $\text{H}_2\text{C}_2\text{O}_4$ in absence of H_2O is described; MeOH is given up slowly at room temp. and rapidly at 60° ; H_2O converts it into the dihydrate. An attempt to prepare a similar compound with EtOH was unsuccessful. The prep. of $\text{ZnC}_2\text{O}_4, 2\text{C}_5\text{H}_5\text{N}$ by adding $\text{C}_5\text{H}_5\text{N}$ to ZnC_2O_4 in absence of H_2O is described; heat converts it into ZnC_2O_4 , and H_2O into $\text{ZnC}_2\text{O}_4, 2\text{H}_2\text{O}$. $\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{C}_2\text{O}_4$, m.p. 149° , has been prepared by addition of the reagents in EtOH solution. The absence of compounds in other mol. ratios has been confirmed by X-ray analysis.

LII. The thermal decomp. of $\text{ZnC}_2\text{O}_4, 2\text{H}_2\text{O}$ has been followed by determining d , sedimentation velocity, and resistance to stirring, and by means of photomicrographs. In the first stage ($\text{ZnC}_2\text{O}_4, 2\text{H}_2\text{O} \rightarrow \text{ZnC}_2\text{O}_4$) the particle size gradually increases and the mass becomes more homogeneous; in the second stage ($\text{ZnC}_2\text{O}_4 \rightarrow \text{ZnO}$) these changes are reversed. E. S. H.

Appearance of intermediate stages, highly magnetic and catalytically very active, in the thermal formation of zinc-chromium spinels. G. F. HÜTTIG, H. KITTEL, and H. RADLER (Naturwiss., 1932, 20, 640; cf. this vol., 1009).—In the formation of ZnCr_2O_4 by heating equimol. proportions of ZnO and Cr_2O_3 an unstable intermediate product possessing ferromagnetic properties, high catalytic power, and a characteristic X-ray spectrum is formed.

W. R. A.

Non-metal halogen compounds. III. Saturation pressures of boron trifluoride. E. POHLAND and W. HARLOS (Z. anorg. Chem., 1932, 207, 242—245; cf. this vol., 132).—The relation between v.p. and temp. for solid BF_3 is expressed by $\log p = -1176.6/T + 1.75 \log T - 0.0032084T + 6.6293$; for liquid BF_3 , $\log p = -1174.4/T + 1.75 \log T - 0.013350T + 8.0536$. BF_3 has m.p. -128° (obs.) and b.p. -99.9° (by extrapolation). BF_3, HCN , prepared by direct addition, has m. p. -40° (under pressure; at room temp. the gas is completely dissociated).

E. S. H.

Oxonium salt from titanium tetrachloride and ethyl ether. A. DIMITRIOS and E. LADIKOS (Praktika, 1930, 5, 449—454; Chem. Zentr., 1932, i, 1648).— $\text{TiCl}_4, 2\text{Et}_2\text{O}$, from TiCl_4 and anhyd. Et_2O , is very hygroscopic and is rapidly decomposed by H_2O .

A. A. E.

Preparation of optically identical solutions of impure dyes by means of the step photometer. C. URBACH (Biochem. Z., 1932, 251, 447—451).—A photometric method is described which makes possible the repeated prep. of optically identical solutions of impure dyes, Ti-yellow being taken as an example.

Behaviour of germanium tetrachloride and related chlorides, especially arsenious chloride, with concentrated hydrochloric acid. E. R. ALLISON and J. H. MÜLLER (J. Amer. Chem. Soc., 1932, 54, 2833—2840).—Complete removal of AsCl_3 , SbCl_3 , SnCl_4 , and TiCl_4 from GeCl_4 can be effected by extraction with conc. HCl . The distribution of AsCl_3 between conc. HCl and GeCl_4 was studied at 0° .

H. F. J. (c)

Synthesis of homoplex poly-compounds of antimony bromide. A. C. VOURNASOS (Praktika, 1930, 5, 324—331; Chem. Zentr., 1932, i, 1642—1643).—The following compounds $\text{X}_2\text{Sb}_3\text{Br}_{11}$ are described: $\text{X} = \text{K}, \text{Na}, \text{Li}, \text{NH}_4 (2\text{H}_2\text{O})$; $\text{X}_2 = \text{Ba} (2\text{H}_2\text{O}), \text{Cd}$.

A. A. E.

Rhenium trioxide. II. W. BILTZ and G. A. LEHRER [with K. MEISEL] (Z. anorg. Chem., 1932, 207, 113—120).—When heated, mixtures of oxides of Re yield ReO_3 and Re. The proportion of metal present is proportional to the intensity of the Re X-ray lines. J. W. S.

Blue anhydrous iron phosphate. G. TAMMANN and H. O. VON SAMSON-HIMMELSTJERNA (Z. anorg. Chem., 1932, 207, 319—320).—The blue colour produced by heating at 700° FePO_4 which has been pptd. by $(\text{NH}_4)_2\text{HPO}_4$ is due to the reducing action of H_2 formed by decomp. of $(\text{NH}_4)_2\text{HPO}_4$. The compound is probably $2\text{FeO}\cdot\text{P}_2\text{O}_5$. E. S. H.

Roasting and reduction relations of spathic iron ore. J. KLARDING (Z. anorg. Chem., 1932, 207, 246—250; cf. A., 1931, 1096).—The decomp. of siderite at 900° involves the reactions (a) $\text{FeCO}_3 = \text{FeO} + \text{CO}_2$ and (b) $3\text{FeO} + \text{CO}_2 = \text{Fe}_3\text{O}_4 + \text{CO}$. E. S. H.

Complex cyanides of iron and hexamethylene-tetramine. A. PERRET and A. GISLON (Bull. Soc. chim., 1932, [iv], 51, 751—757).—The following compounds are described:

$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{C}_6\text{H}_{12}\text{N}_4\cdot 5\text{H}_2\text{O}$;
 $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{C}_6\text{H}_{12}\text{N}_4\cdot 3\text{H}_2\text{O}$;
 $\text{Li}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{C}_6\text{H}_{12}\text{N}_4\cdot 5\text{H}_2\text{O}$, and
 $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}_2]\cdot 2\text{C}_6\text{H}_{12}\text{N}_4\cdot 5\text{H}_2\text{O}$: all are dissociated in aq. solution. $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ forms a series of mixed crystals with hexamethylenetetramine. No evidence could be found for the existence of the compounds $\text{K}_3\text{Fe}(\text{CN})_6\cdot \text{C}_6\text{H}_{12}\text{N}_4\cdot 9\text{H}_2\text{O}$ and $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot \text{C}_6\text{H}_{12}\text{N}_4\cdot 11\text{H}_2\text{O}$ of Ray and Sarkar. H. A. P.

Thiocyanates of bi- and ter-valent iron. A. ROSENHEIM, E. ROEHRICH, and L. TREWENDT (Z. anorg. Chem., 1932, 207, 97—110).—By the interaction of EtOH solutions of RCNS (R =alkali metal) and FeCl_3 , there are formed the compounds $\text{R}_4[\text{Fe}(\text{CNS})_6]\cdot x\text{H}_2\text{O}$ containing Fe^{II} . The corresponding derivatives of Fe^{III} are formed only in aq. solution. With $\text{R}_3\text{Fe}(\text{CNS})_6$ pyridine gives the compound $\text{C}_5\text{H}_5\text{N}[\text{Fe}(\text{C}_5\text{H}_5\text{N})_2(\text{CNS})_4]$ (cf. Reinicke's salt and corresponding Mo^{III} and V^{III} compounds; A., 1931, 697; this vol., 31). The acid of the above salt yields characteristic Tl and Cd salts. The compounds of this series are stable in org. solvents but hydrolysed by H_2O . Boiling $\text{C}_5\text{H}_5\text{N}$ reduces them to $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_2]$, which in boiling CHCl_3 loses part of its $\text{C}_5\text{H}_5\text{N}$ to give $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_2(\text{CNS})_2]$. Atm. oxidation of a CHCl_3 solution of $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_2]$ gives $[\text{Fe}_3(\text{C}_5\text{H}_5\text{N})_{10}(\text{CNS})_9]$ corresponding with Fe_3O_4 and probably $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_6][\text{Fe}(\text{C}_5\text{H}_5\text{N})_2(\text{CNS})_4]_2$. This is most probably the same compound as obtained by Spacu (A., 1914, i, 1089) by the action of $\text{C}_5\text{H}_5\text{N}$ on $\text{Fe}(\text{CNS})_3$ at room temp., and previously regarded as a β -isomeride of $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_2]$. Quinoline yields a compound $\text{C}_9\text{H}_7\text{N}[\text{Fe}(\text{C}_9\text{H}_7\text{N})_2(\text{CNS})_4]$ on reaction with $\text{R}_4[\text{Fe}(\text{CNS})_6]\cdot x\text{H}_2\text{O}$. The action of $\text{C}_5\text{H}_5\text{N}$ on $\text{Fe}(\text{CNS})_3$ yields a compound of approx. composition $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2(\text{CNS})_2]\text{CNS}$. J. W. S.

Reduction of ilmenite in the gaseous phase. V. S. SUTROKOMSKI, E. V. SNOPOVA, and N. I. ROTKOV (Min. Suir, 1931, 6, 522—527).— Fe_2O_3 in oxidised ilmenite or titanomagnetite is reduced with H_2 to Fe at high temp. CH. ABS.

Appearance of highly magnetic intermediate stages in the thermal decomposition of nontronite. W. GEILMANN, W. KLEMM, and K. MEISEL (Naturwiss., 1932, 20, 639—640; cf. this vol., 1008).—The nontronite was heated up to 1200°, and samples were

taken at different high temps. Between 300° and 500° κ decreases slightly due to the loss of H_2O of constitution. At 800° κ increases and is dependent on the applied field. This indicates the formation of an unstable ferromagnetic intermediate compound in the decomp. W. R. A.

"Chloramine" as reagent in volumetric analysis. O. TOMICEK and B. SUCHARDA (Coll. Czech. Chem. Comm., 1932, 4, 285—299).—A detailed account of work already noted (this vol., 825).

Precision with which concentrations of solutions of hydrochloric acid and sodium hydroxide may be determined with the immersion refractometer. E. R. WASHBURN and A. L. OLSEN (J. Amer. Chem. Soc., 1932, 54, 3212—3218).—Equations are given for computing the concn. of HCl or NaOH from the reading of the instrument and the precautions necessary are stated. A difference of 0.1 in the scale reading corresponds with a difference in normality of 0.0048 for HCl and 0.0036 for NaOH. All the results obtained at 20°, 25°, and 30° agreed within these limits. W. T. H. (c)

Use of adsorption indicators in titrations of halides of limited or reversible ionisation. A. J. BERRY (Analyst, 1932, 57, 511—514).—Phenosafranine, tartrazine, and "pyrazolone jaune" are the only adsorption indicators which have been found satisfactory. With weak electrolytes, such as Hg or Tl halides, determinations are difficult, if not impossible. With complex compounds of the type $[\text{ClCo}(\text{NH}_3)_5]\text{Cl}_2$ adsorption indicators may be used to trace the rate of ionisation in solutions. T. McL.

Potentiometric determination of small quantities of iodide in presence of large quantities of chloride and bromide. R. FLATT and A. BONAME (Bull. Soc. chim., 1932, [iv], 51, 761—769).—The mixture is titrated potentiometrically with 0.1N-KMnO₄. I is liberated and later forms ICl. Br is not liberated until this second phase of the reaction is complete. By working in fairly conc. HCl solution and observing the potential rise corresponding with the formation of ICl, it is possible to determine I' in presence of 1000 times the amount of Br' and any amount of Cl'. E. S. H.

Specific reaction of iodides. C. I. KRUISHEER (Z. anal. Chem., 1932, 89, 196—197).—The solution is mixed with an equal vol. of conc. HCl and saturated with SO_2 ; if I' is present a yellow colour appears which may be extracted with $\text{C}_5\text{H}_{11}\cdot\text{OH}$. A. R. P.

Determination of the sulphate ion by precipitation as barium sulphate. J. N. FRIEND and W. N. WHEAT (Analyst, 1932, 57, 559—562).—Precautions to be observed for the prevention of adsorption of alkali salt in the BaSO_4 ppt. are described. E. B. H.

Use of ultra-violet light for the detection of traces of sulphites. J. GRANT and J. H. W. BOOTH (Analyst, 1932, 57, 514—515).—0.25 mg. of SO_2 may be detected by oxidation and the formation of quinine sulphate. HCl is used to liberate SO_2 as quinine phosphate is fluorescent, and oxidising agents must be free from S compounds. T. McL.

Sensitive reaction for the detection of thio-sulphate and its separation from sulphide, sulphite, sulphate, tetrathionate, and thiocyanate. G. SPACU and P. SPACU (Z. anal. Chem., 1932, 89, 192—196).— $S_2O_3^{2-}$ in neutral or feebly alkaline solutions yields a cryst. violet ppt. of the compound $[Ni en_3]S_2O_3$ with solutions of $[Ni en_3](NO_3)_2$, whereas S^{2-} , SO_3^{2-} , SO_4^{2-} , $S_2O_6^{2-}$, and CNS^- yield no reaction. $(NH_4)_2S$ decomposes the ppt., but Na_2S is without action. A. R. P.

Determination of tellurium as crystalline tellurium and as tellurium dioxide. O. E. CLAUDER (Z. anal. Chem., 1932, 89, 270—282).—Cryst. Te is pptd. quantitatively from solutions containing 15—20% HCl, and only small amounts of org. acids or H_2SO_4 by adding a 5—10% solution of H_3PO_3 , $N_2H_4 \cdot H_2SO_4$, semicarbazide + HCl, $NH_2OH \cdot HCl$, H_2SO_3 , or $TiCl_3$, and warming gradually. The ppt. is readily washed and dried, and does not oxidise in the air. With special precautions the determination may be made in presence of moderate amounts of Sb, Bi, Cu, or Pb. TeO_2 is pptd. quantitatively from a hot solution containing HCl and NH_4Cl by adding 20% aq. hexamethylenetetramine. The TeO_2 is washed, dried, and weighed. This determination may be made in presence of excess of H_2SeO_3 . A micro-determination by the same method is also described. H. J. E.

Optical determination of sodium nitrite. K. WEBER (Chem.-Ztg., 1932, 56, 642—643).—Unlike all other colourless inorg. salts, $NaNO_2$ absorbs radiation between 3000 and 4000 Å. For λ 3660 Å., the % absorption $A = 100(1 - 10^{-3.02cp})$, where c is the concn. of the solution (g. per 100 c.c.) and p the thickness of the layer in cm. $NaNO_2$ in brine, preserving salt, etc. may be determined by fluorometric observation of the absorption to within 0.0015%, calc. for a 10% salt solution; a 0.1% solution of quinine sulphate in $N \cdot H_2SO_4$ is recommended as the fluorescent solution. H. F. G.

Direct titration of nitrates with titanous chloride using alizarin as an adsorption indicator. A. W. WELLINGS (Trans. Faraday Soc., 1932, 28, 665—667).—0.01N- and 0.1N-solutions of NO_3^- can be determined by titrating with $TiCl_3$, using alizarin as an adsorption indicator. When sufficient H_2O is present, the $TiCl_3$ is hydrolysed on boiling, and the colour change occurs at the surface of the colloidal TiO_2 particles. E. S. H.

Determination of phosphate and glycerophosphate ions by the mercurimetric method. A. IONESCO-MATTU and (MME.) A. POPESCO (Bull. Soc. chim., 1932, [iv], 51, 769—774).—The method (cf. B., 1928, 690) has been applied successfully to the determination of PO_4^{3-} and $C_3H_7(OH)_2PO_4^{2-}$. E. S. H.

Titration of arsenic precipitated by hypophosphorous acid. B. S. EVANS (Analyst, 1932, 57, 492—494; cf. B., 1929, 1046).—Certain filter-papers give a blue colour with I which is stable to As_2O_3 , but preliminary treatment of the pulp with Br in dil. HCl prevents the formation of the colour. C_6H_6 is added as an indicator in the initial titration, starch being added for the end-point. T. McL.

Colorimetric determination of silica. E. J. KING (Contr. Canad. Biol. Fish., 1931, 7, No. 8—11, D, No. 1—4, 121—125).—An apparatus compensating for the natural colour of the H_2O is employed. 10% NH_4 molybdate (2 c.c.) and 50 vol.-% H_2SO_4 (4 drops) are added to H_2O (100 c.c.), the resulting colour being matched against an artificial standard of picric acid (25.6 mg. in 1 litre of $H_2O = 50$ mg. of SiO_2 in 1 litre). CH. ABS.

Microdetermination of carbon in the organic state in water. M. PICON.—See B., 1932, 818.

Analysis of gaseous elements in metals. N. A. ZIEGLER (Trans. Electrochem. Soc., 1932, 62, 175—187; cf. B., 1928, 573).—The sample is melted in a graphite crucible in vac. by means of a high-frequency induction furnace, and the gases evolved (CO , H_2 , and N_2) are measured by a deflexion manometer after expansion into a known vol. Manometer readings after oxidation and selective freezing out of H_2O and CO , are obtained, and separate re-vaporisation of H_2O and CO_2 gives a check on the proportions of H_2 and O_2 determined by difference. The method has an accuracy of about 0.002% and is especially advantageous for small samples of low gas content. H. J. T. E.

Determination of caesium in presence of rubidium and other alkali metals. N. A. TANANAEV and E. P. HARMASCH (Z. anal. Chem., 1932, 89, 256—262).—Cs is pptd. as a cryst. $Cs_3Bi_2I_9$ by adding a hot solution of BiI_3 in HI to the conc. solution containing Cs alone, or with other alkali metals. The ppt. is washed with aq. $Cs_3Bi_2I_9$, then with cold H_2O , dried $1\frac{1}{2}$ hr. at 140 — 150° , and weighed. An accuracy >99% is obtained. H. J. E.

Determination of traces of silver in presence of both copper and chloride. N. KAMEYAMA and S. MAKISHIMA (J. Soc. Chem. Ind. Japan, 1932, 35, 372—373B).—The Cu is removed by adding NaOH to the solution, heating, and filtering; if sufficient Cl⁻ is present no Ag is lost. The Ag may then be determined colorimetrically with rhodanine; 0.05 mg. of Ag in 100 c.c. of 4N-NaCl containing a little NaOH may be detected, and the intensity of the coloration is proportional to the quantity of Ag present. If the solution is nearly neutral the trace of Cu²⁺ remaining interferes. The method is suitable for the determination of 0.1—0.001% of Ag in refined Cu. H. F. G.

Determination of calcium by the filtration method. H. T. BUCHERER and F. W. MEIER (Z. anal. Chem., 1932, 89, 171—173).—Titration of the ammoniacal Ca solution containing a little EtOH with 0.1N- $Na_2C_2O_4$ at 80° is recommended. A. R. P.

Determination of the insoluble matter in calcium hypochlorite. A. VASSILIEV and H. STUTZER.—See B., 1932, 770.

Rapid gravimetric analysis without ignition of precipitates (washing with alcohol and ether). A. A. VASSILIEV and A. K. SINKOVSKAJA (Z. anal. Chem., 1932, 89, 262—268).—Dick's method of washing the ppt. with EtOH and Et_2O and drying in a vac. desiccator instead of igniting (cf. A., 1929, 901; 1931, 453) gave trustworthy results for Ca, Ba, Ni, SO_4 , and Mg. H. J. E.

Precipitation of barium sulphate in presence of salts of thorium and uranium. L. A. VASILEVA (Uchen. Zapiski Kazan. Gos. Univ., 1930, 90, 15—26).—The ppt. contains Th and U from Th⁺⁺⁺ and UO₂⁺⁺; UO₂⁺⁺ probably forms a solid solution in BaSO₄ and complex Ba, Th, and UO₂ sulphates are probably formed. CH. ABS.

Gravimetric micro-analysis of beryllium silicate rocks. H. THURNWALD and A. A. BENEDETTI-PICHLER (Mikrochem., 1932, 11, 200—220).—Full details are given of the determination of SiO₂, PO₄^{'''}, Al, Be, Mg, and Ca in a few mg. of the mineral, together with the results of applying the methods described to a 27-mg. sample of kolbeckite. H. F. G.

Use of a sulphate-hydrogen sulphate buffered solution for precipitation of zinc sulphide. C. E. P. JEFFREYS and E. H. SWIFT (J. Amer. Chem. Soc., 1932, 54, 3219—3228).—The pptn. of ZnS from such a solution is complete even at [H⁺] as high as 2.5×10^{-2} . Ni, Fe, Mn, Cr, and Al, but not Co, may be quantitatively separated from Zn by this pptn. High [Cl⁻] increases the solubility of ZnS. A procedure is outlined for quant. pptn. of Zn and its separation from the other metals. The temp. should be maintained at 500° when igniting ZnSO₄ and at 900° when igniting to ZnO. C. E. P. J. (c)

Liquid amalgams in volumetric analysis. S. KANEKO and C. NEMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 343b).—Practical notes are given as to the reduction of solutions with Zn etc. amalgam prior to titration with KMnO₄ solution. H. F. G.

Luminescence analysis. IV. Fluorescence of zinc oxide. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1932, 61, 69—86).—The following fluorescence colours are shown by various samples of ZnO: yellowish-brown, golden-orange (preps. obtained at relatively low temp.), dark brown (prepared by decomp. of the basic carbonate at 300°), olive, greenish-yellow, bright green (preps. obtained by ignition of ZnO in a reducing atm.). A definite relationship between fluorescence colour and physical properties does not appear to exist. The degree of fluorescence is diminished by pulverisation. The action of moist CO₂ on ZnO (giving the salt 5ZnO.2CO₂.4H₂O) is accompanied by changes in fluorescence which can be followed with a step photometer (A., 1931, 453). H. B.

Testing of tap water for small quantities of lead and copper. N. SCHOORL.—See B., 1932, 818.

Mechanism of precipitation processes. X. Reaction between lead acetate and iodide ions. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1932, 207, 129—132; cf. A., 1931, 182, 582, 1021).—The formation of PbI₂ is favoured by high [H⁺] and a low mol. ratio Pb(OAc)₂:KI. Opposite conditions favour the pptn. of Pb(OH)I. Mixtures are often produced in this reaction. Pb(OH)I is pptd. when Pb(NO₃)₂ reacts with KI in presence of NH₄OAc. PbI₂ is converted into Pb(OH)I by boiling with aq. NaOAc. The solubility of Pb(OH)I is 0.074 g.-mol. per litre at 16°. E. S. H.

Electrolytic deposition of copper from nitric acid solution and a simple electrolytic separation

of copper and lead. H. BJØRN-ANDERSEN (Z. anal. Chem., 1932, 89, 178—187).—Deposition of Cu from HNO₃ solutions is retarded and the pptn. of the last traces of Cu prevented by the formation of HNO₂ at the cathode, and these effects are greater the higher is the acid concentration. Quant. deposition of Cu is obtained by neutralising the solution or by addition of CO(NH₂)₂, which, besides destroying the HNO₂ in solution, retards formation of this acid at the cathode. For the electrolytic separation of Cu and Pb the solution is made 1.5N with HNO₃ and electrolysed with 2 amp. at 70°, using a Pt dish anode and a Pt gauze cathode; after 30 min. two thirds of the acid is neutralised with aq. NH₃ and electrolysis continued for another 30 min. to complete deposition of PbO₂ and start that of Cu at the cathode. CO(NH₂)₂ is added and electrolysis continued at 55° until no further Cu remains in the electrolyte. Both anode and cathode are washed with H₂O, then with EtOH, and dried, the former at 200° and the latter at 50°.

A. R. P.

Determination of minute amounts of copper in presence of iron and certain other metals. L. A. HADDOCK and N. EVERS (Analyst, 1932, 57, 495—499).—Cu is adsorbed on Fe(OH)₃. Fe⁺⁺⁺, or Cr⁺⁺⁺, may be kept in solution by citric acid and NH₃ at $p_H > 9$; Al, Zn, and Sn are dissolved in NaOH and aq. NH₃ before the addition of Na diethyldithiocarbamate. Cu diethyldithiocarbamate is formed and extracted with CCl₄; the colour is proportional to the amount of Cu present. T. McL.

Rapid determination of mercury. G. SPACU and P. SPACU (Z. anal. Chem., 1932, 89, 187—191).—The neutral or feebly ammoniacal Hg⁺⁺ solution is treated at 100° with an excess of KI and boiling conc. aq. [Cu pn₂]SO₄ (pn=propylenediamine), whereby the Hg is pptd. completely on cooling as the dark bluish-violet cryst. compound [Cu pn₂]HgI₄ (21.81% Hg). The ppt. is washed with 0.1% aq. KI containing 0.1% [Cu pn₂]SO₄, then with 96% EtOH, and finally with Et₂O, dried in a vac. desiccator, and weighed.

A. R. P.

Separation of aluminium from iron by the thiosulphate method. A. K. KUTARKINA (Uchen. Zapiski Kazan. Gos. Univ., 1930, 90, 156—161).—The separation by addition of Na₂S₂O₃ in slightly acid solution is more complete if the solution is boiled for nearly 1 hr.; double filtration is advisable. Excess of NH₄⁺ should be avoided. CH. ABS.

Potentiometric analysis in the steelworks laboratory. P. DICKENS and G. THANHEISER.—See B., 1932, 801.

Electrometric determination of iron in felspar. A. K. LYLE, jun.—See B., 1932, 723.

Volumetric analysis utilising titanous sulphate solution. S. KANEKO and C. NEMOTO (J. Soc. Chem. Ind. Japan, 1932, 35, 348—349b).—A solution of Ti₂(SO₄)₃ prepared by reducing a solution of Ti(SO₄)₂ (8 g. of TiO₂ and 60 g. of K₂SO₄ per litre) with Zn-Hg may be employed for the direct titration of Fe⁺⁺⁺ salt solutions, NH₄CNS being used as indicator. The Ti₂(SO₄)₃ solution is standardised by adding an excess of Fe alum and titrating the FeSO₄ formed with KMnO₄. KClO₃ and KBrO₃ may be determined by

adding a solution to an acidified solution of FeSO_4 , and titrating the Fe^{+++} formed. H. F. G.

Determination of iron in aluminium. L. SZEGO.—See B., 1932, 802.

Ferrocyanides and some of their [analytical] applications. C. T. GASPARY ARNAL (Ann. Chim. Analyt., 1932, [ii], 14, 342—351).—A summary. J. W. S.

Separation of nickel and cobalt and their determination by the filtration method. H. T. BUCHERER and F. W. MEIER (Z. anal. Chem., 1932, 89, 161—171).—In one portion of the solution Ni and Co together are determined by titration with 8-hydroxyquinoline at 70° in very dil. AcOH containing NaOAc, and in another portion the Ni alone is determined by titration with 0.3% dimethylglyoxime in 1:1 COMe_2 - H_2O in a solution containing 2% AcOH and some NaOAc. If Co is in excess of the Ni, sufficient standard Ni solution should be added in the second titration to make the Ni:Co ratio at least 1:1. The end-point in each case is determined by filtration of a small portion of the solution and addition of more reagent to the filtrate. A. R. P.

Alkaline persulphate as an analytical reagent. W. M. DEHN and D. A. BALLARD (J. Amer. Chem. Soc., 1932, 54, 3264).—Heating with $\text{K}_2\text{S}_2\text{O}_8$ in presence of KOH is recommended for the pptn. of $\text{Co}(\text{OH})_3$ and $\text{Ni}(\text{OH})_3$, and for the oxidation of simple and complex CN compounds and $\text{S}_2\text{O}_3^{--}$. W. T. H. (c)

Titration of bivalent tin with potassium chlorate. R. M. KULVARSKAJA (Z. anal. Chem., 1932, 89, 199—201).—The conc. HCl solution of Sn^{++} is titrated with N- or 0.1N- KClO_3 , using 1 drop of 0.1N- FeCl_3 as indicator, a yellow colour (FeCl_3) appearing at the end-point. As^{+++} and Sb^{+++} do not interfere. A. R. P.

Determination of small quantities of antimony in copper and its alloys. W. BOEHM and W. RAETSCH.—See B., 1932, 801.

Determination of bismuth as phosphate in presence of organic compounds. P. P. SOLODOVNIKOV (Uchen. Zapiski Kazan. Gos. Univ., 1929, 39, 873—875).—Moser's method can be employed if a little HNO_3 is added and the solution is filtered as soon as it clears after addition of Na_2HPO_4 . The ppt. may be washed with 90% EtOH when sparingly sol. org. substances are present. If EtOH is present in the solution less HNO_3 need be added. CH. ABS.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXIII. Quantitative separation of tantalum, niobium, titanium, and zirconium. W. R. SCHOELLER and A. R. POWELL (Analyst, 1932, 57, 550—554).—Tannin separates quantitatively Ta, Nb, and Ti from Zr, Th, and Al, the former group being pptd. from slightly acid oxalate solution and the latter from slightly alkaline oxalate solution. E. B. H.

Micro-m.p. apparatus. P. MULLER (Ann. Chim. Analyt., 1932, [ii], 14, 340—341; cf. this vol., 36).—A m.p. apparatus which permits the microscopic

observation of the substance during the determination is described. J. W. S.

Hortvet cryoscope. D. HENVILLE (Analyst, 1932, 57, 569—570).—Improvements to prevent leakage of Et_2O , to stir efficiently, to avoid parallax in reading the thermometer, and to obtain ice when required are suggested. E. B. H.

Continuously operating laboratory furnaces. F. SEIDENSCHNUR (Chem. Fabr., 1932, 317—318).—The electrically-heated furnace described is suitable for use in research on the carbonisation of coal, the degassing of solid fuels, tar distillation, catalytic gas reactions, vapour-phase oil refining, etc. Its capacity permits a daily throughput of 5—15 kg. of coal. H. F. G.

Photo-electric colorimetry. V. Applications of the "Sperrschicht" type of photo-electric cell. R. H. MÜLLER (Mikrochem., 1932, 11, 353—368).—The short-circuit current of the "Sperrschicht" cell ($\text{Cu-Cu}_2\text{O-Cu}$ etc.) is proportional to the intensity of the incident light, and such cells are therefore very suitable for colorimetric work. Typical measurements are described. The light filter and the thickness and concn. of solution used must be chosen with care; small variations of voltage across the light source may introduce large errors. H. F. G.

Photo-electric cell in micro-acidimetry. H. M. PARTRIDGE and R. A. SMITH (Mikrochem., 1932, 11, 311—325).—In the method described a photo-electric cell, in conjunction with a suitable light filter, is employed to observe the colour change of the indicator used (bromothymol-blue); 5 c.c. of 0.007N-acid may be titrated with an error of 1 part in 750 parts. H. F. G.

Photo-electric polarimeter. G. BRUHAT and P. CHATELAIN (Compt. rend., 1932, 195, 370—372).—The polarimeter is on the half-shadow principle, the pencils of light being separated after traversing the polarimeter tube; a double monochromator and K cell are used, the photo-electric current, of the order of 10^{-9} amp., being amplified about 10^6 times. The method avoids the necessity of determining or compensating absorption (cf. A., 1931, 1026), and is accurate to 0.1%. C. A. S.

Constant-temperature cells for microscopic observations. J. B. M. COPPOCK, J. COLVIN, and J. HUME (Chem. and Ind., 1932, 700—701).—A cell for use below 40° consists of a cemented glass cell held inside a larger one, with H_2O at a const. temp. flowing between. For temp. between 150° and 400° a metal box suitably insulated and heated electrically is employed. Light is admitted by a glass window, and the sample is placed in a SiO_2 bowl. T. McL.

Demountable cell for the X-ray investigation of liquids. S. ZEIDENFELD (J. Sci. Instr., 1932, 9, 260—261).—A cell adaptable to the photographic recording of liquid haloes is described. N. M. B.

Lindemann glass for protecting air-sensitive substances when examined by long X-rays. A. SCHLEEDE and M. WELLMANN (Z. Krist., 1932, 83, 148—149).—Ordinary Lindemann glass (Li Be borate) is readily devitrified when heated. A glass suitable for long X-ray work is prepared by fusing in a Pt

crucible a mixture of Li_2CO_3 (4.4), Be carbonate (1.4), and H_3BO_3 (18.5) until a homogeneous melt is obtained. C. A. S.

Apparatus for quantum yields of gas reactions by actinometry. G. S. FORBES, G. B. KISTIAKOWSKY, and L. J. HEIDT (J. Amer. Chem. Soc., 1932, 54, 3246—3249).—An apparatus for quant. study of photochemical gas reactions attended by pressure changes is described. Two quartz cells may be exposed alternately, one for the reaction being studied and the other for determination of the quantum yield of $\text{UO}_2\text{C}_2\text{O}_4$, using monochromatic light of the same wave-length. Brief variations of light energy are followed by measurement of the energy flux through a monochromator with a thermopile. L. P. H. (c)

Heterochrome determinations with the Pulfrich photometer. E. MAYER (Physikal. Z., 1932, 33, 665—670).—The Pulfrich photometer can be used for heterochrome determinations, giving results in agreement with those obtained by other methods.

A. J. M.
Intensity of illumination in spectrographs. O. OLDENBERG (J. Opt. Soc. Amer., 1932, 22, 441—455).—The intensity of the spectrum from a concave grating is calc. A cylindrical lens in front of the plate appears to be the only device capable of increasing intensity without reducing dispersion and resolving power. J. W. S.

Quartz double monochromator and vario-illuminator with mirrors (instead of lenses) for the range 0.2—3 μ . C. LEISS (Z. Physik, 1932, 77, 412—414).—The apparatus is described.

A. J. M.
Light filters for the mercury lamp. E. J. BOWEN (J.C.S., 1932, 2236—2239).—Light filters and their arrangement for obtaining monochromatic light from the Hg lamp are described. Data are presented for their transmission and their stability under illumination under different energy conditions.

J. W. S.
Zero-current thermionic valve galvanometer. H. M. PARTRIDGE [with S. J. BRODERICK] (Mikrochem., 1932, 11, 337—352).—A simple triode circuit is described which is particularly useful when high-resistance (e.g., glass) or easily polarised electrodes are used. The device operates at the no-current point. H. F. G.

Automatic electrometric titrations using a valve. W. KORDATZKI and P. WULFF (Z. anal. Chem., 1932, 89, 241—256).—Details of an apparatus for recording the whole titration curve automatically are given. The apparatus may be modified for conductometric titrations. H. J. E.

Compensated thermionic electrometer. K. G. COMPTON and H. E. HARING (Trans. Electrochem. Soc., 1932, 62, 195—206).

Recent progress in electro-organic chemistry. C. J. BROCKMAN (Trans. Electrochem. Soc., 1932, 62, 265—270).

Electrolysis stand. E. REICHEL (Z. anal. Chem., 1932, 89, 173—177).—The stand contains a support for the beaker, an adjustable micro-burner below,

and a support with two parallel arms which carry the electrodes one on each side of the top of the beaker. Connexions are made between the electrodes and the arms of the support through narrow slits in the top of the beaker. In this way corrosion of the supports and contamination of the beaker contents are avoided.

A. R. P.
Hydrogen electrode vessel. A. J. LINDSEY (Analyst, 1932, 57, 573).—A description of a small vessel, capacity 5—7 c.c., which can be easily cleaned, about 3 min. being required for saturation of the solution with H_2 . E. B. H.

Automatic suction and drop apparatus. E. LÖWENSTEIN (Chem.-Ztg., 1932, 56, 683—684).—An apparatus for the automatic suction of liquid into a pipette and the adjustment of its vol. is described.

M. S. B.
Vacuum micro-distillation. R. A. SMITH (Mikrochem., 1932, 11, 221—226).—The Pregl apparatus has been modified in such a manner that the temp. of the vapour above the boiling liquid can be measured (by a thermocouple) and fractional distillation may be carried out. H. F. G.

Micro-determination of vapour density. I. Determination of mol. wt. J. B. NIEDERL and W. J. SASCHKE. **II. Determination of b.p.** J. B. NIEDERL and I. B. ROUTH (Mikrochem., 1932, 11, 237—250, 251—273).—I. Niederl's original apparatus has been improved, and the necessary corrections for the expansion of the vessel with temp. and for the v.p. of Hg and capillary effects have been determined. Tests with various pure liquids show the method to be at least as accurate as the usual macro-methods. The v.p. and b.p. may be determined simultaneously and repeatedly on one sample (about 10 mg.), and during both heating and cooling.

II. The b.p. of a pure liquid may be determined sharply in the modified apparatus, whilst for mixtures the entire b.-p. range may be determined graphically. Results are given for EtOH , NH_2Ph , thymol, CCl_4 , and C_6H_6 . Various methods of calculating the b.p. to 760 mm. are compared. H. F. G.

Torsion method for measuring very small vapour pressures. K. NEUMANN and E. VÖLKER (Z. physikal. Chem., 1932, 161, 33—45).—The vessel containing the substance under examination is suspended by a torsion fibre in a space which is then evacuated. Vapour escapes from the vessel through two holes, in such a position as to establish a torque; from the resulting deflexion the v.p. can be calc. The method may be used to measure v.p. of 10^{-2} to 10^{-4} mm. with an error of 0.5—1.5%. From the v.p. of Hg and K the chemical consts. are calc. as 1.91 ± 0.06 and 1.105 ± 0.05 , respectively. R. C.

Applicability of the shaking flask. H. BARSON (Chem.-Ztg., 1932, 56, 622).—A dimensional drawing is given of a flask provided with a ground-glass stopper (with spring clip) traversed by a sealed-in glass tube which outside the flask is closed by a glass tap and inside the flask reaches nearly to the bottom, where its constricted end is bent through 180° . The flask can be used alone for ordinary purposes and after attachment of the stopper can serve in place of a separating funnel in the determination of fats etc. D. F. T.

Vacuum filtration apparatus. R. RIPAN (Z. anal. Chem., 1932, 89, 198).—The apparatus comprises a glass head which fits into the usual conical filtration flask and is provided with two side-bulbs and a movable head for holding the filtering crucible. The lower part of the upper head is bent sideways so that by rotating it the main filtrate can be collected in the flask and the various wash-waters separately in the two side-bulbs. A. R. P.

Pressure stopcock. R. N. EVANS (Ind. Eng. Chem., 1932, 24, 856).—The plug of a stopcock is prevented from being dislodged by a wire passing through a hole in the protruding end and holding a glass collar firmly against the shell. The collar may have one concave surface which together with the degree of stiffness of the wire allows the tension to be modified. C. A. K.

Burette with means for automatic filling and adjustment to zero. J. LEWIN (Bull. Soc. Chim. biol., 1932, 14, 1101—1103).

Two types of laboratory pumps for pumping mercury. P. B. SHIVOTINSKI (Ukrain. Chem. J., 1931, 6, [Sci.], 241—244).—Apparatus is described. R. T.

Apparatus for the continuous extraction of liquids by low-boiling solvents. R. T. LESLIE.—See B., 1932, 710.

Apparatus for determining oxygen in gases. K. W. HETZEL.—See B., 1932, 770.

Constant-level regulator for water-baths. T. B. VINYCOMB and A. I. VOGEL (J.C.S., 1932, 2088).—An all-metal swivel joint const.-level regulator is described. F. J. W.

Gas-heated water drying oven with recovery of distillate. E. RUPP (Chem.-Ztg., 1932, 56, 611).—The bottom of the oven which suffers wear from the effect of the gas burners is a separate unit into which the remainder of the oven fits. C. I.

Twin-bomb method for the accurate determination of pressure-volume-temperature data and a simple method for the accurate measurement of high pressures. E. W. WASHBURN (Bur. Stand. J. Res., 1932, 9, 271—278).—Constructional and experimental procedure is outlined. W. R. A.

Simple manometer utilising a non-volatile liquid of low density. C. G. MALMBERG and W. W. NICHOLAS (Rev. Sci. Instr., 1932, [ii], 3, 440—443).—A closed-end manometer, in which Bu phthalate is used instead of Hg, is described. The accumulation of gas in the closed end and its removal therefrom are discussed. W. R. A.

Diamond windows for withstanding very high pressures. T. C. POULTER and F. BUCKLEY (Physical Rev., 1932, [ii], 41, 364—365; cf. this vol., 827).—Diamond windows are superior to glass or fused quartz, permitting pressures up to 21,500 atm. even with H₂O and alcoholic solutions. N. M. B.

Geochemistry.

Occurrence of silica in the waters of the Passamaquoddy Bay Region. H. M. KING (Contr. Canad. Biol. Fish., 1931, 7, No. 8—11, D, Nos. 1—4, 129—137).—Only where H₂O movement was not marked the SiO₂ content varied with depth. Vals. decreased during summer. Tributary fresh H₂O contained more SiO₂ than bay H₂O. CH. ABS.

Salts in river waters near Damascus. V. FROLOW (Compt. rend., 1932, 195, 426—428; cf. this vol., 829).—The max. salt content in all the rivers occurs in Nov., at the beginning of the rains, 3 months earlier than at Palmyra; the min. is in the spring. C. A. S.

Problem of desert crusts. B. V. PIASKOVSKI (Pedology, Russia, 1931, 26, 96—107).—Many of the crusts formed on rocks in the R. Dnieper contain Mn; such crusts are pptd. from H₂O and the discovery of crusts in any region does not indicate a desert type of climate. CH. ABS.

Determination of minerals in platinum concentrates from the Transvaal by X-ray methods. F. A. BANNISTER [with M. H. HEY] (Min. Mag., 1932, 23, 188—206).—Previous bulk analyses of the concentrates from the platiniferous norites of the Bushveld have led to uncertain results. For the present analyses each minute grain was first submitted to a detailed X-ray examination and the grains were sorted into different lots, but not more than a few mg. of each

kind of material could be so collected. The following minerals were determined. Cooperite, PtS, has the tetragonal space-group D_{2h}^2 and the unit cell (a 4.91, c 6.10 Å.) contains 4 mols. Laurite, RuS₂, has the pyrite structure with a 5.59 Å. Braggite, (Pt,Pd,Ni)S, a new mineral, containing Pd 18.1, Ni 4.7%, has the tetragonal space-group D_{2h}^2 and the unit cell (a 6.37, c 6.58 Å.) contains 8 mols. Sperryite, PtAs₂, has the pyrite structure with a 5.926—5.934 Å. Platinum, as minute bright cubes (a 3.91 Å.), and as magnetic dull prisms and plates (a 3.87 Å.). Two other minerals remained undetermined. These results were confirmed by the X-ray examination and analysis of synthesised material. PtS (a 4.92, c 6.12 Å., d 9.0, $d_{\text{calc.}}$ 10.1), PtS₂ (a 3.54, c 5.02, d 7.2, 7.86), and PdS (a 6.37, c 6.58, $d_{\text{calc.}}$ 6.87, corresponding with braggite) were the only sulphides formed. The stable existence of PdS₂ is doubtful. L. J. S.

Distinction of pyrite from marcasite in nodular growths. F. A. BANNISTER (Min. Mag., 1932, 23, 179—187).—The nodules of FeS₂ of common occurrence in the English Chalk (and often popularly supposed to be "thunderbolts") have often been referred to marcasite. X-Ray photographs and examination of polished surfaces in reflected polarised light show, however, that this material consists wholly of pyrite. Nodular growths of marcasite appear to be rare, but stalactites from Mineral Point, Wisconsin, were determined as marcasite. L. J. S.

Legrandite, a new zinc arsenate. J. DRUGMAN and M. H. HEY [with F. A. BANNISTER] (Min. Mag., 1932, 23, 175—178).—A small specimen of blende from an old collection from Flor de Peña mine, Lampazos, Mexico, shows bright yellow radiating needles with the composition As_2O_5 42.02, ZnO 46.68, Fe_2O_3 2.14, MnO 0.05, H_2O 9.36=100.25. This agrees only approx. with a formula $\text{Zn}_3\text{As}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$, and the monoclinic unit cell (a 12.70, b 7.90, c 10.18 Å., $\beta=75^\circ 35'$) would contain 4.54 such mols. The formula is therefore written $\text{Zn}_{14}(\text{AsO}_4)_9\text{OH} \cdot 12\text{H}_2\text{O}$, with 1 mol. in the unit cell. d 4.01, n_α 1.675, n_β 1.690, n_γ 1.735. L. J. S.

Changed composition of an anorthoclase-bearing rock-glass. L. HAWKES and H. F. HARWOOD (Min. Mag., 1932, 23, 163—174).—Analyses of the glass and of the separated crystals of anorthoclase from the glassy selvage of a felsite dike in Iceland indicate that the crystals cannot have grown from a liquid having the composition of the glass. The suggestion is therefore made that the glass has since suffered a change in composition by the loss of K_2O and SiO_2 and the addition of Na_2O . Glasses are more liable to metasomatic change than crvst. rocks.

L. J. S.

Bultfonteinite, a new fluorine-bearing hydrous calcium silicate from South Africa. J. PARRY, A. F. WILLIAMS, and F. E. WRIGHT (Min. Mag., 1932, 23, 145—162).—This new mineral was found in the Bultfontein and Dutoitspan diamond mines at Kimberley and in the Jagersfontein mine in Orange River Colony. It forms pale pink globular aggregates of radiating needles and has much the appearance of natrolite. Analysis gives the formula $2\text{Ca}(\text{OH},\text{F})_2\text{SiO}_2$. From the manner in which the mineral is decomposed by H_2O and by dil. acids the formula is written as $2\text{Ca}(\text{OH})_2\text{SiO}_2 + \text{CaF}_2 \cdot \text{Ca}(\text{OH})_2$. The minute crystals are triclinic, but much complicated by polysynthetic twinning; d 2.73, n_α 1.587, n_β 1.590, n_γ 1.597. The mineral is related to afwillite (A., 1925, ii, 429) with the addition of $\text{Ca}(\text{OH})_2$ and CaF_2 , and its nearest ally is custerite.

L. J. S.

X-Ray spectra of Borschtschovotschny (Transbaikalia) monazites. K. K. MATVEEV (Bull. Acad. Sci. U.R.S.S., 1932, 1329—1346).—A description of the spectra given by granite magma and pegmatite monazites from Transbaikalia. R. T.

Bakal (S. Ural) magnesite. L. M. MIROPOLSKI (Bull. Acad. Sci. U.R.S.S., 1932, 829—832).—The rocks consist of dolomite, with zones of transition to magnesite, which, again, in various horizons passes into siderite.

R. T.

Genesis of the Perunna-La Zarza pyritic ore body, Spain. G. WILLIAMS (Bull. Inst. Min. Met., 1932, No. 336, 33 pp.).

Volcanic rocks from Ruwenzori, Uganda. A. HOLMES and H. F. HARWOOD (Quart. J. Geol. Soc., 1932, 88, 370—439).—Petrographical descriptions are given of volcanic rocks of Pleistocene age and their parentage is discussed. Analyses are given of turjaite, leucitite lapilli, olivine-leucitite, and potash-ankaratite. The rocks contain small but appreciable amounts of Ba and Sr.

L. J. S.

Obsidianites in the Philippine Islands. T. HODGE-SMITH (Philippine J. Sci., 1932, 48, 581—585).—Small spheroidal or cylindrical bodies with pitted and grooved surfaces are found in alluvium. They consist of black glass (olive-brown and optically isotropic in thin chips), d 2.441—2.448, and contain SiO_2 70.88, TiO_2 0.86, Al_2O_3 12.33, Fe_2O_3 1.20, FeO 4.32, MnO trace, MgO 2.62, CaO 3.97, Na_2O 1.61, K_2O 2.39, ign. 0.18=100.36. They are compared with australites and billitonites, and are believed to be of meteoric origin.

L. J. S.

Uranothorites from the Arendal district, Norway. E. GLEDITSCH and B. QVILLER (Phil. Mag., 1932, [vii], 14, 233—243).—Chemical analysis and determination of Ra content indicate a deficiency of Pb, probably due to ground-waters, and that Th-Pb has been lost in greater proportion than U-Pb. Age estimates are much lower than the expected vals.

N. M. B.

Letovicite and accompanying [minerals]. J. SEKANINA (Z. Krist., 1932, 83, 117—122).—Both S-I and S-II and S-I paramorphs of S-II occur in the dumps of abandoned coal mines at Letovice (Lettowitz) and Boskovice (Boskowitz) in Czechoslovakia. With them are found slightly turbid colourless crystals of the new mineral letovicite, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, d 1.81, n_α 1.501, n_γ — n_α 0.025. This is best prepared artificially by heating at 200° 3 parts of $(\text{NH}_4)_2\text{SO}_4$ and 1 part of H_2SO_4 , and crystallising the cold crvst. mass from a little H_2O ; the product has d 1.831, n_α 1.499, n_γ — n_α 0.027 (cf. J.C.S., 1923, 123, 476).

C. A. S.

Actual state of Mont Pelée. ROMER (Compt. rend., 1932, 195, 393—396).—The material erupted during 1929 consists of vitreous or quartziferous dacitoids. Various fumaroles produce alunogen (temp. 90°), gypsum (temp. 86°), or NH_4Cl . A sample of gas emitted (temp. 180°) contained CO , 3.6, SO_2 5.5, N_2 74, O_2 16.5%, with a trace of HCl.

C. A. S.

X-Ray diffractions by volcanic glasses and ashes. M. HIRATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 237—244).—The X-ray diffraction figures of glassy rocks and volcanic ashes from various parts of Japan are of two types; either there is only one diffraction ring which contracts a little when heated, or there are two diffraction rings of nearly equal intensity, and on heating the outer ring is diminished in intensity, whilst the inner contracts a little to approach the form of the first type, the diffraction diagram as a whole resembling that of fused SiO_2 . It is concluded that the H_2O contained in such rocks is not in its ordinary liquid state, but is intimately connected within the mol. arrangement.

J. W. S.

Occurrence of feebly radioactive lateritic soil in Japan. S. IMORI, J. YOSHIMURA, and S. HATA (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, 11, 901—909).—Analyses for soil previously described (cf. A., 1931, 459) are given. A new chemical criterion for determining the lateritisation of soils and clays is described.

N. M. B.

"Mummified" lignin. G. L. STADNIKOV (Brennstoff-Chem., 1932, 13, 247).—A sample of shale of

unknown origin was found to contain fibres of lignin sufficiently well preserved to exhibit all the characteristic lignin reactions. The material contained no cellulose. A. B. M.

Role of micro-organisms in peat formation. S. A. WAKSMAN (Brennstoff-Chem., 1932, 13, 241—247; cf. B., 1929, 965; 1930, 933, 960).—The author's experimental results bearing on the problem are collected and discussed. It is concluded that peat formation is essentially a micro-biological process; even if chemical reactions, *e.g.*, oxidation, reduction, and hydrolysis, play a part therein the explanation of the greater part of the changes which occur in the transformation of plant material into peat must be sought for in the activity of the soil bacteria, fungi, and other micro-organisms. A. B. M.

Is petroleum formed from algæ? A. F. VON STAHL (Petroleum, 1932, 28, No. 27, 9—10).—A discussion. E. D.

Formation of mineral oil, asphalt, and coal. E. BERL, A. SCHMIDT, H. BIEBESHEIMER, and W. DIENST (Naturwiss., 1932, 20, 652—655).—All mineral oil has not been formed in exactly the same way.

The carbonisation of cellulose in alkaline media give rise to a substance which will give mineral oil on hydrogenation, and asphalt on cracking. In nature this could be brought about by CaO or dolomite deposits. It is possible to give chemical explanations. A. J. M.

Origin of coal. E. BERL, A. SCHMIDT, and H. KOCH (Angew. Chem., 1932, 45, 517—519).—A critical review of published theories and experimental work. The lignin theory alone does not explain all the facts. Hard coals are produced from material poor in resins, waxes, and lignins, whilst lignite originates in more highly organised plant material. Lignite does not subsequently become converted into coal. H. F. G.

Origin of coal. O. HORN (Naturwiss., 1932, 20, 647—652).—A summary. A. J. M.

Properties of coals as determined by their mode of origin. H. G. A. HICKLING.—See B., 1932, 757.

Occurrence of quartz in bituminous coals. D. J. W. KREULEN (Brennstoff-Chem., 1932, 13, 312).—Bands of quartz have been found in a Russian anthracite. A. B. M.

Organic Chemistry.

Free radicals and unsaturated compounds. P. WALDEN (Inst. Internat. Chim. Solvay, 1928, 431—523; Chem. Zentr., 1932, i, 1511).—A review. L. S. T.

Common basis of intramolecular rearrangements. F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 3274—3283).—Many of the "abnormal" reactions of org. chemistry, including most intramol. rearrangements, are correlated by the following simple assumptions. A non-ionic linking between an atom such as C or N and an electronegative atom or group is broken during the reaction; the electronegative group takes with it a completed octet of electrons, and the atom is thus left with a sextet. This deficiency of two electrons may induce a migration of an electron pair from an adjacent atom, thus giving rise to "abnormal" or rearranged products. In the case of CO compounds a C with an open sextet may be formed by the addition of a positive ion to the O. In this case, also, the presence of the open sextet induces rearrangement. C. J. W. (b)

Absence of rearrangement of the isobutyl group during the formation of magnesium isobutyl bromide and its relation to the theory of rearrangements. F. C. WHITMORE and A. R. LUX (J. Amer. Chem. Soc., 1932, 54, 3448—3454).—No rearrangement (to *tert.*-Bu compounds) occurs when Bu^{*i*}Br is converted into the Grignard reagent and then into Bu^{*i*}OH by the action of O₂. The possible relation of these facts to the theoretical consideration of rearrangements and of the Grignard reaction is indicated. C. J. W. (b)

Chlorination of neopentane. G. H. FLEMING and F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 3460—3461).—Chlorination of neopentane is complete

in 15 min. at room temp.; a chloride (I), b. p. 24°/80 mm., f. p. -20°, and a small quantity of a dichloride, b. p. 35°/8 mm., are obtained. (I) contains 6% of *tert.*-halide, the amount of which is increased only slightly when (I) is heated at 140° for 1.5 hr. A Grignard reagent could not be prepared from (I). C. J. W. (b)

Production of butenes by pyrolysis of the normal monochlorobutanes. P. E. WESTON and H. B. HASS (J. Amer. Chem. Soc., 1932, 54, 3337—3343).—The thermal decomp. of α - (I) and β - (II) -chlorobutanes in absence and presence of anhyd. CaCl₂ (as catalyst) is studied. In absence of CaCl₂, decomp. of (I) at 550° and of (II) at 500° is homogeneous; (I) gives Δ^{α} -butene (III), but (II) affords (III) and *cis*- and *trans*- Δ^{β} -butenes, the composition of the product from (II) being the same at 450°, 500°, and 550°. In presence of CaCl₂ at 450°, (I) and (II) give the three butenes [relatively little (III) is formed]. It is not known whether the butenes rearrange in contact with the catalyst or whether the catalyst causes the reaction to proceed so that the Δ^{β} -butenes are formed directly from the chlorobutanes. C. J. W. (b)

Behaviour of amylene under dark electric discharge. D. MENECHINI and I. SORGATO (Gazzetta, 1932, 62, 621—632).—Amylene vapour mixed with H₂ and subjected at atm. pressure to an electrical discharge in an ozoniser yields 85% of liquid products (C₅H₁₂ isomerides, isopropylacetylene, etc.); in the gas formed, C₂H₂ derivatives predominate. Amylene alone, or mixed with N₂, does not give the saturated liquid products which are obtained with H₂. Under a corona discharge, with H₂, the amount of amylene transformed is much less, but the changes are more profound, and free C is formed. E. W. W.

Catalytic partial oxidation of alcohols in the vapour phase. IV. W. L. FAITH, P. E. PETERS, and D. B. KEYES.—See this vol., 1004.

Dehydration of diethylcarbinol. F. A. KARNATZ and F. C. WHITMORE (J. Amer. Chem. Soc., 1932, 54, 3461).—Dehydration of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ in a flow reactor at 40 lb. pressure and at $365\text{--}410^\circ$ with a H_3PO_4 catalyst on SiO_2 gel gives a mixture of olefines, b.p. $65\text{--}70^\circ$. Ozonolysis of the mixture gives CH_2O , MeCHO , EtCHO , and PrCHO , showing the formation of normal and rearranged products. C. J. W. (b)

Neopentyl alcohol and its rearrangement products. F. C. WHITMORE and H. S. ROTHROCK (J. Amer. Chem. Soc., 1932, 54, 3431—3435).—Neopentyl alcohol (I) is stable to heat and to reagents such as I , K_2CO_3 , and traces of HCl ; cold conc. H_2SO_4 gives some neopentyl H sulphate. The chloride could not be obtained by saturation of (I) with HCl at -10° and then heating at $62\text{--}65^\circ/206$ hr., or with SOCl_2 . (I) and PBr_3 give 14% of bromide, which is not formed using 48% HBr . With HBr at 40° no bromide results, but at 65° (I) is slowly converted into a mixture of approx. 72% *tert.*-amyl bromide, 8% of (probably) *sec.*-isoamyl bromide, and 20% of one or more primary bromides. The composition of the mixture is not changed by heating to 105° .

C. J. W. (b)

Preparation of alcohols by high-pressure reduction of fats. R. ODA (J. Soc. Chem. Ind. Japan, 1932, 35, 349—352b).—80—90% reduction to the corresponding alcohol occurs when stearic acid, *Et* stearate, soya, castor, and olive oils are reduced with H_2 at $320^\circ/120\text{--}140$ atm. for 20—30 min. in the presence of a 20% Cu-kieselguhr catalyst. With coconut oil, even after a second reduction with fresh catalyst, the crude product has sap. val. 80—90, but with excess H_2 this val. is reduced to 29.0, and from the product a mixture of alcohols is obtained (cf. B., 1931, 12). No reduction occurs in Et_2O , C_6H_6 , or EtOH as solvent. No ethers of the alcohols from coconut oil with cellulose or $\text{C}_5\text{H}_{11}\text{OH}$ could be obtained, but the alkoxides with $(\text{CH}_2\text{Br})_2$ give a glycol ether, m.p. about 15° .

J. W. B.

Reaction of acid iodides with ethers. E. L. GUSTUS and P. G. STEVENS (J. Amer. Chem. Soc., 1932, 54, 3461—3462).—The (cleavage) reaction between AcI (and its Cl substituted derivatives) and aliphatic ethers (and sulphides and oxides) is unimol. *sec.*-Ethers are more readily cleaved into alkyl iodides and esters than are primary ethers; with chloroacetyl iodides, the tendency for fission is diminished by increase of Cl atoms. CCl_3COI does not cleave primary or *sec.*-ethers at room temp. even with ZnI_2 as catalyst.

C. J. W. (b)

Autoxidation of ethyl ether. I. R. NEU (Angew. Chem., 1932, 45, 519—520).—On the average 0.07 g. of I per 10 c.c. was liberated from mixtures of commercial Et_2O (10 c.c.) and 10% KI solution (1 c.c.) after storage in the dark for 10 hr. All the samples contained Fe , and after removal of the Fe the average amount of I liberated after storage in daylight in ordinary glass vessels, with free access of air, for 3 months, was only 0.0009 g. per 10 c.c.

Analytical reactions of alkyl mercaptans in benzene solution. J. R. SAMPEY and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 3404—3409).—The iodometric method (A., 1921, ii, 464) for the determination of mercaptans is applied to C_6H_6 solutions. Two acidimetric methods are given: in one the HI formed by I oxidation is titrated, whilst in the other the HCl liberated by the action of HgCl_2 on the mercaptan is determined. Details are given.

C. J. W. (b)

Analytical reactions of alkyl sulphides in benzene and purified naphtha solutions. J. R. SAMPEY, K. H. SLAGLE, and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 3401—3404).—Alkyl sulphides (in C_6H_6 or in naphtha free from unsaturated hydrocarbons) may be determined by treatment with saturated $\text{Br-H}_2\text{O}$, removal of the slight excess of Br with KI , and removal of the liberated I with $\text{Na}_2\text{S}_2\text{O}_3$; the HBr is extracted with H_2O and titrated with 0.05N- NaOH . Details and precautions are given.

C. J. W. (b)

tert.-Butylmercaptan. H. RHEINBOLDT, F. MOTT, and E. MOTZKUS (J. pr. Chem., 1932, [ii], 134, 257—281).— $\text{Bu}^\text{t}\text{SH}$, b.p. $63.7\text{--}64.2^\circ$ [Hg , m.p. $159\text{--}160^\circ$, Ag , m.p. $268\text{--}270^\circ$ (decomp.), Pb , decomp. 260° , and Na salts; Me , b.p. $101\text{--}102^\circ$, and *Et* thioether, b.p. $56\text{--}57^\circ/109$ mm. (Me_2SO_4 etc. in alkaline solution); CH_2Ph thioether, b.p. $115\text{--}116^\circ/15$ mm. (CH_2PhI and AgSBU^t); *di-tert.*-butyl sulphide, b.p. $72^\circ/71$ mm. ($\text{Bu}^\text{t}\text{I}$ and $\text{Bu}^\text{t}\text{SAg}$); Ac , b.p. $31\text{--}32^\circ/11$ mm., and Bz , b.p. $127^\circ/11$ mm., -derivatives ($\text{Bu}^\text{t}\text{SHg}$ and the acid chloride); 3:5-dinitrobenzoate, m.p. $146\text{--}147^\circ$ ($\text{Bu}^\text{t}\text{SH}$, acid chloride, and pyridine); thionitrite, m.p. -54° , b.p. $38\text{--}39^\circ/55$ mm. ($\text{Bu}^\text{t}\text{SHg}$ and NOCl ; poor yield)], is prepared by interaction of $\text{MgBu}^\text{t}\text{Cl}$ with S (0.8 equiv.) in Et_2O ; it cannot be separated from its Et_2O solution by distillation, and is therefore converted into its Hg salt, and this decomposed by H_2S . The Hg salt also gives HgS and some $\text{Bu}^\text{t}\text{SH}$ on thermal decomp. The mercaptan is oxidised to the disulphide, b.p. $84\text{--}85^\circ/20$ mm. by I or SO_2Cl_2 and alkali, and is regenerated from it by Na and abs. EtOH . It is oxidised by KMnO_4 to *tert.*-butylsulphonic acid, m.p. $115\text{--}116^\circ$ (decomp.) (K and Ag salts; Me , m.p. 116° , and *Et*, m.p. $114\text{--}5^\circ$, esters). *tert.*-Butylsulphonic acid is obtained as its Mg salt by action of SO_2 on $\text{MgBu}^\text{t}\text{Cl}$; its Ag salt with MeI gives *Me tert.*-Bu sulphone, m.p. $78\text{--}79^\circ$ (decomp.).

H. A. P.

Complex compounds of iridium. I. Compounds with organic sulphides. P. C. RAY and N. ADHIKARI (J. Indian Chem. Soc., 1932, 9, 251—257).— IrCl_4 is slowly reduced by alkyl sulphides, especially in the presence of EtOH , and the following complex compounds were isolated: $\text{IrCl}_3\cdot 3\text{Me}_2\text{S}$, $\text{IrCl}_3\cdot 2\text{Me}_2\text{S}$, $\text{Ir}_2\text{Cl}_5\cdot 4\text{Me}_2\text{S}$, $\text{IrCl}_3\cdot 3\text{Et}_2\text{S}$, $\text{Ir}_2\text{Cl}_5\cdot 4\text{Et}_2\text{S}$, $2\text{IrCl}_3\cdot 3\text{Et}_2\text{S}$. The compounds $\text{IrCl}_3\cdot 3\text{Alk}_2\text{S}$ are non-electrolytes and the formula $[(\text{Alk}_2\text{S})_3\text{IrCl}_3]$ is suggested.

A. G.

Action of chloramine-T on disulphides containing the S-S linking. J. R. ALEXANDER and H. MCCOMBIE (J.C.S., 1932, 2087).—With cold aq. chloramine-T $\beta\beta$ -dichlorodiethyl disulphide gives β -chloroethyl-p-toluenesulphonimidodisulphine-p-toluene-

sulphonylimine, m.p. 154°. Et_2S_2 and Ph_2S_2 give the corresponding Et and Ph compounds, m.p. 187—188° and 149—151° (Na salt, m.p. 225°), respectively.

R. S. C.

Reduction of aliphatic sulphonic acid salts with phosphorus pentabromide and phosphorus tribromide. W. H. HUNTER and B. E. SORENSON (J. Amer. Chem. Soc., 1932, **54**, 3364—3367).— MeSO_3K and $\text{PBr}_5 + \text{PBr}_3$ give 26% of Me_2S_2 ; EtSO_3K similarly gives 54% of Et_2S_2 , whilst with PBr_5 41% of EtSO_3Br results. BuSO_3K and 1 mol. of PBr_5 give 66% of *butanesulphonyl bromide*, b.p. 101—102°/11 mm.; 3.5 mols. of PBr_5 give 49% of Bu_2S_2 , b.p. 227—229°/735 mm., whilst a mixture of PBr_5 and PBr_3 affords 52% of Bu_2S_2 (also formed in 63% yield with PBr_3 alone). *Na isopentanesulphonate*, PBr_5 , and PBr_3 give 55% of *diisoamyl disulphide*; $\text{CH}_2\text{Ph}\cdot\text{SO}_3\text{Na}$ similarly affords 87% of $(\text{CH}_2\text{Ph})_2\text{S}_2$, whilst PBr_5 alone gives 70% of CH_2PhBr ; $\text{CHPh}(\text{SO}_3\text{K})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{PBr}_5 + \text{PBr}_3$ give 80% of $\text{CHBrPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, whilst PBr_5 affords 62% of $\text{CHBrPh}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$. *Ethanesulphonamide*, m.p. 57—58°, and *dibutyl trisulphide*, b.p. 119—121°/6 mm., are described. The SO_2Br group is more easily replaced by Br (PBr_5) when attached to an aliphatic radical than when attached to an aromatic nucleus. The presence of Ph on the C attached to SO_2Br facilitates the replacement of the latter by Br.

C. J. W. (b)

Thiolmethiononic acid. H. J. BACKER (Rec. trav. chim., 1932, **51**, 775—782).—Interaction of K thiosulphomethionate with aq. AgNO_3 gives a colloidal suspension of *K Ag thiolmethionate* ($-1\text{H}_2\text{O}$): $\text{CH}(\text{S}_2\text{O}_3\text{K})(\text{SO}_3\text{K})_2 + 2\text{AgNO}_3 + \text{H}_2\text{O} = \text{CH}(\text{SK})(\text{SO}_3\text{Ag})_2 + 2\text{KNO}_3 + \text{H}_2\text{SO}_4$ (cf. hydrolysis of $\text{Ag}_2\text{S}_2\text{O}_3$ to Ag_2S). The free acid ($+2\text{H}_2\text{O}$), m.p. 94—95°, is prepared from the Ba salt ($+8\text{H}_2\text{O}$), and is characterised by a transient blue coloration with FeCl_3 (sensitive test for Fe^{+++}); it titrates as a dibasic acid to Me-orange, and tribasic to phenolphthalein. The K , H , Ba H ($+3\text{H}_2\text{O}$), K_3 , Ti_3 , Ag_3 ($+2\text{H}_2\text{O}$), NH_4 Ag_3 ($+1\text{H}_2\text{O}$), Pb_3 ($+8\text{H}_2\text{O}$), and *strychnine* ($+6\text{H}_2\text{O}$) salts are described. The structure assigned is confirmed by the oxidation of the acid or its salts to $\text{CH}(\text{SO}_3\text{H})_3$ by Cl_2 or Br ; H_2O_2 , HNO_3 , or KMnO_4 give H_2SO_4 .

H. A. P.

Alcoholysis of esters by mixed magnesium alcoxides and phenoxides. D. IVANOV and T. ROUSTCHEV (Compt. rend., 1932, **195**, 467—469).—If, in the reversible reaction $\text{RCO}_2\text{R}' + \text{R}''\text{O}\cdot\text{MgX} \rightleftharpoons \text{RCO}_2\text{R}'' + \text{R}'\text{O}\cdot\text{MgX}$, both R' and R'' are alkyl radicals, the heavier R'' partly replaces R' . If R' is aryl and R'' alkyl, R'' partly replaces R' , the reverse reaction occurring only very slightly. With esters of dicarboxylic acids symmetrical and mixed esters result. The following mixed *Et isoamyl* esters were thus obtained in the yields stated in parentheses: *oxalate*, b.p. 112—114°/20 mm. (26.1%); *carbonate*, b.p. 175—176°/18 mm. (23.6%); *malonate*, b.p. 120—122°/17 mm. (20%).

R. S. C.

Acid salts of fatty acids. T. G. LEVI (Gazzetta, 1932, **62**, 709—716).—By treating fatty acids, HX , with less than the calc. amount of KOH , and washing out the excess of acid with EtOH or Et_2O , the follow-

ing salts, $\text{KX}\cdot\text{HX}$, are prepared: *formate*, m.p. 105—110°, *propionate*, m.p. 85—140°, *butyrate*, m.p. 85—140°, *valerate*, m.p. 55—120°, *hexoate*, *octoate*, m.p. 80—130°, and *erucate*, m.p. 55—120°, all decomposing in Et_2O to KX and HX ; *undecoate*, m.p. 90—160°, *laurate*, m.p. 80—150°, *myristate*, m.p. 95—160°, and *stearate*, m.p. 100—160°, all stable to Et_2O . All the above are stable to cold C_6H_6 , but decompose in hot C_6H_6 . The non-existence (cf. A., 1930, 1162) of salts of the types $2\text{KX}\cdot\text{HX}$, and $\text{KX}\cdot 2\text{HX}$ (A., 1929, 677) is confirmed.

E. W. W.

Electrochemical production of formates from carbon dioxide. M. A. RABINOVITSCH and A. P. MASCHOVETZ.—See this vol., 1005.

Use of keten in the preparation of simple and mixed acid anhydrides. C. D. HURD and M. F. DULL (J. Amer. Chem. Soc., 1932, **54**, 3427—3431).—Mixed anhydrides, RCO_2Ac , are prepared readily from keten and acids (RCO_2H). AcOH gives Ac_2O (nearly quant.); PrCO_2H affords $\text{PrCO}\cdot\text{OAc}$ containing some of the simple anhydrides; BzOH in Et_2O yields AcOBz (quant. yield) which on distillation at 18 mm. gives Ac_2O and Bz_2O . AcOBz and NH_2Ph afford BzOH , NHAcPh , and a little NHBzPh . Furoic acetic anhydride is also obtained in quant. yield; with NH_2Ph it gives furoic acid and NHAcPh , whilst vac. distillation affords some furoic anhydride. Distillation at atm. pressure causes rapid and complete pyrolysis to the *s*-anhydrides.

C. J. W. (b)

Effect of varying conditions of catalytic hydrogenation of fatty oils on nature of reaction product. H. A. WATERMAN, J. A. VAN DIJK, and C. VAN VLODRUP (Rec. trav. chim., 1932, **51**, 653—666; cf. this vol., 601).—Hydrogenation of arachis oil at 180°/1 atm. or more with Ni-kieselguhr catalysts (Wilbuschewitsch's and Normann's methods) leads to preferential reduction of linoleic to oleic glycerides ("homogeneous hardening"), whilst at room temp./1 kg. per sq. cm. with a Pt-active C catalyst saturated acids are formed from oleic acid ("heterogeneous hardening"). Similar results are obtained with Et oleate (containing 16% linoleate and 1.5% saturated esters) and Et linoleate.

H. A. P.

Phenacyl esters of oleic acid series. W. KIMURA.—See this vol., 946.

Autoxidation of the double linking. P. RONA, R. ASMUS, and H. STEINECK.—See this vol., 1003

Preparation of triglycerides of fatty acids. P. E. VERKADE, J. VAN DER LEE, and (FRL.) W. MEERBURG (Rec. trav. chim., 1932, **51**, 850—852).—*Glycerol trisridecoate*, m.p. 42.7°, *triundecoate*, m.p. 29.9°, and *trinonoate*, m.p. 8.7°, are prepared by heating an excess of the acid with glycerol and a little Zn dust in CO_2 at 130°→240°/150—120 mm. In the case of trinonoin the excess of acid was removed by distillation, and in the other cases by neutralisation with KOH in 96% EtOH or in Et_2O , and crystallisation.

H. A. P.

Doubly conjugated system in α - and β -elaeostearic acids. R. S. MORRELL and H. SAMUELS (J.C.S., 1932, 2251—2254).—Maleic anhydride and α -elaeostearic acid give an *adduct*

Me·[CH₂]₃·R·CH·CH·[CH₂]₇·CO₂H (R = annexed formula), m.p. 62·5°, oxidised by KMnO₄ in boiling COMe₂ to azelaic acid (36% of calc.) and much tarry material (oxidised by acid KMnO₄ to small amounts of valeric and azelaic acids).

β-Eläostearic acid similarly gives the adduct Me·[CH₂]₃·CH·CH·R·[CH₂]₇·CO₂H, m.p. 77°, oxidised to valeric acid (63% of calc.), an unidentified substance, C₁₄H₂₁O₈, m.p. 91°, and much tar (oxidised to a little azelaic acid). Me β-eläostearate affords an adduct, m.p. 61°. The maleic anhydride adduct of the β-acid glyceride has a marked power of association; the adduct of the α-acid glyceride has not. Maleic anhydride could not be combined with coumarin, vinyl acetate, anthraquinone, acrylic acid, or citraconic anhydride. H. B.

Reactions of tung oil and eläostearic acid. J. MARCUSSE.—See B., 1932, 850.

Odour and constitution. II. Alkoxy-acids and their esters. B. ROTHSTEIN (Bull. Soc. chim., 1932, [iv], 51, 838—845).—In the series OR·CH₂·COR' the odour rapidly diminishes in intensity and persistence in the order R=Me>Et>Pr^β>Bu^β. The influence of olfactive radicals is greater when present as alkoxy than as ester groups. Methoxy- (chloride, b.p. 99°/1 atm.), ethoxy-, isopropoxy-, b.p. 113°/21 mm. (chloride, b.p. 127°), and isobutoxy-, b.p. 118°/18 mm. (chloride, b.p. 59°/22 mm.) -acetic acids are prepared by interaction of CH₂Cl·CO₂H with the appropriate Na alkoxide. The following esters are prepared in almost theoretical yield by interaction of the appropriate acid chloride and alcohol in presence of pyridine in CHCl₃: CH₂Ph, b.p. 136°/16 mm., phenylethyl, b.p. 148·5—149°/18 mm., geranyl, b.p. 151—152°/16 mm., and citronellyl methoxyacetate, b.p. 149—150°/16·5 mm.; CH₂Ph, b.p. 143°/16 mm., β-phenylethyl, b.p. 156°/17 mm., γ-phenylpropyl, b.p. 167°/16 mm., cinnamyl, b.p. 179°/15 mm., terpenyl, b.p. 157°/20 mm. citronellyl, b.p. 157—158°/16·5 mm., and geranyl ethoxyacetate, b.p. 163°/17 mm.; CH₂Ph, b.p. 149°/17 mm., β-phenylethyl, b.p. 158°/16 mm., γ-phenylpropyl, b.p. 169°/16 mm., geranyl, b.p. 164—165°/15 mm., and citronellyl, b.p. 161—162°/15 mm., isopropoxyacetates; CH₂Ph, b.p. 154°/17 mm., β-phenylethyl, b.p. 166°/15 mm., cinnamyl, b.p. 191°/15 mm., geranyl, b.p. 175°/17 mm., and citronellyl isobutoxyacetate, b.p. 170°/16 mm. H. A. P.

Identification of α-ethoxypropionic acid. A. DEMOLIS and G. A. R. KON (J.C.S., 1932, 2283).—The acid is converted by SOCl₂ into the chloride, b.p. 32°/13 mm., and thence into the amide, m.p. 64°, and anilide, m.p. 66—67°. H. B.

Allyl laevulate and its derivatives. P. P. T. SAH and T. MA (J. Amer. Chem. Soc., 1932, 54, 3271—3273).—Allyl laevulate, b.p. 133—136°/40 mm. (semicarbazone, m.p. 126—127°; phenylhydrazone, m.p. 79—80°), obtained in 60% yield by direct esterification (HCl) of the acid, and Cl₂ in CCl₄ give 40% of βγ-dichloropropyl laevulate, b.p. 199—202°/40 mm. (semicarbazone, m.p. 104—106°; phenylhydrazone, m.p. 73—75°). βγ-Dibromopropyl laevulate (semicarbazone, m.p. 101—102°; phenylhydrazone, m.p. 98—99°) has b.p. 208—210°/40 mm. The Cl- and Br-

esters are also obtained from the corresponding alcohols. C. J. W. (b)

d-Tartaric acid hydrates. M. ORLOVA and A. MOROSOV (Z. Krist., 1932, 83, 150—152).—By exposing aq. solutions of d-tartaric acid of varying concn. to temp. down to -40°, hydrates nC₄H₄O₆·mH₂O, where n : m is 1 : 20, 1 : 10, 1 : 7, 2 : 3, and 3 : 1, have been prepared; the first three melt below room temp., the two last are moderately permanent. C. A. S.

δ-Lactones formed by oxidation of aldoses with bromine water. H. S. ISBELL (Bur. Stand. J. Res., 1932, 8, 615—624).—Oxidation of α- and β-d-mannose and α- and β-l-rhamnose with Br in H₂O saturated with CO₂ at 20° in presence of BaCO₃ (which reacts with free sugar acids, but not with their lactones) confirms the conclusion (this vol., 834) that the oxidation products are δ-lactones, since only 1—2% of the product is neutralised by the BaCO₃. After removal of excess of Br and BaCO₃, the presence of the δ-lactone was confirmed by plotting the time-p_H and time-[α] curves for the initially neutral solution so obtained. Determination of unchanged reducing sugar (Scales, A., 1919, ii, 435) and of total lactone permits the calculation of the amount of product neutralised by BaCO₃ during the oxidation. The larger proportion of neutralisation found with α- (24%) and β- (10·6%) -lactose, β-cellobiose (25·4%), and β-maltose (3·4%) is ascribed to the greater ease of hydrolysis of the lactones of these sugars. The β-forms of the sugars are more easily oxidised than the α, and the formation of a δ-lactone from both α- and β-d-mannose confirms the pyranose structure of both forms. J. W. B.

Properties of d-mannuronolactone. W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1932, 54, 3409—3412).—d-Mannuronolactone is isolated from the hydrolysis products of the alginic acids from *Laminaria saccharina* and *Fucus serratus*. Data on the mutarotation of the lactone are given and the approx. val. for the rotation of the equilibrated mixture of the α- and β-forms of the free acid is calc. to be [α]_D²⁰ +12°. Cinchonine, m.p. 154° (decomp.), [α]_D²⁰ +113·3° in H₂O, cinchonidine, m.p. 154° (decomp.), [α]_D²⁰ -78·3° in H₂O, and brucine, m.p. 147° (decomp.), [α]_D²⁰ -23·1° in H₂O, mannuronates are prepared. C. J. W. (b)

Photochemical reduction of carbon dioxide in aqueous solution. M. QURESHI and S. S. MOHAMMAD.—See this vol., 1006.

Photolysis of aliphatic aldehydes. I. Propaldehyde. P. A. LEIGHTON and F. E. BLACET.—See this vol., 1006.

Preparation of keten from acetone. J. AL (Angew. Chem., 1932, 45, 545—546).—Yields of keten of the order of 90% are obtained by passing COMe₂ vapour through a quartz tube containing (in order of decreasing activity) pumice and V₂O₅, quartz, or pumice, at 675—690°. H. F. G.

Electrolytic reduction of aliphatic ketones to hydrocarbons. S. SWANN, jun.—See this vol., 1005.

Preparation of acetone from acetic acid. H. BERGSTROM and K. N. CEDERQUIST (Iva, 1931,

22—23, 47—48).—AcOH passed over a mixture of CaO and ThO₂ at 423° gives a 90·8% yield of COMe₂; CaCO₃, MgO, and ZnO are much less active.

CH. ABS.

Alcoholysis and hydrolysis of $\alpha\gamma$ -diketones and β -keto-esters. R. CONNOR and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 3420—3427).—The alcoholysis and hydrolysis of various $\alpha\gamma$ -diketones and β -keto-esters at 150—250°/about 100 atm. are investigated. EtOH dried over Al(OEt)₃ is inactive for the alcoholysis of $\alpha\gamma$ -diketones, but EtOH containing the trace of H₂O not removed by CaO is rather active; Al(OEt)₃ is a very active catalyst for the alcoholysis. CH₂Bz₂, which is resistant to alcoholysis in presence of HCl at 60° and atm. pressure, is readily cleaved at 200° either by dry EtOH or EtOH containing Al(OEt)₃. Branching of the chain adjacent to one CO group decreases the rate of alcoholysis with dry EtOH (as with EtOH-HCl). The ratio of the products formed in the cleavage of an $\alpha\gamma$ -diketone is a function of the conditions under which alcoholysis occurs. The keto-esters are much more resistant to alcoholysis than the diketones; the latter are alcoholysed at 150° at about the same rate as are the keto-esters at 250°. EtOH dried over Al(OEt)₃ is not an active reagent for the cleavage of the esters; Al(OEt)₃ is an active catalyst. CH₂Ac·CO₂Et does not undergo alcoholysis at all readily at 200° even with moist EtOH, but does so at 250°. Et α -methyl- and α -benzyl-acetoacetate are alcoholysed as rapidly as CH₂Ac·CO₂Et, but the Me₂ and Et₂ derivatives are very resistant to cleavage. Excellent yields of ketones were obtained by hydrolysis of several β -keto-esters with H₂O at 200°. $\alpha\alpha$ -Dialkylated β -keto-esters are stable towards H₂O at 200°; they can be freed from monoalkylated β -keto-esters by such treatment. Hydrolysis of these dialkylated esters is effected by alkali at 250°. CH₂Ac·CO₂Et is hydrolysed to COMe₂ (97% yield); Et α -benzylacetoacetate gives 97% of 8-phenylbutan- β -one; CAcMe₂·CO₂Et affords 50% of COMePr^{*β*} (with alkali there results 70% of COMePr^{*β*} and 5% of AcOH and Pr^{*β*}CO₂H); CAcEt₂·CO₂Et and dil. EtOH give 49% of γ -ethylpentan- β -one and 45% of unchanged ester at 200°, and 84% of the ketone at 250°; CMe₃·CO₂Et at 200° undergoes 36% hydrolysis; CH₂BzAc and H₂O at 200° give 76% of AcOH and 24% of BzOH.

C. J. W. (b)

Reducing sugars. W. GABRYELSKI and L. MARCHLEWSKI (Biochem. Z., 1932, 250, 385—391).—The presence of OH ions alters the spectrum of glucose and galactose very considerably, due to the formation of products containing aldehydic complexes. The change in spectrum occurs on mixing the sugar solution and the NaOH before any pigment formation has occurred. Immediate neutralisation regenerates the original spectrum but such regeneration does not occur in the later stages.

P. W. C.

Optical rotatory dispersion in the carbohydrate group. I. T. L. HARRIS, E. L. HIRST, and C. E. WOOD (J.C.S., 1932, 2108—2120).—The rotatory dispersions of various sugar derivatives have been measured over the range λ 6708—2380. Sucrose (cf. Lowry and Richards, A., 1925, ii, 265), α -methylmannofur-

anoside and its tetra-acetate, and β -methylmannopyranoside tetra-acetate exhibit simple dispersion, whilst the following show complex dispersion: α -methylgluco-pyranoside and -furanoside, α -methylmannopyranoside (I) and its tetra-acetate, α - and β -methylglucopyranoside tetra-acetates, " γ "-methylmannopyranoside tetra-acetate [3:4:6-triacetyl- β -mannopyranose 1:2-orthomethylacetate], α -cellobiose octa-acetate, and 4- β -glucosido- α -mannose octa-acetate. In these cases deviation from simple dispersion throughout the visual region is small and is always of the same sign; the character of the dispersion does not account for the failure of many of the substances [especially (I)] to conform with Hudson's isorotation rules (A., 1926, 714; 1930, 747). The difference between the mol. rotations of α -methylgluco-, $[\alpha]_D^{20} +118^\circ$, and α -methylmanno-, $[\alpha]_D^{20} +108^\circ$ in H₂O, -furanoside varies from Hudson's calc. vals.

H. B.

Hydroxymethylfurfuraldehyde as an impurity in hexoses. G. VAN KLEET (Rec. trav. chim., 1932, 51, 692—694).—Hydroxymethylfurfuraldehyde is present in crude glucose and is removable by recrystallisation. It is oxidised with difficulty by OI', and may cause a positive Selivanov or Ihl-Pechmann reaction after oxidation of an impure hexose with I and NaOH.

H. A. P.

Precipitation of sugars and polyhydric alcohols by metallic hydroxides in an alkaline medium. II. Mechanism of precipitation and practical conclusions. P. FLEURY and J. COURTOIS (J. Pharm. Chim., 1932, [viii], 16, 145—161).—When alkali is added to various metal salts in presence of glucose or mannitol the latter is removed from solution in the ppt., the results previously found in the case of Cu (cf., A., 1930, 196; this vol., 368) holding for other metals. The hydroxides probably combine with the sugar or alcohol to form a compound of similar constitution to K Sb tartrate, which then exists in the form of its alkali salt stabilised by the presence of excess of the alkali. The dissolution of the ppt. which may occur in presence of an excess of alkali is due to peptisation with the resultant formation of a colloidal solution. Fe is most effective in removing the sugar or alcohol from solution. The metals are best employed in the form of acetates. NaOH is not suitable. Aq. NH₃ and especially Ba(OH)₂ are satisfactory. It is best to add alternately small quantities of the salt solution and of the alkali to the cooled solution of the sugar or alcohol and finally to shake the mixture for 15—30 min.

W. O. K.

Crystalline α -methylglucofuranoside (γ -methylglucoside) and its derivatives. W. N. HAWORTH, C. R. PORTER, and A. C. WAINE (J.C.S., 1932, 2254—2258).— α -Methylglucofuranoside 5:6-monocarbonate (I), m.p. 130°, $[\alpha]_D^{20} +130^\circ$ in MeOH, separates from the residues from the prep. of its β -isomeride (II) (A., 1930, 196). A mixture, m.p. 106—107°, of (I) and (II) is occasionally obtained during the action of MeOH-HCl on isopropylidene-glucose carbonate; acetylation gives α -, m.p. 110—111°, $[\alpha]_D^{20} +148^\circ$ in COMe₂, and β -, m.p. 164°, $[\alpha]_D^{20} -41^\circ$ in COMe₂, -2:3-diacetylmethylglucofuranoside

5:6-monocarbonates, separable through their differing solubilities in aq. pyridine. The α -diacetate and (I) are hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to α -methylglucofuranoside (III), m.p. 62–63°, $[\alpha]_D^{20} +118^\circ$ in H_2O , which is not hydrolysed by zymoin or emulsin, but is so by 0.01N-HCl at 95–100° ($k_{\text{base } 10} \times 10^5 = 4500$) (yielding glucose). β -Methylglucofuranoside, $[\alpha]_D^{20}$ about -77° in H_2O , has not been obtained cryst. (III) is methylated to 2:3:5:6-tetramethyl- α -methylglucofuranoside, b.p. 91°/0.04 mm., m.p. 11°, $[\alpha]_D^{20} +106.5^\circ$ in MeOH, hydrolysed by 0.01N-HCl at 95–100° ($k \times 10^5 = 1500$) to 2:3:5:6-tetramethylglucofuranose, distils at 130° (bath temp.)/0.01 mm., $[\alpha]_D^{20} -7.6^\circ$ in H_2O (oxidised by Br to tetramethyl- γ -gluconolactone), also formed by similar hydrolysis ($k \times 10^5 = \text{approx. } 1900$) of 2:3:5:6-tetramethyl- β -ethylglucofuranoside, distils at 118–120° (bath temp.)/0.1 mm., which is prepared by methylation (Me_2SO_4 , alkali) of β -ethylglucofuranoside 5:6-monocarbonate in 50% aq. COMe_2 followed by Purdie's reagents. α -Ethylglucofuranoside 5:6-carbonate, m.p. 138–140°, $[\alpha]_D^{20} +117^\circ$ in EtOH, is isolated from the mother-liquors from the prep. of the β -isomeride (*loc. cit.*); its 2:3-Ac₂ derivative has $[\alpha]_D^{20} +143^\circ$ in COMe_2 . α - and β -Ethylglucofuranosides have $[\alpha]_D^{18} +101^\circ$ and -86° in H_2O , respectively. H. B.

Hemiacetals of aldehydogalactose penta-acetate and their optical properties. M. L. WOLFROM and W. M. MORGAN (J. Amer. Chem. Soc., 1932, 54, 3390–3393).—Crystallisation of aldehydogalactose penta-acetate from the appropriate alcohol gives the following hemiacetals: *Me*, m.p. 123°, $[\alpha]_D^{20} +3.0^\circ \rightarrow -7.7^\circ \rightarrow +15^\circ$ (initial, min., and final vals. in CHCl_3 ; this order is followed below); *Et*, m.p. 133°, $+1.5^\circ \rightarrow -7.5^\circ \rightarrow +6^\circ$; *Pr*, m.p. 130°, $+4.2^\circ \rightarrow -8.2^\circ \rightarrow +4.5^\circ$; *Pr* ^{β} , m.p. 144°, $-1^\circ \rightarrow -12^\circ \rightarrow -7^\circ$; *Bu* ^{β} , m.p. 123°, $+6^\circ \rightarrow -7^\circ \rightarrow +1^\circ$; cyclohexyl, m.p. 136°, $0^\circ \rightarrow -12^\circ \rightarrow -3^\circ$. The optical behaviour supports the open-chain intermediate theory of sugar mutarotation.

C. J. W. (b)

Synthesis of cellobiose. K. FREUDENBERG and W. NAGAI (Naturwiss., 1932, 20, 578).—Acetobromoglucose in dioxan reacts with β -glucosan and Ag_2CO_3 to give a mixture of tetra-acetylglucosido-derivatives of β -glucosan, which, after treatment with 50% H_2SO_4 , was acetylated to cryst. cellobiose octa-acetate.

W. R. A.

Constitution of allolactose. M. POLONOVSKI and A. LESPAGNOL (Compt. rend., 1932, 195, 465–467).—Human milk contains, besides gynolactose and allolactose (I), glucosides and glucoproteins. (I), $[\alpha] +25^\circ$, gives, when hydrolysed, a mixture of sugars, $[\alpha] +65^\circ$. It is hydrolysed by emulsin and, when kept for 14 days at 37° with aq. KCN and then hydrolysed by 1% H_2SO_4 , gives galactose (II). The osazone, m.p. 176°, of (I) with boiling 5% HCl gives (II). (I) is, therefore, 3- or impure 6- β -galactosidyl-d-glucose.

R. S. C.

Nitrogenous glucosides. I. Utilisation of glucosecarbimides for glucoside syntheses. T. B. JOHNSON and W. BERGMAN (J. Amer. Chem. Soc., 1932, 54, 3360–3363).—Bromoglucose tetra-acetate and AgCNO in xylene give two isomeric tetra-acetyl-

d-glucose-l-carbimides, m.p. 92° (I) and 120° (II) (cf. Fischer, A., 1914, i, 662), and s-octa-acetyl-d-di-glucosylcarbamide, m.p. 164°, $[\alpha]_D^{20} -3.7^\circ$ in CHCl_3 (hydrolysed to s-d-diglucosylcarbamide). (I) rearranges into (II) when heated. (II) and amyl alcohol boiled for 30 min. give tetra-acetyl-d-glucose amylourethane, m.p. 88°, $[\alpha]_D^{20} -6.61^\circ$ in Et_2O ; the β -chloroethylurethane, m.p. 114°, $[\alpha]_D^{20} -11.6^\circ$ in Et_2O , is similarly prepared. C. J. W. (b)

Osmometric investigation in dilute solutions of polysaccharides. I. Molecular size of the α -dextrin of Schardinger (α -di- and α -tetra-amylose). M. ULMANN (Biochem. Z., 1932, 251, 458–477).—The doubtful existence of Pringsheim's α -diamylose and its identity with α -tetra-amylose as indicated chemically by Mickleley (A., 1930, 1414; this vol., 255) are confirmed by osmotic measurements. Boiling an aq. solution of α -tetra-amylose for 2 hr. does not effect any change. If small amounts of alkali are added to an α -amylose solution, the osmotic pressure at first slowly and then rapidly increases until the final vals. almost reach those required by α -diamylose. If the p_H is then readjusted to neutrality, the osmotic pressure does not change, the reaction being irreversible. If, however, the amylose is recovered by careful evaporation at room temp. the product on redissolving in H_2O gives again a val. for a tetra-amylose. If the p_H of a tetra-amylose solution be adjusted to the acid side, the osmotic pressure gives vals. corresponding with an octa- to hexadeca-saccharide.

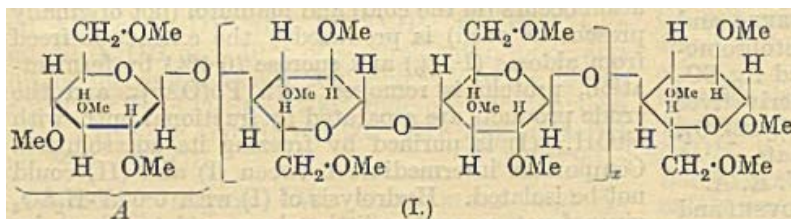
P. W. C.

Natural polyglucans. IV. Carbohydrates of the Jerusalem artichoke. H. H. SCHLUBACH and H. KNOOP (Annalen, 1932, 497, 208–234; cf. Tanret, A., 1893, i, 385, 617).—Inulin (I), $[\alpha]_D^{18} -39.9^\circ$ in H_2O (10–15%), dilævan (II), $[\alpha]_D^{18} -22.3^\circ$ in H_2O (20–30%), impure diaraban, $[\alpha]_D^{18} -62.9^\circ$ in H_2O (1%), and a series of products, $[\alpha]_D^{18} +40^\circ$ to $+120^\circ$ (5–10%), are isolated from the tubers by extraction with H_2O in presence of CaCO_3 [whereby a fermentation occurs (in the cold) and mannitol (not originally present as such) is produced]; the extract is freed from aldoses (1.9%) and sucrose (6.4%) by fermentation, protein is removed with $\text{Pb}(\text{OAc})_2$, and the crude products are separated by fractional pptn. with EtOH. (I) is purified by freezing its aq. solution. Compounds intermediate between (I) and (II) could not be isolated. Hydrolysis of (I) with 0.05N- H_2SO_4 gives fructose and a little glucose (determined by Willstätter and Schudel's or Auerbach and Bodlander's method); under the same conditions sucrose gives a slight excess of glucose. The aldose val. of (I) is undoubtedly due to the presence of small amounts of difficultly separable impurities; (I) is built up solely of fructose units. Methylation of (I), $[\alpha]_D^{20} -37^\circ$, gives trimethylinulin, m.p. 146.5–147°, $[\alpha]_D^{20} -49^\circ$ in CHCl_3 (cf. Haworth and Learner, A., 1928, 510), which is depolymerised ($\text{EtOH-H}_2\text{C}_2\text{O}_4$) and then hydrolysed (0.25% HCl) to 3:4:6-trimethylfructose, b.p. 110–114°/0.05 mm., $[\alpha]_D^{18} +26.3^\circ$ in CHCl_3 [osazones, m.p. 77–79° and 127–128° (cf. Haworth and Learner, *loc. cit.*)], also formed by methylation and subsequent degradation of (II). Hydrolysis of (II) with dil. H_2SO_4 gives fructose and

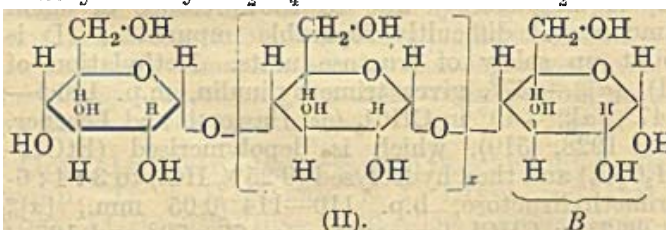
a considerable amount of a substance oxidised by hypoiodite. H. B.

Thermal degradation of inulin to a fructose anhydride. H. H. SCHLUBACH and H. ELSNER (Annalen, 1932, 497, 201—207).—Inulin heated with $(\text{CH}_2\text{OH})_2$ at $140^\circ/15$ mm. for 72 hr. gives a product, M 230, $[\alpha]_D^{25} +29.6^\circ$, which is not identical with levan, since on methylation (Ag_2O , MeI , MeOH) it affords pentamethyl- γ -fructose (impure) [hydrolysed by 1% HCl to (mainly) 1:3:4:6-tetramethylfructose (I)] and a hexamethyldihexose anhydride, b.p. $152^\circ/0.01$ mm. [converted by successive treatment with $\text{EtOH}-\text{H}_2\text{C}_2\text{O}_4$ and dil. HCl into a trimethylhexose (II), b.p. $90-93^\circ/0.01$ mm., $[\alpha]_D^{25} +25^\circ$ in CHCl_3 , similar to 3:4:6-trimethylfructose (III)]. (II) and $\text{NHPh}\cdot\text{NH}_2$ in 20% AcOH give a small amount of an oily osazone containing 2 OMe groups, whilst (III) affords an osazone, m.p. 126° , containing 3 OMe; (I) similarly furnishes an oily osazone containing 2 OMe only. Depolymerisation of inulin with NH_2Bz at 140° gives a complex mixture of degradation products. H. B.

Polysaccharides. X. Molecular structure of cellulose. W. N. HAWORTH and H. MACHEMER. **XI. Molecular structure of glycogen.** W. N. HAWORTH and E. G. V. PERCIVAL (J.C.S., 1932, 2270—2277, 2277—2282).—X. Cellulose acetate "C" (COMe_2 -sol.) is prepared by a modification of Barnett's method; this is free from degradation products and is completely deacetylated and methylated by one treatment with Me_2SO_4 and alkali under the conditions previously described (A., 1931, 941). Hydrolysis of the methylated cellulose [as (I)] with cold saturated aq. HCl , separation of the methylglucoses, conversion of these into the methylglucosides, and subsequent fractionation gives tetramethylmethylglucoside = 0.6% of tetramethylglucose [derived from A in (I)]. This indicates that the cellulose prep. consists of not less than 100 and not more than 200 β -glucose units, and has, therefore, a mol. wt. of 20,000—40,000. Cellulose is a straight chain of β -glucopyranose units linked through positions 1:4.



XI. Glycogen triacetate, $[\alpha]_D^{25} +170^\circ$ in CHCl_3 , prepared by acetylation with Ac_2O -pyridine, is methylated by Me_2SO_4 and alkali in COMe_2 . The



methylated glycogen (free from degraded material) is hydrolysed (as above); 9% of tetramethylgluco-

pyranose is isolated, indicating that glycogen is represented as (II), (where x has a min. val. of 10). The terminal "aldose" unit (B) in glycogen, starch, and cellulose may be modified by oxidation to the acid (or lactone) group. The originals must be consulted for details. H. B.

Determination of the composition of additive compounds of cellulose. G. CHAMPETIER (Compt. rend., 1932, 195, 499—501).—A comparison of the method (A., 1931, 941) with that of Schwarzkopf (this vol., 836). F. R. S.

Acetolysis of cellulose. V. Water-soluble dextrins from cellulose. K. HESS and F. KLAGES (Annalen, 1932, 497, 234—247).—Crude cryst. H_2O -sol. dextrins (A), obtained essentially by the method previously described (A., 1931, 827), are separated by pptn. from aq. solution with MeOH into three groups of products: (a) $[\alpha]_D^{25} +13^\circ$ to $+14^\circ$ in H_2O , I val. ~ 20 (corresponds with cellohexaose), (b) $[\alpha]_D^{25} +15^\circ$ to $+16^\circ$, I val. 23 (cello-pentaose), (c) $[\alpha]_D^{25} +15^\circ$ to $+19^\circ$, I val. ~ 28 (cello-pentaose and -tetraose); the non-cryst. residue (B) from the combined mother-liquors from (A) has $[\alpha]_D^{25} +22.6^\circ$, I val. 38.2 (it is stated in a footnote that cryst. cellotriose has probably been isolated from B). Methylation (Me_2SO_4 , alkali) of these products shows that they are not homogeneous; hendecamethylcellotriose is obtained from (c) whilst tetradecamethylcellotetraose and higher products are obtained from (a), (b), and (c). The same interferences (Röntgen diagram) are shown by (a)—(c) as by hydrocellulose. H. B.

Action of fluorosulphonic acid on cellulose. C. H. MÖLLERING (J. pr. Chem., 1932, [ii], 134, 209—214).—Cellulose dissolves in 3—4 times its wt. of cold FSO_3H eventually to a clear brown, viscous liquid, which mixes in H_2O to a clear solution; titration with alkali suggests that a mixture of tetra- with a little tri-fluorosulphonyl ester has been formed.

Attempts to isolate the ester or its Ac derivative, or to dissolve cellulose in an equiv. amount of FSO_3H , failed, but removal of excess of FSO_3H from the aq. solution with Pb carbonate and evaporation of the filtrate under reduced pressure gave a solid which on analysis appeared to be a mixture of FSO_3K and a K cellulose fluorosulphonate.

Rearrangements involved in the action of nitrous acid with *n*-butylamine. F. C. WHITMORE and D. P. LANGLOIS (J. Amer. Chem. Soc., 1932, 54, 3441—3447).— NaNO_2 and NH_2Bu in dil. HCl give BuOH 25%, *sec.*- BuOH 13.2%, BuCl 5.2%, *sec.*- BuCl 2.8%, butenes 36.5%, high-boiling material 7.6%, and traces of Bu nitrites. Branched-chain Bu derivatives are not formed. The relation of these facts to the mechanism of rearrangements is discussed. C. J. W. (b)

Sulphonation of amino-acids, polypeptides, and diketopiperazines. II. P. BAUMGARTEN, I. MARGGRAFF, and E. DAMMANN (Z. physiol. Chem., 1932, 209, 145—165; cf. A., 1928, 534).—The following derivatives were obtained by sulphonation of the corresponding NH_2 -acids etc. with *N*-pyridinium-

sulphonic acid : *glycine-N-sulphonic acid* [K_2 (+ H_2O), Na_2 (+ H_2O), $Cu K_2$ (+ H_2O), $3Ag_2 K_2$ (+ H_2O) salts], *alanine-N-sulphonic acid* [$4K_2$ salt (+ $EtOH$)], *leucine-N-sulphonic acid* [K_2 , $2Cu$ (+ $3KOAc$), $5Ag_2 K_2$ (+ $24H_2O$) salts], *aspartic-N-sulphonic acid* [K_3 (+ K H aspartate), $2K_3$ (+ $AcOH$) salts], *glutamic-N-sulphonic acid* [K_3 (+ K H glutamate + H_2O), $2K_3$ (+ $AcOH$) salts], *serine-N-sulphonic acid* [$5K_2$ (+2 serine mols.), K_2 salts], *oxyproline-N-sulphonic acid* (K_2 salt), *tyrosine-ON-disulphonic acid* ($K_3 + K_2 H$ salt), *cystine-NN'-disulphonic acid* [$4K_4$ salt (+ $3AcOH$)], *arginine-N-sulphonic acid* [$4K$ salt (+ $KOAc$)], *ornithine-NN'-sulphonic acid* [$4K_3$ salt (+ $3AcOH$)], *histidine-NN'-disulphonic acid* ($K_3 + K_2 H$ salt (+ $\frac{1}{2}AcOH$)), *proline-N-sulphonic acid* (K_2 salt), *tryptophan-N-sulphonic acid* (K_2 salt), *glycyl-glycine-N-sulphonic acid* [K_2 salt (+ H_2O)], *diglycyl-glycine-N-sulphonic acid* [K_2 salt (+ H_2O)], *leucyl-glycine-N-sulphonic acid* [K_2 salt (+ $2H_2O$)], *glycyl-serine-N-sulphonic acid* [K_2 salt (+ $\frac{1}{2}EtOH$)], *glycyl-tyrosine-ON-disulphonic acid* [K_3 salt (+ $EtOH$)], *histidylhistidine-NN'-trisulphonic acid* [K_4 salt (+ H_2O)], *diketopiperazine-NN'-disulphonic acid* [*pyridinium* (+ $\frac{1}{2}EtOH$), K_2 (also + $EtOH$), Ba (+ $2H_2O$) salts]. The free sulphonic acids are readily hydrolysed in aq. solution, the peptide acids even in alkaline solution at the peptide linking. Hydrolysis of diketopiperazinedisulphonic acid first yields the diglycyl derivative and finally glycinesulphonic acid.

J. H. B.

Deamination of ethyl β -methylaminopropionate. W. B. THOMAS and S. M. McELVAIN (J. Amer. Chem. Soc., 1932, 54, 3295—3298).—Et β -methylaminopropionate (I) reacts with Et β -bromo- α -methylpropionate or Et α -methylacrylate giving Et β -methyliminodipropionate, formed by elimination of NH_2Me (or its salt) from 2 mols. of (I).

C. J. W. (b)

Isolation of norleucine and evidence of its identity. Thermodynamic data based on the dissociation pressures of the compounds which the isomeric leucines form with ammonia and hydrogen chloride. E. J. CZARNETZKY and C. L. A. SCHMIDT (J. Biol. Chem., 1932, 97, 333—343).—Hydrolysis of ox spinal cord by H_2SO_4 and purification by the Cu and Zn salts, dissolution in $AcOH$, and 10 crystallisations from H_2O gives *d*-norleucine, $[\alpha]^{25} +22.5^\circ$ in 20% HCl , in 0.22% yield. Identity with the synthetic compound is shown by its crystal structure and that of the Ag and Cu salts. Measurement of the pressure resulting when NH_3 or gaseous HCl is gradually admitted with shaking to a solid NH_2 -acid in presence of a little H_2O vapour gives the dissociation pressure of the resulting compound, which is characteristic of the NH_2 -acid used. Breaks in the straight lines obtained indicate mixtures and the position of the break allows the relative quantity of the components of the mixture to be estimated. The identity of natural and synthetic norleucine is confirmed by this method. Dissociation pressures are also recorded for the compounds of *dl*-leucine, *-iso*-leucine, and *-nor*leucine with HCl and NH_3 , whence are calc. the changes in free energy, heat content, and entropy due to the dissociations. The vals. obtained differ from those for unsubstituted fatty

acids, which supports the theory that NH_2 -acids exist in the solid state as "Zwitterions," since combination will then take place only when a sufficiently high energy level has been reached to cause a H atom to migrate and an electron to shift.

R. S. C.

Oxidation of thiol compounds with hydrogen peroxide. I. Oxidation of cysteine with hydrogen peroxide. A. SCHÖBERL (Z. physiol. Chem., 1932, 209, 231—238).—Free cysteine and its Na salt are rapidly oxidised to cystine by H_2O_2 . The reaction velocity is depressed in HCl and oxidation proceeds only in presence of catalysts such as Cu^{++} and Fe^{++} . The latter catalyst is the more active, but is more sensitive to acid.

J. H. B.

Action of nitrous acid with trimethylacetamide. F. C. WHITMORE and D. P. LANGLOIS (J. Amer. Chem. Soc., 1932, 54, 3438—3441).— NH_2Ac and HNO_2 give a quant. yield of $AcOH$, whilst $CMe_3 \cdot CO \cdot NH_2$ affords more than 90% of the calc. amounts of N_2 and $CMe_3 \cdot CO_2H$. Rearrangements do not occur in reactions involving the $CMe_3 \cdot CO$ group; this is in marked contrast with the analogous neopentyl derivatives.

C. J. W. (b)

Hofmann rearrangement of *tert*-butylacetamide and its significance in the theory of rearrangements. F. C. WHITMORE and A. H. HOMER (J. Amer. Chem. Soc., 1932, 54, 3435—3437).—Hofmann rearrangement of $CMe_3 \cdot CH_2 \cdot CO \cdot NH_2$ gives a quant. yield of neopentylamine; the failure of the migrating neopentyl group to rearrange to *tert*-amyl is discussed in its bearing on the mechanism of rearrangement. A "negative" neopentyl group is apparently stable, whereas a "positive" neopentyl group undergoes rearrangement to *tert*-amyl and related compounds. $CMe_2Et \cdot CO \cdot NH_2$ is rearranged to *tert*-amylamine.

C. J. W. (b)

Electro-organic reductions. R. H. MCKEE and C. J. BROCKMAN.—See this vol., 1005.

Electrolytic reduction of nitrobenzene to azoxybenzene. C. KERNS.—See this vol., 1005.

Mechanism of the reduction of sulphonyl bromides with phosphorus tribromide. W. H. HUNTER and B. E. SORENSON (J. Amer. Chem. Soc., 1932, 54, 3368—3374).—The following steps are postulated in the reduction of RSO_2Br to R_2S_2 : $RSO_2Br + PBr_3 \rightarrow RSOBr + POBr_3$; $RSOBr + PBr_3 \rightarrow R_2SBr + POBr_3$; $2R_2SBr \rightleftharpoons R_2S_2 + Br_2$; $Br_2 + PBr_3 \rightleftharpoons PBr_5$; $R_2SBr + PBr_3 (Et_2O) \rightleftharpoons RSPBr_4$; $RSPBr_4 + 4H_2O \rightarrow RSH + H_3PO_4 + 4HBr$. $p\text{-}C_6H_4Me \cdot SOCl$ and PBr_3 give 54% of *di-p*-tolyl disulphide, also obtained similarly from $p\text{-}C_6H_4Me \cdot SO_2Br$. $o\text{-}NO_2 \cdot C_6H_4 \cdot SBr$ and PBr_3 in Et_2O give 15% of *di-o*-nitrophenyl disulphide, which with PBr_5 in Et_2O affords 40% of $o\text{-}NO_2 \cdot C_6H_4 \cdot SBr$. *o*-Nitrobenzenesulphonyl bromide, m.p. $63\text{--}64^\circ$, from the disulphide and Br in $AcOH$, with PBr_3 gives $o\text{-}NO_2 \cdot C_6H_4 \cdot SBr$ and some disulphide; hydrolysis of the reaction product with H_2O affords $o\text{-}NO_2 \cdot C_6H_4 \cdot SH$. PBr_3 does not react with *di-o*-nitrophenyl disulphide in Et_2O . $o\text{-}NO_2 \cdot C_6H_4 \cdot SBr$ and PBr_3 in Et_2O (followed by hydrolysis) give $o\text{-}NO_2 \cdot C_6H_4 \cdot SH$; in C_6H_6 the disulphide results.

C. J. W. (b)

Syntheses with magnesium triarylvinyl bromides. Penta-arylallyl alcohols. C. F. KOELSCH (J. Amer. Chem. Soc., 1932, 54, 3384—3389).—Benzylidenefluorene dibromide and KOH in dil. EtOH give 85—89% of α -phenyl- β -diphenylenevinyl bromide, m.p. 127°, the Grignard reagent (I) of which with BzCl affords α -phenyl- β -diphenyleneacrylophenone, m.p. 300—303°, and with CO₂ gives α -phenyl- β -diphenyleneacrylic acid, m.p. 182—183° (amide, m.p. 128—129°). Mg triphenylvinyl bromide (II) and CPh₂ in PhMe give pentaphenylallyl alcohol (III), m.p. 108—109°, and a little $\alpha\alpha\beta\gamma\delta\delta$ -hexaphenylbutadiene, m.p. 213—214°. (I) and CPh₂ give $\alpha\alpha\beta$ -triphenyl- γ -diphenyleneallyl alcohol (IV), m.p. 217—219°, whilst (II) and fluorenone give $\beta\gamma\gamma$ -triphenyl- α -diphenyleneallyl alcohol (V), m.p. 150—151°. Dehydration of (III) with H₂SO₄, HCl, or AcCl in AcOH gives 1:1:2:3-tetraphenylindene (VI), m.p. 149—150°, whilst (IV) or (V) gives 2:3-diphenyl-1-diphenyleneindene (VII), m.p. 174—175°. Oxidation of (VI) with CrO₃ in AcOH gives *o*-benzoyltriphenylcarbinol or diphenylphthalide, whilst (VII) gives BzOH and *o*-benzoylbenzophenone-*o*'-carboxylic acid and a neutral compound, C₂₅H₁₈O₃ (?), m.p. 204—206°. 9-Hydroxy-9-*o*-tolylfluorene has m.p. 118—119°. C. J. W. (b)

Substitution in compounds containing two or more phenyl groups. II. Nitration of 3-methyldiphenyl. W. S. M. GRIEVE and D. H. HEY (J.C.S., 1932, 2245—2247; cf. this vol., 838).—Nitration of 3-methyldiphenyl gives the 4-NO₂ derivative; homonuclear substitution predominates (cf. *loc. cit.*). The product of nitration is oxidised (CrO₃, AcOH) to 6-nitro-*m*-toluic acid (obtained similarly from 4-nitro-*m*-xylene), converted by HNO₃ (*d* 1.37) at 100° into 4:4'-dinitro-3-methyldiphenyl, m.p. 197° (reduced to 3-methylbenzidine), and on reduction (SnCl₂, EtOH-conc. HCl) and subsequent acetylation affords 4-acetamido-3-methyldiphenyl, m.p. 166° [synthesised from 6-nitro-*m*-toluidine and C₆H₆ by Gomberg and Bachmann's method (A., 1924, i, 1295) and oxidised by neutral KMnO₄ to 4-acetamidodiphenyl-3-carboxylic acid, m.p. 205—206°]. Nitration of 3- and 4-methyldiphenyl shows a certain parallelism to the substitution reactions of 3- and 4-methylazobenzene (Burns *et al.*, A., 1929, 58). H. B.

Electrochemical oxidation of naphthalene using a new type electrode. E. G. WHITE and A. LOWY.—See this vol., 1005.

Synthesis of alkylphenanthrenes. III. 1:2:7-, 1:3:7-, and 1:6:7-Trimethylphenanthrenes. R. D. HAWORTH and (in part) F. M. BOLAM (J.C.S., 1932, 2248—2251; cf. this vol., 839).—2-C₁₀H₇Me, EtCOCl, and AlCl₃ in cold PhNO₂ give 6-methyl-2-naphthyl Et ketone, b.p. 198—200°/15 mm., m.p. 61—62°, converted by KOH at 250° into 6-methyl-2-naphthoic acid and by Br in CCl₄ into 6-methyl-2-naphthyl α -bromoethyl ketone, m.p. 92—93°. This and CHNa(CO₂Et)₂ in C₆H₆ afford (after hydrolysis and subsequent decarboxylation) β -6-methyl-2-naphthoylbutyric acid, m.p. 118—120°, the Me ester, b.p. 195—198°/0.2 mm., of which with MgMeI gives γ -6-methyl-2-naphthyl- β -methyl- Δ^{β} -pentenoic acid. Reduction of this with red P and HI and subsequent

treatment with H₂SO₄ yields 4-keto-1:2:7-trimethyl-1:2:3:4-tetrahydrophenanthrene, b.p. 195—198°/0.5 mm. [semicarbazone, m.p. 217—218° (decomp.)], which when reduced (Clemmensen) and then dehydrogenated (Se) gives 1:2:7-trimethylphenanthrene, m.p. 120—121° (picrate, m.p. 148—149°, styphnate, m.p. 169—170°; quinone, m.p. 209—210°; quinoxaline, m.p. 184—185°).

Methylsuccinic anhydride and 2-C₁₀H₇Me give (cf. *loc. cit.*) β -6-methyl-2-naphthoylisobutyric acid, m.p. 182—183° (Me ester, b.p. 230—240°/15 mm., m.p. 88—89°), converted by way of γ -6-methyl-2-naphthyl- α -methyl- Δ^{β} -pentenoic acid, m.p. 150—151°, and 4-keto-1:3:7-trimethyl-1:2:3:4-tetrahydrophenanthrene, b.p. 190—195°/0.4 mm., into 1:3:7-trimethylphenanthrene, m.p. 68—69° (picrate, m.p. 163—164°; styphnate, m.p. 160—161°; quinone, m.p. 174—175°; quinoxaline, m.p. 201—202°). Succinic anhydride and 2:3-C₁₀H₆Me₂ give β -6:7-dimethyl-2-naphthoylpropionic acid, m.p. 179—180° (Me ester, b.p. 235—240°/12 mm., m.p. 95—96°), converted by KOH at 250° into 6:7-dimethyl-2-naphthoic acid, m.p. 254—255° (Me ester, m.p. 147—148°) [also obtained by hydrolysis of 2-cyano-6:7-dimethylnaphthalene (prepared by distillation of Na 6:7-dimethylnaphthalene-2-sulphonate and KCN)], and by way of γ -6:7-dimethyl-2-naphthyl- Δ^{β} -pentenoic acid, m.p. 155—156°, and 4-keto-1:6:7-trimethyl-1:2:3:4-tetrahydrophenanthrene, b.p. 190—192°/0.4 mm. (semicarbazone, m.p. 200—202°), into 1:6:7-trimethylphenanthrene, m.p. 123—124° (picrate, m.p. 165—166°; styphnate, m.p. 111—112°; quinone, m.p. 221—222°; quinoxaline, m.p. 189—190°). The above trimethylphenanthrenes differ from the methylpimanthrenes obtained from *d*-pimaric and *iso*-agathidicarboxylic acids (cf. *loc. cit.*). H. B.

Polynuclear aromatic hydrocarbons. XIII. Condensation with 1- and 2-chloromethylnaphthalenes. E. CLAR and L. LOMBARDI (Gazzetta, 1932, 62, 539—544).—When 1-C₁₀H₇·CH₂Cl is condensed (AlCl₃ in CS₂) with 2-C₁₀H₇Me, and the product is distilled from Cu, the resulting hydrocarbon mixture is shown spectroscopically to contain naphtha-2':3':2:3-phenanthrene (A., 1929, 922). This is removed by addition of maleic anhydride to a solution of the mixture in boiling C₆H₆Me₂, when 1':4'-endo-naphtha-2':3':2:3-phenanthrene- $\alpha\beta$ -succinic anhydride is formed, dissolved in dil. NaOH, isolated, and decomposed by heat. The residue contains 1:2:5:6- and probably 1:2:7:8-dibenzanthracenes (cf. this vol., 747). Condensation of 1- with 2-C₁₀H₇·CH₂Cl gives the same products, together with a complex polymeride. The compounds described (A., 1931, 1233) as 2':3'-naphtho- and 7:7'-dimethyl-2':3'-naphtho-3:4-phenanthrene are re-examined and found to be 1:2:5:6-dibenzanthracene and 2':2''-dimethyl-1:2:5:6-dibenzanthracene, respectively; the names of the former are therefore to be eliminated from the literature, together with those of their quinones and of 3:4-phthalyl- and dimethyl-3:4-phthalyl-phenanthrene (*loc. cit.*). E. W. W.

Orthoformanilides and their transformation into the corresponding leuco-bases. A. GIACALONE (Gazzetta, 1932, 62, 577—582).—CH(OEt)₃

heated with NH_2Ph , or *o*- or *m*-toluidine gives a compound of the type $\text{CH}(\text{NHR})_3$, which when heated at $165\text{--}170^\circ$ with the hydrochloride of the amine is converted into a CHPh_3 derivative. Attempted acylation of the first product leads only to the acyl derivative of the amine. Amine hydrochlorides with $\text{CH}(\text{OEt})_3$ yield hydrochlorides of the type $\text{CH}(\text{NHR})_3\cdot\text{HCl}$. The following are obtained. *Trianilinomethane*, m.p. 138° [hydrochloride, m.p. 240° (decomp.)], and *p*-leucaniline; *tri-o-toluidinomethane*, m.p. $150\text{--}151^\circ$ [hydrochloride, m.p. $212\text{--}213^\circ$], and $4:4':4''$ -triamino- $3:3':3''$ -trimethyltriphenylmethane; *tri-m-toluidinomethane*, m.p. 123° [hydrochloride, m.p. $221\text{--}222^\circ$ (decomp.)], and $4:4':4''$ -triamino- $2:2':2''$ -trimethyltriphenylmethane, m.p. 260° . E. W. W.

Syntheses by means of magnesylurethanes. R. BINAGHI (Gazzetta, 1932, 62, 469—477).—Phenylurethane (I) undergoes the quant. reaction: $\text{NHPh}\cdot\text{CO}_2\text{Et} + \text{EtMgBr} = \text{MgBr}\cdot\text{NPh}\cdot\text{CO}_2\text{Et} + \text{C}_2\text{H}_6$, the Mg derivative (II) decomposing with H_2O to (I), and forming compounds with Et_2O and with $2\text{C}_5\text{H}_5\text{N}$. From (II) are derived: with BzCl , *N*-benzoylphenylurethane, m.p. $160\text{--}161^\circ$ (strongly doubly refracting, hydrolysed to benzanilide) which is different from the "benzoylphenylurethane" of Wheeler and Johnson (A., 1903, i, 693); with PhCHO , *N*-phenylurethanophenylcarbinol, m.p. $225\text{--}227^\circ$; with COPh_2 , *N*-phenylurethanodiphenylcarbinol, m.p. $75\text{--}76^\circ$; with $\text{CH}_2\text{Ph}\cdot\text{OAc}$, *bis*-*N*-(phenylurethano)methylcarbinol, m.p. $112\text{--}114^\circ$. E. W. W.

Oxidation of *s*-tribromoaniline by chromic anhydride in acid solution. II. Mechanism. W. H. HUNTER and C. SLY (J. Amer. Chem. Soc., 1932, 54, 3348—3353; cf. A., 1926, 839).—The properties of *s*-hexabromohydrazobenzene (I) show that it cannot be an intermediate in the production of a pentabromoquinoneimine obtained by oxidation of $\text{s-C}_6\text{H}_2\text{Br}_3\cdot\text{NH}_2$ with CrO_3 in acid solution. It is probable that N analogues of the type postulated (*loc. cit.*) in the oxidation of *s*-halogenophenols are involved. (I) and $2:4:2':4'$ -tetrabromohydrazobenzene (II), m.p. $123\text{--}124^\circ$ (Ac_2 derivative, m.p. $178\text{--}179^\circ$) (obtained in 80% yield from the corresponding azo-compound, m.p. 211° , which results in 40% yield from $2:4\text{-C}_6\text{H}_3\text{Br}_2\cdot\text{NH}_2$ and KMnO_4 in aq. pyridine and in 50—60% yield by reduction of *s*-hexabromoazobenzene with Zn and NH_4Cl and then oxidising with CrO_3 in AcOH), do not undergo the semidine rearrangement. In presence of a mineral acid, oxidation and reduction to the corresponding azobenzene and aniline occur; in presence of a reducing agent also, fission to the anilines occurs. C. J. W. (b).

Nitration of *o*-chlorodimethylaniline. C. F. VAN DUIN (Rec. trav. chim., 1932, 51, 878—886).—*o*-Chlorodimethylaniline (*picrate*, m.p. 132°) is conveniently prepared from *o*-chloroaniline and Me_2SO_4 . Nitration in H_2SO_4 at room temp. is slow and gives the 5- NO_2 -derivative, m.p. $64\text{--}65^\circ$, only; the constitution of this is proved by synthesis from 2-chloro-5-nitroaniline and Me_2SO_4 . Nitration in 10% aq. HNO_3 in presence of HNO_2 gives the 4-, m.p. 78° (I), and 6- NO_2 -derivative, b.p. $92\text{--}93^\circ/6\text{ mm.}$ (II),

and 2-chloro-4-nitro(mono)methylaniline, m.p. $116\text{--}117^\circ$ (III) (nitrosoamine, m.p. $95\text{--}96^\circ$; decomposed by boiling EtOH). (I) is also obtained by methylation of 2-chloro-4-nitroaniline, and by interaction of 1:2-dichloro-4-nitrobenzene and NHMe_2 in EtOH at 160° . The structure of (II) follows from its synthesis from 1:2-dichloro-3-nitrobenzene and NHMe_2 , its stability to NHMe_2 at 160° , and its conversion by further nitration (HNO_3 , d 1.51) into 2-chloro-4:6-dinitrophenylmethylnitroamine, m.p. $91\text{--}92^\circ$, also obtained by nitration of 2-chloro-4:6-dinitromethylaniline, m.p. 133° (nitrosoamine). The last-named is prepared from 1:2-dichloro-4:6-dinitrobenzene and NH_2Me at room temp.; NHMe_2 , similarly, gives 2-chloro-4:6-dinitrodimeethylaniline, m.p. $90\text{--}91^\circ$. The structure of (III) is similarly proved by its synthesis from 1:2-dichloro-4-nitrobenzene and 20% NH_2Me in EtOH at $120\text{--}130^\circ$. 2-Chloro-6-nitromethylaniline, m.p. $49\text{--}50^\circ$, is obtained from 1:2-dichloro-3-nitrobenzene and NH_2Me . Improvements are effected in the prep. of *o*-chloroacetanilide and its mononitration mixture. All m.p. are corr. H. A. P.

Action of *o*-toluidine on pyruvylhydroxamic acid. E. PRINCIVALLE and F. COSSU (Gazzetta, 1932, 62, 575—577).—Pyruvylhydroxamic acid NaHSO_3 compound (A., 1923, i, 1236) heated in AcOH with *o*-toluidine does not yield a quinoline, but *N*-acetyl-*N'*-*o*-tolylcarbamide. E. W. W.

Nitration of α - and β -naphthylamine derivatives. II. Nitration of methyl and ethyl β -naphthylcarbamates and *N*- β -naphthyl-*N'*-ethylcarbamide. C. GROENEVELD (Rec. trav. chim., 1932, 51, 783—811).—Nitration of *Me* β -naphthylcarbamate (I), m.p. $112\text{--}113^\circ$ (from $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, ClCO_2Me , and Na_2CO_3 in C_6H_6 at the b.p.), with HNO_3 (d 1.45) gives 1:8-, m.p. $226\text{--}227^\circ$ (decomp. ?), and 1:6-, m.p. 212° , $-(\text{NO}_2)_2$ -derivatives, identified by hydrolysis by NH_3 in MeOH at 100° to the known dinitronaphthylamines. Nitration of (I) or further nitration of its $(\text{NO}_2)_2$ -derivatives with HNO_3 (d 1.52) gives the 1:6:8- $(\text{NO}_2)_3$ -derivative (II), m.p. $228\text{--}230^\circ$ (decomp.) (similarly identified). The *Et* 1:8-, m.p. 178° , and 1:6- $(\text{NO}_2)_2$, m.p. $185\text{--}186^\circ$, and 1:6:8- $(\text{NO}_2)_3$, m.p. $215\text{--}216^\circ$ (decomp.) (III), -derivatives are similarly prepared and identified; unlike the *Me* compounds, they may be prepared from the nitronaphthylamine and ClCO_2Et .

N- β -Naphthyl-*N'*-ethylcarbamide, m.p. $183\text{--}184^\circ$, is prepared by interaction of $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ with EtNCO . Nitration (HNO_3 , d 1.52) at -10° to -5° gives *N'*-nitro-*N*-1:6:8-trinitro-2-naphthyl-*N'*-ethylcarbamide, $\text{C}_{10}\text{H}_4(\text{NO}_2)_3\cdot\text{NH}\cdot\text{CO}\cdot\text{NEt}_2$, m.p. 101° (decomp.), which is decomposed by H_2O into 1:6:8-trinitro- β -naphthylamine, and by MeOH and EtOH into the corresponding urethanes, (II) and (III). A literature survey of the nitration of β -naphthylamine derivatives is given. H. A. P.

Diphenyl series. II. C. FINZI and A. MANGINI (Gazzetta, 1932, 62, 664—677).—2:4'-Diaminodiphenyl (A., 1931, 613) is nitrated by EtNO_3 in H_2SO_4 to 4-nitro-2:4'-diaminodiphenyl (I), m.p. $177\text{--}178^\circ$, the constitution of which is proved by

conversion into 4'-nitro-4-aminodiphenyl and into 4-nitrodiphenyl. Diazotisation of (I) under suitable conditions also yields 4-nitro-4'-amino-2-hydroxy-, m.p. 145—146°, 4-nitro-2-hydroxy-, m.p. 200—201°, and 4-nitro-2:4'-dihydroxy-diphenyl, m.p. 187°. 2'-Amino-4-acetamidodiphenyl (*loc. cit.*) is nitrated to 4'-nitro-2'-amino-4-acetamidodiphenyl (II), m.p. 225° (whence 4'-nitro-4-acetamido- and 4'-nitro-4-amino-diphenyl), and to 3:4'-dinitro-2'-amino-4-acetamidodiphenyl (III), m.p. 240—241° [whence 3:4'-dinitro-4-acetamido-, new m.p. 239° (cf. A., 1927, 656), and 3:4'-dinitro-diphenyl]. 2:4'-Diacetamidodiphenyl is nitrated to 4-nitro- (IV), m.p. 236—237°, and to 4:3'-dinitro-2:4'-diacetamidodiphenyl (V), m.p. 225—226°, also obtainable from (I) or (II), and (III) or (IV), respectively. Hydrolysis of (V) gives 4:3'-dinitro-2:4'-diaminodiphenyl, m.p. 199—200°, whence 3:4'-dinitro-, new m.p. 187° (cf. A., 1928, 166), 3'-nitro-4-amino-, m.p. 127°, and 3-nitro-diphenyl are successively prepared, and prove the constitutions of the new compounds, which agree with the general readiness of diphenyls to nitrate in the 4-position. E. W. W.

Behaviour of phenylhydrazones with condensing agents. II. A. GIACALONE (Gazzetta, 1932, 62, 582—587; cf. A., 1931, 1416).—Phenylhydrazones of aldehydes are condensed in presence of ZnCl_2 or of slightly diluted H_2SO_4 and $\text{CH}(\text{OEt})_3$ to the following products. From *p*-tolualdehyde, *pp'*-4:4'-dimethylbenzylidenedihydrazino-*p''*-methyltriphenylmethane, m.p. 200° (blackening); from *m*- and *p*-nitrobenzaldehydes, *m*-nitro-*pp''*-3:3'- and *p*-nitro-*pp''*-4:4'-dinitrobenzylidenedihydrazinotriphenylmethane, m.p. 175° and 195°, respectively; from *o*- and *m*-chlorobenzaldehydes, *o*-chloro-*pp''*-2:2'- and *m*-chloro-*pp''*-3:3'-dichlorobenzylidenedihydrazinotriphenylmethane, m.p. about 75° and about 90°, respectively. E. W. W.

Some azoxyamide derivatives. Z. E. JOLLES (with O. ORSATTI and W. CAMIGLIERI) (Gazzetta, 1932, 62, 588—597; cf. A., 1922, i, 1072).—Benzeneazocarbonanilide [*Br*₃-derivative, m.p. 195° (decomp.)] is oxidised by H_2O_2 -AcOH to benzeneazoxycarbonanilide, $\text{O}:\text{NPh}:\text{N}:\text{CO}:\text{NPh}$, m.p. 136° (decomp. 155°) [*Br*-derivative, m.p. 157° (decomp.)], forming *p*-bromoaniline on hydrolysis; NO_2 -derivative, m.p. 182° (decomp.). *p*-Chlorobenzeneazocarbonamide, now prepared from *p*-chlorophenylsemicarbazide and FeCl_3 , is oxidised by H_2O_2 -AcOH to *p*-chlorobenzeneazoxycarbonamide, m.p. 192—192.5° (azo- β -naphthol derivative, m.p. 162.5°), and *pp'*-dichloroazoxybenzene. E. W. W.

Reactions in liquid hydrogen sulphide. IX. Reactions between persulphides of hydrogen and organic compounds. W. B. KING and J. A. WILKINSON (J. Amer. Chem. Soc., 1932, 54, 3070—3073).—H persulphides react with styrene and amylene, adding the $\text{S}:\text{S}$ group at the double linking (an oxidation reaction); they reduce $(\text{NPh})_2$ to $(\text{NPh})_2$. Reaction between diazonium chlorides and persulphides occurs with explosive violence unless it is regulated by a solvent such as CS_2 . F. S. (b)

Manufacture of aromatic monoacyldiamines. A. CARPMAEL. From I.G. FARBERIND. A.-G.—See B., 1932, 763.

Manufacture of diacylated diamines. Soc. CHEM. IND. IN BASLE.—See B., 1932, 763.

Acyl derivatives of *o*-aminophenol. I. C. B. POLLARD, C. E. SPARKS, and M. L. MOORE (J. Amer. Chem. Soc., 1932, 54, 3283—3286).—A study of the *ON*-diacyl derivatives of $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, where one of the acyl groups was always β -phenylpropionyl, has been made. In five of the six cases studied, isomerides were obtained depending on the order of introduction of the acyl groups. Complete rearrangement occurred (in five cases) during hydrolysis; in four cases the heavier and more acidic group, whilst in the other case the heavier and less acidic group, was attached to N. *o*- β -Phenylpropionamidophenol (I) has m.p. 131.5—132°. The following *o*- β -phenylpropionamidophenyl esters are prepared: *acetate*, m.p. 79.5—81°; *propionate* (II), m.p. 113.5—115.5°; *valerate*, m.p. 74—75.5°; *isovalerate*, m.p. 92—93°; *phenylacetate* (III), m.p. 90—92°; *benzoate*, m.p. 116.5—118.5°. The following derivatives of *o*-aminophenyl β -phenylpropionate are also described: *Ac*, m.p. 124.5—126°; *propionyl* (IV), m.p. 102.5—104.5°; *valeryl*, m.p. 72.5—74°; *isovaleryl*, m.p. 73.5—74°; *phenylacetyl* (V), m.p. 81—83°; *Bz*, m.p. 122.5—124.5°. (II) and (IV) give a mixed m.p. of 110—115°, indicating that each might be an equilibrium mixture; each substance is, however, hydrolysed to (I). Hydrolysis of (III) and (V) gives approx. 60% of (I) and 40% of *o*-phenylacetamidophenol. Hydrolysis of the other derivatives affords (I). C. J. W. (b)

Tautomerism of *p*-benzoquinoneoxime and *p*-nitrosophenol. L. C. ANDERSON and M. B. GEIGER (J. Amer. Chem. Soc., 1932, 54, 3064—3070).—Absorption curves of several derivatives of *p*-benzoquinoneoxime are given. Conclusions are reached regarding structure and ratio of isomeric forms. F. S. (b)

Halogen derivatives of monohydroxydiphenylmethane and their antibacterial action. E. KLARMANN, L. W. GATES, and V. A. SHTERNOV (J. Amer. Chem. Soc., 1932, 54, 3315—3328).—The following are prepared by *C*-benzylation of halogenophenols or by halogenation of hydroxydiphenylmethanes: 3-chloro-4-, b.p. 155—160°/5 mm.; 3-bromo-4-, b.p. 152—154°/3 mm.; 3-chloro-2-, b.p. 144°/4 mm.; 4'-chloro-4-, b.p. 175—177°/4 mm., m.p. 85.5°; 5-chloro-2-, b.p. 160—162°/3.5 mm., m.p. 48.5°; 5-bromo-2-, b.p. 189—192°/3.5 mm.; 4'-chloro-2-, b.p. 168—171°/4 mm., m.p. 61.5°; 3:4'-dichloro-4-, b.p. 160—164°/3 mm., m.p. 64°; 3-chloro-4'-bromo-4-, b.p. 182°/3 mm., m.p. 65°; 5-chloro-3-methyl-2-, b.p. 147—149°/4.5 mm., m.p. 55°; 4'-chloro-3-methyl-2-, b.p. 167—172°/4 mm., m.p. 48°; 5-chloro-4(6)-methyl-2-, b.p. 176—178°/4.5 mm.; 5-chloro-4:6-dimethyl-2-, b.p. 182—185°/4 mm., m.p. 68.5°; 4'-bromo-4:6-dimethyl-2-, b.p. 194—196°/4 mm., m.p. 101.5°, and 5-chloro-3-isopropyl-6-methyl-2-, b.p. 175°/3 mm., -hydroxydiphenylmethanes. All the above compounds are potent bactericides; some of them are extremely active towards *Staphylococcus aureus* and *Streptococcus haemolyticus*. Certain regularities in the relation be-

tween the antibacterial action and composition are found. Thus, halogen in the *p*-position to OH causes a greater antibacterial efficiency than when in the *o*-position. The 4'-chloro-2-hydroxy- is more effective than the 4'-chloro-4-hydroxy-derivative towards the above bacteria, but less effective against *E. typhi* and *E. paratyphenteriae*. The monobromo-derivatives of both the 2- and 4-OH derivatives are less effective than the corresponding Cl analogues towards *E. typhi* and *E. paratyphenteriae*, but more so against *S. aureus* and *S. haemolyticus*. The dihalogen derivatives are also highly bactericidal. The presence of 1 or 2 Me groups causes a considerable increase in germicidal potency towards the cocci only. Me and Pr² together reduce the bactericidal action on all 4 micro-organisms. The above substances appear to show a typically bactericidal rather than a bacteriostatic behaviour, when compared, e.g., with bacteriostatic dyes. The effect of EtOH used in the prep. of solutions employed in the bacteriological tests is studied. Concns. not germicidal *per se* impair the antibacterial action of the *o*-chloro-2-derivative; an explanation for this is suggested on the basis of an assumed shift of the partition equilibrium of the dissolved substance between the bacteria and the H₂O-EtOH phase. The effect of using dil. alkali in the prep. of the solutions on their germicidal action is also studied. C. J. W. (b)

Thiophenols. Action of benzhydrol, triphenylcarbinol, and the corresponding chlorides. C. FINZI and V. BELLAVITA (Gazzetta, 1932, 62, 699—709).—Thiophenols combine with CHPh₂·OH or CPh₂·OH in H₂SO₄, or with CHPh₂Cl or CPh₂Cl in acid, alkali, or pyridine, to products in which primary substitution in each case is in the SH group. The following are described: *Ph* CHPh₂ sulphide, m.p. 78°; *S*: *p*-bis(diphenylmethyl)thiophenol, m.p. 121° (using CHPh₂·OH with hot H₂SO₄, or AlCl₃; α - and β -naphthyl CHPh₂ sulphides, m.p. 77.5° and 123°, respectively; *S*: 4-bis(diphenylmethyl- α -thionaphthol, m.p. 148°; *Ph* CPh₂ sulphide, m.p. 106°; α - and β -naphthyl CPh₂ sulphides, m.p. 121° and 134°, respectively; *S*: 1-bis(triphenylmethyl- β -thionaphthol, m.p. 82°; *o*- and *p*-tolyl CPh₂ sulphides, m.p. 145° and 147°, respectively; 2:4-dinitrophenyl CPh₂ sulphide, m.p. 190° (from 4-chloro-*m*-dinitrobenzene and CPh₂·SH or from 2:4-dinitrothiophenol and CPh₂Cl); 2:4:2':4'-tetramethylthioltriphenylcarbinol, m.p. 141° [from *m*-C₆H₄(SMe)₂, CPh₂Cl, and AlCl₃], and 2:4-dimethylthioltriphenylcarbinol, m.p. 144—145° [from *m*-C₆H₄(SMe)₂, CPh₂Cl, and AlCl₃]. E. W. W.

Constitution of tribromoguaiacol. A. ZANGIROLAMI (Gazzetta, 1932, 62, 570—575).—Tribromoguaiacol, m.p. 117° (cf. A., 1893, i, 313), must be the 4:5:6-compound, since it is obtainable from 6-bromoguaiacol (J.C.S., 1908, 93, 792) and Br. It is also apparently obtained when 6-bromo-5-nitroguaiacol (J.C.S., 1917, 111, 917) is reduced to 6-bromo-*o*-aminoguaiacol (hydrochloride, decomp. 230°; sulphate, decomp. 200°), diazotised, treated with KBr, and the mixed product brominated. E. W. W.

Decomposition of acyl derivatives of 3:5:3':5'-tetranitro-2:2'-dihydroxydiphenyl into 1:3:6:8-tetranitrodiphenylene oxide and an acid anhydride. J. VAN ALPHEN (Rec. trav.

chim., 1932, 51, 715—725).—The following diacyl derivatives of 3:5:3':5'-tetranitro-2:2'-dihydroxydiphenyl are decomposed by heating alone or in PhNO₂ to the corresponding acid anhydride and 1:3:6:8-tetranitrodiphenylene oxide (I) (cf. this vol., 267): *dipropionate*, m.p. 139°; *diisobutyrate*, m.p. 133°; *di-p-chlorobenzoate*, m.p. 233°; *di-p-bromobenzoate*, m.p. 204°; *di-p-anisate*, m.p. 199°; *di-m-ethoxybenzoate*, m.p. 118°; *di-p-ethoxybenzoate*, m.p. 188° (impure); *di(phenylacetate)*, m.p. 174.5°; *phthalate*, m.p. > 200° (indef.; decomp.), and *di-p-nitrobenzoate*, m.p. 221°. The action of *p*-toluenesulphonyl chloride on the diphenol in aq. NaOH at 95—100°, or on its K salt in COMe₂ at the b.p. gave (I) unaccompanied by any acyl derivative; ClCO₂Et and the K salt at 100° gave a similar result. (I) was not formed, however, by the action of conc. H₂SO₄ at 140° or of 7% oleum at 15° on the diphenol. 3:5:3':5'-Tetrabromo-2:2'-diacetoxydiphenyl, m.p. 118°, is stable at 250° and at higher temp. decomposes without formation of the corresponding diphenylene oxide. No other formation was observed on heating 2:2'-diacetoxydiphenyl, its 5:5'-(NO₂)₂-derivative, m.p. 204°, 3:5:3':5'-tetranitro-4:4'-diacetoxydiphenyl, or 2:4-dinitro- or 2:4:6-trinitro-phenyl acetates. H. A. P.

Configurative relationships of phenylmethyl-, cyclohexylmethyl-, and methylhexyl-carbinols and of their homologues. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1932, 97, 379—391).—Previous conclusions (A., 1930, 1178) are in part confirmed and in part corrected. Freudenberg's rule is not universally true. The contribution of the cyclohexyl group has an opposite direction of rotation from that of the hexyl group when the members of the two series are configuratively related. The following substances were prepared, mainly by the Grignard (A) or malonic ester (B) syntheses: *cyclohexylmethylcarbinol* (A), resolved by the strychnine salt, $[\alpha]_D^{20} +48.6^\circ$ in abs. EtOH, of the *H* phthalate, gives the *d*-carbinol, b.p. 105°/35 mm., $[\alpha]_D^{20} +5.11^\circ$; *cyclohexyl-n-propylcarbinol* (A), resolved by the strychnine salt, $[\alpha]_D^{20} -1.55^\circ$ in abs. EtOH, of the *H* phthalate, gives the *l*-carbinol, b.p. 127°/25 mm., $[\alpha]_D^{20} -17.03^\circ$; *cyclohexylethylcarbinol* (A), resolved by the strychnine salt, $[\alpha]_D^{20} +13.3^\circ$ in abs. EtOH, of the *H* phthalate, gives the *l*-carbinol, b.p. 106°/19 mm., $[\alpha]_D^{20} -8.09^\circ$; *cyclohexyl-n-butylcarbinol* (A), resolved by the strychnine salt, $[\alpha]_D^{20} -2.06^\circ$ in abs. EtOH, of the *H* phthalate, gives the *l*-carbinol, b.p. 135°/25 mm., $[\alpha]_D^{20} -12.87^\circ$; CHPhPr·OH, resolved similarly, gives the *l*-carbinol, b.p. 120°/15 mm., $[\alpha]_D^{20} -23.3^\circ$ (homogeneous) and -35.8° in C₆H₆ [acetate, b.p. 134°/30 mm., $[\alpha]_D^{20} -55.1^\circ$ in C₆H₆ and -57.32° (homogeneous)]; the cinchonidine salt of *d*-phenyl-*n*-butylcarbinol *H* phthalate, $[\alpha]_D^{20} +11.5^\circ$ in Et₂O, gives the *d*-carbinol, b.p. 130°/15 mm., $[\alpha]_D^{20} +17.2^\circ$ (homogeneous) and $+31.3^\circ$ in C₆H₆; *l*- α -phenylethyl chloride, b.p. 90°/26 mm., $[\alpha]_D^{20} -16.9^\circ$ (from CHPhMe·OH and SOCl₂), yields (B) *d*- β -phenylbutyric acid, b.p. 134°/4 mm., $[\alpha]_D^{20} +2.85^\circ$; *d*- α -phenylpropyl chloride, b.p. 86°/14 mm., $[\alpha]_D^{20} +19.82^\circ$ (similarly prepared), yields (B) *d*- β -phenylvaleric acid, solid, b.p. 150°/6 mm., $[\alpha]_D^{20} +5.44^\circ$ in C₆H₆; *l*- α -phenyl-*n*-butyl chloride, b.p.

115°/30 mm., $[\alpha]_D^{25} -26.19^\circ$, yields (B) d- β -phenyl-n-hexoic acid, b.p. 155°/4 mm., $[\alpha]_D^{25} +7.95^\circ$; l- α -phenyl-n-amyl chloride, b.p. 120°/15 mm., $[\alpha]_D^{25} -24.62^\circ$; α -phenylethyl acetate, b.p. 120°/35 mm., $[\alpha]_D^{25} +26.8^\circ$ (homogeneous) and $+28.9^\circ$ in C_6H_6 ; d- α -phenylpropyl acetate, b.p. 130°/35 mm., $[\alpha]_D^{25} +53.7^\circ$ in C_6H_6 and $+55.34^\circ$ (homogeneous); l- α -phenyl-n-amyl acetate, b.p. 140°/20 mm., $[\alpha]_D^{25} -37.3^\circ$ in C_6H_6 and -37.9° (homogeneous). R. S. C.

Tautomerism of hydroxytriarylcarbinols. III. L. C. ANDERSON and M. B. GEIGER (J. Amer. Chem. Soc., 1932, 54, 3058—3064).—The effect of substitution is shown in the absorption spectra curves of the corresponding methane, coloured carbinol, and fuchsone of 3-chloro-, 3-bromo-, 3:5-dichloro-, and 3:5-dibromo-4-hydroxytriphenylcarbinols, together with the curves of the colourless carbinols of the last three compounds. F. S. (b)

Heteropolarity. XVI. Diphenyl-green dyes. W. DILTHEY, W. BRANDT, W. BRAUN, and W. SCHOMMER (J. pr. Chem., 1932, [ii], 134, 188—208).—A p-Ph substituent in the aldehyde component of malachite-green and similar dyes has a bathochromic influence on shade, apparently due to an absorption band not present in the visible spectrum of the parent type, the main band being altered but little in position. The dye salts ($RCIO_4$) are less stable to hydrolysis, and the halochromism in H_2SO_4 is abnormal. 4'-Aminophenyl-4-diphenylcarbinol, m.p. 189—190° (Ac_2 derivative, m.p. 157—158°), is prepared by reduction of the corresponding ketone with Zn and NaOH in MeOH. p-Dimethylaminophenyl 4-diphenyl ketone (I), m.p. 127—128° [picrate, m.p. 159—160° (decomp.); oxime, m.p. 225—230°], is prepared by interaction of p-dimethylaminobenzoyl chloride, Ph_2 , and $AlCl_3$ in $PhNO_2$. It is reduced as above to the corresponding carbinol, m.p. 139—141°. pp'-Tetramethyldiaminodiphenyl-4-diphenylcarbinol, m.p. 145°, is prepared by condensation of (I) with $NPhMe_2$ and $POCl_3$ or by oxidation of pp'-tetramethyldiaminodiphenyl-4-diphenylmethane (II), m.p. 191°, with PbO_2 and HCl. It is reduced to (II) by Zn and AcOH, and with acids gives diphenyl-green-A [perchlorate, m.p. 222° (decomp.); chloride]. (II) is prepared by interaction of diphenyl-4-aldehyde with $NPhMe_2$ and $POCl_3$ at 100°. The following methane bases are similarly prepared and oxidised to dyes. Bis-4-diethylaminophenyl-, dimorphic, m.p. 132°, 143—144° [carbinol base, m.p. 148°; diphenyl-green-B (perchlorate, m.p. 205°)], bis-4-benzylmethylaminophenyl-, m.p. 113° {diphenyl-green-C [perchlorate, m.p. 200° (decomp.)]}, and bis-4-benzylethylaminophenyl-4'-diphenylmethane, m.p. 97° {diphenyl-green-D [perchlorate, m.p. 210° (decomp.)]}. H. A. P.

Manufacture of alkamines of the type $Ar\cdot CH(OH)\cdot CHR\cdot NR'R''$. I. G. FARBENIND. A.-G.—See B., 1932, 792.

Chemical structure and optical rotation. III. Configurative relationship of disubstituted propionic acids containing a cyclohexyl group. Correction of previous work. P. A. LEVENE and R. A. MARKER (J. Biol. Chem., 1932, 97, 563—583; cf. A., 1931, 1413).—The sign of $[\alpha]$ given previously

(loc. cit.) for γ -phenylhexoic acid (A) and the substances prepared from it should be changed from — to +. The levorotation of γ -phenylhexane, obtained by reduction of the bromide prepared from (A), is due to partial unsaturation; the hydrocarbon is dextrorotatory after catalytic reduction (colloidal Pd). Other hydrocarbons, similarly prepared, are, however, saturated. These corrections lead to the conclusion that all β -phenyl- β -alkylpropionic acids rotate in the same direction (contrast loc. cit.). Reduction of β -phenylbutyric acid, but not of the homologues, to the cyclohexyl compound results in a change of direction of rotation; all the carbinols, halides, and hydrocarbons of the cyclohexyl series rotate in the opposite direction to the corresponding phenyl compounds. Unless otherwise stated, reductions reported below were carried out by H_2 and PtO_2 in AcOH. Reduction of β -phenylbutyric acid gives l- β -cyclohexylbutyric acid (I), b.p. 145°/4 mm., $[\alpha]_D^{25} -0.26^\circ$; β -phenylbutyl alcohol gives d- β -cyclohexylbutyl alcohol, b.p. 128°/15 mm., $[\alpha]_D^{25} +2.71^\circ$, which with PBr_3 yields the d-bromide, b.p. 126°/15 mm., $[\alpha]_D^{25} +5.20^\circ$. d- β -Phenylbutane (II), $[\alpha]_D^{25} -6.82^\circ$, gives d- β -cyclohexylbutane, b.p. 174°, $[\alpha]_D^{25} +0.79^\circ$. Crystallisation of the quinine salt of the dl-acid obtained from α -cyclohexylethyl bromide and Et_2 malonate gives (I), having $[\alpha]_D^{25} -0.75^\circ$, the Et ester, b.p. 104°/3 mm., $[\alpha]_D^{25} -1.44^\circ$, of which with Na and EtOH gives l- β -cyclohexylbutyl alcohol, b.p. 128°/15 mm., $[\alpha]_D^{25} -2.69^\circ$; this with PBr_3 gives the corresponding bromide, b.p. 135°/15 mm., $[\alpha]_D^{25} -6.6^\circ$, which by Grignard reactions affords d- β -cyclohexylbutane, b.p. 174°, $[\alpha]_D^{25} +0.45^\circ$, and l- γ -cyclohexylvaleric acid, b.p. 149°/3 mm., $[\alpha]_D^{25} -2.17^\circ$. The Et ester, b.p. 133°/7 mm., $[\alpha]_D^{25} -2.14^\circ$, of this with Na and EtOH gives l- δ -cyclohexyl-n-amyl alcohol, b.p. 134°/15 mm., $[\alpha]_D^{25} -2.98^\circ$, giving with PBr_3 the bromide, b.p. 146°/16 mm., $[\alpha]_D^{25} -6.56^\circ$, whence (Grignard) l- β -cyclohexylpentane, b.p. 88°/15 mm., $[\alpha]_D^{25} -0.81^\circ$, was obtained. β -Phenylhexane, $[\alpha]_D^{25} +1.96^\circ$, gives l- β -cyclohexylhexane, b.p. 101°/18 mm., $[\alpha]_D^{25} -0.90^\circ$. β -Phenylvaleric acid, $[\alpha]_D^{25} -14.2^\circ$ in C_6H_6 , gives l- β -cyclohexylvaleric acid (III), b.p. 153°/5 mm., $[\alpha]_D^{25} -1.53^\circ$. γ -Phenyl-n-amyl alcohol, $[\alpha]_D^{25} -4.54^\circ$, gives d- γ -cyclohexyl-n-amyl alcohol (IV), b.p. 135°/15 mm., $[\alpha]_D^{25} +2.22^\circ$, yielding with PBr_3 the bromide, b.p. 135°/15 mm., $[\alpha]_D^{25} +2.76^\circ$. γ -Phenylhexane, $[M]_D^{25} +0.92^\circ$, gives d- γ -cyclohexylhexane (V), b.p. 111°/28 mm., $[\alpha]_D^{25} -0.89^\circ$. γ -Phenylheptane, $[\alpha]_D^{25} +0.97^\circ$, gives l- γ -cyclohexylheptane, b.p. 112°/15 mm., $[\alpha]_D^{25} -0.68^\circ$. α -Phenylpropyl bromide and Et_2 malonate give dl- β -cyclohexylvaleric acid, resolved by the quinine salt into (III), b.p. 148°/4 mm., $[\alpha]_D^{25} -1.38^\circ$, the Et ester, b.p. 118°/6 mm., $[\alpha]_D^{25} -0.82^\circ$, of which with Na and EtOH yields (IV), b.p. 119°/5 mm., $[\alpha]_D^{25} 2.00^\circ$. β -Phenylhexoic acid, $[\alpha]_D^{25} -2.48^\circ$, gives l- β -cyclohexylhexoic acid (VI), b.p. 155°/4 mm., $[\alpha]_D^{25} -0.39^\circ$. γ -Phenylhexan- α -ol, $[\alpha]_D^{25} +2.51^\circ$, gives l- γ -cyclohexylhexan- α -ol, b.p. 141°/15 mm., $[\alpha]_D^{25} -0.19^\circ$, yielding with PBr_3 the bromide, b.p. 145°/15 mm., $[\alpha]_D^{25} -0.62^\circ$. δ -Phenyl-octane, $[M]_D^{25} +1.18^\circ$, gives δ -cyclohexyloctane, b.p. 123°/15 mm., $[\alpha]_D^{25} -0.29^\circ$. α -cyclohexylbutyl bromide and Et_2 malonate give dl- β -cyclohexylhexoic acid, resolved with difficulty by the quinine salt to (VI), $[\alpha]_D^{25} +2.04^\circ$, the

Et ester, b.p. 126°/4 mm., $[\alpha]_D^{25} +1.54^\circ$, of which led to *d*- γ -cyclohexan- α -ol, b.p. 127°/4 mm., $[\alpha]_D^{25} -0.79^\circ$, the corresponding *bromide*, b.p. 145°/15 mm., $[\alpha]_D^{25} -1.38^\circ$, and (V), $[\alpha]_D^{25} +0.57^\circ$. *d*- β -Phenylheptioic acid (VII), $[M]_D^{25} +47.6^\circ$, gives *d*- β -cyclohexylheptioic acid, b.p. 155°/2 mm., $[\alpha]_D^{25} +4.6^\circ$. α -Phenylpropyl chloride, $[M]_D^{25} +30.62^\circ$, and $MgMeI$ give (II), b.p. 63°/15 mm., $[\alpha]_D^{25} +1.18^\circ$. α -Phenyl-*n*-amyl chloride, $[M]_D^{25} -45.06^\circ$, and Et_2 malonate give (VII), b.p. 165°/4 mm., $[\alpha]_D^{25} +8.00^\circ$, the *Et* ester, b.p. 128°/2 mm., $[\alpha]_D^{25} -2.98^\circ$, of the *l*-isomeride of which led to *l*- γ -phenylheptan- α -ol, b.p. 150°/10 mm., $[\alpha]_D^{25} -1.45^\circ$, the corresponding *bromide*, b.p. 132°/4 mm., $[\alpha]_D^{25} -10.4^\circ$, *d*- γ -phenylheptane, b.p. 112°/15 mm., $[\alpha]_D^{25} +0.75^\circ$, and *l*- γ -cyclohexylheptane, b.p. 112°/15 mm., $[\alpha]_D^{25} -0.54^\circ$. R. S. C.

***o*-Chlorobenzoic acid by the action of chlorine on saccharin.** P. BERTOLO and A. BERTOLO (*Gazzetta*, 1932, 62, 487—493).—Saccharin is oxidised by $KClO_3$ and dil. HCl (1 in 4) at the b.p. to *o*-chlorobenzoic acid, free from *m*- and *p*-isomerides.

E. W. W.

Absorption in ultra-violet and chemical reactivity of organic compounds. (MME.) RAMART-LUCAS and J. HOCH (*Bull. Soc. chim.*, 1932, [iv], 51, 824—838).—A detailed description of work already published (cf. this vol., 211). In the series $Ph \cdot [CH_2]_n \cdot CO_2H$ the effect of *o*-Me groups (mesityl in place of *Ph*) is to diminish the mutual effect of the chromophores. γ -Mesitylpropyl bromide (I), b.p. 163°/20 mm. [prepared by the route $C_6H_2Me_3 \cdot [CH_2]_2 \cdot CO_2H \rightarrow \cdot COCl \rightarrow \cdot CO \cdot NH_2 \rightarrow \cdot CH_2 \cdot OH$ (Na and $EtOH$) $\rightarrow \cdot CH_2Br$ (PBr_3)], is converted by KCN into γ -mesitylbutyronitrile, b.p. 177°/18 mm., which on alkaline hydrolysis gives the corresponding acid, m.p. 87°. δ -Mesityl-*n*-valeric acid, m.p. 64°, b.p. 213°/18 mm. (amide, m.p. 131°), is prepared by condensation of (I) with $CHNa(CO_2Et)_2$, hydrolysis of the resulting $Et_2\gamma$ -mesitylpropylmalonate, b.p. 222°/18 mm., with KOH in $EtOH$, and decarboxylation of the resulting acid, m.p. 140°, by heat. Reduction of δ -mesitylvaleramide with Na and abs. $EtOH$ gives ϵ -mesitylpentan- α -ol, b.p. 183—184°/16 mm. (phenylurethane, m.p. 97°), the corresponding bromide, b.p. 185°/18 mm., of which is converted by KCN and subsequent hydrolysis into ϵ -mesityl-*n*-hexoic acid, m.p. 70°. Interaction of α -dibromodecane in excess with $NaOPh$ gives mainly α -*diphenoxydecane*, m.p. 85°, and a little α -bromo- κ -phenoxydecane, b.p. 230—245°/35 mm., converted by the malonate synthesis into λ -phenoxylauric acid, m.p. 81°. The action of $AlCl_3$ on phenoxyacetyl chloride in C_6H_6 gives, in addition to coumarone (15% of theory), ω -phenoxyacetophenone, b.p. 210—215°/15 mm.; the yield of coumarone is not increased by carrying out the reaction in CS_2 . H. A. P.

Nuclei of *cis*-cinnamic acid. II. A. W. K. DE JONG (*Rec. trav. chim.*, 1932, 51, 695—698; cf. this vol., 612).—Crystal nucleus formation in liquid *cis*-cinnamic acid is favoured by light and by the *trans*-acid; the cryst. forms that separate depend to some extent on the temp. Light petroleum (b.p. 40—50°) and H_2O have little or no effect. H. A. P.

New choladienic acid. V. DEULOFEU (*Z. physiol. Chem.*, 1932, 210, 30—32).—Catalytic hydro-

genation (PtO_2) of 7:12-diketocholanic acid at 60° gives 7:12-dihydroxycholanic acid, m.p. 206—208°. The latter, on distillation in vac., affords ϵ -choladienic acid, m.p. 184—185°, which on catalytic hydrogenation takes up $2H_2$, yielding cholanic acid.

J. H. B.

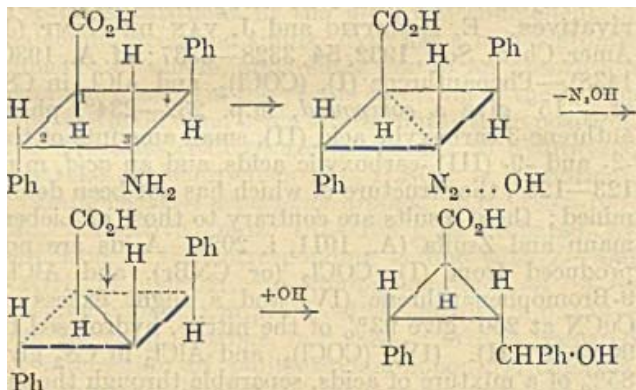
Bromination of dehydrodeoxycholic acid and of dehydrocholic acid. II. T. NOGUCHI (*Z. physiol. Chem.*, 1932, 209, 249—252; cf. A., 1931, 1293).—Hydrolysis of monobromodehydrodeoxycholic acid (I) with dil. aq. KOH gives 2-hydroxydehydrodeoxycholic acid (II), m.p. 197° (decomp.) (Ac derivative, m.p. 235°). Oxidation of (II) with CrO_3 in $AcOH$ opens the ring between C_2 and C_3 giving deoxybilanic acid. Hence the Br in (I) is attached at C_2 of ring I. Similarly CrO_3 oxidation of 2-hydroxydehydrocholic acid gives bilanic acid, indicating a similar position for Br in monobromodehydrocholic acid. J. H. B.

Phenanthrene series. II. Phenanthrene-carboxylic acids and 9-bromophenanthrene derivatives. E. MOSETTIG and J. VAN DE KAMP (*J. Amer. Chem. Soc.*, 1932, 54, 3328—3337; cf. A., 1930, 1438).—Phenanthrene (I), $(COCl)_2$, and $AlCl_3$ in CS_2 at -15° give a compound, m.p. 232—234°, phenanthrene-3-carboxylic acid (II), small amounts of the -2- and -9- (III) -carboxylic acids, and an acid, m.p. 123—125°, the structure of which has not been determined; these results are contrary to those of Liebermann and Zsuffa (A., 1911, i, 202). Acids are not produced from (I), $COCl_2$ (or $CNBr$), and $AlCl_3$. 9-Bromophenanthrene (IV) and a slight excess of $CuCN$ at 260° give 93% of the nitrile, hydrolysed to 90% of (III). (IV), $(COCl)_2$, and $AlCl_3$ in CS_2 give 85% of a mixture of acids, separable through the Me esters; 9-bromophenanthrene-3(or 6)-carboxylic acid (V), m.p. 283—284° (Me ester, m.p. 155—155.5°, oxidised to Me phenanthraquinone-3-carboxylate), and at least two other acids are formed. Debromination of the Me ester by H (Pd) gives the Me ester of (II). (IV), $AcCl$, and $AlCl_3$ give 70% of 9-bromo-3(or 6)-acetylphenanthrene, m.p. 150—151° (semicarbazone, m.p. 265—265.5°; oxime, m.p. 142.5—143°), oxidised ($NaOCl$) to (V). C. J. W. (b)

Retene. II. α -Retenecarboxylic acid and its derivatives. M. T. BOGERT and T. HASSELSTROM (*Proc. Nat. Acad. Sci.*, 1932, 18, 417—421).—Acetylretene (A., 1931, 1297) and alkaline $NaOBr$ in $MeOH$ give the (α)-retenecarboxylic acid (I), m.p. 237.5—238.5° (all m.p. are corr.) (anilide, m.p. 224.5—225.5°), of Komppa and Wahlforss (*ibid.*, 226), which is oxidised by CrO_3 - $AcOH$ to α -retenequinonecarboxylic acid, decomp. above 252° (lit. m.p. 237—240°) [quinoxaline, decomp. above 272°, from o - $C_6H_4(NH_2)_2$; Me ester, m.p. 197.5—198.5° (quinoxaline, m.p. 187—188.5°)], and reduced (as Na salt) by Na and isoamyl alcohol to α -octahydroretenecarboxylic acid, m.p. 181—182°, the alkali salts of which behave as true resins. An amorphous compound, hydrolysed by aq. Na_2CO_3 to the Na salt of (I), is also formed during the prep. of (I) by Komppa and Wahlforss' method (*loc. cit.*). H. B.

Theory of ring-contraction and related rearrangements. F. SCHENCK (*J. pr. Chem.*, 1932,

[ii], 134, 215—248).—The hypothesis tentatively advanced (A., 1928, 174) in explanation of the conversion of the stereoisomeric truxillamic and truxinamic acids (cf. this vol., 158, 159) by NOBr or HNO₂ into corresponding forms of 2-phenyl-3-hydroxybenzylcyclopropane-1-carboxylic acid (I) is inadequate; thus, it should lead to the same intermediate form in the case of both α - and γ -truxillic acids, whereas actually different end-products are obtained. It is now suggested that the conversion of $\cdot\text{NH}_2$ into $\cdot\text{N}_2\cdot\text{OH}$ lessens the attraction of C for N, and that the resulting partial-valency adjustments lead successively to a strengthening of the 2:3- and 2:4-linkings and weakening of the 1:2- and 1:4-linkings, compensated by a partial-valency linking between the 1:3-positions. Elimination of N₂ then leads to formation of the cyclopropane ring by fission of the 1:2- or 1:4-linking, the $\text{CHPh}\cdot\text{OH}$ groups thus formed taking the place of the original NH₂ group. In the truxillic series fission takes place in both directions, but in the truxinic series it occurs between the Ph



groups only. The hypothesis is generally applicable to rearrangements involving the migration of hydrocarbon radicals, and explanations of the retropinacolin, pinacone-pinacolin, semipinacolin, and benzil-benzilic acid transformations are given.

The three remaining isomerides of (I) demanded by theory are isolated by reduction of the Me esters of the 3-benzoyl-2-phenylcyclopropane-1-carboxylic acids (for brevity the former are referred to as "oxy-acids," and the latter as "ketonic acids"; for numeration cf. A., 1928, 174 *et seq.*) with $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH . Reduction of ketonic acid I Me ester gives the lactone, m.p. 168—169°, of oxy-acid Ib, m.p. 171—172° (decomp.) [Me ester, m.p. 171—172° (CH_2N_2)], and a small amount of the Pr^i ester of oxy-acid IVa. Oxy-acid Ib is isomerised to IIIb by fusion with KOH, and to the lactone of Ia by 15% HCl at room temp. Ketonic acid II gives OH-acids IIa and IIb as lactones, the latter in preponderating amount. From ketonic acid III the Pr^i ester, m.p. 125.5—126.5°, of oxy-acid IIIb (2^l-phenyl-3^l-hydroxybenzylcyclopropane-1^c-carboxylic acid), m.p. 188—189° (Me ester, m.p. 104—105°), alone is obtained; it does not give any appreciable amount of lactone with Ac_2O at 100°. Reduction of the Me ester of ketonic acid IV, and hydrolysis of the product gives a mixture of oxy-acids IVa and IVb (2^c-phenyl-3^l-hydroxybenzylcyclopropane-1^c-carboxylic acid) [oxy-acid IVa, m.p. 152—153° (Me ester, m.p. 125—126°;

Pr^i ester, m.p. 125—126°); oxy-acid IVb, m.p. 151—152° (Me ester, m.p. 82—83°)]; on reoxidation both give the original ketonic acid. The relative configurations of Ph and CO₂H in the new isomerides are confirmed by ring-fission with $\text{AcOH}-\text{H}_2\text{SO}_4$, which gives the stereoisomeric forms of α -(acetoxymethyl)- β -benzylidenepropionic acid (Pr^i ester of acid, m.p. 151.5—152.5°, has m.p. 109—110°). H. A. P.

Substitution products of *o*- α -naphthoylbenzoic acid. E. H. JOHNSON, V. WEINMAYR, and R. ADAMS (J. Amer. Chem. Soc., 1932, 54, 3289—3295).—*o*- α -Naphthoylbenzoic acid (I) and Br in boiling AcOH give 69.5% of *o*-5'-bromo-1'-naphthoylbenzoic acid (II), m.p. 203—204°; the 5'-Cl-derivative (III) has m.p. 179—180° (94.4% yield). Bromination of (I) in presence of a trace of FeCl_3 and Fe at room temp. gives 57.3% of the 5':8'-Br₂-derivative (IV), m.p. 260—261°, also formed by brominating in 93% H_2SO_4 at 50° or by further bromination of (II); the 5':8'-Cl₂-derivative (V) has m.p. 242°. Fusion of (II) with alkali affords 5-hydroxy- α -naphthoic acid. (II) and conc. H_2SO_4 at 115—117° give Bz-4-bromo-1:2-benzanthraquinone, m.p. 231—232° (oxidised to anthraquinone-1:2-dicarboxylic acid); (IV) similarly affords the 1:4-Br₂-derivative, m.p. 265—266°, whilst (III) and (V) give the 4-Cl-, m.p. 232°, and the Cl₂-derivative, two forms, m.p. 267—268° and 304°, respectively. (II) and HNO_3 in H_2SO_4 give the 8'-NO₂-derivative, m.p. 228—230°; reduction (catalytic or with Fe and acid) gives a light brown amorphous product characteristic of 8-amino-1-ketonaphthalene. (III) gives an 8'-NO₂-derivative, m.p. 233—234°. (II) and conc. HNO_3 in Ac_2O give 32% of *o*-5':8'-dinitro-1'-naphthoylbenzoic acid, m.p. 262—263° (decomp.). C. J. W. (b)

Preparation of amines from carboxylic acids by means of azoimide. M. OESTERLIN (Angew. Chem., 1932, 45, 536—537).—*p*-Methoxyhydrocinamic acid reacts readily with N_3H in presence of conc. H_2SO_4 , the 2:4-dimethoxy-compound reacts but slightly, and the trimethoxy- not at all. With benzoic, phenylacetic, and hydrocinnamic acids, 85%, 75%, and 70% yields of the corresponding amines are obtained. *o*-, *m*-, and *p*-Nitrobenzoic acids react readily, but with *o*- and *p*-aminobenzoic acids only traces of the diamines are formed. Phthalic acid yields only anthranilic acid. With aliphatic dicarboxylic acids the yield of amine depends on the distance between the two CO₂H groups; adipic acid yields 80% of putrescine and succinic acid only 8% of $\text{C}_2\text{H}_4(\text{NH}_2)_2$, whilst $\text{CH}_2(\text{CO}_2\text{H})_2$ and its aromatic derivatives do not react. Lævulic acid reacts explosively, yielding NH_2Me . NH₂-acids cannot be further aminated with N_3H , and heterocyclic acids such as the pyridine- and quinoline-carboxylic acids do not react. With cinnamic acid styrylamine is most probably formed, but it decomposes immediately into phenylacetaldehyde and NH_3 ; a considerable quantity of NH_2Ph is formed also.

H. F. G.

Synthesis of depsides. T. CURRIE and A. RUSSELL (J.C.S., 1932, 2263—2265).—Excellent yields of depsides are readily obtained by condensing

an acid chloride with the Na salt of a hydroxy-aldehyde in COMe_2 and oxidation of the resulting aldehyde by KMnO_4 in aq. MeOH. The name *p*-dibenzoic acid is assigned to *p*-benzoyloxybenzoic acid. The following compounds were thus prepared: 3:3':4'-trimethoxy-*p*-, m.p. 124°, 3':4'-dimethoxy-*o*-, m.p. 102°, -*m*-, m.p. 120°, and -*p*-, m.p. 109°, 4'-methoxy-*o*-, m.p. 85°, -*m*-, m.p. 102°, and -*p*-, m.p. 113°, and 3:4'-dimethoxy-*p*-benzoyloxybenzaldehyde, m.p. 136°; 3:3':4'-trimethoxy-*p*- (II), m.p. 216—218°, 3':4'-dimethoxy-*o*-, m.p. 152°, -*m*-, m.p. 167°, and -*p*-, m.p. 211—212°, 4'-methoxy-*o*-, m.p. 132°, -*m*-, m.p. 196°, and -*p*-, m.p. 212°, and 3':4'-dimethoxy-*p*-benzoyloxybenzoic acid, m.p. 171°. The acid chloride of (II) has m.p. 129°. R. S. C.

Condensation of certain γ -ketonic esters with aromatic aldehydes. C. F. H. ALLEN and G. F. FRAME (Canad. J. Res., 1932, 6, 605—613).—The preps. of benzylidene-*p*-chloro-, -*p*-bromo-, and -*p*-methoxy-acetophenone are modified. KCN, AcOH, and the appropriate ketone in EtOH at 35° give γ -keto- α -phenyl- γ -*p*-bromo-, m.p. 124°, and -*p*-methoxy-phenylbutyronitrile, m.p. 62° (*Me* esters, m.p. 129° and 97°, respectively); the *Et* ester of the corresponding *p*-Cl-compound has m.p. 63°. These esters, the appropriate aldehyde, and NaOMe (not piperidine or NPhEt_2) in hot MeOH yield the following lactols

(A), $\text{O} \cdot \text{CR}'(\text{OH}) \gg \text{C} \cdot \text{CH}_2\text{R}$, of substituted γ -keto- α -*diphenyl- β -benzyl- Δ^a -butenoic acid*: $\text{R} = \text{Ph}$, and $\text{R}' = \text{p-C}_6\text{H}_4\text{Cl}$ (I), m.p. 134°, $\text{p-C}_6\text{H}_4\text{Br}$, m.p. 155°, and p-anisyl , m.p. 119°; $\text{R} = \text{piperonyl}$, and $\text{R}' = \text{p-C}_6\text{H}_4\text{Cl}$ (II), m.p. 174°, $\text{p-C}_6\text{H}_4\text{Br}$, m.p. 171°, and p-anisyl , m.p. 162°. (A) are insol. in NaHCO_3 , sol. in cold, aq. NaOH (pptd. unchanged by acids), unchanged by O_3 or dissolution in conc. H_2SO_4 , do not give aromatic acyl derivatives or phenylurethanes, react with 3 mols. of MgMeI to evolve 1 mol. of CH_4 , and are oxidised by KMnO_4 to the substituted benzoic acids, whilst with CrO_3 in AcOH 1:2-diketones are also formed, of which the following are new (m.p. in parentheses being those of the quinoxaline derivatives): *p-chloro*-, m.p. 103° (m.p. 132°), *p-bromophenyl*-, m.p. 122° (m.p. 143°), and *p-anisyl benzyl* 1:2-diketone, m.p. 96° (m.p. 138°); *p-chlorophenyl piperonyl* 1:2-diketone, m.p. 161.5 (decomp.) (m.p. 161°). (I) with SOCl_2 or AcCl gives γ -chloro- α -phenyl- γ -*p*-chlorophenyl- β -benzyl- Δ^a - γ -butenolactone (III), m.p. 137°; the corresponding *p-bromophenyl* compound (IV) has m.p. 132°. (III) with AgOAc gives the γ -aceto-compound, m.p. 157° [hydrolysed to (I) by conc. aq. NH_3 at 30°], also formed from (I), Ac_2O , and a trace of H_2SO_4 , and with MeOH gives the γ -OMe-compound, cryst., rapidly hydrolysed by hot KOH -MeOH to the *K* salt of the acid (V) corresponding with (I). (IV) yields similarly the corresponding γ -OMe-compound, m.p. 75°. The *Ag* salt of (V) and MeI in dry Et_2O give the *Me* ester, m.p. 87°, hydrolysed to (I) by hot KOH -MeOH. The constitution of (A) is proved by the above reactions, but the open-chain form also exists, as (I) forms an oxime, m.p. 160°. (A) is presumed to be formed by elimination of H_2O from the aldehyde and the β - CH_2 group of the keto-ester, followed by

migration of the ethylenic linking, thus indicating that in arylated γ -keto-esters the CO group confers greater mobility on the α -H atom than does the CO_2Me group. The stability of the lactol is considered to be due to the branching of the chain.

R. S. C.

Friedel-Crafts reaction with phenolic acids. P. C. MITTER and H. C. RAY (J. Indian Chem. Soc., 1932, 9, 247—250).—*Me* salicylate, $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ (I), and AlCl_3 in $\text{s-C}_2\text{H}_5\text{Cl}$ give *o*-4'-hydroxy-3'-carboxybenzoylbenzoic (4-hydroxybenzophenone-3:2'-dicarboxylic acid, m.p. 248° [*Me*₂ ester, m.p. 130—131°; *Me* ether (II), m.p. 232° (*Me*₂ ester, m.p. 105—106°)], identical with the phthalylsalicylic acid of Limpricht (A., 1899, i, 292) and reduced by Zn dust and AcOH—conc. HCl to α -*p*-hydroxyphenylphthalide-3'-carboxylic acid, m.p. 211—212° [*Me* ether, m.p. 164°, prepared by similar reduction of (II)]. *Me* *o*-cresotate and (I) similarly give 4-hydroxy-5-methylbenzophenone-3:2'-dicarboxylic acid, m.p. 258—261° (decomp.) [*Me*₂ ester, m.p. 103—104°; *Me* ether, m.p. 197—198° (*Me*₂ ester, m.p. 90°)], reduced to α -4'-hydroxy-5'-methylphenylphthalide-3'-carboxylic acid, m.p. 204—205° (*Me* ester, m.p. 114—115°; *Me* ether, m.p. 160°). *Me* *p*-cresotate and *m*- and *p*-OH- $\text{C}_6\text{H}_4\text{CO}_2\text{Me}$ do not react with (I) under the above conditions. H. B.

Displacement of atoms and groups in the naphthalene nucleus. J. G. KERKHOFF (Rec. trav. chim., 1932, 51, 739—754).—The displacement of substituents in the C_{10}H_8 series follows the rules postulated by Blanksma (A., 1902, i, 600, 715; 1904, i, 565) for the C_6H_5 series, e.g., OH, NH_2 , and alkyl groups promote replacement in the *o*- and *p*-positions. The ready replacement of groups in the α - but not β -positions may then be regarded as due to the behaviour of the fused ring as an *o*-substituent to the former. These principles are illustrated by the bromination and nitration of 1-hydroxy-4-naphthaldehyde (I), and the α - and β -naphthoic acids and 1- and 2- $\text{C}_{10}\text{H}_7\text{SO}_3\text{H}$.

Bromination of (I) [azine (+6 H_2O), m.p. 225—235°; *p*-nitrophenylhydrazone, m.p. 238—239 (decomp.); semicarbazone, m.p. 225°; semioxamazone, m.p. 268° (decomp.)] in AcOH gives the 2-*Br*-derivative (II), m.p. 144° [azine, m.p. 246° (decomp.); phenylhydrazone, m.p. 122° (decomp.); *p*-nitrophenylhydrazone, m.p. 218—219° (decomp.); semicarbazone, decomp. 219—222° (no m.p.); semioxamazone, m.p. 247—248°]; further bromination gives 2:4-dibromo- α -naphthol. Nitration (HNO_3 , *d* 1.4, in AcOH) of (I) or (II) gives 2:4-dinitro- α -naphthol only. α -Naphthoic acid gives the 5-*Br*-derivative without loss of CO_2 ; nitration of this, however, gives an indefinite product, m.p. 140—145°, from which the CO_2H group has been completely eliminated. Bromination of 1- $\text{C}_{10}\text{H}_7\text{SO}_3\text{H}$ in H_2O results in partial replacement of the 1- SO_3H group with formation of 1:6- $\text{C}_{10}\text{H}_6\text{Br}_2$ (?) (about 33%); nitration, similarly, gives 1:8-dinitro- or 1:3:8-trinitro-naphthalene according to conditions, and nitronaphthalenesulphonic acids. Little or no loss of SO_3H was observed in the nitration or bromination of 2- $\text{C}_{10}\text{H}_7\text{SO}_3\text{H}$. Nitration of 1- $\text{C}_{10}\text{H}_7\text{Br}$ occurred without replacement of Br and gave the 4:5-, m.p. 174°, and 4:8-(NO_2)₂-derivatives. The

literature m.p. of 4 : 5-dinitro- α -naphthylamine (245°) (Ac derivative, 245°) and α -naphthylmethylamine (259°) are confirmed (cf. A., 1902, i, 753). 4 : 8-Dinitro- α -naphthylmethylamine, m.p. 145°, is similarly prepared. H. A. P.

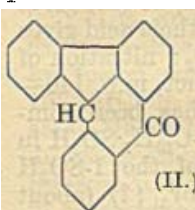
Hydrolysis of lignin with 12% hydrochloric acid. M. PHILLIPS and M. J. GOSS (J. Amer. Chem. Soc., 1932, 54, 3374—3377).—Lignin is isolated from maize cobs, oat hulls, and spruce wood by the method of Willstatter and Zechmeister (A., 1913, i, 955), by the EtOH and aq. NaOH methods, and by Freudenberg and Harder's modification (A., 1927, 342) of Urban's method. Distillation with 12% HCl gives CH_2O (in appreciable quantity) only with the lignins isolated from oat hulls and spruce wood by Freudenberg and Harder's method (cf. *loc. cit.*). The results are discussed from the point of view of the probable presence of the methylenedioxy-group in the lignin mol. C. J. W. (b)

Manufacture of aldehydes and intermediate products [perfumes]. W. W. GROVES. From I. G. FARBERIND. A.-G.—See B., 1932, 793.

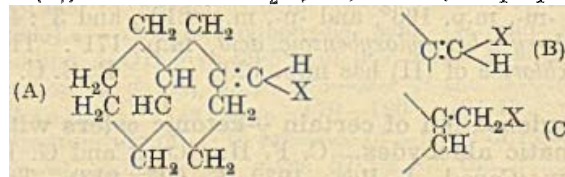
Cyclic ketones. III. R. POGGI and P. SALTINI (Gazzetta, 1932, 62, 678—686; cf. A., 1931, 1057).—6-Benzylidene-2-methylcyclohexanone forms an *oxime*, m.p. 147—148.5°; 6-benzylidene-3-methylcyclohexanone a *semicarbazone*, m.p. 173—180°. 4-Methylcyclohexanone yields 6-benzylidene-, m.p. 51—52° (*semicarbazone*, m.p. 190—191°; *oxime*, m.p. 144.5—145.5°), and 2 : 6-dibenzylidene-4-methylcyclohexanone [Br_4 -derivative, m.p. 192° (decomp.)]. 2-Benzylcyclohexanone [oxime, new m.p. 133—135° (cf. A., 1926, 744)] gives 6-benzylidene-2-benzylcyclohexanone, m.p. 77°. 2-Benzylidene-4-methylcyclohexanone is hydrogenated (Pt-black) to 2-benzyl-4-methylcyclohexanone [*semicarbazone*, m.p. 186° (decomp.)]; *oxime*, m.p. 131°; 6-benzylidene derivative, m.p. 50—75°]. E. W. W.

Triphenylmethane derivatives with linked benzene nuclei. VII. Ketomethylenephenyldiphenylenemethane. R. WEISS and E. KNAPP (Monatsh., 1932, 61, 61—68).—Fluorenone and $\text{o-C}_6\text{H}_4\text{Me-MgBr}$ give 9-hydroxy-9-o-tolylfluorene (I), m.p. 121—123° (*acetate*, m.p. 174—177°) [in one case 9-o-tolylfluorene (+0.25 H_2O), m.p. 129—130.5°, m.p. (anhyd.) 133° (NO_2 -derivative, m.p. 156—157°), was produced], oxidised by alkaline KMnO_4 to o-diphenylenephthalide (the lactone of 9-hydroxy-9-phenylfluorene-2'-carboxylic acid), m.p. 226—229°.

This is reduced (Na-Hg, EtOH) to 9-phenylfluorene-2'-carboxylic acid, m.p. 243—246° (*Me ester*, m.p. 112—114°), converted by P_2O_5 in C_6H_6 into ketomethylenephenyldiphenylenemethane (II), decomp. 249°. (I) and fuming HNO_3 in cold AcOH give a NO_2 -derivative, m.p. 155—157° [$(\text{NO}_2)_2$ -derivative, m.p. 222—223°], reduced (SnCl_2 , conc. HCl, AcOH) to an amino-9-o-tolylfluorene, m.p. 131—134° [isolated by addition of aq. NH_3 and $(\text{NH}_4)_2\text{S}$ to the evaporated reaction mixture; when the mixture is basified with aq. NaOH, an oily product (*hydrochloride*, decomp. 200°) is obtained]. H. B.



Three-carbon tautomerism in dicyclic systems. I. Comparison of corresponding compounds of *trans*- β -decalin and cyclohexane. II. Effect of an α -methyl group on tautomerism in *trans*- β -decalin compounds. III. Comparison between corresponding compounds of *trans*-hexahydroindene and cyclopentane. IV. Effect of an α -methyl group on tautomerism in *trans*-hexahydroindene compounds. R. S. THAKUR (J.C.S., 1932, 2120—2138, 2139—2147, 2147—2157, 2157—2167).—I. Isomerides of the types (A), (B), and (C), in which $\text{X}=\text{CO}_2\text{H}$, Me, and Ac, are prepared.

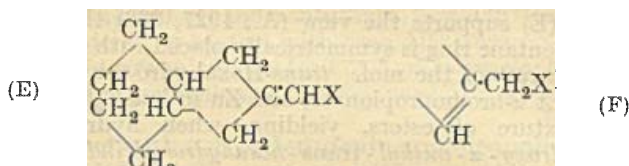


Their interconversions take place to an extent and (excepting the acids) at a rate very similar to those of the corresponding cyclohexane compounds, thus indicating that the strain factor either operates with equal force in both series or plays no determining part in the equilibrations. The apparent mobility of the acids in the *trans*- β -decalin series is lowered by the insolubility of the K salts in conc. aq. KOH. The percentage of Δ^2 -form (C) in mixtures can in all cases be determined by I (modified method in some cases). *trans*- β -Decalone (modified prep.; yield 86%) gives by the Reformatsky reaction a mixture of two isomeric forms of *Et 2-hydroxy-trans-decalin-2-acetate*, b.p. 140—150°/1 mm. (average yield 67%), hydrolysed by cold 10% NaOH-MeOH to Δ^2 (or Δ^1)-*trans-octahydronaphthyl-2-trans-beta-decalone*, m.p. 125—126° [*semicarbazone*, m.p. 209—210° (decomp.)]; *oximes*, m.p. 180—190° and 198—203° (decomp.)], and three forms of 2-hydroxy-trans-decalin-2-acetic acid, (I) m.p. 140—141° after sintering, (II) m.p. 116—118° (lit. 102°), and (III) m.p. 88°. (III) is possibly a eutectic mixture of (I) and (II). The crude mixture of acids and boiling Ac_2O give a liquid and a mixture of *trans-decahydronaphthylidene-2-acetic acids*, separable by partial esterification into $\alpha\beta$ -acids, (IV), m.p. 143° (lit. 145°) (*dibromide*, m.p. 155°; *amide*, m.p. 187—188°; *Et ester*, b.p. 160°/7 mm.), and (V), m.p. 95—96° (*dibromide*, m.p. 143—144°; *amide*, m.p. 145—147°; *Et ester*, b.p. 160°/9 mm., converted by O_3 into *trans-beta-decalone*). The acid chlorides of (IV) and (V) (prepared by SOCl_2 below 40°) isomerise when distilled, but give nearly pure amides with NH_3 in Et_2O if not heated. Under certain conditions, instead of (IV) and (V), there were obtained 2-methylenetrans-decalin, b.p. 81—83°/9 mm. [nitrosochloride gives *nitrolpiperidides*, m.p. 197—198° (decomp.) and 153—154°], and Δ^2 -*trans-octahydronaphthalene-2-acetic acid* [cf. (C)] (VI), m.p. 99—100° (lit. 100—101°) (*Et ester*, b.p. 153—154°/9 mm.) (also obtained from the $\alpha\beta$ -acid, pyridine, and Ac_2O , first at 100° and then at 130°). The crude hydroxy-ester with boiling $\text{POCl}_3\text{-C}_6\text{H}_6$ or cold pyridine- SOCl_2 gives a mixture, whence (VI) [*dibromide*, m.p. 99—100° (lit. 100—101°); *amide* (prepared from distilled acid chloride), m.p. 181—182°] was isolated. The pure ester of (VI) with O_3 in CHCl_3 gives *trans-cyclohexane-2- γ* -

carbethoxyacetone-1-acetic acid (*semicarbazone*, m.p. 164°), and (in another experiment) *trans-cyclohexane-1:2-diacetic acid* (VII), *trans-cyclohexane-2-acetone-1-acetic acid* [*semicarbazone*, m.p. 195—196° (decomp.)], and a liquid acid, further oxidised by hot, dil. HNO_3 to (VII). Equilibrium mixtures of (IV), (V), and (VI) (boiling 20—25% aq. KOH) contain 12+1% of $\alpha\beta$ -acid. Partial esterification of (V) gives (IV) and the ester of (VI), but not (V). (IV) and (V) in CHCl_3 are slowly (? and partly) converted into (VI) by ultra-violet light. The esters of (IV), (V), and (VI) give with NaOEt no OEt -compound, but an equilibrium mixture containing 40% of $\alpha\beta$ -esters. The distilled acid chloride, b.p. 154—155°/8 mm., of (IV) with ZnMeI in PhMe gives the *semicarbazone* (VIII), m.p. 186—187°, of *trans-decahydronaphthylidene-2-acetone*, a small amount of an *isomeride*, m.p. 199°, and a mixture of (IV) and (VI), but often a low-melting, inseparable, possibly eutectic mixture (IX) of *semicarbazones* is obtained. The distilled acid chloride of (V) gives similar products, but in one experiment the *semicarbazone* (X), m.p. 134—135°, of Δ^2 -*trans-octahydronaphthyl-2-acetone* was obtained, whilst (II) gives also (VIII) and (IX). Use of MgMeI and ZnMe_2 led to similar products. By the Blaise-Maire reaction the acid chloride, b.p. 145—146°/11 mm., of (VI) gave (X), whilst some (VI) was regenerated. (VIII), best with $\text{H}_2\text{C}_2\text{O}_4$, yields the *ketone*, b.p. 149—150°/15 mm., oxidised to decalone by 3% KMnO_4 . (X) and an *isomeride*, m.p. 175° (obtained from an $\alpha\beta$ -acid chloride in one Blaise-Maire reaction), with $\text{H}_2\text{C}_2\text{O}_4$ or Al-Hg give the *ketone*, b.p. 145°/15 mm. The equilibrated (NaOPr) mixture of these ketones contains 35% of the $\alpha\beta$ -components. This mixture with Et_2S sodiummalonate gives a gum, changed by hot 20% aq. KOH to *decalin-2-spirocyclohexane-2':6'-dione*, decomp. 185°. *trans- β -Decalone*, COMe_2 , and NaOEt give a mixture of ketones, yielding (IX), whereas, when $\text{Mg}(\text{OBu})_2$ is used, the product gives gummy *semicarbazones*.

II. As in the *cyclohexane* series, substitution by an α -Me group to give type (D) $\text{C}(\text{Me})\text{X}$ from type (A) greatly retards the tautomeric mobility of the acids and esters of the *trans- β -decalin* series, and displaces the equilibrium largely to the $\alpha\beta$ -side. *trans- β -Decalone*, $\text{Et } \alpha$ -bromopropionate, and Zn in hot C_6H_6 give a mixture of isomeric *Et 2-hydroxy-trans-decalin-2- α -propionates*, b.p. 170—172°/9 mm. (76% yield), hydrolysed by cold 10% $\text{NaOH-MeOH-H}_2\text{O}$ to the corresponding acids, (I) m.p. 156—157°, and (II) m.p. 110—114°, and Δ^2 -*trans-octahydronaphthyl-2- β -decalone*. The mixed ester with cold pyridine and SOCl_2 gives *Et Δ^2 -octahydronaphthalene-2- α -propionate* (III), b.p. 163—164°/19—20 mm., hydrolysed by cold $\text{NaOH-MeOH-H}_2\text{O}$ to the corresponding acid (IV), b.p. 148—149°/approx. 1 mm. (acid chloride, b.p. 155—156°/17 mm.; *amide*, m.p. 133—134° after sintering). The constitution of (III) is proved by ozonolysis to *trans-cyclohexane-1-acetic acid-2-methyl Et ketone* [*semicarbazone*, m.p. 203° (decomp.)]. The crude mixture of (I) and (II) with boiling Ac_2O yields *trans-decahydronaphthylidene-2- α -propionic acid* (V), m.p. 95—96° [*amide*, m.p. 206—207°, gives with Br in CHCl_3 the *dibromide*, m.p.

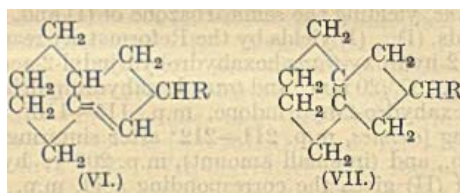
175—176° (decomp.), and (?) α -*bromo- Δ^2 -octahydronaphthalene-2- α -propionic acid*, m.p. 145—146° (decomp.); *Et ester* (VI), b.p. 169°/16 mm.]. The undistilled chloride of (V) and ZnMeI in Et_2O at -40° give the anhydride and a little α -methyl-*trans-decahydronaphthylidene-2-acetone* (VII) (*semicarbazone*, m.p. 209—210°), whereas the distilled chloride gives a product containing mostly the $\beta\gamma$ -isomeride. The acid chloride, b.p. 159—161°/19 mm., of (III) with ZnMeI gives pure α -methyl- Δ^2 -*trans-octahydronaphthyl-2-acetone* (VIII), b.p. 153—154° (*semicarbazone*, m.p. 194°), also obtained from Δ^2 -*trans-octahydronaphthyl-2-acetone*, MeI , and "mol." Na in Et_2O , and with a little (VII) from (I) [? or (II)]. Equilibration of (IV) and (V) is too slow for measurement; the equilibrium mixture (NaOEt) of (III) and (VI) contains 10% of (VI), the mobility of the substances being one hundredth of that of the unsubstituted esters; heating (VIII) with NaOEt indicated at most a trace of isomerisation.



III. Substances of types (E) and (F) ($\text{X}=\text{CO}_2\text{H}$, CO_2Et , and Ac) are prepared and found to show very high mobility, equilibrium being very much on the $\alpha\beta$ -side. The *cyclopentane* series is the only series resembling these compounds, but the large amount of $\beta\gamma$ -form in the equilibrium mixture of *cyclopentane* acids is anomalous. The prep. of *trans-cyclohexane-1:2-diacetic acid* from *trans- β -decalol* and -*decalone*, and thence of *trans-hexahydro-2-hydrindone* (I) is modified. (I) is purified by hydrolysis of the *semicarbazone* by $\text{H}_2\text{C}_2\text{O}_4$ or dil. H_2SO_4 ; when 50% aq. HCl is used, this gives also a substance, m.p. 150—152°, possibly *di-trans-hexahydro-2-hydrindylidene-hydrazine*, yielding the *semicarbazone* of (I) and, with dil. acids, (I). (I) yields by the Reformatsky reaction *Et 2-hydroxy-trans-hexahydrohydrindyl-2-acetate* (II), b.p. 167°/20 mm., and *trans-hexahydrohydrindylidenehexahydro-2-hydrindone*, m.p. 115—116° after sintering [*oximes*, m.p. 211—212° after sintering and decomp., and (in small amount), m.p. 206°]; hydrolysis of (II) gives the corresponding acid, m.p. 87—88°, which with boiling Ac_2O does not give an AcO -compound, but yields *trans-hexahydrohydrindylidene-2-acetic acid* (III), m.p. 151—152° [*dibromide*, m.p. 147—148°; acid chloride, b.p. 153—154°/16 mm.; *amide*, m.p. 154—155°; *anhydride*, m.p. 116—118°; *Et ester* (IV), b.p. 158°/19 mm.]. (II) with P_2O_5 (with or without C_6H_6), POCl_3 and C_6H_6 , or pyridine and SOCl_2 gives mixtures of esters, hydrolysed by 10% $\text{NaOH-MeOH-H}_2\text{O}$ to mixtures of (III) and *trans-hexahydrohydrindenyl-2-acetic acid* (V), m.p. 66—67° [*dibromide*, m.p. 135°; *amide*, m.p. 160—161° after sintering; *Et ester* (VI), b.p. 133—135°/11—13 mm.]. The acid chloride of (III) with ZnMeI gives *trans-hexahydrohydrindylidene-2-acetone* (VII), b.p. 134°/10 mm. [*semicarbazone*, m.p. 221—222° (decomp.)], oxidised in AcOEt by O_3 to *trans-hexahydrohomophthalic acid* and *trans-hexa-*

hydro-2-hydrindone, and giving with Et_2 sodiomalonate *Et cyclohexane-3:5-dione-1(2')-spiro-trans-hexahydrohydrindene-2-carboxylate*, m.p. 156—157° [hydrolysed by 20% aq. KOH to *cyclohexane-3:5-dione-1(2')-spiro-trans-hexahydrohydrindene*]. (VII) is unchanged by $N\text{-NaOEt}$. The equilibrium mixture of (IV) and (VI) contains $98.5 \pm 0.5\%$ of (IV), that of (III) and (V) about 90% of (III). Kandiah's data (A., 1931, 728) for many of the above compounds are corrected.

IV. Substitution of an $\alpha\text{-Me}$ group in substances of types (E) and (F) shifts the position of the equilibrium to the $\alpha\beta$ -side and retards the mobility of the system. The mobility of the ketones cannot, however, be measured. The resemblance between the *trans*-hexahydrindene and the *cyclopentane* compounds is less than that between the *trans*- β -decalin and *cyclohexane* compounds, but this is inexplicable, as is also the high mobility of the first-mentioned series. The absence of isomerides amongst compounds of type (E) supports the view (A., 1927, 238) that the *cyclopentane* ring is symmetrically placed with respect to the rest of the mol. *trans*-Hexahydro-2-hydrindone, $\text{Et } \alpha\text{-bromopropionate}$, and Zn in hot C_6H_6 give a mixture of esters, yielding, when hydrolysed, 2-hydroxy- α -methyl-*trans*-hexahydrohydrindene-2-acetic acid, m.p. 119—120° [*Et* ester (II), b.p. 156—157°/11 mm.], dehydrated by boiling Ac_2O to α -methyl-*trans*-hexahydrohydrindylidene-2-acetic acid (I), m.p. 196—197° [*Me* ester (II), m.p. 43—45°; *Et* ester (III), b.p. 154°/10 mm.; acid chloride, b.p. 163°/10 mm.; amide, m.p. 205°; dibromide, m.p. 182—183° (decomp.)], oxidised by KMnO_4 to *trans*-hexahydrohydrindone. (II) with P_2O_5 in C_6H_6 or pyridine and SOCl_2 gives a mixture of esters, hydrolysed to (I) and impure α -methyl-*trans*-hexahydroindanyl-2-acetic acid (IV), b.p. 154—155°/1—2 mm. [*Et* ester (V), b.p. 134°/10 mm.]; the last acid contained some isomeride, (VI) or (VII) ($\text{R}=\text{CHMe}\cdot\text{CO}_2\text{H}$), m.p. 89—90° after sintering (amide, m.p. 185—186° after



sintering), best separated by partial esterification. The acid chloride, b.p. 163°/10 mm., cryst., with ZnMeI gives α -methyl-*trans*-hexahydrohydrindylidene-2-acetone (VIII), b.p. 144—148°/9 mm. [semicarbazone, m.p. 206—208° (decomp.)], converted by O_3 into *trans*-hexahydro-2-hydrindone, and yielding with Et_2 sodiomalonate an oily ester, hydrolysed by 20% aq. KOH to 2-methylcyclohexane-3:5-dione-1(2')-spiro-*trans*-hexahydrohydrindene, m.p. 164—165°. The sodio-derivative of (VIII) with BzOH gives a product yielding a semicarbazone, m.p. 213°, or *trans*-hexahydrohydrindyl-2-acetonesemicarbazone, m.p. 180°, according to the conditions used. *trans*-Hexahydrohydrindylidene-2-acetone, "mol." Na , and MeI or EtI in hot Et_2O give a mixture of $\alpha\beta$ - and $\beta\gamma$ -unsaturated ketones [semicarbazone of (?) $\beta\gamma$ -form, m.p. 175—177°]. (VIII) is unaffected by $N\text{-NaOEt}$ —

EtOH . Equilibrium mixtures of (I) and (IV) and of (III) and (V) contain 90 and 98%, respectively, of the $\alpha\beta$ -form. Hydrolysis of (V) by $\text{NaOH-MeOH-H}_2\text{O}$ gives a mixture of (I) and (II). R. S. C.

Mixed benzoin. VIII. Determinations of structures. Question of isomerides. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1932, 54, 3302—3309; cf. A., 1931, 1294).—The following new benzoin is reported: 3:4-diethoxybenzoyl-*o*-chlorophenylcarbinol, m.p. 63° [from $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ and 3:4-(OEt) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$] [oxime (I), m.p. 61°], and its 4'-methoxy-3'-ethoxy-, m.p. 103° [oxime (II), m.p. 113°], and 3'-methoxy-4'-ethoxy-, m.p. 120° [oxime (III), m.p. 114°], analogues; *p*-dimethylaminobenzoyl-3:4-methylenedioxyphenylcarbinol, m.p. 136° [oxime (IV), m.p. 145°]. Oxidation of the benzoin (in EtOH) with a slight excess of Fehling's solution gives 2-chloro-3':4'-diethoxy-, m.p. 110°; 2-chloro-4'-methoxy-3'-ethoxy-, m.p. 150°; 2-chloro-3'-methoxy-4'-ethoxy-, m.p. 132°, and 4'-dimethylamino-3:4-methylenedioxy-, m.p. 174°, -benzils. The following deoxy-compounds are prepared by the method previously described: 3':4'-diethoxyphenyl *o*-chlorobenzyl ketone, m.p. 95° (anti-oxime, m.p. 105°); 4'-methoxy-3'-ethoxy-, m.p. 98° (anti-oxime, m.p. 130°), and 3'-methoxy-4'-ethoxy-, m.p. 121° (anti-oxime, m.p. 167°) -phenyl *o*-chlorobenzyl ketones; 4'-dimethylaminophenyl 3:4-methylenedioxybenzyl ketone, m.p. 140° (anti-oxime, m.p. 152°). anti-4'-Dimethylaminophenyl *m*-chlorobenzyl ketoxime, m.p. 146°; anti-3':4'-methylenedioxyphenyl *p*-chlorobenzyl ketoxime, m.p. 119°; *o*-chlorophenylacet-3':4'-diethoxyanilide, m.p. 178°, -4'-methoxy-3'-ethoxyanilide, m.p. 165°, and -3'-methoxy-4'-ethoxyanilide, m.p. 166°; *m*-chlorophenylacet-4'-dimethylaminoanilide, m.p. 178°; *p*-chlorophenylacet-3':4'-methylenedioxyanilide, m.p. 195°; 3:4-methylenedioxyphenylacet-4'-dimethylaminoanilide, m.p. 170°; *p*-dimethylaminobenzoyl-*m*-chlorophenylcarbinoloxime (V), m.p. 148°, and 3:4-methylenedioxybenzoyl-*p*-chlorophenylcarbinoloxime (VI), m.p. 178°, are described. The Beckmann reaction (PhSO_2Cl and alkali) with the oximes (I)—(VI) gives: (I) $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ (88%) and 3:4-(EtO) $_2\text{C}_6\text{H}_3\cdot\text{CN}$ (87%); (II) $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ (73%) and 3:4- $\text{EtO}(\text{MeO})\text{C}_6\text{H}_3\cdot\text{CN}$ (44%); (III) $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ (65%) and 3:4- $\text{MeO}(\text{EtO})\text{C}_6\text{H}_3\cdot\text{CN}$ (60%); (V) *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ (52%) and *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ (62%); (VI) *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ (38%) and piperonitrile (47%); (IV) piperonal (77%) and *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ (63%). *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, hippuric acid, Ac_2O , and NaOAc give the azlactone, m.p. 164°, hydrolysed by 10% NaOH to *m*-chlorophenylpyruvic acid, m.p. 145°, oxidised by alkaline H_2O_2 to *m*-chlorophenylacetic acid, m.p. 74°. 3:4-Diethoxybenzaloxime, m.p. 98°, is dehydrated by Ac_2O to 3:4-diethoxybenzonitrile, m.p. 68°. 4-Methoxy-3-ethoxybenzaloxime, m.p. 98°, 4-methoxy-3-ethoxybenzonitrile, m.p. 70°, and 3-methoxy-4-ethoxybenzaloxime, m.p. 100°, are prepared. The question of the formation of pairs of isomeric mixed benzoin (by the KCN condensation) is discussed; it is considered that reported cases of the occurrence of such pairs of isomerides require further substantiation. In naming benzoin the authors suggest using primes for the numbered substituents

on the C_6H_6 ring next to the CO group (in the case of oximes, the C:NOH group); thus *o*-chlorobenz-veratrolin is 2-chloro-3':4'-dimethoxybenzoin.

C. J. W. (b)

Complex salts of hydroxyquinones. II. A. MANGINI and R. STRATTA (Gazzetta, 1932, 62, 686—699; cf. this vol., 164).—The following are described: the *Co*, decomp. 210—215°, *Cu* (+2H₂O), decomp. above 300°, *UO₂*, *Ni*, *Zn* (+H₂O), *Pb* (+H₂O), *Cd* (+2½H₂O), *Hg* (+H₂O), and *basic Fe* salts of 2-hydroxy- α -naphthaquinone; the neutral *Ni* salt of naphthazarin; the *acid Ni* (+1½H₂O), and neutral *Ni* (+½H₂O) and *Cu* salts of 1:8-dihydroxyanthraquinone; the neutral *Cu* (+H₂O) and *Co* (+½H₂O), and the *acid Ni* (+3H₂O) salts of chrysophanic acid [1:8-dihydroxy-2(or 3)-methylantraquinone]. The colours of salts of these hydroxyquinones are tabulated; spectroscopic examination shows that salt-formation involves chelation.

E. W. W.

Perylene and its derivatives. XXXVI. A. ZINKE (Monatsh., 1932, 61, 1—14).—Perylene dissolves in cold conc. H₂SO₄ with the following colour changes: green, bluish-green, blue (red fluorescence), bluish-violet, reddish-violet; perylenesulphonic acids and perylene-3:10-quinone (I) (probably formed by way of the 3:10-disulphonic acid) are produced. (I) is formed in quant. yield from perylene and traces of HNO₃ and FeSO₄ in cold conc. H₂SO₄.

[With G. HAUSWIRTH.] Dichloroperylene-3:10-quinone heated with PhOH, K₂CO₃, and Cu powder gives *diphenoxyperylene-3:10-quinone*; di-(3-methyl-4-isopropylphenoxy)- and di-*p*-chlorophenoxyperylene-3:10-quinones are prepared similarly. A compound, C₄₀H₂₀O₃, not reducible (vat), is obtained using β -C₁₀H₇OH. Perylene-3:9-quinone (II) and Cl₂ in PhNO₂ containing a little I give an unstable adduct, which when crystallised from PhNO₂ passes into a violet substance [probably a mixture of Cl₂- and Cl₃-derivatives of (II)], oxidised by MnO₂ and conc. H₂SO₄ to anthraquinone-1:5-dicarboxylic acid (III); substitution occurs in the quinonoid nuclei. Analogous results are obtained using Br. (II) and HNO₃-AcOH give a (NO₂)₂-derivative [corresponding (NH₂)₂-derivative], also oxidised (bleaching powder) to (III).

1-Hydroxyperylene, BzCl, and AlCl₃ in CS₂ give a 1-hydroxydibenzoylperylene, m.p. 227—228°, which is not converted into a dye (isoviolanthrone) when heated with AlCl₃ in absence or presence of MnO₂.

[With W. BLANK.] 3:9-Dibenzoylperylene (IV) does not react with *p*-OMe.C₆H₄.MgI nor does (?) 3:9-dianisoylperylene with MgPhI. (IV) and MgPhBr give 3:9-di-(α -hydroxydiphenylmethyl)perylene, m.p. 327—328°. (I) is reduced (partly) to the quinol by MgMeI and MgPhBr.

[With V. GRIMM.] Phenanthrene-1:8:9:10-tetracarboxylic dianhydride (A., 1931, 730) and fuming HNO₃ at 250° give mellitic acid. H. B.

Manufacture of 1-aldehydanthraquinone and its nuclear substitution products. A. CARPMAEL. From I. G. FARBENIND. A.-G.—See B., 1932, 764.

Manufacture of alkyl ethers of amino- β -hydroxyanthraquinones. J. Y. JOHNSON. From I. G. FARBENIND. A.-G.—See B., 1932, 765.

Manufacture of vat dyes [dibenzopyrene-quinones; dibenzoylnaphthalene derivatives]. I. G. FARBENIND. A.-G.—See B., 1932, 765.

Constitution of marmelosin. I. B. B. L. DIKSHIT and S. DUTT (J. Indian Chem. Soc., 1932, 9, 271—279).—Marmelosin (I) (A., 1930, 1628), C₁₃H₁₂O₃, m.p. 103°, $[\alpha] +36^\circ$ in EtOH (*Ac*, m.p. 214°, *Bz*, m.p. 119—120°, and *NO₂*, m.p. 97°, derivatives; *phenylurethane*, m.p. 245°; *Br*-derivative *dibromide*, m.p. 82°), is reduced by Zn dust and AcOH to *dihydromarmelosin*, m.p. 238° [*Ac* derivative, m.p. 176°, formed by reductive acetylation of (I)], gives an additive compound, m.p. 156°, with HBr (1 mol.), and is dehydrated by warm 75% H₂SO₄ or with PCl₅ to *anhydromarmelosin*, m.p. 76°. KOH-fusion of (I) gives H₂C₂O₄ and an *acid*, C₁₃H₁₈O₆, m.p. 245°, which is also formed (together with a little succinic acid) by oxidation of (I) with alkaline KMnO₄. (I) may be an $\alpha\beta$ -unsaturated lactone. When an alkaline solution of (I) is acidified, (I) and a substance, m.p. 146° [convertible into (I) in contact with conc. HCl], are produced.

(I) occurs only in the fruit of *Aegle marmelos* (Indian Bel) and predominates in the inner layer of the pulp.

H. B.

Constitution of hederagenin and oleanolic acid.

I, II, III. Z. KITASATO and C. SONE (Acta Phytochim., 1932, 6, 179—222, 223—225, 305—314).—I. Hederagenin, C₃₁H₅₂O₄, is isolated from the saponin of *Sapindus mukurossi* (cf. A., 1925, i, 947, 948; 1930, 1293; 1931, 1159) [*diphenylurethane*, m.p. 155—158°; *thionylethyl* derivative, m.p. 269°; *-oxychlorophosphine*, m.p. 275°; *-phosphoric acid*, m.p. 286° (decomp.); γ -*keto-methyl* derivative, m.p. 190—193°, and its *oxime*, m.p. about 190° (decomp.); γ -*keto*-derivative, m.p. > 300°, and its *oxime*; *bromo-methyl* derivative, m.p. 147°; *bromodiacyldehydrolactone*, m.p. 223° (decomp.); *bromodehydrolactone*, m.p. 210°; *dibromolactone*, m.p. 251—253° (decomp.); *dibromodiacyl-lactone*, m.p. 216—217° (decomp.); *tribromolactone*, m.p. 217°; *bromothionyldehydrolactone*, m.p. 212—213° (decomp.); “*bromothionyl-lactone*,” C₃₁H₄₇SB₂, m.p. 257°; *nitrode*-(6)-*hydrodinitrate*, m.p. 229°]. Acetyloleanolic acid on oxidation yields the δ -*keto*-acetyl-lactone, m.p. 227—280° [*oxime*, m.p. 222° (decomp.); *Br*-derivative, m.p. 225—226° (decomp.)], hydrolysis of which gives the δ -ketolactone, m.p. > 300°, which on reduction yields the δ -ketodehydrolactone, m.p. 277° [*dioxime*, m.p. 223° (decomp.); *Br*-derivative, m.p. 225° (decomp.)]. Similarly were prepared δ -ketohederageninlactone, m.p. > 300° [*diacetyl oxime*, m.p. about 200° (decomp.); *Me* derivative, m.p. 220°], δ -ketoacetylmethyloleanolic acid, m.p. 224°, and δ -ketomethyloleanolic acid, m.p. 197°. Oxidation of bromohederageninlactone yields *bromohedragone-lactone* (with 1½ mol. AcOH), m.p. 200—202° [*oxime*, (+1½ mol. AcOH), m.p. 225° (decomp.)], which is reduced (Zn dust, AcOH) to *hedragone*, C₃₃H₄₆O₃, m.p. 253—255° [*oxime*, m.p. 245—246° (decomp.); *dibromolactone*, m.p. 203—204° (decomp.)], the *Me* derivative and *oxime* being identical with substances described by Jacobs (A., 1926, 1250). Hedragone on further reduction gives *hedragenin*, m.p. 261—263° (*Ac* derivative, m.p. 247—250°; *acetylmethyl* derivative, m.p. 175°). Dehydrogenation of hederagenin

bv Se yields $C_{10}H_5Me_3$. The sapogenin from *Panax* is identical with oleanolic acid. The hæmolytic and toxic properties of the saponin of *S. mukurossi* were determined.

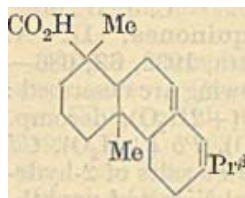
II. δ -Ketoacetyloleanolic acid lactone oxidised with $HNO_3 + AcOH$ yields a di-acid (I), $C_{33}H_{50}O_8$, m.p. $>300^\circ$ (Me ester, m.p. 269—270°). Similarly, δ -keto-diacythederageninlactone yields a dinitrodi-acid, m.p. 274° (decomp.).

III. Hydrolysis of (I) yields oleanolic acid lactone di-acid, m.p. $>300^\circ$. MeOH-KOH converts ϵ -bromo- δ -ketodehydro-oleanolic acid lactone into ϵ -oxy- δ -keto-oleanolic acid lactone, m.p. 285°. Hedragone treated with $HNO_3 + AcOH$ followed by reduction with Zn dust yields ketohedragone di-acid, m.p. $>300^\circ$ (decomp.), whilst treatment with KBr gives a substance, m.p. $>300^\circ$, which is either hedragone di-acid or hedragilic acid. Oxidation of hedragone gives the δ -ketolactone, m.p. 234—236° [oxime, m.p. 208—210° (decomp.)], which with KBr yields hedragil-lactone tri-acid, m.p. 288—289° (decomp.). The above data are applied to a consideration of the structural formulæ of hederagenin and oleanolic acid, based on a picroene ring structure.

F. O. H.

Constitution of abietic acid. F. VOCKE (Annalen, 1932, 497, 247—264).—Reduction (H_2 , PtO_2 , AcOH) of abietic acid (I) gives tetrahydroabietic acid (II), m.p. 190° (not sharp), $[\alpha]_D +11.1^\circ$ in 96% EtOH, the Me ester of which with $MgPhBr$ affords a carbinol, $C_{32}H_{44}O$, m.p. 155°, oxidised (CrO_3 , AcOH) to $BzOH$ and $COPh_2$. (II) and conc. H_2SO_4 at 60° give CO (about 70%), CO_2 (about 30%), a hydrocarbon, $C_{19}H_{31}$, b.p. 128°/1 mm., and a viscous oil (sol. in H_2SO_4). The formation of CO from (I) and conc. H_2SO_4 at 50—60° indicates that the CO_2H of (I) is attached to a *tert*-C atom. The acid $C_{11}H_{16}O_6$ (III), prepared from (I) by Levy's method (A., 1929, 1448), and conc. H_2SO_4 at 100—140° give 2 mols. of CO; 1-methylhexahydrophthalic acid, m.p. 165° [prepared by reduction (H_2 , Pd-black, AcOH) of the adduct from citraconic anhydride and butadiene], similarly gives 1 mol. of CO at 100—140°, whilst *cis*- and *trans*-hexahydrophthalic acids afford about 1 mol. of CO at 195—250° and 230—250°, respectively. (III), Br, and red P at 100° (bath) (after mixing in the cold) give a mixture of the bromoanhydrotetracarboxylic acid (IV), m.p. 215° (slight decomp.), its acid bromide, (V), m.p. 207° (not sharp) (stable to cold H_2O), the anhydrotetracarboxylic acid (IV, Br=H), m.p. 178° (cf. Ruzicka *et al.*, A., 1931, 736), and its acid bromide, m.p. 160° (also stable to cold H_2O); the chloride of (III) and Br at 100° (tube) afford (after treatment with moist HCO_2H) a compound, $C_{11}H_{13}O_5Br_3$, m.p. 150°. (IV) and (V) heated with 2N-NaOH give (by loss of HBr and CO_2) 1:3-dimethyl- Δ^2 -tetrahydrophthalic acid, m.p. 183° (decomp.) (Me ester, m.p. 132°), converted by aq. H_2SO_4 (1:1) at 120—100°

glutaric acid. (III) is probably 1:3-dimethylcyclohexane-1:2:3-tricarboxylic acid. The formation of methylretene from methylabietin (Ruzicka and Meyer, A., 1922, i, 829) may involve migration of Me. (I) appears to be best represented by the annexed constitution.



trans-Hexahydrophthalic acid, Br, and red P at 70—80° give a little Br-derivative, m.p. 172°, also formed similarly from, reduced (Zn dust, AcOH) to, *cis*-hexahydrophthalic acid.

H. B.

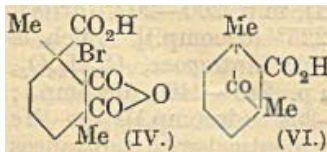
Thermal decomposition of natural and artificial caoutchouc in presence of aluminium chloride. N. D. ZELINSKI and N. S. KOSLOV (Annalen, 1932, 497, 160—170).—Caoutchouc ("pale crêpe") heated with 10% of $AlCl_3$ gives saturated ($KMnO_4$), b.p. 34—240°, and unsaturated (A), b.p. 70—250°/9 mm., hydrocarbons; with 20% of $AlCl_3$, saturated hydrocarbons, b.p. 34—300°, are produced. (A) heated with 10% of $AlCl_3$ also gives saturated hydrocarbons, b.p. 29—290°. Dehydrogenation of the "benzine" fraction (B), b.p. 70—150°, with Pt-asbestos at 300° affords a product containing 13% of aromatic hydrocarbons [by absorption in oleum (7% SO_3)]; (B) contains cyclo-alkanes other than hexanes. A fraction, b.p. 120—126°, is similarly dehydrogenated to a product containing 41% of xylenes. The gaseous products of the original decomp. are saturated. Caoutchouc from *Scorzonera Tau-Sagis* with 10% of $AlCl_3$ gives a mixture, b.p. 22—235° to 70—250°/15 mm., of hydrocarbons all the fractions of which contain unsaturated ($KMnO_4$) material; further treatment with 10% of $AlCl_3$ affords a saturated mixture, b.p. 30—267°. The original mixture contains cyclohexane derivatives, other cycloalkanes, unsaturated hydrocarbons possessing a terpene odour, and a fraction resembling dipentene.

Synthetic caoutchouc (from butadiene and Na) also gives a mixture of cyclohexane derivatives and other cycloalkanes when heated with $AlCl_3$.

H. B.

Modifications of guttapercha hydrocarbon. II. A. W. K. DE JONG (Rec. trav. chim., 1932, 51, 699—705; cf. this vol., 275).—On heating, the spongy modification contracts markedly in vol. between 61° and 64.5° (55—63° in less pure samples), after which it expands normally at the same rate as the α -modification, of which it is composed. The contraction represents the m.p. range, but is not observed if the hydrocarbon has been previously pulverised. The β -form is less dense than the α -, and both expand on melting. The spongy form was purified by crystallisation from C_6H_6 ; it undergoes autoxidation.

Natural and synthetic rubber. X. Constituents of rubber hydrocarbon. XI. Constituents of milled rubber hydrocarbon. T. MIDGLEY, jun., A. L. HENNE, and M. W. RENOLL (J. Amer. Chem. Soc., 1932, 54, 3343—3348, 3381—3383).—X. By means of fractional pptn. (B., 1931, 853) and by the use of a "standard pptn. point" (the temp. at which a sudden increase of turbidity occurs in a slowly-cooled solution of 0.85% rubber, 28.55% abs. EtOH,



into the lactone (VI), m.p. 146°, and oxidised (O_3 and then CrO_3 in AcOH) to a malonic acid derivative, the Me ester, b.p. about 150° (bath)/12 mm., of which is hydrolysed by 2N-HCl at 160—180° to α -methyl-

and 70.6% of C_6H_6) it is concluded that the original rubber specimen consisted of a sol. portion (>20%) containing several individuals, a single sol. component (>50%), and an insol. portion (<20%). The larger portion is characterised by a "standard pptn. point" of 35°. It is suggested that the more sol. fractions are generated during the washing and sheeting of the original coagulum.

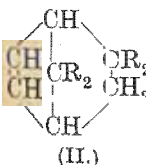
XI. Investigation of the composition of milled rubber by a method based on fractional pptn. from C_6H_6 -EtOH shows that it consists of a continuous series of undefined components, without a single predominating individual. C. J. W. (b)

Asymmetric synthesis. XI. A. MCKENZIE and P. D. RITCHIE (Biochem. Z., 1932, 250, 376—384).—(–)Menthyl anisoformate, m.p. 62.5–63°, has $[\alpha]_{D}^{20} -58.6^\circ$ in $CHCl_3$, -44.2° in $COMe_2$, -45.0° in C_6H_6 , -30.6° in CS_2 , and -45.9° in EtOH. Mutation was not observed in these solutions, a striking difference from (–)menthyl benzoylformate. The asymmetric syntheses by Grignard reactions of (–)methylanisylglycolic acid, m.p. 146–147°, $[\alpha]_{D}^{25} -61.7^\circ$ in EtOH, from (–)menthyl anisoformate and of (+)methylanisylglycolic acid, m.p. 146–147°, $[\alpha]_{D}^{25} +61.0^\circ$, from (–)menthyl pyruvate are described. P. W. C.

Studies in stereochemical structure. IV. Esters of (–)menthol and the (–), (+), and *r*-mandelic acids. R. ROGER (J.C.S., 1932, 2168–2180).—The rotatory dispersions of *d*-mandelic acid, Et *d*(–), and (–)menthyl *d*(–)-mandelate are normal and complex, that of (–)menthyl *r*- is simple, and that of (–)menthyl *l*(+)-mandelate is complex and anomalous in certain solvents. The dispersions of (–)menthyl *d*(–)- and *l*(+)-mandelates may be complicated by induced asymmetry in the C-COR group. The evidence for the existence of (–)menthyl *r*-mandelate as a true racemic compound in solution is examined. F. R. S.

The enzyme model of Bredig and Fajans. P. RONA and F. REUTER.—See this vol., 966.

Hydrocarbons corresponding with particular campher-like substances. II. *apoisoFenchene* (camphenylene), *apocyclene*, and *apobornylene*. G. KOMPPA and T. HASSELSTROM (Annalen, 1932, 497, 116–130).—*dl*-*apoBornyl* (= *dl*- α -fenchocamphoryl) chloride (I) heated with NH_2Ph gives a mixture of hydrocarbons containing *apocyclene* (not affected by $KMnO_4$) and *apoisofenchene* (II, $R'=Me$, $R=H$) (oxidised by $KMnO_4$ to *trans*-*apofenchocamphoric* acid). (I) and amyl-alcoholic K amyloxide at 230° give *apobornylene* (II, $R=Me$, $R'=H$), oxidised to *apocamphoric* acid. Treatment of α -fenchocamphoronehydrazone with EtOH-HgCl₂ in cold EtOH-KOH affords *apocyclene*, b.p. 137.5°/756 mm., m.p. 41–42° (cf. A., 1922, i, 1167), whilst reduction of (I) with Na and EtOH gives *apobornylene* and *apocamphane*. *dl*- β -Fenchocamphoryl chloride does not undergo rearrangement when heated with aq. $Ca(OH)_2$ and is converted by K amyloxide at 230° into *apoisofenchene*, b.p. 134.5–135.5°/762 mm., m.p. 24.5–25° [*nitroschloride*, m.p. 144–145° (decomp.)].



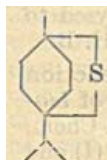
Camphenilonehydrazone and EtOH-HgCl₂ in EtOH-KOH give *apocyclene*, the hydrochloride (III), b. p. 76–77°/11 mm., m.p. 44–46°, of which is probably a stereoisomeride of (I). (III) and KOPh at 150° afford pure *apocyclene* (m.p. 38.5–39.5°), whilst (III) and aq. $Ca(OH)_2$ at 80° give (probably) a stereoisomeride (IV), b.p. 196–198°, m.p. 85.5–86.5°, of α -fenchocamphorol. (IV) is oxidised by $KMnO_4$ to *apocamphoric* acid and by $K_2Cr_2O_7$ -dil. H_2SO_4 to α -fenchocamphorone. The acetate from (III) and AgOAc in AcOH is hydrolysed by EtOH-KOH to a product, b.p. 78–81°/6.5 mm., containing *isofenchyl* alcohol; the acetate from (I) [which reacts less readily than (III)] is hydrolysed to solid (impure) α -fenchocamphorol. H. B.

Catalytic action of silica gel in the reaction of camphene and oxalic acid. Synthesis of *isoborneol*. T. KUWATA and S. TATEGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 303–304B).—Camphene (I) and anhyd. $H_2C_2O_4$ react thus: (I) (2 mols.) + $2H_2C_2O_4$ *isobornyl* H oxalate (m.p. 40.5°) (2 mols.) *isobornyl* oxalate (m.p. 114–115°) + $H_2C_2O_4$. Reaction is extremely slow below 100° and polymerised material results above 150°; a 65% yield of *isoborneol* (II) is obtained only with difficulty (cf. G.P. 193,301). Reaction occurs below 100° with silica gel as catalyst; the yield of (II) is increased to 75%. The yield of borneol from pinene and $H_2C_2O_4$ is <75%; polymerised material is formed from the intermediate bornyl H oxalate. H. B.

Constitution of bornylaniline. J. J. RITTER and H. O. MOTERN (J. Amer. Chem. Soc., 1932, 54, 3458).—Lipp and Stutzinger's observation (this vol., 398) that the "bornylaniline" of Ullmann and Schmid (A., 1911, i, 70) is identical with the product from camphene and NH_2Ph is confirmed. Reduction of camphoranil with Na and NH_2Ph gives a *sec*-amine, the Ac derivative of which has m.p. 112–113° (Lipp and Stutzinger give 123°). C. J. W. (b)

Higher β -homologues of camphoric acid, and β -homocamphor. F. SALMON-LEGAGNEUR (Bull. Soc. chim., 1932, 51, [iv], 807–824).—A fuller account of work already published (cf. A., 1931, 626; this vol., 399). The Me ester (I) of camphoceanaldehydic acid [*Et* ester, b.p. 144–145°/13 mm. (*semicarbazone*, m.p. 158–160°)] gives with Zn and Et bromoacetate *Et* β -campholide- β -acetate, $C_8H_{14} \begin{smallmatrix} <CO \\ CH(CH \cdot CO Et) \end{smallmatrix} >O$, m.p. 52–53° (cf. A., 1931, 626), hydrolysed by 20% H_2SO_4 at 100° to the corresponding *acid*, m.p. 213°, but by aq. KOH to α -carboxycamphocean- β -acrylic acid (*Me* ester, b.p. 188°/15 mm.). Reduction of (I) with H_2 -PtO₂ gives the *ester* $C_8H_{14}(CH_2 \cdot OH) \cdot CO_2Me$, b.p. 158–162°/19 mm., cyclised by aq. KOH to β -campholide, m.p. 218°. The oxime of (I) is converted by $SOCl_2$ into camphoric acid mononitrile. Inter-action of $SOCl_2$ (1 mol.) with oximino- β -homocamphor (1 mol.) (cf. this vol., 399) gives a *compound*, $C_{22}H_{32}O_3N_2$, m.p. 200–205°. The thermal decomp. of Pb α -carboxycamphocean- β -propionate gives, in addition to β -homocamphor, a *diketone*, $C_{22}H_{32}O_2$ (or $C_{22}H_{36}O_2$?), m.p. 290–291° (block), probably $C_8H_{14} \begin{smallmatrix} <CO \cdot CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CO \end{smallmatrix} >C_8H_{14}$, or a dehydrogenation product. H. A. P.

Sulphur compounds of terpenes. II. Constitution of sulphur compound from the action of sulphur on dipentene. III. Action of sulphur on cyclic terpene alcohols. IV. Action of sulphur on linalyl acetate and linalool. A. NAKATSUCHI (J. Soc. Chem. Ind., Japan, 1932, 35, 376—379B).—II. Under the conditions previously used (A., 1931, 95) dipentene heated with S gives a *sulphide*, $C_{10}H_{18}S$ (I), b.p. $223^{\circ}/759$ mm., m.p. -23° (*dibromide*, m.p. 143°), which gives additive compounds with $AuCl_3$ and MeI. Oxidation of (I) with $KMnO_4$ gives successively the *cryst. compounds*, $C_{10}H_{18}O_2S$, m.p. 65.5° , $C_{10}H_{18}O_3S$, m.p. 150° , and $C_{10}H_{18}O_4S$, m.p. 227.5° .



T

III. Dihydro- α -terpineol heated with S at 160° first eliminates H_2O , further treatment giving the same result as $\Delta^{8(9)}$ -*p*-menthene; the product gives a compound $C_{10}H_{17}SAu$ with $AuCl_3$. α -Terpineol and terpinyl acetate similarly lose H_2O or $AcOH$, giving, finally, *p*-cymene and (?) (I). No reaction occurs with menthol.

IV. Linalool and its acetate similarly heated with S eliminate H_2O or $AcOH$ and afford *p*-cymene, dipentene, a *terpene*, $C_{10}H_{16(14)}$, b.p. $186-187^{\circ}/774$ mm., m.p. $-26-81^{\circ}$, a *compound*, $C_{10}H_{18}S$ ($AuCl_3$ and MeI additive compounds) (probably a mixture of different types containing the C-S-C and C-S groups), and higher S derivatives. J. W. B.

Ethyl 5-nitrofurfurylidene-malonate and α -cyano- β -5-bromofurylmalonate. Stability of furan compounds towards acids. H. GILMAN and R. V. YOUNG (Rec. trav. chim., 1932, 57, 761—768).—The product of nitration of Et furfurylidene-malonate (I) (A., 1895, i, 651) is the 5- NO_2 -derivative [synthesis from 5-nitrofurfuraldehyde (II) and Et malonate]. The product of bromination of Et α -cyano- β -furylacrylate (A., 1894, i, 488) is identical with the product of interaction of (II) and $CN\cdot CH_2\cdot CO_2Et$ in presence of $NaOEt$, and is therefore the 5-, and not the β -Br-derivative. Many negatively substituted furan derivatives have good stability towards acids (including the halogen acids); thus, (I) may be nitrated with HNO_3 (*d* 1.5). H. A. P.

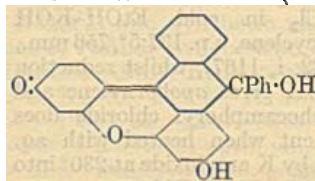
Dimethylfuroic acids. H. GILMAN and R. B. BURNER (Rec. trav. chim., 1932, 51, 667—672).—Details are given for the prep. of 2:5-dimethylfuran-3-carboxylic acid [4-Br-derivative, m.p. 181° (decomp.); α -naphthalide, m.p. 148°]. Nitration of its Et ester in Ac_2O gives the 4- NO_2 -ester, b.p. $119-120^{\circ}/20$ mm., hydrolysed by 20% HCl to the free acid, m.p. 176° , and 3-nitro-2:5-dimethylfuran, b.p. $88-92^{\circ}/9$ mm. (also formed by nitration of 2:5-dimethylfuran). The 5- NO_2 -, m.p. 182° , and 5-Br-, m.p. 104° (decomp.), derivatives of 2:4-dimethylfuran-3-carboxylic acid [best prepared by the method of Anschütz (A., 1891, 172)] are similarly prepared. It is decarboxylated by Cu-bronze and quinoline to 2:4-dimethylfuran ($HgCl_2$ -derivative, m.p. 112°). H. A. P.

Experiments on the synthesis of anthocyanins. XIV. Cyanenin chloride, malvenin chloride, and an indication of the synthesis of cyanin chloride. A. LÉON and R. ROBINSON (J.C.S., 1932, 2221—2224).—Cyanenin and malvenin chlorides (also

picrates), the 5-glucosidyl derivatives of cyanidin and malvidin chlorides, have been synthesised by the method used for pelargonidin chloride (A., 1931, 1423) and are identical with the products of hydrolysis of cyanin and malvin chlorides. Condensation of crude 2-*o*-benzoylphloroglucinaldehyde with the intermediate for chrysanthemin (*loc. cit.*) gives traces of (probably) cyanin chloride. E. E. J. M.

Stability of coumarinic acids derived from 1:2- $\beta\alpha$ -naphthapyrones. B. B. DEY, R. H. RAO, and Y. SANKARANARAYANAN (J. Indian Chem. Soc., 1932, 9, 281—289).—Acidification of alkaline solutions of 1:2- $\beta\alpha$ -naphthapyrone (I) (modified prep. given) and its 3-Me and 3- $CO_2H\cdot CH_2$ derivatives regenerates the pyrones, i.e., the intermediate coumarinic acids are unstable. The 4-Me and 4- $CO_2H\cdot CH_2$ derivatives similarly afford stable (i.e., isolable) coumarinic acids which are not convertible into the *trans*-forms (coumaric acids) by the usual methods, but which pass into the original pyrones at the m.p. when crystallised from hot $AcOH$, or when kept in a desiccator for several days. The pyrone ring is rendered unstable by Cl, Br, or NO_2 in the 3-position; these groups are removed by boiling alkali when the 4-position is unsubstituted. The following are prepared: *trans*- β -2-hydroxy-1-naphthylacrylic acid (II), m.p. 165° (decomp.), in small amount from (I) and 40% KOH ; *cis*- β -2-hydroxy-1-naphthylcrotonic acid (III), m.p. 146° (decomp.), from 4-methyl-1:2- $\beta\alpha$ -naphthapyrone; *cis*- α -chloro- β -2-hydroxy-1-naphthylcrotonic acid, m.p. 148° (decomp.), from 3-chloro-4-methyl-1:2- $\beta\alpha$ -naphthapyrone; *cis*- β -2-hydroxy-1-naphthylglutaconic acid, m.p. 174° (decomp.) (cf. Dey, J.C.S., 1915, 107, 1606), from 1:2- $\beta\alpha$ -naphthapyrone-4-acetic acid; *trans*- β -2-hydroxy-1-naphthylitaconic acid, m.p. 79° , from 1:2- $\beta\alpha$ -naphthapyrone-3-acetic acid by Sen and Chakravarti's method (A., 1930, 913); *cis*- β -2-hydroxy-1-naphthyl- β -methylitaconic acid, m.p. 154° (decomp.), from 4-methyl-1:2- $\beta\alpha$ -naphthapyrone-3-acetic acid; *trans*- β -2-hydroxy-1-naphthyl- α -methylacrylic acid, m.p. 138° (Me ester, m.p. 130°), from 3-methyl-1:2- $\beta\alpha$ -naphthapyrone by Sen and Chakravarti's method; *cis*- β -(?)-nitro-2-hydroxy-1-naphthylcrotonic acid, m.p. 271° (decomp.), from (?)-nitro-4-methyl-1:2- $\beta\alpha$ -naphthapyrone, m.p. 273° (sinters at 268°) [prepared from (III) and fuming HNO_3 in Ac_2O]. 3-Bromo-1:2- $\beta\alpha$ -naphthapyrone, m.p. 165° (decomp.), from (I) and Br in CS_2 and sunlight, is converted by 30% KOH in $EtOH$ into β -naphthafurancarboxylic acid, m.p. 192° . 3-Nitro-1:2- $\beta\alpha$ -naphthapyrone, m.p. 244° , from (II) and HNO_3 , and 30% KOH give 1-aldehydo- β -naphthol. H. B.

Dye derived from 10-hydroxy-9-phenyl- γ -anthranol. T. PAVOLINI (L'Ind. Chimica, 1932, 7,



877—879).—Condensation of *o*-benzoylbenzoic acid with resorcinol yields a compound, named *rodonine*, m.p. $157-158^{\circ}$, of the probable constitution annexed. In slightly acid solution it dyes wool and silk yellow and in slightly

alkaline solution coral-pink. It serves as an indicator, changing sharply from yellow in neutral or acid solution to pink with green fluorescence in alkaline solution; its use for determining the acidity of coloured liquids like wine, beer, and vinegar is suggested.

T. H. P.

Rotenone. XXIII. Structure of rotenone. F. B. LaFORGE (J. Amer. Chem. Soc., 1932, 54, 3377—3380).—Rotenone, the lactone corresponding with rotenonic acid (I), is partly converted into derritol (II) by Zn and EtOH-KOH. (I) and Me_2SO_4 in 5% KOH give the *Me* ester, m.p. 138°, of *methyl-rotenonic acid*, m.p. 179—180° (tetrahydro-derivative, m.p. 184—186°). (II) and $\text{CO}_2\text{Et}\cdot\text{COCl}$ in pyridine give rotenone; this is a convenient method of prep. A structure is proposed for rotenone; it is identical with that of Butenandt and McCartney (this vol., 619).

C. J. W. (b)

Ring fission of pyridine. A. TREIBS (Annalen, 1932, 497, 297—301).—Pyridine (1 mol.) and CHCl_3 (1 mol.) in cold 15% NaOH (3—5 mols.) give first an unstable red dye and then (after 1—7 months) HCN and a little β -vinylacrylic acid: $\text{C}_5\text{H}_5\text{N} + \text{CHCl}_3 + 5\text{NaOH} = \text{C}_5\text{H}_5\text{O}_2\text{Na} + \text{NaCN} + 3\text{NaCl} + 3\text{H}_2\text{O}$; glutacondialdehyde is not an intermediate. Red dyes are similarly produced using CHBr_3 , CHI_3 , CCl_4 , CPhCl_3 , and $\text{CCl}_3\cdot\text{CO}_2\text{H}$, but not with 2:6-dimethyl- and 2:4:6-trimethyl-pyridine, quinoline, and 2-methylquinoline. 2-Methylpyridine, $\text{CCl}_3\cdot\text{CO}_2\text{H}$, and aq. NaOH give HCN and sorbic acid.

H. B.

The Rosenmund aldehyde synthesis in the pyridine series. R. GRAF (J. pr. Chem., 1932, [ii], 134, 177—187).—4:6-Dichloropyridine-2-aldehyde, m.p. 74° (phenylhydrazone, m.p. 195—197°), 5:6-dichloropyridine-3-aldehyde, m.p. 69—70° (phenylhydrazone, m.p. 158°), and 2:6-dichloropyridine-4-aldehyde, m.p. 46—47° (phenylhydrazone, m.p. 157—158°), are obtained, together with some of the corresponding dichloropyridines, from the appropriate carboxyl chlorides ($\text{H}_2\text{-Pd-BaSO}_4$). The reaction fails with less highly negatively substituted derivatives, e.g., nicotinic, 4-chloropicolinic, dipicolinic, isocinchomeric, quinaldinic, and 2-chloroquinoline-4-carboxylic acids. The aldehydes are converted by 50% aq. KOH into the corresponding alcohols, viz., 4:6-dichloro-2-pyridylcarbinol, m.p. 84° (Bz derivative, m.p. 53—54°), 5:6-dichloro-3-pyridylcarbinol, m.p. 76—78° (Bz derivative, m.p. 103—104°), and 2:6-dichloro-4-pyridylcarbinol, m.p. 131—132° (Bz derivative, m.p. 119—120°). 2:3-Dichloropyridine has m.p. 69°.

H. A. P.

Preparation of pyridine-*o*-thiol- and -*o*-sulphocarboxylic acids. E. SUCHARDA and C. TROSKIEWICZ (Rocz. Chem., 1932, 12, 493—499).—The following substances have been prepared by the action of KSH on the corresponding chloropyridine-carboxylic acids: 2-thiopyridine-3-carboxylic acid, m.p. 270°, yielding on oxidation 2-sulphopyridine-3-carboxylic acid, m.p. 282°, 3-thiopyridine-2-carboxylic acid, m.p. 183.5°, 2:2'-dicarboxy-3:3'-dipyridyl disulphide, m.p. 206°, yielding on oxidation the corresponding 3-sulphonic acid, m.p. 343°, 3-thiopyridine-4-carboxylic acid, m.p. 225°, and 4:4'-dicarboxy-3:3'-dipyridyl disulphide, m.p. 307—308°,

giving on oxidation the corresponding 3-sulphonic acid, m.p. 318°.

R. T.

Action of halogens on polycyclic indole derivatives. II. Bromination of the acyl derivatives of 8:9:10:11-tetrahydro- $\alpha'\beta'$ -naphthacarbazole and 7:8:9:10-tetrahydro- $\alpha\beta$ -naphthacarbazole. S. G. P. PLANT and (MISS) M. L. TOMLINSON (J.C.S., 1932, 2192—2195).—Bromination of 7-acetyl-8:9:10:11-tetrahydro- $\alpha'\beta'$ -naphthacarbazole in AcOH gives the 5-*Br*-compound, m.p. 199°, hydrolysed to 5-bromo-8:9:10:11- $\alpha'\beta'$ -naphthacarbazole, m.p. 115—120°, also prepared from cyclohexanone-4-bromo-2-naphthylhydrazine (corresponding Bz compounds similarly obtained; 5-bromo-7-benzoyl-, m.p. 158—159°). *Et* 8:9:10:11-tetrahydro- α' -naphthacarbazole-7-carboxylate, m.p. 121°, is brominated to the 5-*Br*-derivative, m.p. 180—181°; the 5-bromo-11-acetyl-, m.p. 126—127°, and 5-bromo-11-benzoyl-, m.p. 115°, derivatives are hydrolysed to 5-bromo-7:8:9:10-tetrahydro- $\alpha\beta$ -naphthacarbazole, m.p. 116° (prepared by the indole synthesis from cyclohexanone and 4-bromo-1-naphthylhydrazine, m.p. 139°). Orientation problems arising from these results are discussed.

F. R. S.

Platinum with a co-valency of four: diquinolinoplatinous chlorides. E. G. COX, H. SAENGER, and W. WARDELAU (J.C.S., 1932, 2216—2221).—Cold aq. K_2PtCl_4 with quinoline gives a solid which when extracted with CHCl_3 gives the β -dichloride, $\text{Pt}(\text{C}_9\text{H}_7\text{N})_2\text{Cl}_2\cdot 2\text{CHCl}_3$ (I), for which crystallographic data are given; this in boiling quinoline gives the α -dichloride $\text{Pt}(\text{C}_9\text{H}_7\text{N})_2\text{Cl}_2$ (II) but no tetraquinolinous salt. (I) with $\text{C}_5\text{H}_5\text{N}$ gives quantitatively tetrapyridinoplatinous chloride $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}_2$ (III), giving with K_2PtCl_4 a plato-salt, $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4][\text{PtCl}_4]$ and with dil. HCl α -dipyridinoplatinous chloride; with aq. $\text{C}_5\text{H}_5\text{N}$ (I) gives mixtures of (III) with β -dipyridinodiquinolinoplatinous chloride, $\text{Pt}(\text{C}_5\text{H}_5\text{N})_2(\text{C}_9\text{H}_7\text{N})_2\text{Cl}_2$, (plato-salt; α -pyridinoquinolinoplatinous chloride). (II) reacts similarly but much less rapidly; α -tetrapyridino- and α -dipyridinodiquinolinoplatinous chlorides and their plato-salts are described. With moist Ag_2O (I) gives the β -base $\text{Pt}(\text{C}_9\text{H}_7\text{N})_2(\text{OH})_2$ (β -dibromide); (II) reacts very slowly, giving only traces of the α -base.

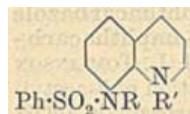
E. E. J. M.

Synthesis of quinoline derivatives. K. DZIEWONSKI and J. MOSZEW (Rocz. Chem., 1932, 12, 482—492).—The chief product of reaction of $\text{CS}(\text{NHPh})_2$ or $\text{CO}(\text{NHPh})_2$ with COPhMe is 4-anilino-2-phenylquinoline, m.p. 190° [hydrochloride, m.p. 265—266°; picrate, m.p. 235—236°; *NO*-derivative, m.p. 203°; *Ac* derivative, m.p. 160°; compound with 0.5 mol. $\text{C}_6\text{H}_5\text{Br}_2$, m.p. 297—298°; 1:2:3:4-tetrahydro-derivative, m.p. 138—139° (picrate, m.p. 163°)]. COME_2 and di-*p*-tolylthiocarbamide yield 4-*p*-tolylamino-2-phenyl-6-methylquinoline, m.p. 162° [hydrochloride, m.p. 324°; nitrate, m.p. 171°; picrate, m.p. 241°; *NO*-derivative, m.p. 189°; *Ac* derivative, m.p. 154°; compound with $\text{C}_6\text{H}_5\text{Br}_2$, m.p. 262—263°; tetrahydro-derivative, m.p. 113° (picrate, m.p. 203°)].

R. T.

Molecular dissymmetry dependent on restriction of rotation about a single linking. II. Opti-

cally active 8-benzenesulphonylethylamino-1-ethylquinolinium salts. W. H. MILLS and J. G. BRECKENRIDGE (J.C.S., 1932, 2209—2216).—The following 8-benzenesulphonyl compounds having the annexed formula are described: -aminoquinoline (I),



m.p. 133.5°; -ethylaminoquinoline (II), m.p. 136.5° [prep. by mixing EtOH solutions of (I) and KOEt and heating the resulting K derivative (III) with EtI at 115°]; -ethylamino-1-methylquinolinium iodide (IV), m.p. 169.5° [prep. by heating (II) with Me₂SO₄ at 100° and treating the resulting methosulphate, m.p. 192°, with aq. KI] [d- α -bromocamphor--sulphonate (V), [α]_D²⁰ +59.4° in CHCl₃]; -ethylamino-1-ethylquinolinium iodide, m.p. 173°, from (II) and Et₃SO₄, giving a gummy d-bromocamphorsulphonate (VI), the cryst. anhyd. form of which was obtained by pptn. of its EtOH solution with Et₃O [dihydrate (VII), m.p. 104—107°]; -d-ethylamino-1-ethylquinolinium iodide (VIII), from (VII) and conc. aq. KI; -1-ethylamino-1-ethylquinolinium d-bromocamphorsulphonate (IX), prep. by evaporation of a solution of (VI) in EtOAc-MeOH [l-iodide (X)]; -n-propylaminoquinoline, m.p. 66.5°, from (III) and PrI at 120° [methosulphate, m.p. 168°; methiodide, m.p. 162°; d-bromocamphorsulphonate, m.p. 170° [trihydrate (XI), m.p. 105°, [α]_D²⁰ +58.8° in CHCl₃]]; -benzylaminoquinoline, m.p. 124°, from (III) and CH₃PhBr at 160° (methosulphate, m.p. 219°; methiodide, m.p. 176°). (VII), (VIII), (IX), and (X) in which R' is Et all show mutarotation, which is described in detail; (V) and (XI) in which R' is Me do not.

E. E. J. M.

Oxidation of optochin. C. C. VERNON and H. U. RESCH (J. Amer. Chem. Soc., 1932, 54, 3455—3456).—Oxidation of optochin with CrO₃ in acid solution gives 6-ethoxyquinoline-4-carboxylic acid, m.p. 288.5°.

C. J. W. (b)

Quinoline compounds. VII. U. BRAHMACHARI and J. M. DAS-GUPTA (J. Indian Chem. Soc., 1932, 9, 203—206).— β -6-Methoxy-8-quinolylamino- α -dimethylamino- and - α -diethylamino-propane (dihydrochlorides, m.p. 180° and 175°, respectively) are prepared from the α -NH₂-compound (this vol., 281, 522) and MeI and EtI, respectively. β -8-Quinolylamino-, β -6-methyl-8-quinolylamino-, and β -6-methoxy-2-methyl-8-quinolylamino- α -dimethylaminopropane dihydrochlorides, m.p. 200—205°, 210°, and 218°, respectively, are similarly prepared. These compounds could not be prepared from aminoquinolines and β -bromo- α -dialkylaminopropanes. 8-Allylaminoquinoline and fuming HBr at 100° (bath) give 8- β -bromopropylaminoquinoline, hydrolysed by aq. Na₂CO₃ to 8- β -hydroxypropylaminoquinoline (hydrochloride, m.p. 170—172°), also formed from 8-aminoquinoline and CH₂Cl-CHMe-OH; 8- β -hydroxypropylamino-6-ethoxyquinoline (hydrochloride, m.p. 165°) is similarly prepared. 8-Aminoquinoline and Et lactate at 130° give 8- α -hydroxypropionamidoquinoline (hydrochloride, m.p. 182—185°), also formed when 8-aminoquinoline lactate is heated at 175°. 8- α -Hydroxypropionamido-6-ethoxyquinoline (hydrochloride, m.p. 177°) is similarly prepared.

H. B.

Synthetic experiments in the benzylisoquinoline series. I. C. SCHOPF, H. PERREY, and I.

JÄCKH. II. Preparation of 6-hydroxy-1-3'-hydroxy-4'-methoxybenzyl-N-methyltetrahydroisoquinoline and laudanoline 4'-methyl ether. C. SCHOPF, I. JÄCKH, and H. PERREY (Annalen, 1932, 497, 47—58, 59—68).—I. β -3 : 4-Dimethoxyphenylpropionhydrazide, m.p. 132—133°, is converted by the usual method into the azide, which when heated with CH₂Ph-CO₂H in C₆H₆ gives phenylacet- β -3 : 4-dimethoxyphenylethylamide. Rapid treatment of β -m-benzoyloxyphenylpropionhydrazide (I), m.p. 135—137° (sinters at 130°), with aq. NaNO₂ in cold AcOH-C₆H₆ affords the azide, which with CH₂Ph-CO₂H and 3-benzoyloxy-4-methoxyphenylacetic acid, m.p. 126—130° (prepared from benzylisovanillin by way of the azlactone and pyruvic acid), gives phenylacet-, m.p. 81—86°, and 3-benzoyloxy-4-methoxyphenylacet- (II), m.p. 101—106°, β -m-benzoyloxyphenylethylamide, respectively. Slow treatment of (I) with NaNO₂ gives some sec.- β -m-benzoyloxyphenylpropionhydrazide, m.p. 190—192°, as a by-product. (II) and PCl₅ in CHCl₃ give 6-benzoyloxy-1-3'-benzoyloxy-4'-methoxybenzyl-3 : 4-dihydroisoquinoline hydrochloride (III) (+2H₂O), m.p. 127—128° (decomp.); the free base (IV) undergoes ready autoxidation and with MeI affords a compound, probably C₃₂H₃₀O₄NI, m.p. 188—190°. The following compounds are described: s-di-(β -m-benzoyloxyphenylethyl)carbamide, m.p. 166—168°; β -3-benzoyloxy-4-methoxyphenylpropionhydrazide, m.p. 138—140°; 3 : 4-dibenzoyloxyphenylacetic acid, m.p. 109°.

II. β -3 : 4-Dibenzoyloxyphenylpropionhydrazide, m.p. 138°, is converted [as (I)] into the azide which with 3-benzoyloxy-4-methoxyphenylacetic acid gives 3-benzoyloxy-4-methoxyphenylacet- β -3 : 4-dibenzoyloxyphenylethylamide, m.p. 137° (sinters at 124°), cyclised by PCl₅ in CHCl₃ to 6 : 7-dibenzoyloxy-1-3'-benzoyloxy-4'-methoxybenzyl-3 : 4-dihydroisoquinoline hydrochloride, m.p. 179—181°. Successive treatment of this with NaOEt and MeI in EtOH and N₂ gives the methiodide, m.p. 185—187°, of the free base; treatment of this with AgOAc in aq. AcOH and subsequent reduction (Zn dust) affords 6 : 7-dibenzoyloxy-1-3'-benzoyloxy-4'-methoxybenzyl-N-methyl-tetrahydroisoquinoline (laudanoline 6 : 7 : 3'-tribenzyl 4'-methyl ether), m.p. 86—87°, debenzylated by HCl (d 1.12) in 2N-AcOH to laudanoline 4'-Me ether, m.p. 120—122° (decomp.) (sinters at 110°) (demethylated by 48% HBr to laudanoline). 6-Benzoyloxy-1-3'-benzoyloxy-4'-methoxybenzyl-3 : 4-dihydroisoquinoline methiodide, m.p. 120° (sinters at 100°) [obtained by successive treatment of (III) with NaOEt and MeI in EtOH and N₂], is converted into the methochloride (+H₂O), m.p. 145—147°, which is debenzylated to the 6 : 3'-dihydroxy-analogue (V) [corresponding methopicate, m.p. 208—209° (sinters at 198°)] and reduced by Zn dust and 50% AcOH to the 6 : 3'-dibenzyl ether of 6-hydroxy-1-3'-hydroxy-4'-methoxybenzyl-N-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline [picrate, m.p. 183—184° (sinters at 175°)] [also prepared by reduction of (V) with Zn dust and 30% AcOH or catalytically]. Debonylation of (IV) gives 6-hydroxy-1-3'-hydroxy-4'-methoxybenzyl-3 : 4-dihydroisoquinoline [picrate, m.p. 148—152° (sinters at 140°)], reduced (H₂, PtO₂, dil. HCl, or Zn dust, 30% AcOH) to 6-hydroxy-1-3'-hydroxy-4'-methoxybenzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline (VI), m.p.

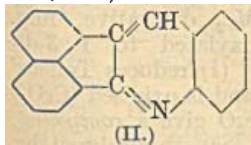
210—212° (sinters at 206°) [*picrate*, m.p. 130—132° (sinters at 120°); Ac_3 derivative, m.p. 103—105° (sinters at 95°)], also obtained by reduction (H_2 , PtO_2 , $AcOH$) of (III) and subsequent debenzoylation. (VI) and keten in N - $AcOH$ give an impure N - Ac derivative. Reduction of (IV) (as acetate) with Zn dust and 50% $AcOH$ gives a compound, $C_{31}H_{31(29)}O_3N(+3H_2O?)$, m.p. 140—142°, hydrolysed by 20% HCl to 50% of (VI) and resinous material; with 60% $AcOH$, a substance, $C_{26}H_{27}O_4N$, m.p. 166—168°, is also produced, whilst the use of 30% $AcOH$ leads to 6% of a compound, $C_{31}H_{31}O_3N$, m.p. 150—152°, and a mixture of substances [hydrolysed to (VI) in 15% yield].

A hydrochloride, $C_{31}H_{28}O_4NCl \cdot H_2O$, of the autoxidation product of (IV) is described. H. B.

Phenanthridine series. II. Nitro- and amino-phenanthridines. G. T. MORGAN and L. P. WALLS (J.C.S., 1932, 2225—2231).—5-Nitro- and 4-nitro-2-acetamidodiphenyls and 2-o-nitrobenzamide-5-nitrodiphenyl, m.p. 167° (prep. from 5-nitro-2-xenylamine and o-nitrobenzoyl chloride), give with $POCl_3$ 3-nitro-(I) and 7-nitro-9-methylphenanthridines and 3-nitro-9-o-nitrophenylphenanthridine, m.p. 210°, 243—245°, and 227°, respectively; the yield of the last two is small. Reduction (Fe) of (I) gives 3-amino-9-methylphenanthridine, m.p. 152°, the Ac derivative of which with Me_2SO_4 gives 4-acetamido-9:10-dimethylphenanthridinium methosulphate, decomp. about 225°, hydrolysis of which with 5*N*- HCl gives the chloride, m.p. about 275° (decomp.) (dihydrate), which has no therapeutic val.

An improvement in Pictet and Hubert's process for preparing phenanthridine (IV) is described. The *dinitrate* and *nitrate*, m.p. 169—171°, with conc. H_2SO_4 give three mononitro-derivatives, m.p. 260—262°, 160—163°, and 156—158°, and a substance subliming at 220/6 mm. (IV) reacts with $NaNH_2$ or with NH_3 in hot $NPhMe_2$ in presence of Na to give 9-amino-phenanthridine (V), m.p. 195.5° [acetate, m.p. 206—209°; lactate, m.p. 202—204° (decomp.)]; Ac derivative, m.p. 193.5° (does not form quaternary salts), together with a brown base which gives highly-coloured solutions in acids. With HNO_2 (V) is not diazotised, but gives only phenanthridone identical with that obtained when either o-xenylcarbamide [2-diphenylcarbamide], m.p. 157—158.5°, or methyl-o-xenyl [methyl-2-diphenyl] carbamate, m.p. 61°, obtained from o-xenylcarbimide with NH_3 or $MeOH$, respectively, is fused with $ZnCl_2$. E. E. J. M.

Acenaphthenone. II. Indole and acridine derivatives. A. C. SIRCAR and M. D. R. GOPALAN (J. Indian Chem. Soc., 1932, 9, 297—301).—Acenaphthindole, m.p. 235°, and its N - Me derivative, m.p. 204°, are prepared by Robinson and Thornley's method (A., 1927, 158) from acenaphthenone (I) and $NHPh \cdot NH_2$ and $NPhMe \cdot NH_2$, respectively. *Pheno* - $\alpha\beta$ - acenaphthacridine [2:3-1:8-naphthquinoline] (II), m.p. 181°, is obtained from (I) and o- $NH_2 \cdot C_6H_4 \cdot CHO$ by Friedlander's method (A., 1883, 1148; 1892, 1106). Reduction of o-nitrobenzylidene-acenaphthenone, m.p. 157°, with Fe and fuming HCl in



$EtOH$ gives a little (II) and a substance, decomp. 236—240°. H. B.

Syntheses of 19-ketophenanthridindocoline, 3-benzoylcarbazole, and 3:6-dibenzoylcarbazole. S. G. P. PLANT and (Miss) M. L. TOMLINSON (J.C.S., 1932, 2188—2192).—Carbazole and o- $NO_2 \cdot C_6H_4 \cdot COCl$ afford 9-o-nitro-, m.p. 148—150°, reduced to 9-o-aminobenzoylcarbazole, m.p. 160—162°, which on diazotisation in $MeOH-H_2SO_4$ gives 19-ketophenanthridindocoline (cf. this vol., 168). 9-Benzoylcarbazole heated with $AlCl_3$ at 120° is isomerised to the 3-Bz compound (phenylhydrazone, m.p. 219°), converted by Ac_2O and $BzCl$, respectively, into 3-benzoyl-9-acetyl-, m.p. 154°, and 3:9-dibenzoyl-carbazole, m.p. 170°. 3-Benzoylcarbazole has been synthesised by oxidising with S 6-benzoyltetrahydrocarbazole, m.p. 167—168°, obtained by heating the product of condensing cyclohexanone and p-hydrazinobenzophenone with H_2SO_4 . Benzoylation of carbazole in CS_2 in presence of $AlCl_3$ gives 3:6-dibenzoylcarbazole (I), m.p. 258°, which forms 3:6:9-tribenzoyl-, m.p. 224°, 3:6-dibenzoyl-9-acetyl-, m.p. 270°, and -9-phenacetyl-carbazole, m.p. 190—191°, with the appropriate reagent. 4-Bromo-3-nitrobenzophenone, p-amino-benzophenone, and K_2CO_3 yield 2-nitro-, m.p. 150°, reduced to 2-amino-4:4'-dibenzoyldiphenylamine, m.p. 153°, converted by $NaNO_2$ into 5:4'-dibenzoyl-1-phenylbenzotriazole, m.p. 195°, which is decomposed at 380° to (I). 2-Bromo-3-nitrobenzophenone, m.p. 76° (lit. 115°), and NH_2Ph give 2-nitro-, reduced to 2-amino-6-benzoyldiphenylamine, m.p. 118—119°, forming with $NaNO_2$, 7-benzoyl-1-phenylbenzotriazole, m.p. 154°, which could not be converted into 1-benzoylcarbazole. F. R. S.

Structure of C-substituted derivatives of barbituric acid. D. MAROTTA and G. ROSANOVA (Atti R. Accad. Lincei, 1932, [vi], 15, 753—755).—Diazo-methane converts 5:5-diethylbarbituric acid into a mixture of an O-ether (a syrup) and the N -ether obtained by Fischer and Dilthey (A., 1905, i, 35).

T. H. P.

isoVioluric acid (alloxan-6-oxime). D. DAVIDSON and M. T. BOGERT (Proc. Nat. Acad. Sci., 1932, 18, 490—496).—isoBarbituric acid (A., 1925, i, 1188) and HNO_2 give isovioluric acid (alloxan-6-oxime) (+2 H_2O), m.p. (anhyd.) about 250° (decomp.) [5-phenylhydrazone, m.p. 268° (decomp.)], rearranged by dil. HCl to violuric acid, oximated to alloxan-5:6-dioxime, m.p. 242° (decomp.) [reduced by 20% (NH_4) $_2S$ to 5:6-diaminouracil], and reduced [(NH_4) $_2S$] to isouramil, not melted at 290° (5-O- Ac derivative, not melted at 275°), which is hydrolysed by dil. HCl to dialuric acid and oxidised by dil. HNO_3 to alloxan.

H. B.

Creatine and creatinine. II. Alleged acyl derivatives of creatine. H. R. ING (J.C.S., 1932, 2198—2200).—Acetylation of creatine gives s-(N -acetylsarcosyl)acetylcarbamide (I), m.p. 177—178°, and 1-methylhydantoin, and not diacetylcreatine (cf. Erlenmeyer, A., 1895, i, 310), since (I) reacts with aq. NH_3 to form acetylcarbamide and N -acetylsarcosine amide, m.p. 140—141°. Phthalylldicreatine (Urano, A., 1907, i, 192) is dicreatinine phthalate, m.p. 223° (decomp.). F. R. S.

Formation of the piperazine ring. K. H. SLOTTA and R. BEHNISCH (Annalen, 1932, 497, 170—180).— β -Dimethylaminoethyl alcohol (I), p - $C_6H_4Me \cdot SO_2Cl$, and Na_2CO_3 in C_6H_6 give 1:1:4:4-tetramethylpiperazinium di- p -toluenesulphonate (II), decomp. 335° (corresponding *dipicrate*, decomp. 315°), also obtained from p - $C_6H_4Me \cdot SO_3Ag$ and 1:1:4:4-tetramethylpiperazinium di-iodide or dichloride [prepared from $NMe_2 \cdot CH_2 \cdot CH_2Cl$ (cf. Knorr, A., 1904, i, 938)]. β -Diethylaminoethyl alcohol (III) similarly affords 1:1:4:4-tetraethylpiperazinium di- p -toluenesulphonate (IV), m.p. 285° (corresponding *dipicrate*, m.p. 277°, and *dichloroaurate*, decomp. 236—237°), also formed from β -chloroethyl p -toluenesulphonate and NH_4Et_2 at 120°. Similarly, $PhSO_2Cl$ with (I) and (III) gives 1:1:4:4-tetramethyl-, decomp. above 340° (*dipicrate*, decomp. 315°), and 1:1:4:4-tetraethyl-, m.p. 258—260° (*dipicrate*, m.p. 277°), -piperazinium dibenzenesulphonates, respectively. β - N -Methyl- and -ethyl-anilinoethyl alcohols with $ArSO_2Cl$ give deep blue products. (II) and (IV) are converted by $EtOH$ - KOH into 1:4-dimethyl- and -diethyl-piperazine, respectively. $PhOH$, (II), and $EtOH$ - KOH at 130° give ω -dimethylaminophenetole; ω -diethylaminophenetole, b.p. 120°/10 mm., and o -anisyl β -diethylaminoethyl ether are similarly prepared from (IV) and $PhOH$ and guaiacol, respectively. p - $C_6H_4Me \cdot SO_2Cl$ and (III) in pyridine give β -diethylaminoethylpyridinium p -toluenesulphonate, m.p. 166° (not sharp) (corresponding *picrate*, m.p. 143°, and *chloroaurate*, m.p. 212°). H. B.

Substituted piperazines. IV. Stereoisomeric bispentamethylenepiperazines. GODCHOT and MOUSSERON. V. Aminoalcohols. MOUSSERON (Bull. Soc. chim., 1932, [iv], 51, 774—782, 782—807).—IV. 2-Chlorocycloheptanone, b.p. 98—100°/1 atm., prepared by chlorination of suberone in presence of $CaCO_3$, gives with cold NH_3 - $EtOH$ bispentamethylenepiperazine, m.p. 137—138° [*picrate*; *chloroplatinate*; *hydrochloride* (+2 H_2O)], in 12% yield. Unlike the corresponding tetramethylene compound (this vol., 625), this is not reduced by Na and $EtOH$ or Na and $C_5H_{11} \cdot OH$, but with H_2 - Pt gives three of the five possible stereoisomeric piperazines, isolated as $(NO)_2$ -derivatives, viz., α -, m.p. 74—75° [*chloroplatinate*; $(NO)_2$ -derivative, decomp. 230° without melting], β -, m.p. 100—101° [*dipicrate*, m.p. 165°; *chloroplatinate*, decomp. 250°; *dihydrochloride* (+8 H_2O)]; $(NO)_2$ -derivative, m.p. 186—187°; solubility of urate 1 in 1510 of H_2O at 15°], and γ -bispentamethylenepiperazine, m.p. 58—59° [*dipicrate*, decomp. 220°; *chloroplatinate*, decomp. 230°; *dihydrochloride* (+8 H_2O)], decomp. 250°; $(NO)_2$ -derivative, m.p. 148—149°; solubility of urate 1 in 24.6 of H_2O at 15°]. α -Chlorocyclooctanone, b.p. 96—98°/6 mm., similarly prepared, did not give a piperazine derivative with NH_3 .

V. Interaction of α -halogeno-alcohols or the corresponding ethylene oxides with piperazine and its C -substituted derivatives gives a mixture of mono- and bis- N -substitution products. These are separated either by crystallisation from the aq. reaction mixture, and recovery of the more sol. mono-derivative by steam-distillation and pptn. as $HgCl_2$ derivative, or by action of CS_2 , which combines with

the former only to give a dithiocarbamate, which is decomposed by boiling aq. KOH . The following are described: N -(2-hydroxycyclopentyl)-, m.p. 83—84° [*picrate*; *dithiocarbamate*, decomp. 200°; *chloroplatinate*, decomp. 250°; *dihydrochloride* (+3 H_2O), decomp. 230°; *mercurichloride*]; NN' -bis-2-hydroxycyclopentyl-, m.p. 202—203° [*picrate*; *chloroplatinate*, decomp. 250°; *dihydrochloride* (+3 H_2O), decomp. 200°]; N -2-hydroxycyclohexyl- (I), m.p. 67—68° [*picrate*, decomp. 200°; *dithiocarbamate*, m.p. 205° (decomp.); *chloroplatinate*, decomp. 250°; *dihydrochloride* (+1 H_2O); *mercurichloride* ($C_{10}H_{20}ON_2 \cdot 2HCl \cdot 2HgCl_2$)]; NN' -bis-2-hydroxycyclohexyl- (II), m.p. 204—206° [*picrate*, m.p. 215° (decomp.); *chloroplatinate*, decomp. 270°; *dihydrochloride* (+4 H_2O), decomp. 240°]; -bis-2'-hydroxycyclohexyl-2:5-dimethyl-, m.p. 225° (*chloroplatinate*, decomp. 260°); N -2-hydroxycycloheptyl-, m.p. 41—42° [*picrate*, decomp. 225°; *dithiocarbamate*, decomp. 235°; *chloroplatinate*; *dihydrochloride* (+4 H_2O), m.p. 220°]; NN' -bis-2-hydroxycycloheptyl-, m.p. 78—79° [*dipicrate*; *chloroplatinate*; *dihydrochloride* (+6 H_2O), m.p. 225°]; N -2-hydroxycyclooctyl-, m.p. 39° [*dipicrate*, decomp. 250°; *dithiocarbamate*, decomp. 220°; *chloroplatinate*, decomp. 260°]; NN' -bis-2-hydroxycyclooctyl-, m.p. 84—85° [*dipicrate*, decomp. 270°; *chloroplatinate*, decomp. 270°]; N -1-hydroxy-2-indanyl-, m.p. 72—73° (*dipicrate*, decomp. 240°; *dithiocarbamate*, decomp. 220°; *chloroplatinate*, decomp. 245°), and NN' -bis-(1-hydroxy-2-indanyl)-piperazine, decomp. 200° without melting (*dipicrate*; *chloroplatinate*). The C_6 , C_7 , and C_8 derivatives possess marked local anaesthetic action. It was not found possible to condense tetramethyl- or bistetramethylene-piperazines with o -chlorocyclohexanol or with cyclohexene oxide. Interaction of 2-chlorocyclohexanone with excess of piperazine hydrate at 140° gives N -2-ketocyclohexylpiperazine, m.p. 4° [*dithiocarbamate*, m.p. 165° (decomp.); *chloroplatinate*, decomp. 210°], and NN' -bis-2-ketocyclohexylpiperazine, m.p. 113—114° (*picrate*, decomp. 140°; *dihydrochloride*, m.p. 185°; *chloroplatinate*). The former is reduced by Na and $EtOH$ to the corresponding alcohol (I), but by H_2 - Pt to a stereoisomeride of (I), m.p. 105—106° (*dithiocarbamate*, m.p. 155°; *picrate*, m.p. 150°; *chloroplatinate*, decomp. 225°); from the latter both (II) and its stereoisomeride, m.p. 160—161° (*picrate*, m.p. 180°), are formed by either method, Na and $EtOH$ giving mainly (II), and Pt - H_2 mainly its stereoisomeride. H. A. P.

Syntheses of 2-iminazolone-4-carboxylic acid and 2-iminazolone. G. E. HILBERT (J. Amer. Chem. Soc., 1932, 54, 3413—3419).—Anhyd. tartaric acid is added to oleum (13% SO_3) below 10° and the mixture treated with $CO(NH_2)_2$ at 80°, whereby 2-iminazolone-4-carboxylic acid (I), m.p. 261° (decomp.) (*Et* ester, m.p. 255°; 1:3- Me_2 derivative, m.p. 229—230° (decomp.)), decarboxylated to 1:3-dimethyl-2-iminazolone, results. (I) reduces Tollens' reagent and Ag_2O in aq. NH_3 , and is oxidised (CrO_3) to parabanic acid. (I) and Ac_2O give a compound, $C_{10}H_{10}O_6N_4$ (?), not melted at 300°, hydrolysed by KOH to a salt, $C_8H_2O_4N_4K_2$. (I) heated at 220°/2 mm. for 6 hr. gives 2-iminazolone, decomp. 250—251

(1:3-Ac₂ derivative, m.p. 105—106°), which is probably identical with the "isoiminazolone" of Fenton and Wilks (J.C.S., 1909, 95. 1329).

C. J. W. (b)

NN'-Substituted pyrimidine and purine derivatives. IV. 5-Substitution products of 3-phenyl-1-methylbarbituric acid. B. HEPNER and S. FRENKENBERG (J. pr. Chem., 1932, [ii], 134, 249—256).—3-Phenyl-1-methylbarbituric acid reacts with PhCHO, PhN₂Cl, and HNO₃ to give the *CHPh*. derivative, m.p. 102—104°, 3-phenyl-1-methylalloxan-5-phenylhydrazone, m.p. 210—214°, and 3-phenyl-1-methylviolic acid (+1H₂O), m.p. 91° (decomp.), respectively. The last-named is reduced by Zn and HCO₂H (d 1.22) to 5-formamido-3-phenyl-1-methylbarbituric acid, m.p. 248° (decomp.). The 5-bromo-5-alkyl derivatives of phenylmethylbarbituric acid, prepared by bromination in CHCl₃ (5-bromo-3-phenyl-1-methyl-, m.p. 161°, 5-bromo-3-phenyl-1-methyl-5-n-propyl-, m.p. 89°, and -5-isopropyl-, m.p. 95°, -barbituric acids) are converted by aq. alkalis, NH₃, or amines into hydantoin derivatives with elimination of HBr and CO₂; N-phenyl-N'-methyl-5-isopropylhydantoin, m.p. 170° (*Br*-derivative, m.p. 127°, stable to alkalis), is thus prepared. The dibromides, m.p. 118—120° and 108°, respectively, of 3-phenyl-5-allyl-1-methyl-5-n-propyl-, and -5-isopropyl-barbituric acid, and the tetrabromide, m.p. 168°, of 3-phenyl-5:5-diallyl-1-methylbarbituric acid are described. N-Phenyl-N'-methylcarbamide is conveniently prepared by desulphurisation of the thiocarbamide with H₂O₂ and the calc. quantity of NaOH.

H. A. P.

Gluciminazole and its thiol. H. PAULY and E. LUDWIG (Z. physiol. Chem., 1932, 209, 247—248).—Gluciminazole (A., 1922, i, 953) forms crystals (+2½H₂O), m.p. 120°, $[\alpha]_D^{20}$ -19.6°. The corresponding thiol has m.p. 205° (temp. raised 1° in 10 sec.).

J. H. B.

Colouring matters of bacteria. II. Chlororaphin and "xanthoraphin," a contribution to the chemistry of quinhydrone. F. KÖGL and B. TÖNNIS (Annalen, 1932, 497, 265—289).—The identity of chlororaphin (I), m.p. 228—229° (in N₂), with a quinhydrone-like complex of mol. proportions of phenazine-1-carboxylamide (II) and dihydrophenazine-1-carboxylamide (III) is confirmed (cf. A., 1930, 929). Zerevitinov determinations of active H give the following vals.: (I) 3, (II) 1, (III) variable results, phenazine 0, dihydrophenazine 2; the val. for (I) indicates that (III) possesses an unsym. structure (cf. *loc. cit.*). o-C₆H₄Br·NO₂, 3:4-(NH₂)₂·C₆H₃·CO₂H, Na₂CO₃, and CuCl in amyl alcohol and N₂ at 185—190° give (probably) a mixture, m.p. 228—229°, of 4-amino-3-o-nitroanilino- and 3-amino-4-o-nitroanilino-benzoic acids, which when reduced (SnCl₂, conc. HCl, AcOH) and then oxidised (H₂O₂) affords phenazine-2-carboxylic acid, m.p. 292—293° (amide, m.p. 312°, which forms a green "quinhydrone," chars at 240°, with its H₂-derivative).

[With H. J. GROENEWEGEN.] "Xanthoraphin," the H₂O-sol. intermediate in the production of (I), is identical with oxychlororaphin [*i.e.* (II)] (cf. *loc. cit.*). Addition of phenazine-1-carboxylic acid to the culture solution (asparagine, glycerol, MgSO₄, Na

phosphate, CaCl₂, and FeSO₄ in H₂O) causes approx. twelve- and five-fold increases in the amount of (II) after 4 and 10 days, respectively; the use of K phenazine-1-carboxylate leads to an approx. eleven-fold increase of (II) after 4 days and about 71% of the salt is consumed. KOBz has little effect, K nicotinate causes decreases in the amount of (II) and the wt. of the bacteria (*B. chlororaphis*), but K picolinate increases the amount of (II) by 387% and the wt. of the bacteria by 46% [whilst picolinic acid (51%) is recovered and 3% of picolinamide is formed]. The amount of (II) is doubled by addition of o-C₆H₄(OH)₂ and pyrocatechol-o-carboxylic acid.

H. B.

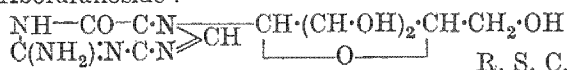
Dyes derived from phenanthraquinone: fluorenophenanthrazines. P. C. DUTTA, D. PRASAD, and S. C. DE (J. Indian Chem. Soc., 1932, 9, 211—213).—The following are prepared from 1:2-diaminofluorene and the appropriate phenanthraquinone (the colour given is the shade on wool): fluoreno-phenanthrazine, m.p. 279—280° (yellow); -2- (this and the following compounds have m.p. above 290°) (chocolate-brown) and -4-nitro- (deep brown), -2:7- (yellow) and -4:5-dinitro- (chocolate), -2-bromo- (brown), -2- (chocolate-brown) and -4-amino- (deep brown), -2:7-diamino- (yellowish-brown), -2- (chocolate) and -4-hydroxy- (greenish-brown), and -2:7-dihydroxy-phenanthrazines (greenish-brown). The compounds are pptd. unchanged from their deep blue solutions in conc. H₂SO₄ by H₂O; they possess deeper shades than the corresponding phenanthra-phenazines and -naphthazines.

H. B.

Prodigiosin, the red pigment of *Bacillus prodigiosus*. II. F. WREDE (Z. physiol. Chem., 1932, 210, 125—128; cf. A., 1929, 1469).—Analyses of prodigiosin and of its perchlorate confirm the formula C₂₀H₂₅ON₃. It contains one OMe group and 2 active H atoms [*Zn* salt, (C₂₀H₂₁ON₃)₂Zn, m.p. 176°] and resembles a dipyrrolylmethene.

J. H. B.

Ring structure of guanosine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1932, 97, 491—495).—Guanosine hydrate, NaOAc, and boiling Ac₂O give triacetylguanosine, m.p. 224—225°, which with Me₂SO₄ and NaOH in aq. COMe₂ affords trimethyl-N-methylguanosine (hydrochloride, amorphous, decomp. 98°). This with 4% HCl (85°; 8 hr.) gives 2:3:5-trimethylribose, oxidised by hot, conc. HNO₃ to i-dimethoxysuccinic acid. Guanosine is, therefore, a ribofuranoside:



R. S. C.

Tetrazole derivatives. R. STOLLE [with K. EHLMANN, D. RIEDER, H. WILLE, H. WINTER, and F. HENKE-STARK] (J. pr. Chem., 1932, [ii], 134, 282—309; cf. A., 1922, i, 689).—Interaction of NHMe·CS·NH₂ with Pb carbonate and NaN₃ in EtOH in CO₂ gives 5-amino-1-methyltetrazole, m.p. 222° (Ac, m.p. 164°, *CHPh*., m.p. 157°, and N-NO-, explodes 177°, -derivatives). It is converted by Ca(OCl)₂ in warm H₂O into 1:1'-dimethyl-5:5'-azotetrazole, m.p. 182° (decomp.), which is reduced by H₂S in faintly acid solution to the hydrazo-compound (+1H₂O), m.p. 158° (decomp.). 5-Amino-1-phenyltetrazole [hydrochloride, m.p. 155—165° (de-

comp.); $+AgNO_3$, m.p. 183° (decomp.); $CHPh$, m.p. 119° , $N-(CH_2Ph)_2$, m.p. 107° , and $N-NPh.N$, decomp. 130° , derivatives], is similarly formed from $NHPh.CS.NH_2$, and converted into 1:1'-diphenyl-5:5'-azo-, m.p. 228° (decomp.), and α :5'-hydrazino-tetrazole ($+2EtOH$), m.p. 190° (decomp.) (Ac_2 derivative, m.p. 195°). Its $N-NO$ -derivative (Ag salt, decomp. 224°) is decomposed to 5-hydroxy-1-phenyltetrazole (I) by hot aq. $NaOH$, and reduced by Zn and 10% aq. $AcOH$ or by $Na-Hg$ to 5-hydrazino-1-phenyltetrazole, m.p. 125° (decomp.) [$CHPh$, m.p. 205° , and CMe_2 , m.p. 146° (decomp.), derivatives], which is also the product of interaction of (II) (below) with $N_2H_4.H_2O$, and is converted by HNO_2 into 5-azido-1-phenyltetrazole, m.p. 99° [hydrolysed by $NaOH$ in aq. $EtOH$ to (I)]. 5-Chloro-1-phenyltetrazole, m.p. 124° , is prepared from the 5- NH_2 -compound with HNO_2 in warm HCl (Cu is beneficial), or from (I) and $POCl_3$ at the b.p. The 5- Br -compound (II), m.p. 151° , is prepared similarly, and also by bromination of 1-phenyltetrazole (accompanied by a by-product, m.p. 225° , when Fe is used as catalyst) or (in H_2O) of 5-thiol-1-phenyltetrazole or the corresponding disulphide, and is hydrolysed to (I) by conc. aq. KOH . 5-Phenylhydrazino-1-phenyltetrazole (*loc.cit.*), prepared from (II) and $NHPh.NH_2$, is oxidised by HgO in xylene to 5-benzeneazo-1-phenyltetrazole, m.p. 168° . α -Allylamino-1-phenyltetrazole, m.p. 108° , is prepared from $NHPh.CS.NH.C_3H_5$ by the general method, or from (II) and allylamine at 100° . *p*-Chlorophenylthiocarbamide, m.p. 183° , prepared by heating $C_6H_4Cl.NH_2.HSCN$ at 100° , is converted by NaN_3 and PbO into 5-amino-*p*-chlorophenyltetrazole, m.p. 213° (decomp.).

The following are prepared by similar methods: 1:1'-bis-*p*-chlorophenyl-5:5'-azotetrazole, m.p. 228° (decomp.); α -amino-*m*-chlorophenyl-, m.p. 173° (decomp.); 5-amino-*p*-aminophenyl-, m.p. 200° (decomp.); 5-amino-*o*-anisyl-, m.p. 172° ; 1:1'-bis-*o*-anisyl-5:5'-azo-, m.p. 190° (decomp.); 5-amino-1-*p*-phenetyl-, m.p. 197° (hydrochloride, decomp. 190° ; Ac_2 , m.p. 145° , and NO_2 , decomp. 117° , derivatives); 1-*p*-phenetyl-5-hydrazino-, m.p. 158° (decomp.) (hydrochloride, decomp. 180° ; sulphate; $CHPh$ derivative, m.p. 171°); 1-*p*-phenetyl-5-azido-, m.p. 72° ; 5-chloro-1-*p*-phenetyl-, m.p. 99° ; 5-hydroxy-1-*p*-phenetyl-, m.p. 168° ; 1:1'-bis-*p*-phenetyl-5:5'-azo-, m.p. 223° (decomp.) (converted by O_3 or H_2O_2 in warm aq. alcoholic $NaOH$ into 5-amino- and 5-hydroxy-1-*p*-phenetyl-tetrazoles); 1:1'-bis-*p*-phenetyl-5:5'-hydrazo- ($+2EtOH$), m.p. 167° (decomp.); 5-*p*-phenetyl-amino-1-*p*-phenetyl-, m.p. 197° (from the thiocarbamide); 5-amino-1-*m*-xyl-, m.p. 198° ; α -amino-1- α -naphthyl-, m.p. 194° (Ac derivative, m.p. 214°); 1:1'-bis- α -naphthyl-5:5'-azo-, m.p. 180° (decomp.) (stable to H_2O_2 in $AcOH$); 5-amino-1- β -naphthyl-, m.p. 193° ; and 1:1'-bis- β -naphthyl-5:5'-azotetrazole, decomp. 204° . The product of interaction of 1-phenyltetrazole and $MgMeI$ gives with $BzCl$, not the expected 5- Bz derivative, but benzoylphenylcyanamide, a fission product. H. A. P.

Oxidation of uric acid by iodine. J. MORE (J. Pharm. Chim., 1932, [viii], 15, 545—550).—When uric acid is oxidised by aq. I containing $Na_2B_4O_7$.

and NH_4 salts, an unstable compound, $C_4H_{10}O_3N_6$ is formed, readily decomposing into NH_4 oxalurate.

A. L.

Acetylation of uric acid [and methyl derivatives]. H. BILTZ and H. PARDON (J. pr. Chem., 1932, [ii], 134, 310—334).—Acetylation of methyluric acids with hot Ac_2O occurs in position 7 if this is free; an 8-acetoxanthine derivative is formed if this is substituted, but either position 3 or 9 is free, otherwise no action takes place. Thus 1:3:9-trimethyluric acid gives the 7- Ac derivative (I), dimorphic, m.p. 235° , whilst the three isomeric trimethyluric acids are unaffected. Similarly, 3-methyl- and 1:3-dimethyl-uric acids give 7- Ac derivatives, m.p. 300° (decomp.), and 304° (decomp.), respectively, the structure of which is confirmed by their methylation by CH_2N_2 (carefully freed from H_2O and $MeOH$) to (I).

9-Methyluric acid is conveniently prepared by action of Me_2SO_4 and alkali on uric acid and separation of the mixed 3- and 9- Me derivatives by the usual means. With Ac_2O it gives the 7- Ac derivative, slow decomp. $>300^\circ$, converted quantitatively by pure CH_2N_2 into 6:8-dihydroxy-2-methoxy-7-acetyl-1:9-dimethylpurine (II), m.p. 150° ; this on heating at 180° isomerises to (I), and on hydrolysis with HCl in $EtOH$ at the b.p. gives 6:8-dihydroxy-2-methoxy-1:9-dimethylpurine, m.p. 275° , which, when heated above its m.p., similarly gives 1:3:9-trimethyluric acid among other products. 7-Acetyl-1:9-dimethyluric acid, m.p. 282° (decomp.), also gives (II) with CH_2N_2 .

The Ac derivative of 7-methyluric acid (A., 1921, i, 606) is converted by CH_2N_2 into 8-acetoxycaffeine (III), m.p. 135° [re-solidifies and re-melts 340° (decomp.)], identified by deacetylation by heat or by alcoholic HCl to 1:3:7-trimethyluric acid; it is therefore 8-acetoxy-7-methylxanthine. 1:7-Dimethyluric acid, similarly, gives 8-acetoxy-1:7-dimethylxanthine, m.p. 272° (decomp.), which with CH_2N_2 gives (III). Acetylation of 1-methyluric acid gives 8-acetoxy-7-acetyl-1-methylxanthine, decomp. $>300^\circ$, which on methylation with pure CH_2N_2 gives 8-acetoxy-7-acetyl-1:3-dimethylxanthine, m.p. 125° (identity confirmed by alkaline hydrolysis to 1:3-dimethyluric acid); CH_2N_2 in presence of $MeOH$, however, removes the 7- Ac group and gives (I), whilst in presence of piperidine this group is replaced by Me and 8-methoxycaffeine, m.p. 176° , is produced. Uric acid is slowly converted by 2000 parts of Ac_2O at 100° into 8-acetoxy-7-acetyl-xanthine, from which the OAc group is displaced by cold H_2O , and 7-acetyluric acid; the former gives (I) with CH_2N_2 . Methylation of acetyl-3:9-dimethyluric acid (A., 1921, i, 614) with Me_2SO_4 and $NaOH$ (CH_2N_2 is without action) gives a mixture of 3:9-dimethyl-, 3:7:9-trimethyl-, and tetramethyl-uric acids, and thus affords no evidence of structure (cf. following abstract). H. A. P.

Reactions of 7-acetyl-3:9-dimethyluric acid H. BILTZ and H. PARDON (J. pr. Chem., 1932, [ii], 134, 335—352).—Chlorination of 7-acetyl-3:9-dimethyluric acid (I) in $CHCl_3$ gives 4-chloro-3:9-

dimethyl-Δ^{5,7}-isouric acid (II), m.p. 175° (decomp., sinters at 80°), but in pure, dry AcOH 4-chloro-5-acetoxy-7-acetyl-3 : 9-dimethyl-4 : 5-dihydrouic acid (III), m.p. 171° (decomp.) (previously described as the 1-Ac compound; cf. A., 1921, i, 609), is formed, whilst from the mother-liquors the corresponding 5-OH-compound (IV) is slowly pptd. on addition of H₂O. (IV) is also formed by chlorination in wet AcOH or by hydrolysis of (III); it is unaffected by cold H₂O, but at the b.p., or with 30% aq. AcOH or NH₃ in boiling EtOH gives 1 : 7-dimethylspiro-dihydantoin, m.p. 265° ("4-hydroxy-3 : 9-dimethyl-Δ^{5,7}-isouric acid," *loc. cit.*); it is stable to EtOH, not reducible to 3 : 9-dimethyluric acid (V), and, unlike the corresponding 3 : 7-Me₂ compound, is completely decomposed by NaOEt. With warm Ac₂O in AcOH it gives a Cl-free compound, m.p. 202°. (III) liberates I from HI with formation of (V), and is converted by warm EtOH into 3 : 9-dimethyluric acid glycol monoethyl ether, m.p. 174°; with CH₂N₂ it gives 4-chloro-5-acetoxy-7-acetyl-1 : 3 : 9-trimethyldihydrouic acid (VI), m.p. 185° (decomp.), the structure of which, and, therefore, of (I) also, is proved by its formation by chlorination of 7-acetyl-1 : 3 : 9-trimethyluric acid in Ac₂O. Hydrolysis of (VI) with warm H₂O gives 1-acetylisoapocaffeine, and reduction with HI in AcOH gives 1 : 3 : 9-trimethyluric acid.

Methylation of (IV) with CH₂N₂ gives the 5-Me ether, m.p. 143°, hydrolysed by conc. HCl at room temp. to 7-acetyl-3 : 9-dimethyluric acid glycol monoethyl ether, m.p. 205° (decomp.), which is further hydrolysed by NH₃ in EtOH to the Ac-free ether, m.p. 214°. Replacement of the 4-Cl group of (IV) occurs on treatment with amines in EtOH at room temp.; at the b.p., or where interaction is vigorous, simultaneous removal of the 7-Ac group occurs. 5-Hydroxy-4-piperidyl-, m.p. 208° [hydrochloride, m.p. 200° (decomp.); chloroaurate, m.p. 174° (decomp.)]; 7-Ac derivative, m.p. 198°, 5-hydroxy-4-anilino-7-acetyl-, m.p. 182°, 5-hydroxy-4-methylamino-, m.p. 186° [picrate, m.p. 186° (decomp.)], and 5-hydroxy-4-amino-7-acetyl-3 : 9-dimethyl-4 : 5-dihydrouic acid, m.p. 218° [picrate, m.p. 298° (decomp.)] (not hydrolysed by NH₃ in EtOH or by HCl), are thus prepared.

H. A. P.

Chlorophyll. XXIII. Synthesis of phylloerythrin. Conversion of phæoporphyrin *a*₅ into phæoporphyrin H. FISCHER and J. RIEDMAIR (Annalen, 1932, 497, 181—193; cf. this vol., 625).—Deoxophylloerythrin (I) (improved prep. given; cf. A., 1930, 932, where it is termed isophæoporphyrin *a*₃) in conc. H₂SO₄ treated with oleum (50% SO₃) containing S, gives about 10% of phylloerythrin (II) (Me ester, m.p. 264°), identical with the natural product. (I) is oxidised by CrO₃-AcOH to phylloporphyrin (III) and by K₂CrO₇-conc. H₂SO₄ to (III) and a trace of (II). Treatment of phæoporphyrin *a*₅ with oleum-S [as for (I)] gives phæoporphyrin *a*₇; ring fission accompanies oxidation. H. B.

Constitution of bile pigments. VIII. Synthesis of a coprobilirubin and work preliminary to a bilirubin synthesis. H. FISCHER and E. ADLER (Z. physiol. Chem., 1932, 210, 139—167;

cf. this vol., 627).—5-Bromo-3 : 4'-di-β-carboxyethyl-4 : 3' : 5'-trimethylpyrromethene hydrobromide when heated with KOAc in AcOH gives 5-hydroxy-3 : 4'-di-β-carboxyethyl-4 : 3' : 5'-trimethylpyrromethene (I), m.p. 265°, and coprobilirubin (II), decomp. 292° (Me₂ ester dihydrochloride, m.p. 199—200°; Cu salt, m.p. 300°). Treatment of (I) with Br in AcOH affords an acid (III), C₁₈H₂₀O₅N₂, m.p. 275° (Me₂ ester hydrochloride, m.p. 239—240°; Me₂ ester, m.p. 243°). Fusion of (III) with resorcinol had no effect, but (II) gave 5-hydroxy-3 : 4'-di-β-carboxyethyl-4 : 3'-dimethylmethene (IV), m.p. 225°. Treatment of (IV) with CH₂O regenerated (II). Reduction of (II) with HI gave cryptopyrrolecarboxylic acid. Reduction of (IV) or of (I) with Na-Hg gave leuco-derivatives. Reduction of 5-hydroxy-4 : 3' : 5'-trimethyl-3 : 4'-diethylpyrromethene with HI gave the corresponding methane (V), m.p. 149°. Fusion of the blue stage (VI) (Cu salt) of ætiomesobilirubin with resorcinol afforded 5-hydroxy-4 : 3'-dimethyl-3 : 4'-diethylpyrromethene (VII), m.p. 197°, which again gave ætiomesobilirubin with CH₂O-HCl. Gentle reduction of (VI) with HI afforded the methane (V) and the methane, m.p. 115°, corresponding with (VII).

The brominated acetylpyrromethene (VIII) (A., 1924, i, 80) with NaOAc in AcOH exchanges one Br for OH, giving a product (IX), C₁₄H₁₅O₂N₂Br, m.p. not below 300°. With Zn dust-AcOH (IX) gives a product, C₁₄H₁₅O₂N₂Br, m.p. 297° (decomp.). Treatment of Et α-methyl-levalate with NH₃ in EtOH gave a substance, m.p. 245—260°, probably bis-5-hydroxy-2 : 4-dimethylpyrrole. Mesobilirubin forms a Cu salt. SO₂Cl₂ converts 3-acetyl-5-carbethoxy-2 : 4-dimethylpyrrole (X) into 3-acetyl-5-carbethoxy-4-methyl-2-chloromethylpyrrole (XI), m.p. 119°. In boiling H₂O, (XI) gives the corresponding 2-hydroxymethyl derivative, m.p. 123°, and 3 : 3'-diacetyl-5 : 5'-dicarbethoxy-4 : 4'-dimethylpyrromethane, m.p. 200°. With EtOH, (XI) gives the corresponding 2-ethoxymethyl derivative, m.p. 92°. When warmed with NH₂Ph (XI) affords a substance, C₁₇H₁₈O₃N₂, m.p. 204—205°. With 3 mols. of SO₂Cl₂ (X) yields 3-acetyl-5-carbethoxy-4-methyl-2-dichloromethylpyrrole (XII), m.p. 158°, which in hot H₂O gives 2-formyl-3-acetyl-5-carbethoxy-4-methylpyrrole (XIII), m.p. 103° (dioxime, m.p. 193°). With hydrazine hydrate, (XIII) affords a pyridazine derivative (hydrazide in position 5). With 4 mol. of SO₂Cl₂, (X) gave no crvst. Cl-derivative, but on boiling with EtOH there was obtained probably 3 : 3'-dichloro-5 : 5'-dicarbethoxy-4 : 4'-dimethylpyrromethene (XIV), m.p. 193°. With Br and (X) a product, m.p. 229° (decomp.), was obtained, possibly the analogue of the product formed with 4 mols. of SO₂Cl₂. Bromination of (XII) in AcOH gave a substance, C₉H₁₀O₂NCl₂Br, m.p. 112°, which when boiled with EtOH gave the product, C₁₁H₁₂O₃NBr, m.p. 108—109°.

Condensation of (XI) with cryptopyrrole afforded a product, C₁₉H₂₅O₂N₂Cl, decomp. at 282°, with cryptopyrrolecarboxylic acid, a product, C₂₂H₃₁O₄N₂Cl, decomp. at 200°, and with opsopyrrole a product, C₁₈H₂₃O₂N₂Cl, m.p. 337° (decomp.). The last is hydrolysed by NaOH, yielding a substance, C₁₆H₁₉O₂N₂Cl. J. H. B.

Fluorescence spectra of bilipurpurin. C. DHÉRE (Compt. rend., 1932, 195, 336—338).—By crushing the crystals of bilipurpurin Me ether against the inside of a test-tube dark red rays are visible. The fluorescence spectrum of bilipurpurin in pyridine or CHCl_3 resembles that of protoporphyrin. The spectrum in CS_2 , and the effect of alkalis, EtOH, and AcOH on it, are described. H. D.

Acetylcarnitine. R. KRIMBERG and W. WIT-TANDT (Biochem. Z., 1932, 251, 229—234; cf. A., 1927, 1058).—*Acetylcarnitine*, $\text{C}_8\text{H}_{14}\text{O}_3\text{N}_2$, m.p. 145° (decomp.), $[\alpha]_D^{25} -19.52^\circ$ [chloride, m.p. 181° (decomp.); *chloroaurate*, m.p. 128° ; *chloroplatin-ate*, m.p. 187°], obtained in 70% yield by cold acetylation of *l*-carnitine (from meat extract) and treatment of the chloride so obtained with Ag_2O , yields betaine on oxidation with $\text{Ba}(\text{MnO}_4)_2$. With HgCl_2 acetylcarnitine yields a mixture of cryst. substances. Acetylcarnitine chloride is stable in air. W. McC.

Thiazoles. XVIII. Synthesis of 2-phenylbenzthiazole-5-carboxylic acid and derivatives. M. T. BOGERT and H. G. HUSTED (J. Amer. Chem. Soc., 1932, 54, 3394—3397).— $\text{o-SH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$ is most conveniently prepared from the Zn salt and conc. HCl. The 3- NO_2 -derivative, m.p. $100\text{--}101^\circ$ (all m.p. are corr.), of $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CN}$ and Na_2S_2 give 86% of *di*-2-nitro-4-cyanophenyl disulphide, chars about 235° and liquefies about 335° , reduced to 2-amino-4-cyanothiophenol (I), decomp. about 250° . 2-Anilinobenzthiazole is best prepared from di-*o*-aminophenyl disulphide and PhNCO . *o*-Cyano-2-phenylbenzthiazole (II), m.p. $196.6\text{--}197.7^\circ$ (NO_2 -derivative, m.p. 256°), obtained in 20% yield from the Zn salt of (I) and BzCl or in 30% yield using PhCHO , is hydrolysed by 75% H_2SO_4 at 80° to 23% of the amide, m.p. 247.2° , of 2-phenylbenzthiazole-5-carboxylic acid, m.p. 273° (Me ester, m.p. $171\text{--}172^\circ$, obtained in 5% yield from the Ag salt and MeI).

C. J. W. (b)

Aminobenzthiazoles. XIII. Corrected data for the 2-alkylamino- β -naphthathiazole series. G. M. DYSON, R. F. HUNTER, and R. W. MORRIS (J.C.S., 1932, 2282—2283).—The revised m.p. of the *s*- α -naphthylalkylthiocarbamides previously described (A., 1926, 718) are: methyl-, 198° ; ethyl-, 121° ; *n*-propyl-, $101\text{--}102^\circ$; *n*-butyl-, 100° ; *n*-amyl-, 104° ; *iso*amyl-, 95° ; *n*-heptyl-, $65\text{--}66^\circ$. The alleged 2-alkylamino- β -naphthathiazoles (A., 1927, 263) obtained by bromination of naphthylalkylthiocarbamides are mixtures containing probably 8-bromo-2-alkylamino- β -naphthathiazoles. Pure 2-alkylamino- β -naphthathiazoles are obtained by refluxing the naphthylalkylthiocarbamides in CHCl_3 with slight excess of Br, and have the following m.p.: 2-methyl-, 161° ; 2-ethyl-, 107° ; 2-*n*-propyl-, 86° ; 2-*n*-butyl-, 67° ; 2-*isobutyl*-, 70° ; 2-*n*-amyl-, 78° ; 2-*iso*amyl-, 90° ; 2-*n*-hexyl-, 70° ; and 2-*n*-heptyl-, 72° .

E. E. J. M.

Electrolytic reduction of saccharin. I. Electrolysis in acid and alkaline solutions. M. MATSUI, T. SAWAMURA, and T. ADACHI (Mem. Coll. Sci. Kyōtō, 1932, A, 15, 151—155).—Saccharin,

suspended in a mixture of EtOH and dil. H_2SO_4 , is reduced at a cathode of Pb, Zn, Hg, or Zn-Hg, below 30° , using 5.5 amp. per 70 sq. cm. to a substance, $\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2\text{S}_2$, m.p. 141° , regarded as a condensation product of hydroxybenzylsultam and benzylsultam,

$\text{SO}_2\text{--}\langle\text{NH--}\text{C}_6\text{H}_4\text{--}\text{CH--N--}\langle\text{CH}_2\text{--}\text{C}_6\text{H}_4\text{--}\rangle\text{--SO}_2$ (result not affected by varying c. d. or concn. of H_2SO_4); and at 50° and 1 amp. per 10 sq. cm., to benzylsultam. If the catholyte contains $\text{NHPh}\cdot\text{NH}_2$, *o*-sulphamido-benzaldehydephenylhydrazone is pptd. under the former conditions. In presence of aq. NaOH at $15\text{--}18^\circ$ and 3 amp. per 70 sq. cm., NH_3Bz , Na_2SO_3 , NH_3 , PhCHO, benzoin, and hydrobenzoin are obtained. D. R. D.

Syntheses and transformations of natural substances under physiological conditions (biogenesis of natural substances). [Introduction.] C. SCHÖPF. I. Alkaloids of *Angostura* bark. Synthesis of 2-methyl- and 2-*n*-amyl-quinoline under physiological conditions. C. SCHÖPF and G. LEHMANN. II. Dehydrogenation of laudanoline and laudanoline 3':4'-dimethyl ether. C. SCHÖPF and K. THIERFELDER (Annalen, 1932, 497, 1—6, 7—21, 22—46).—[Introduction.] Three types of biosynthesis are differentiated: (a) through a highly sp. enzyme action (e.g., starch from CO_2), (b) intermediate enzyme action on cell constituents, and (c) changes involving no enzyme action. Syntheses of natural substances under conditions of type (c) are investigated.

I. $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (*M*/200) and COMe_2 (*M*/100) in aq. solution at p_H 12 and 13 at 25° give (after 7 days) II and 86%, respectively, of 2-methylquinoline (I), which is not produced below 12 even with more conc. solutions. The aldehyde and Me amyl ketone similarly give (at p_H 13) 98% of 2-methyl-3-*n*-butyl-quinoline, m.p. $61\text{--}62^\circ$ (picrate, m.p. 206°) [oxidised (CrO_3 -dil. H_2SO_4) to 2-methylquinoline-3-carboxylic acid (II)], whilst 2-phenylquinoline (III) is produced in quant. yield with COPhMe. It is unlikely that (I) and 2-*n*-amylquinoline (IV) [picrate, m.p. $110\text{--}111^\circ$ (lit. $125\text{--}127^\circ$)] are produced in nature by such condensation; they are probably formed by processes analogous to the following. $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (*M*/200) and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ (*M*/125) at p_H 5—11 and 25° for 8 days give (I), the yield being a max. (66%) at p_H 9; with *M*/50-acid (to overcome self-decomp.) a 90% yield of (I) results after 16 days. Anhydrotris-*o*-aminobenzaldehyde [and no (I)] is produced at p_H 3, whilst (II) is the sole product at p_H 13. (III) and (IV) are similarly formed using $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{H}$ (95% yield at p_H 9) and hexoylacetic acid (70—75% yield at p_H 7—9), respectively; at p_H 13, 2-phenyl-, m.p. 234° (lit. 230°), and 2-*n*-amyl-quinoline-3-carboxylic acid, m.p. 148° [decarboxylated to (IV)], result. The velocity coeff. (*k*) for the reactions with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ at p_H 9, $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{H}$ at p_H 7—9, and hexoylacetic acid at p_H 7—9 are 0.028, about 0.14, and at least 0.01, respectively; *k* decreases with time owing to self-decomp. of the acids.

II. Treatment of papaverine methiodide with NaOEt and subsequent reduction (H_2 , Pt) gives

N-methyl-3:4-dihydroisopapaverine, m.p. 129—130°, reduced (H_2 , PtO_2 , $EtOH$ - $AcOH$) to *dl*-laudanosine, which is demethylated by 48% HBr to *dl*-laudanosoline (I) ($+0.5H_2O$), m.p. 192—194° (becoming red) (sinters at 188—190°) [hydrobromide (II) ($+3H_2O$), m.p. 230—232° (lit. 230°); Ac_4 derivative *picronate*, m.p. 178—179° (sinters at 163°), and *picrolonate*, m.p. 224° (sinters at 220°)]. (II) is dehydrogenated by tetrabromo-*o*-benzoquinone in $AcOH$ to 2:3:11:12-tetrahydroxy-8-methyldibenzotetrahydropyrrocolinium hydrobromide (III) ($+H_2O$), m.p. 262°, m.p. (anhyd.) 275—276° (decomp.) (cf. Robinson and Sugawara, this vol., 527), decomposed by aq. $NaHCO_3$ to the corresponding *phenol-betaine* (IV) ($+H_2O$), m.p. 251° [Ac_4 derivative *hydrobromide*, m.p. 170—172°, and *picronate*, m.p. 207° (decomp.) (sinters at 204°)]; a by-product is a compound, $(C_6HO_2Br)_x$ ($+0.5H_2O$), m.p. 297—300°. (IV) is also produced from (I) by the action of O_2 and Pt -black in N - $AcOH$, O_2 , and $Pd-C$ in dil. Na_2CO_3 , and $K_3Fe(CN)_6$ at p_H 6.9—7.1 (phosphate buffer). (IV) and $BzCl$ in cold pyridine give 2:3:11:12-tetrabenzoyloxydibenzotetrahydropyrrocoline, m.p. 225—227° (sinters at 220°). Methylation (Me_2SO_4 , aq. $NaOH$) of (IV) affords 2:3:11:12-tetramethoxy-8-methyldibenzotetrahydropyrrocolinium methosulphate ($+2.5H_2O$), m.p. 228° (sinters at 115°), degraded (Hofmann) to 5:6-dimethoxy-2-(3':4'-dimethoxy-6'-vinylphenyl)-1-methyldihydroindole, m.p. 128—129° (lit. 124—127°), the methiodide, m.p. 210°, of which is degraded further to 6-dimethylamino-3:4:3':4'-tetramethoxy-6'-vinylstilbene, m.p. 112° (lit. 109—110°), and an isomeride (? *cis*-form), m.p. 92° (sinters at 87°). The former stilbene is oxidised by O_3 in 2*N*- H_2SO_4 to *m*-opianic acid, *m*-hemipinic acid, 6-dimethylaminoveratraldehyde, m.p. 72—73° [also prepared by methylation (MeI , 20% K_2CO_3) of 6-aminoveratrylideneaniline and subsequent hydrolysis], and 6-dimethylamino-6'-aldehyde-3:4:3':4'-tetramethoxystilbene, m.p. 144—146°.

Laudanosoline 3':4'- Me_2 ether (V) ($+EtOH$), m.p. 100—105° (decomp.), m.p. ($EtOH$ -free) 143—145°, prepared by reduction (H_2 , PtO_2 , $EtOH$) of protopapaverine, is oxidised by O_2 and Pt in N - $AcOH$ to probably the 6:7-quinone which is reduced to (V). *dl*-Glaucine heated with aq. HBr gives the hydrobromide, m.p. 238—242° (decomp.), of *dl*-nor-glaucine [Ac_4 derivative, m.p. 176—178° (*hydrobromide*, m.p. 202° (decomp.) (sinters at 191°); *picrolonate*, m.p. 210° (sinters at 178°, softens at 185—186°)]. Successive treatment of corytuberine with 48% HBr and Ac_2O -pyridine gives *tetra-acetylcorytuberoline hydrobromide*, m.p. 230—231° (decomp.) [*picrolonate*, decomp. 209° (sinters at 162°, softens at 180—182°)]. *N*-Methyl-3:4-dihydroisopapaverine and 48% HBr give 3:4-dihydroisopapaveroline methobromide ($+2H_2O$), sinters at 190—194°, melts to a turbid liquid at 226—228°, and becomes yellow at 280—285° [corresponding betaine, m.p. 238—239° (decomp.) (darkens at 200°)].

H. B.

Chemotherapy. III. (Attempts to prepare antimalarials.) Derivatives of cotarnine. G. S. AHLUWALIA, B. D. KOCHHAR, and J. N. RAY (J.

Indian Chem. Soc., 1932, 9, 215—223).—Cotarnine (modified prep. given; cf. J.C.S., 1918, 113, 469) and $m-C_6H_4(OH)_2$ in abs. $EtOH$ at 40—45° give *anhydrocotarninoresorcinol* (1-2':4'-dihydroxyphenylhydrocotarnine) (I) (*hydrochloride*, m.p. 240°). The following are prepared similarly: *anhydrocotarnino-pyrogallol*, m.p. 211°; *-phloroglucinol*, m.p. 170° [*hydrochloride*, m.p. 185° (decomp.)]; *-1-phenyl-3-methylpyrazolone*, m.p. 177°; *-3-methylpyrazolone*, m.p. 199° (decomp.); *-3:5-dimethylpyrazole*, m.p. 140°; *-5-phenyl-3-methylpyrazole*, m.p. 146°; *-1:5-diphenyl-3-methylpyrazole*, m.p. 148°; *-o-*, m.p. 126°, and *-p-phenetidine*, m.p. 126° (*hydrochloride*, m.p. 239°), and *-o-*, m.p. 134°, and *-p-anisidine*, m.p. 124°. The *anhydrocotarnino-p-nitrotoluene* of Hope and Robinson (J.C.S., 1911, 99, 2114) (modified prep. given) is reduced by $SnCl_2$ and aq. HCl at 28—32° to the *NH_2*-derivative, m.p. 95°, converted by the usual method into *anhydrocotarnino-p-cresol*, m.p. 191°.

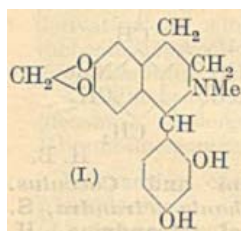
[With K. S. GRAVAL.] Various pharmacological data for some of the above compounds are given.

H. B.

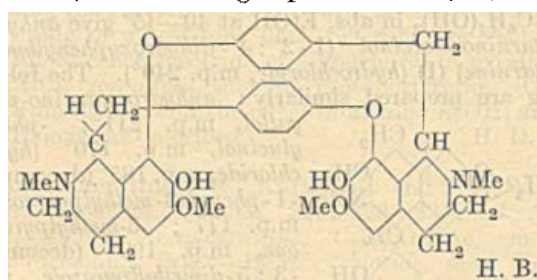
Constitution of isochondodendrine. V. F. FALTIS, S. WRANN, and E. KÜHAS (Annalen, 1932, 497, 69—90).—Experiments on the formation of ethers (Ullmann method) from α -*o*- and *-m*-bromophenyl- β -p-hydroxyphenylethane derivatives are described. $m-C_6H_4Br \cdot CHO$ and $p-OMe \cdot C_6H_4 \cdot CH_2 \cdot CO_2Na$ in Ac_2O at 100—110° give *m-bromo- α -anisylcinnamic acid*, m.p. 169—170°, reduced and demethylated by red P and HI (b.p. 127°) to β -*m-bromophenyl- α -p-hydroxyphenylpropionic acid* (I), m.p. 173—174° (NH_4 salt, m.p. 175°; *Me* ester, m.p. 102—103°), also prepared by reduction of *m-bromo- α -p-hydroxyphenylcinnamic acid*, m.p. 211—212° (*O-Ac* derivative, m.p. 168—169°), and by way of *m-nitro-*, m.p. 187—189°, and *m-amino-*, m.p. 215—218°, α -*p*-hydroxyphenylcinnamic acids and β -*m-aminophenyl- α -p-hydroxyphenylpropionic acid*, m.p. 196—198°. The K salt of (I) heated with Cu powder gives a non-cryst. Br -containing complex mixture. Anisaldehyde and $o-C_6H_4Br \cdot CH_2 \cdot CO_2Na$ afford *p-methoxy- α -o-bromophenylcinnamic acid*, m.p. 167—168°, reduced (H_2 , Pd -black, dil. $NaOH$) to α -phenyl- β -anisylpropionic acid, m.p. 120—121° (*Me* ester, m.p. 59—60°).

Treatment of hemipinic acid in cold 10% KOH with Cl_2 gives 5:6-dichlorohemipinic acid, m.p. 132—133° (*anhydride*, m.p. 122—123°), and its K H salt; with 2*N*- $KOCl$ in 20% KOH , 5-chlorohemipinic acid, (II), m.p. 168—169° (slight decomp.), results. 4(?) : 6-Dibromo-2:3-dimethoxybenzoic acid, m.p. 154°, and a little 5-bromohemipinic anhydride, m.p. 150°, are obtained using $KOBr$. (II) could not be condensed with $p-OH \cdot C_6H_4 \cdot CO_2R$.

Mol. wt. determinations, mainly by Pirsch's method (this vol., 713), on various derivatives of isochondodendrine (III) indicate that (III) is $C_{36}H_{38}O_6N_2$ and not $C_{18}H_{19}O_3N$ (A., 1922, i, 569; 1928, 433); Rast's method gives low results. The structures of (III),



oxyacanthine, berbamine, and phæanthine are discussed; the following is preferred for (III).

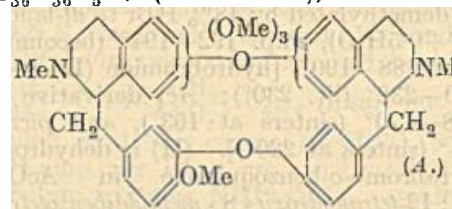


Alkaloids of Sinomenium and Cocculus.
XXXIV. Alkaloids of *Stephania tetrandra*, S. Moore. IV. Constitution of tetrandrine. H. KONDO and K. YANO. **XXXV. Constitution of trilobine and isotriloine.** VI. H. KONDO and M. TOMITA (Annalen, 1932, 497, 90—104, 104—115).—**XXXIV. Tetrandrine (I),** $C_{38}H_{42}O_6N_2$ [and not $C_{19}H_{23}O_3N$ as previously reported (J. Pharm. Soc. Japan, 1928, 552, 108)] [dimethiodide (+2H₂O), m.p. 269° (decomp.)], is converted by the energetic action of HBr into demethyltetrandrine (II) (previously designated demethyltetrandrinol), $C_{34}H_{41}O_6N_2 \cdot 2H_2O$, m.p. 228° [hydrobromide (+2H₂O)]. (I) and HBr (*d* 1.58) at 100° (bath) give (II), a compound, $C_{34}H_{40}O_6N_2(OH)_3(OMe)$, m.p. 190—200°, and a substance, $C_{34}H_{39}O_6N_2(OMe)_2 \cdot 2H_2O$, m.p. 130—140°, $[\alpha]_D^{25} +204.4^\circ$ in $CHCl_3$; shorter treatment affords a compound, $C_{34}H_{31}O_3N_2 \cdot OMe \cdot 2H_2O$, m.p. 240°, $[\alpha]_D^{25} +238^\circ$ in $CHCl_3$. α -Tetrandrinemethylmethine, $C_{40}H_{46}O_6N_2$, m.p. 172° [dimethiodide (+2H₂O), decomp. 235°], and O_3 in cold, very dil. AcOH give 5 : 4'-dialdehydo-2-methoxydiphenyl ether (III) and a dialdehydotrimethoxybis-(β -dimethylaminoethyl)-diphenyl ether [the dimethiodide, decomp. 250°, is degraded (Hofmann) to a dialdehydotrimethoxydivinyldiphenyl ether (IV), m.p. 138—140° (disemicarbazone, decomp. 230—245°)], identical with the ethers obtained similarly from the methylmethine from methoxyacanthine (V) (cf. von Bruchhausen and Gericke, A., 1931, 636). (I) and (V) are isomerides. Further oxidation of (IV) with O_3 in Et₂O affords a tetracarboxytrimethoxydiphenyl ether, decomp. 184—220° (*Me*, m.p. 150°, and *Me*₄, m.p. 152—153°, esters) [also obtained with (III) by ozonolysis of de-*N*-methyltetrandrine, $C_{36}H_{32}O_6$, m.p. 221°], which with KOH at 300—350° gives *m*-hemipinic acid and an acid, $C_{12}H_{14}O(OMe)_3(CO_2H)_3$, m.p. 270—275° (*Me*₃ ester, m.p. 150°). Oxidation of (IV) with O_3 in $CHCl_3$ and subsequent hydrolysis with H_2O affords a hydroxytetra-aldehydodimethoxydiphenyl ether [di-quinoxaline (+H₂O), m.p. 245—250° (decomp.)], from *o*-C₆H₄(NH₂)₂, converted by alkali into a hydroxydicarboxydimethoxydi(hydroxymethyl)diphenyl ether, m.p. 160—190°. β -Tetrandrinemethylmethine, $C_{40}H_{46}O_6N_2$, has m.p. 140°.

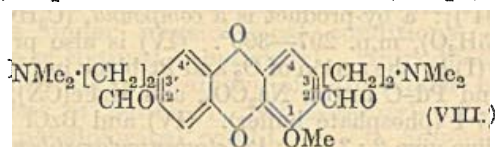
(I) and (V) contain the same diphenyl ether grouping (see A); they differ in the configuration (alternatives suggested) of the trimethoxydi-(*N*-methyltetrahydroisoquinoline) ether residue.

XXXV. Trilobine (VI), m.p. 235°, $[\alpha]_D^{25} +296.3^\circ$ in $CHCl_3$, and isotriloine (VII), m.p. 215°, $[\alpha]_D^{25} +314.8^\circ$ in $CHCl_3$ [previously designated homotri-

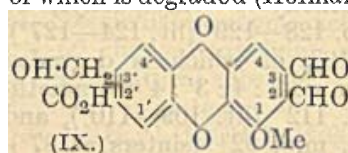
lobine (J. Pharm. Soc. Japan, 1930, 585, 1041)], both $C_{36}H_{36}O_5N_2$ (cf. *loc. cit.*), like methoxy-



acanthin and tetrandrine, are oxidised by $KMnO_4$ to 5 : 4'-dicarboxy-2-methoxydiphenyl ether. Treatment of (VI) with Me_2SO_4 and alkali gives trilobine-methylmethine, $C_{38}H_{40}O_5N_2$, m.p. 106°, oxidised by O_3 in very dil. AcOH to (III) (above) and the dialdehyde (VIII), m.p. 124°. The dimethiodide (+H₂O), m.p.

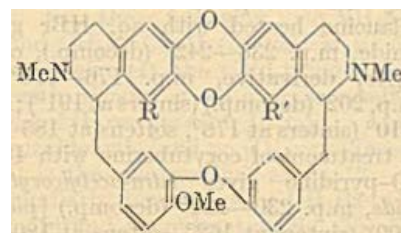


230° (decomp.), of (VIII) is degraded (Hofmann) to the 3 : 3'-divinyl 2 : 2'-dialdehyde (+0.5H₂O), m.p. 195° or above 300° (slow heating) [dioxime (+0.5H₂O), m.p. 206° (decomp.)] [the anil methiodide of which is degraded (Hofmann) to a phenol], oxidised



by O_3 in $CHCl_3$ (and subsequent hydrolysis) to the dialdehydo-acid (IX), m.p. 90—91° (decomp.) (disemicarbazone, m.p. >300°; azine, m.p. <300° 4c derivative, m.p. 165—168°), which is converted by 10% KOH into the corresponding (2 : 3)-phthalide m.p. 286°, and oxidised by $KMnO_4$ to the 2 : 3 : 2' : 3'-tetracarboxylic acid, m.p. 192—197° (decomp.) (*Ag*₄ salt; *Me*₄ ester, m.p. 85°). This with KOH at 250° gives protocatechuic and a trace of gallic (?) acid. isoTrilobinemethylmethine, m.p. 115°, $\alpha_D^{25} \pm 0^\circ$, is also oxidised by O_3 to (III) and (VIII).

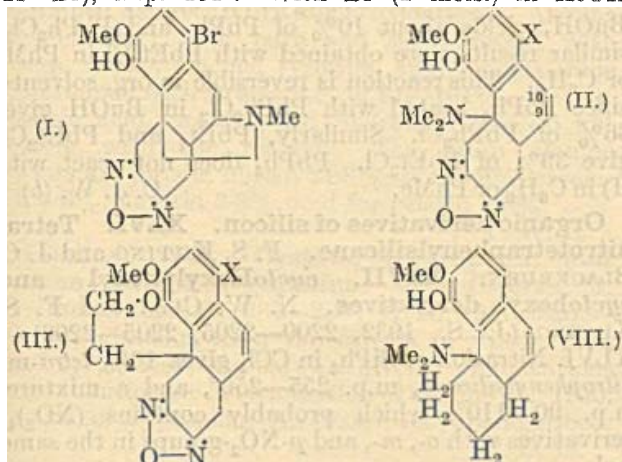
(VI) and (VII) are represented by the following structure; in one case $R=OMe$ and $R'=H$, whilst in the other $R=H$ and $R'=OMe$.



H. B.

Sinomenine and disinomenine. XXXII. Hofmann degradation of 1-bromosinomeninone dioxime, and bromination of the sinomeninone-furazan derivatives. K. GOTO and S. MITSUI (Bull. Chem. Soc. Japan, 1932, 7, 223—233).—Like sinomeninone dioxime (A., 1931, 1172), the corresponding 1-Br-compound when heated with 16.5% KOH gives 1-bromosinomeninonefurazan (I), decomp. 262° [also obtained from sinomeninonefurazan (*loc. cit.*) by the action of Br in AcOH], whilst its methiodide, sinters 220°, decomp. 254°, similarly affords 1-bromo-

de-*N*-methylsinomeninonefurazan (II, X=Br), decomp. 225° [also obtained, in small yield, by bromination of de-*N*-methylsinomeninonefurazan]. The oily methiodide of (II) is converted by 16.5% KOH into NMe₃ and 1-bromodehydro-1-thebenone ketone-(7)-furazan (III, X=Br), m.p. 191°. With Br (2 mols.) in AcOH



de-*N*-methylsinomeninonefurazan (II, X=H) gives the 1:9(?)*-Br*₂-derivative (IV), sinters 194°, decomp. 212°, bromination occurring also at the 9- or 10-position, whilst with 3 Br₂ is obtained a *perbromide*, decomp. 146°, converted by either COMe₂ or H₂SO₃ into (IV). The oily methiodide (not characterised) of (IV) with 16.5% KOH gives 1:9(?)*-dibromodehydro-1-thebenone ketone-(7)-furazan* (V), m.p. 210—211°, also obtained by bromination of either (VI), (VII), or (III)]. Since (V) is stable towards AgOAc-AcOH or KOH-MeOH, the Br is not in the reduced phenanthrene nucleus. Similar bromination (1 mol.) of dehydro-1-thebenone ketone-(7)-furazan (VI) (*loc. cit.*, as III, X=H) gives its 9-*Br*-derivative (VII), m.p. 152—153°, which is different from (III). Similarly de-*N*-methylmethoxydeoxodihydrosinomenine (VIII) with Br (3 mols.) affords the *perbromide* (IX), decomp. 112—113°, of the 1:9-*Br*₂-derivative, decomp. 205°, which is obtained by the action of COMe₂. Treatment of dihydrode-*N*-methylsinomeninonefurazan (as II, X=H and 9:10 double linking reduced) with 1, 2, or 3 Br₂ gives only the 1-*Br*-derivative, sinters 207°, decomp. 221—223° [*hydrobromide*, m.p. 259° (decomp.)], the methiodide of which readily affords 1-bromo-1-thebenone ketone-(7)-furazan, m.p. 202—203°, also obtained by bromination of 1-thebenone ketone-(7)-furazan (*loc. cit.*). (II), (IV), (VII), and (IX) exhibit halochromism in conc. H₂SO₄.

J. W. B.

Sinomenine. XXXIII. Acetolysis of sinomeninone and 1-bromosinomeninone. K. GOTO, H. SHISHIDO, and K. TAKUBO (Annalen, 1932, 497, 289—296).—Sinomeninone methylalcoholate (previously described as sinomenine hydrate) is converted by boiling with Ac₂O and NaOAc into 20% of 4:6-diacetoxy-3-methoxyphenanthrene (I) and 10% of triacetylisothebenine (II), m.p. 167° (sinters at 164°). 1-Bromosinomeninone is similarly converted into 25% of 1-bromo-4:6-diacetoxy-3-methoxyphenanthrene [reduced catalytically to (I)]

and 20% of 1-bromotriacetylisothebenine (III), m.p. 191° (converted by 2*N*-MeOH-NaOH at 80° into 7% of a compound, C₂₀H₂₆O₄NBr, m.p. 253°). Reduction (H₂, Pd-BaSO₄, PdCl₂, AcOH-NaOAc) of (II) or (III) gives triacetyl-9:10-dihydroisothebenine (IV), m.p. 182°; the triacetylisothebenine of Schopf *et al.* (this vol., 290) is (IV). Thebenine and its Ac₃ derivative are similarly reduced to 9:10-dihydrothebenine (*hydrochloride*, m.p. 261°) and triacetyl-9:10-dihydrothebenine, m.p. 120° (decomp.), respectively.

1:5-Dibromosinomeninone hydrobromide, m.p. 197° (decomp.), undergoes conversion (in EtOH) into 1-bromosinomenine hydrobromide.

H. B.

Interaction of phenylarsines with halogeno-phenylarsines. F. F. BLICKE and L. D. POWERS (J. Amer. Chem. Soc., 1932, 54, 3353—3360).—Contrary to Steinkopf and Smie (Ber., 1926, 59, B, 1453), AsPhCl₂ and AsHPh₂ give AsPh₂Cl and arsenobenzene. AsPhCl₂ (2 mols.) and AsHPh₂ (4 mols.) give arsenobenzene (1 mol.) and (AsPh₂)₂ (2 mols.); the latter and an equiv. of AsPhCl₂ give AsPh₂Cl and arsenobenzene. No reaction takes place at room temp. between AsPh₂Cl (or AsHPh₂) and arsenobenzene. AsPhI₂ and AsHPh₂ give di-iododiphenyldiarsyl and (AsPh₂)₂; AsPhI₂ and (AsPh₂)₂ give di-iododiphenyldiarsyl and AsPh₂I. AsPh₂Cl and AsHPh₂ in Et₂O afford (AsPh₂)₂ (which is a satisfactory method of prep.); AsPh₂I reacts similarly. AsPhCl₂ (or AsPhI₂) and AsH₂Ph give arsenobenzene; when 3 mols. of AsPhI₂ are used, the product is di-iododiphenyldiarsyl. AsPh₂Cl (or AsPh₂I) (4 mols.) and AsH₂Ph (2 mols.) give arsenobenzene (1 mol.) and (AsPh₂)₂ (2 mols.).

C. J. W. (b)

Compounds of arsenic acids and hydrochloric acid. J. PRAT (Compt. rend., 1932, 195, 489—491).—Solubility curves of phenyl-, *o*-tolyl-, and *p*-acetamidophenyl-arsinic acids in aq. HCl show the formation of additive compounds, which may be isolated using anhyd. conditions: PhAsO₃H₂·HCl; *o*-C₆H₄·AsO₃H₂·HCl, *p*-NHAc·C₆H₄·AsO₃H₂·HCl.

F. R. S.

Condensation of 4-halogeno-3-nitrophenyl-arsinic acids with aliphatic amino-compounds and phenols. W. D. MACLAY and C. S. HAMILTON (J. Amer. Chem. Soc., 1932, 54, 3310—3315).—The following 3-nitro-4-alkylaminophenylarsinic acids, which do not melt or decompose below 250°, were prepared from 4-chloro-3-nitrophenylarsinic acid, NH₂Alk, and aq. NaOH at 125—135°: *Pr*, *Bu*, *Bu*^β, *amyl*, *isoamyl*, and *β*-hydroxyethyl. Reduction with alkaline Fe(OH)₂ gives the corresponding 3-amino-4-alkylaminophenylarsinic acids. 2-Nitro-4-arsinophenylglycine, decomp. 230—235°, is reduced to 2-hydroxy-3-dihydroquinoxaline-7-arsinic acid. 4-Bromo-3-nitrophenylarsinic acid and ArOH in presence of K₂CO₃, Cu powder, and *amyl* alcohol at 140—150° give 3-nitro-4-aryloxyphenylarsinic acids, do not melt or decompose below 250°; the following are described: 4-*phenoxy*-, 4-*p*-chlorophenoxy-, 4-*p*-tolyl-, 4-*p*-carboxyphenoxy-, 4-*o*-tolyl-, 4-*o*-carboxyphenoxy-, and 4-*p*-nitrophenoxy-. 3-Amino-4-*phenoxy*-, 4-*o*- (I) and -*p*-carboxyphenoxy-, 4-*p*-chlorophenoxy-, and 4-*o*-tolyl-phenylarsinic acids are prepared. The above CO₂H derivatives are prepared by oxidation of the

Me analogues. (I) passes at 200—210°/20 min. into the lactam, not melted at 250°. 4-*p*-Tolyloxyphenyl-arsinic acid, not melted at 250°, prepared in 70% yield from its 3-NH₂-derivative through the diazo-reaction, is oxidised to 4-*p*-carboxyphenoxyphenyl-arsinic acid. Condensation products are not obtained with BuOH, *n*- or *iso*-amyl alcohol, or NH₃Ph.

C. J. W. (b).

Quinoline compounds containing arsenic. IV. Synthesis of derivatives of quinoline-5- and -8-arsinic acids. V. Synthesis of 7:8-triazol-quinoline-5-arsinic acid. R. H. SLATER (J.C.S., 1932, 2104—2108, 2196—2197).—IV. 5-Nitro-, m.p. 95—96°, obtained by replacement of Br by piperidine, is reduced to 5-amino-8-piperidinoquinoline, m.p. 182—183° (*Ac* derivative, m.p. 210—211°), which cannot be converted into the corresponding arsinic acid. 8-Bromo-5-aminoquinoline, m.p. 156—157° (*Ac* derivative, m.p. 179—180°), gives 8-bromoquinoline-5-arsinic acid, m.p. 234—235° (decomp.), in which the Br is unaffected by piperidine [8-chloro-5-aminoquinoline, m.p. 154—155° (*Ac* derivative, m.p. 172—173°), and 8-chloroquinoline-5-arsinic acid, m.p. 226—227° (decomp.), are similarly obtained]. 5-Chloroquinoline-8-arsinic acid, m.p. 284—285° (decomp.), prepared from 5-nitro-8-aminoquinoline, with oleum and KNO₃ yields the 6-NO₂-compound, m.p. 233—234° (decomp.), which gives with piperidine 6-nitro-5-piperidino-, m.p. 259—260° (decomp.), and with aq. KOH, 6-nitro-5-hydroxy-quinoline-8-arsinic acid, m.p. 226—227° (decomp.).

V. 5:7-Dinitro- is reduced by NH₄SH to 5:7-diamino-8-*p*-toluenesulphonamidoquinoline, m.p. 207—208° (decomp.), which, after bis-diazotisation and treatment with Na₃AsO₃, gives a mixture of 7:8-triazolquinoline-5-arsinic acid, m.p. above 310°, and 7:8-triazolquinoline, m.p. 256—257°. F. R. S.

Replacement reactions with the diazonium and acetoxymercuri-groups. J. G. KERKHOFF (Rec. trav. chim., 1932, 51, 755—760; cf. this vol., 1031).—In the naphthalene series, the normal displacement reactions are shown by the diazonium and Hg·OAc groups, the latter occupying a position immediately between the CHO and CO₂H groups. Mercuriation of β-hydroxy-1-naphthoic acid in glacial AcOH at room temp. gives CO₂ and 1-acetoxymercuri-β-naphthol (I), identified by conversion into 1-bromo- and 1-iodo-β-naphthol. The Hg·OAc group in (I) was not replaced by nitration; HNO₃ (*d* 1.4) in EtOH gave the *nitrate* (?), m.p. >260°. Contrary to lit., 3-bromo-4-hydroxy-1-naphthaldehyde is not mercurated by Hg(OAc)₂ in AcOH at the b.p.

H. A. P.

Organic lead compounds. III. Reaction of organic lead salts on mercury and lead aryls. P. R. AUSTIN (J. Amer. Chem. Soc., 1932, 54, 3287—3289; cf. A., 1931, 1317).—Pb diaryl dichlorides react in some cases with Hg diaryls to form the mercuric aryl chlorides and a Pb triaryl chloride. PbPh₂Cl₂ and HgPh₂ give 21% of PbPh₃Cl and 57% of HgPhCl when heated in pyridine for 10 hr. Pb di-*o*-tolyl dichloride and HgPh₂ afford 38% of HgPhCl, but the expected (I) (below) could not be isolated; some PbPh₂Cl₂ is isolated, showing that a further

reaction had taken place. Pb phenyl di-*o*-tolyl chloride (I), m.p. 113—114°, is prepared in 70% yield from the bromide using the method previously described (*loc. cit.*). PbPh₃Cl did not react with HgPh₂ or Hg(CH₂Ph)₂ when heated in various solvents; a small quantity of PbPh₄ resulted from disproportionation of the PbPh₃Cl. PbPh₃Cl, heated in BuOH, yields about 10% of PbPh₄ and PbPh₂Cl₂; similar results were obtained with PbEt₃Cl in PhMe or C₆H₆. This reaction is reversible in org. solvents, since PbPh₄ heated with PbPh₂Cl₂ in BuOH gives 86% of PbPh₃Cl. Similarly, PbEt₄ and PbEt₂Cl₂ give 39% of PbEt₃Cl. PbPh₄ does not react with (I) in C₆H₆ or PhMe.

C. J. W. (b)

Organic derivatives of silicon. XLVI. Tetra-nitrotetraphenylsilicane. F. S. KIPPING and J. C. BLACKBURN. XLVII. *cyclo*Hexylphenyl and *cyclo*hexyl derivatives. N. W. CUSA and F. S. KIPPING (J.C.S., 1932, 2200—2205, 2205—2209).—XLVI. Nitration of SiPh₄ in CCl₄ gives 10% tetra-nitrophenylsilicane, m.p. 255—256°, and a mixture, m.p. 90—110°, which probably contains (NO₂)₄ derivatives with *o*-, *m*-, and *p*-NO₂-groups in the same mol.

XLVII. Mg cyclohexyl bromide and PhSiCl₃ give dicyclohexylphenylsilicyl chloride, b.p. 188—192°/2 mm., m.p. 45—48°, forming with aq. alkali dicyclohexylphenylsilicol (I), m.p. 145—146°, and cyclohexylphenylsilicon dichloride, b.p. 123—125°/0.5 mm., hydrolysed to dicyclo-, m.p. 164—165°, and cyclohexylphenylsilicanediol, m.p. 123—124° (efferv.), which condenses readily to trianhydrotris(cyclohexylphenyl)silicanediol, m.p. 117—118°. (I) cannot be converted into the corresponding oxide or a compound containing Si·C, but gives with HNO₃ or with Br in AcOH, trianhydrotris(dicyclohexyl)silicanediol, m.p. 237—239°. F. R. S.

Rearrangement and hydrogenation of metal alkyls. W. H. ZARTMAN and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 3398—3401).—Ni catalyses the reaction, PbPh₄ → Pb+2Ph₂, which occurs at 200°/100 atm. of H₂. A similar reaction occurs with Pb tetra-*p*-tolyl and Pb tetra-*n*-heptyl and to a very limited extent with ZnBu₄. Ni also catalyses the cleavage of ZnBu₂ and MgPh₂ to C₄H₁₀ and C₆H₆, respectively. Sb(Ph)₃ is recovered unchanged. C. J. W. (b)

Degradation of proteins. III. Proline and hydroxyproline contents of certain proteins. O. FÜRTH and H. MINNIBECK (Biochem. Z., 1932, 250, 18—34).—A method is described which combines those of Van Slyke (determination of non-NH₂-N of the phosphotungstic acid filtrate), Dakin (fractional extraction of the protein hydrolysate with butyl and propyl alcohols), and Kapfhammer and Eck (pptn. of proline with CdCl₂) which permits the determination (in a few g. of protein) of proline and hydroxyproline. The % of proline and hydroxyproline respectively are for gelatin 9.0 and 14.7, for zein 8.4 and 0.8, and for caseinogen 5.7 and 2.1. The method also gives good results for mixtures of proline and hydroxyproline with zein and caseinogen hydrolysates. P. W. C.

Degradation of proteins. IV. Micro-determination of alanine in protein. O. FÜRTH, R.

SCHOLL, and H. HERRMANN (Biochem. Z., 1932, 251, 404—417).—After removal from protein hydrolysates of the dicarboxylic acids by pptn. of the Ca salts with EtOH and of the phosphotungstic acid ppt., the residual NH_2 -acids are converted by HNO_2 into the OH-acids (alanine to lactic acid). The alanine is then determined as MeCHO (KMnO_4 oxidation). Alanine (0.1—0.5 mg.) both pure and when mixed with glycine, valine, leucine, tyrosine, and phenylalanine is determined with an accuracy of 91—104%. Serine, glutamic acid, proline, and hydroxyproline do not interfere with the reaction. The mean alanine contents are for silk fibroin 21.8%, zein 8.9%, caseinogen 5.3%, keratin 3.8%, and for gelatin 2.5%.

P. W. C.

Glutelins. VII. Cystine, tryptophan, and tyrosine content ofutelins. F. A. CSONKA (J. Biol. Chem., 1932, 97, 281—286; cf. A., 1931, 245).—Vals. forutelins from the cereals of wheat, rice, maize, rye, barley, and oats are given. Modifications for the colorimetric determination of cystine (A., 1930, 1604) and of tryptophan (A., 1923, i, 160) are described.

F. O. H.

Micro-determination of carbon and hydrogen in an atmosphere of nitrogen. J. B. NIEDERL and B. WHITMAN (Mikrochem., 1932, 11, 274—300).—The combustion tube is packed with Ag for removal of halogen, PbCrO_3 and CuO for removal of S, Cu for reduction of N oxides, and CuO (no PbO_2), and the combustion is performed in N_2 . Two heating burners are used, and a const.-temp. device is replaced by an arrangement of Cu tube and sheet which conducts enough heat from the burner to prevent condensation in the end of the combustion tube. Full details and results are given. The method requires 22 min., compared with 44 min. for the original Pregl method, and 100 c.c. of N_2 .

H. F. G.

Determination of carbon and hydrogen by the Pregl method applied to explosive liquids. M. FRERI (Gazzetta, 1932, 62, 606—609).—Explosive liquids such as the azide ($\text{C}_3\text{H}_2\text{ON})\text{N}_3$ (A., 1931, 1170) and glyceryl nitrate can be analysed for C and H by the Pregl method if the tube is extended and a long charge of CuO included and progressively heated, and if the sample is gradually heated by a Cu sleeve provided with a thermometer.

E. W. W.

Nitrogen not determined by Kjeldahl method. F. SERIO and S. FIANDACA (Biochem. Z., 1932, 250, 408—413).—The Kjeldahl method determines ureide-, purine-, and guanidine-N quantitatively; gives vals. for pyrrole and pyridine rings and for certain NH_2 -acids (lysine) which are 10—27% lower than by the Dumas method, does not determine NO - and NO_2 -N, and gives vals. for diabetic urine 15% lower than by Dumas and for normal urine and urine of diabetics after treatment with insulin 2—6% lower.

P. W. C.

Determination of the halogen content of organic compounds. P. T. MILLER and C. B. JOHNSON (J. Colo. Wyo. Acad. Sci., 1929, 1, No. 1, 55).—Reduction with Na in $\text{EtOH}-\text{C}_6\text{H}_6$ is followed by titration with AgNO_3 (Mohr).

CH. ABS.

Micro-acetyl determination. A. FRIEDRICH and S. RAPOPORT (Biochem. Z., 1932, 251, 432—446).—

The apparatus and method depending on hydrolysis with *p*-toluenesulphonic acid and determination of AcOH are described. The method is applicable to all compounds which give non-volatile hydrolytic products and substances containing NAc groups, since the base unites with the excess of sulphonic acid.

P. W. C.

Determination of propionic acid. J. B. MCNAIR (J. Amer. Chem. Soc., 1932, 54, 3249—3250).— EtCO_2H is converted into $\text{H}_2\text{C}_2\text{O}_4$ when a mixture of EtCO_2H (5.94 c.c. of 0.1N), Na_2CO_3 (1.5 g.), 3.12% KMnO_4 (17.5 c.c.), and H_2O (27 c.c.) is heated at 100° (bath)/4 hr.; excess of KMnO_4 is removed with EtOH , the MnO_2 filtered off, and $\text{C}_2\text{O}_4^{2-}$ pptd. as CaC_2O_4 (in aq. AcOH solution). EtCO_2H can thus be determined in presence of HCO_2H and AcOH .

W. T. H. (b)

Characterisation of acetone in the presence of aldehydes (formaldehyde, acetaldehyde, propionaldehyde). L. KLING (Bull. Soc. Chim. biol., 1932, 14, 885—895).—The method previously described (A., 1931, 1273) has been modified to avoid loss of COMe_2 during destruction of the aldehyde. The mixture is treated with 5 c.c. of Scott-Wilson reagent, and the mixed ppts. formed are distilled with 5 c.c. of 3% H_2O_2 through boiling 30% KOH solution. Aldehyde is thus oxidised, and the COMe_2 is collected in a further 5 c.c. of Scott-Wilson reagent. The descriptions of the turbidities or ppts. given by various amounts of COMe_2 with different proportions of the above aldehydes present are tabulated.

A. C.

Sensitivity of reagents in the test for phenols. J. CONTZEN (Chem.-Ztg., 1932, 56, 683).—Of 11 tests for phenols all were sensitive in a concn. of 10 mg. phenol per c.c., all but one (the FeCl_3 test) in 1 mg. per c.c., only 2, Landolt's aq. Br test and Udransky's furfuraldehyde test, in 0.1 mg. per c.c., and none in 0.01 mg. per c.c.

M. S. B.

Micro-acidimetry of nitrophenols using the glass electrode. H. M. PARTRIDGE and J. A. C. BOWLES (Mikrochem., 1932, 11, 326—336).—A rapid potentiometric method, using a thermionic valve galvanometer (cf. this vol., 1013), is suitable for titrating nitrophenols having an acid ionisation const. $> 10^{-8}$. Probable error using 9-mg. sample about 0.2%.

H. F. G.

Picrolonates of the alkaline-earth metals. P. L. ROBINSON and W. E. SCOTT (Z. anal. Chem., 1932, 88, 417—431).—From aq. solutions Ca and Sr picrolonates crystallise with $7\text{H}_2\text{O}$, the Mg salt with $2\text{H}_2\text{O}$, and the Ba salt with $4\text{H}_2\text{O}$; the Ca and Sr compounds are isomorphous. From EtOH Ba and Sr picrolonates crystallise with EtOH and are isomorphous, but the Ca compound is quite distinct in cryst. habit. The saturated aq. solution contains per litre, 1.5 mg. of the Ca, 3 mg. of the Mg, 14 mg. of the Sr, and 25 mg. of the Ba salt; excess of Na picrolonate reduces these vals. by about 60%. The use of Na picrolonate in microchemical tests for the alkaline earths is discussed (cf. A., 1931, 1259).

A. R. P.

Sensitivity of some methods for determining adrenaline. H. SATO (Tohoku J. Exp. Med., 1932, 18, 463—474).—The following concns. (mg. per c.c.) can be determined accurately: perfusion of toad

legs 10^{-4} — 10^{-3} , perfusion of rabbit's ear 10^{-5} — 10^{-4} , rabbit intestine segment 4×10^{-5} — 8×10^{-4} , paradoxical cat pupil reaction 10^{-4} — 10^{-3} , blood pressure of pithed frog 5×10^{-3} — 2.5×10^{-2} , Suto-Kojima colorimetric 4×10^{-4} — 5×10^{-3} , Kodama's modification of Folin-Cannon-Denis method 2×10^3 — 4×10^3 . The min. detectable difference and the probable error are given. CH. ABS.

Palladous chloride as a reagent for the detection and determination of purine derivatives and as an oxidising agent. J. M. GULLAND and T. F. MACRAE (J.C.S., 1932, 2231—2236).— PdCl_2 with many purines and alkaloids forms almost quantitatively sparingly sol. complexes from which the bases are easily regenerated by the action of Ag in

aq. suspension. Pptn. depends on the p_H of the solution. The caffeine and theobromine complexes have the formula R_2PdCl_2 . The uses of PdCl_2 as an oxidising agent are described. E. E. J. M.

Determination of arsenic in organo-arsenic derivatives. II. H. N. DAS-GURTA (J. Indian Chem. Soc., 1932, 9, 203—206).—Compounds containing As^{+++} are oxidised by warm H_2O_2 , any mineral acid produced (e.g., HCl from chloroarsines) is neutralised with 0.1N- Na_2CO_3 , the mixture then treated with excess of KI, and the liberated I (from H_2O_2) removed with $\text{Na}_2\text{S}_2\text{O}_3$. As^v in the resulting solution is then determined as previously described (this vol., 763). The above method can be used as a qual. test for As. H. B.

Biochemistry.

Crystalline hæmoglobin from human blood. Z. ASZÓDI (Biochem. Z., 1932, 252, 212—214).—By means of a method described, up to 4 g. of cryst. hæmoglobin can be obtained from 100 c.c. of the blood. W. McC.

Uniformity of the prosthetic group of hæmoglobins of various sources. J. POLDERMANN (Biochem. Z., 1932, 251, 452—457).—The differences in light absorption (both of intensity and of position of max. and min. absorption bands) of a series of chlorohæmin preps. from the bloods both of different animals of the same kind and of different kinds of animals (horse, ox, pig, dog, cat, man) are never greater than the experimental error, and spectrophotometric investigation of these chlorohæmins gives no evidence in favour of difference of prosthetic groups of these hæmoglobins. P. W. C.

Action of parenterally administered iron on blood formation. W. LINTZEL and T. RADEFF (Biochem. Z., 1932, 250, 519—524).—Repeated subcutaneous injection of small amounts of Na Fe^{+++} citrate into rats, accelerates hæmoglobin formation. The substance acts more slowly with parenteral administration than when given by mouth. P. W. C.

Action of manganese and plant ash on growth and on the synthesis of hæmoglobin. J. T. SKINNER, W. H. PETERSON, and H. STEENBOCK (Biochem. Z., 1932, 250, 392—404).—Addition of Mn to a milk diet containing Fe+Cu accelerates considerably the growth of young rats, growth being stimulated equally by 0.0041 mg. as by 0.25 mg. Mn per rat per day. The element appears to stimulate appetite. Such addition of Fe, Cu, and Mn is as active as an acid extract of lucerne containing these three elements in equiv. amounts. Mn exerts no influence on the regeneration of hæmoglobin in anæmic rats and the ash of lucerne is not more active in curing alimentary anæmia than is the equiv. amount of Fe and Cu. P. W. C.

Cryptohæmin. E. NEGELEIN (Biochem. Z., 1932, 250, 577).—The cryptoporphyrin reported by the author as formed on shaking the porphyrin of blood-hæmin in HCl solution with air and irradiating (this

vol., 763) is more probably an artefact arising during isolation. P. W. C.

Relationship between respiration and the pyrophosphate exchange in bird's erythrocytes. W. A. ENGELHARDT (Biochem. Z., 1932, 251, 343—368).—Decomp. of pyrophosphate occurs under anaerobic conditions in nucleated blood corpuscles, resynthesis taking place under aerobic conditions. Not only is the hydrolysis of pyrophosphate reversed by respiration, but the hydrolytic products themselves increase respiration. Adenylpyrophosphate is a constituent of the co-enzyme complex of respiration. P. W. C.

Calcium content of the red corpuscles of human blood. I. Z. VON GULACSY. **II.** S. SCHONBERGER (Biochem. Z., 1932, 251, 162—166, 167—172).—The red corpuscles contain only traces of or no Ca. W. McC.

Micro-determination of chloride in plasma and corpuscles of human blood. S. RASZEJA (Bull. Soc. Chim. biol., 1932, 14, 873—884).—Low results in determining small amounts of Cl^- by Volhard's method, due to interaction of AgCl and CNS^- , are prevented by centrifuging the AgCl before titrating the excess AgNO_3 . With the technique described, Cl^- added to plasma is determined within 0.57%, and the sum of separately determined plasma- and corpuscular Cl^- (3.562 and 1.922 mg. per c.c., respectively) is only 1.38% below that for whole blood (2.854 mg. per c.c.). A val. of 0.711 is deduced for the ratio corpuscle : plasma-vol., the ratio of the chloride concns. being 0.54. The former val. is in agreement with the results of conductivity measurements by Slawinski's method (A., 1929, 1142). The analyses were made at p_H 7.6—7.75 on blood in the fasting state. A. C.

Animal proteases. VIII. Proteolytic enzymes of the white blood-corpuscles of different kinds of animals. H. KLEINMANN and G. SCHARR (Biochem. Z., 1932, 251, 275—328).—The proteinases of aq. and glycerol extracts of horse and rabbit leucocytes were investigated by nephelometric and colorimetric methods, using caseinogen, edestin, gelatin, etc. as substrates. Acid and alkaline glycerol and

acid aq. extracts contain cathepsin and trypsin in approx. equal amounts, whereas alkaline aq. extracts contain chiefly trypsin. By treatment with CHCl_3 (48 hr. at 37°) the ereptic activity of the extracts is destroyed, whilst the tryptic activity is unchanged. Separation of erepsin and trypsin is also effected by kaolin adsorption, the residual solution containing almost all the erepsin and the eluate of the adsorbate containing the proteinases, especially trypsin. Extraction for a short time with neutral glycerol gives almost pure cathepsin. Investigation of exudates shows that whereas horse lymphocytes contain only cathepsin, myelocytes contain also trypsin. Rabbit's mono- and poly-nuclear leucocytes contain cathepsin but no trypsin. The proteolytic activity of cathepsin is increased by H_2S and HCN only when gelatin is used as substrate. The trypsin of horse leucocytes cannot be activated by intestinal enterokinase. Glycerol and to a smaller extent aq. extracts contain dipeptidase, the p_{H} optimum for leucylglycine being 8 and for glycylglycine 7. Autolysis with CHCl_3 destroys dipeptidase activity. P. W. C.

Animal proteases. IX. Proteases in horse and rabbit sera. H. KLEINMANN and G. SCHARR (Biochem. Z., 1932, 252, 145—184; cf. preceding abstract).—The sera contain cathepsin which probably exists combined with the globulin fraction of the serum-protein, but cannot be activated by shaking with CHCl_3 , PhMe, or Et_2O . No diminution in the activity of the protease is caused by treating the sera with kaolin, but when caseinogen is the adsorbent a tryptic enzyme is adsorbed. Edestin adsorbs no enzyme from the sera. As regards activation with HCN and H_2S the cathepsin of the sera resembles that from the blood-corpuscles and organs. Enterokinase (from intestinal mucous membrane) has no effect on the activity of the tryptic enzyme. In the sera the cathepsin exists in an active, the trypsin in an inactive, state. Adsorption on caseinogen activates the tryptic enzyme. W. McC.

Maintenance of a normal plasma-protein concentration in spite of repeated protein loss by bleeding. C. W. BARNETT, R. B. JONES, and R. B. COHN (J. Exp. Med., 1932, 55, 683—693).—Removal of blood-plasma from dogs, followed by return of the red cells, does not lead to a fall in plasma-protein. CH. ABS.

Occurrence of β -*h*-fructosidase in the plasma of horse blood. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1932, 82, 318—319; cf. A., 1930, 499, 1065).—The plasma of horse blood contains an enzyme inactive towards maltose, but capable of inverting sucrose and converting raffinose into melibiose and fructose, with optimum p_{H} 4.7. It is therefore β -*h*-fructosidase, hitherto found only in vegetable organisms. J. H. L.

Extent of noticeable variation in the amount of diastase in blood and urine (Wohlgemuth) under different physiological conditions. K. GERMER (Hospitalstid., 1931, 74, 951—959).—The normal diastase content of 24 hr.-urine lies between 16 and 128, and depends but little on sex or age. Normal blood-diastase lies between 8.8 and 22.8; it is somewhat higher in men than in women and is

independent of the time of day and the ordinary mixed diet. CH. ABS.

Quantitative and reversible reaction of serum with ether and the dependence on temperature. F. SEELICH (Biochem. Z., 1932, 250, 549—559).—Serum unites with large amounts of Et_2O during shaking, forming a gel from which, on keeping, the Et_2O again separates. The amount of Et_2O so absorbed depends on the pretreatment of the serum. P. W. C.

Diffusible serum-calcium by high-pressure ultrafiltration. H. O. NICHOLAS (J. Biol. Chem., 1932, 97, 457—464).—Such filtration through cellophane membranes shows 64% of the total Ca of normal serum to be diffusible. The results at such pressures (150 lb. per sq. in.) are higher but more const. than those obtained at low pressures. F. O. H.

Organic phosphorus compounds in blood. C. BOMSKOV (Z. physiol. Chem., 1932, 210, 67—78).—The various P fractions in the blood of man, dog, and rabbit were determined, making use of the step-photometer. The total org. acid-sol. P compounds are esters from which the P can be eliminated by prolonged hydrolysis. J. H. B.

Determination of bilirubin. E. HERZFELD (Biochem. Z., 1932, 251, 394—403).—A detailed study of the Van den Bergh reaction for determination of bilirubin in serum is described. The tint obtained in the direct determination is often not comparable with that of the standard Co solution, and even after EtOH pptn. although the tint is comparable the results vary from $\frac{1}{10}$ to $\frac{1}{3}$ of those by other methods. P. W. C.

Determination of blood-bile acids. I. Method of Aldrich. K. KUSUI (J. Biochem. Japan, 1932, 15, 399—411).—The method of Aldrich and Bledsoe (A., 1928, 788) was investigated. Adsorption of bile acids occurs during treatment of the filtrate from deproteinised blood with C and Ba(OH)_2 . Hence the method gives low vals (viz., 2.56—5.26 mg. per 100 c.c. of normal human blood). F. O. H.

Determination of blood-glutathione. G. E. WOODWARD and E. G. FRY (J. Biol. Chem., 1932, 97, 465—482).—Sulphosalicylic acid (I) but tungstic acid is suitable for deproteinising blood for glutathione determinations. Following the addition of a further quantity of (I) and of KI, the filtrate is titrated against 0.001N- KIO_3 . Normal human blood gave 0.025—0.041%, whilst 5 cancer cases gave 0.026—0.036%. Reduction of the filtrate by Zn gave an increase of 0.003—0.011%, probably due to oxidised glutathione. Ergothioneine is the only blood constituent to interfere, giving an error of approx. 0.003% in the actual vals. F. O. H.

Optical activity of blood filtrates. I. Preparation and investigation of blood filtrates. H. N. NAUMANN (Biochem. Z., 1932, 251, 266—274).—For the prep. of blood filtrates, neither dialysis nor ultra-filtration can be used without loss of sugar by adsorption, and protein pptn. methods must be relied on. A table summarises the abs. and % errors in the prep. of the filtrates, in polarisation and

determination of sugar by the Hagedorn-Jensen method. Modifications of the method are described and the probable error is reduced to 0.01 c.c. 0.005*N*-thiosulphate, equiv. to 4% on the normal blood-sugar content. P. W. C.

Micro-determination of true blood-sugar. N. DOI (J. Biochem. Japan, 1932, 15, 427—438).—The determination of the reducing val. of 0.2 c.c. of blood by the Hagedorn-Jensen method before and after fermentation by yeast was investigated. Deproteinisation by the Folin-Wu reagent and due regard to the conditions for fermentation are recommended. F. O. H.

Micro-determination of fructose in blood. H. STEINITZ and I. VON RIESEN (Biochem. Z., 1932, 252, 201—204).—The fructose in 0.2 c.c. of blood can be determined by the method described. W. McC.

Influence of proteins, amino-acids, and their derivatives on the regulation of blood-sugar. E. G. SCHENCK (Arch. exp. Path. Pharm., 1932, 167, 201—215).—The changes in the blood-sugar of rabbits after ingestion of NH_2 -acids, glutathione, peptone, and proteins were determined. Glycine is the NH_2 -acid most effective in lowering the blood-sugar, a lowering which summates with that due to simultaneous injection of insulin. Alimentary hyperglycæmia is eliminated by administration of glycine. Valine exhibits the greatest hyperglycæmic activity of the NH_2 -acids investigated. Glutathione, which has practically no action on the blood-sugar level, inactivates insulin *in vitro*, but not *in vivo*. A consideration of the correlation of the structure of the substances with their action on the blood-sugar indicates that the sp. action of insulin depends to some extent on its constituent NH_2 -acids. F. O. H.

Effect of intravenous injection of diastase on the blood-sugar in normal and depancreatized animals. H. E. C. WILSON and F. STRIECK (Biochem. Z., 1932, 251, 199—203).—Since extra pure (but not ordinary) diastase has no hypoglycæmic effect when intravenously injected into rabbits, dogs, or depancreatized dogs, it follows that the reduction in blood-sugar produced both by active and by heat-inactivated diastase is caused by admixtures of unknown nature. W. McC.

Ammonia formation in tortoise blood. II. Formation of a phenolic substance which accompanies the formation of ammonia in hæmolysed tortoise blood. W. MOZOLOVSKI and T. MANN (Biochem. Z., 1932, 250, 487—488).—In the protein-free filtrate of tortoise blood, a substance is present which gives a bluish-green FeCl_3 reaction and on making alkaline a red pigment. The NH_3 formation after hæmolysis is attributed to deamination of an aromatic NH_2 -acid with the formation of the phenolic substance. P. W. C.

Nature of antibody reactions. H. SACHS and H. O. BEHRENS (Biochem. Z., 1932, 250, 352—375).—Addition of tannin to the cholesterolised ox-heart extracts ordinarily employed in the Wassermann test causes either no or only a fleeting increase of the anti-complement action of tannin. Union with comple-

ment on addition of tannin to EtOH extracts of organs is, however, confirmed, using guinea-pig heart extracts. The reaction with tannin is concerned not with antigenic functions but with the colloidal nature of the carriers of antigenic activity. Storage of extract dilutions at a higher temp. effects some change in the colloidal nature of the carrier, so that under suitable conditions an extremely strong reaction with tannin is obtained. Maturing in this way at 56° is much more effective than at 37°. The combinations of complement with tannin and with antibodies are quite different processes. P. W. C.

Significance of the structure of antigens for their production and for the specificity of antibodies. H. ERLENMEYER and E. BERGER (Biochem. Z., 1932, 252, 22—36).—Since no As could be detected in horse sera specifically immunised with the antigen obtained from diazotised atoxyl and the sera it is concluded that antibodies are not in any way produced from antigens. It is impossible to distinguish serologically between antigens produced from $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$, $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$, or $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$, but the antigen from $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Bz}$ can be so differentiated. This shows the importance for serological specificity of the "field" effect of mols. W. McC.

Distribution of protective principle in different protein fractions of horse serum immunised against snake venom. S. M. K. MALLICK and G. C. MAITRA (Indian J. Med. Res., 1932, 19, 951—955).—The active antibody is recovered quantitatively in the pseudoglobulin fraction; the euglobulin and albumin fractions are inactive. CH. ABS.

Effect of hyperthermia, acidosis, and alkalosis on the production of agglutinins. J. DAVESNE and P. HABER (Ann. Inst. Pasteur, 1932, 49, 220—233).—Increase of hyperthermia induced in rabbits by tetrahydro- β -naphthylamine simultaneously with, and after, the immunisation of the animals coincides with an increase in the amount of agglutinins. Acidosis and alkalosis have no effect on the temp. change produced by the injection of the antigen. A. L.

Substances involved in the coagulation of the blood of the new-born. II. Effect of ultra-violet radiation and viosterol. III. Effect of withholding protein and fat from the diet. H. N. SANFORD, T. H. GASTEYER, and L. WYAT (Amer. J. Dis. Children, 1932, 43, 566—568, 569—571).—II. The blood-fibrinogen is increased and the anti-thrombin decreased in both cases.

II. The blood-fibrinogen is decreased. CH. ABS.

Chemical nature of heparin. I. Determination of heparin. A. FISCHER and A. SCHMITZ (Z. physiol. Chem., 1932, 210, 129—133).—Two methods are developed for comparing the heparin content of preps. depending on its power of (a) preventing pptn. of caseinogen solutions and (b) clotting blood, respectively. J. H. B.

Crystalline myoglobin. I. Crystallisation and purification; mol. wt. A. H. T. THEORELL (Biochem. Z., 1932, 252, 1—7).—Although myoglobin (from horse heart or ox; yield 0.5 g. per kg.) has the same Fe content as has hæmoglobin, there are

important differences between the two pigments. Myoglobin has mol. wt. 35,000 or 17,500, is stable within the p_H range 5.5—13, and has isoelectric point at p_H 6.99. The prep. of the cryst. substance (prisms from horse, plates from ox) is described. W. McC.

Titrimetric fat determination in small amounts of organ. P. KINMELSTIEL and H. BECKER (Z. physiol. Chem., 1932, 209, 166—175).—The Kumagawa and Suto method (A., 1908, ii, 331) is modified by direct extraction of the fat with light petroleum. Slightly lower (1½%) but more correct vals. are thus obtained. J. H. B.

Preparation of inosic acid. G. EMBDEN (Z. physiol. Chem., 1932, 210, 194—196).—On keeping liver pulp in distilled H_2O at room temp. adenylic acid is rapidly deaminated; inosic acid accumulates and is readily isolated from the solution. J. H. B.

Skin and the nitroprusside reaction. E. NISHIMURA (Japan. J. Dermat., 1931, 31, 1015—1028).—The nitroprusside reaction was practically the same for man, cats, rabbits, guinea-pigs, mice, and frogs. SH-compounds are present in almost all the internal organs. CH. ABS.

Age changes in inorganic constituents of sound human teeth. H. M. LUNDSTROM (Amer. J. Med. Sci., 1931, 182, 152).—The Mg:Ca and $PO_4:CO_3$ ratios increase with age. CH. ABS.

Reaction of mastic in cerebrospinal fluid. L. G. CORDERO (Anal. quim. farm., Chile, 1931, 1, 105—113).—Colloidal mastic coloured with Sudan III is readily prepared and gives trustworthy results. CH. ABS.

Gastric secretion. IV. Variations in the chlorine content of gastric juice and their significance. F. HOLLANDER (J. Biol. Chem., 1932, 97, 585—604).—For pure gastric juice collected from dogs with Pavlov pouches an abs. parallelism exists between the total and neutral Cl' on the one hand and the total acidity on the other. This fact indicates that pure gastric juice is a mixture of a parietal secretion of isotonic HCl containing no fixed base with an alkaline mucous secretion of an isotonic fluid, the principal constituents of which are neutral chlorides and H carbonates. Thus the max. acidity attained by gastric juice under normal conditions is that of a solution of HCl which contains no neutral Cl' and is isotonic with the blood. F. O. H.

Self-protective mechanism of the stomach against the corrosive action of hydrochloric acid. N. HENNING and L. NORPOTH (Arch. exp. Path. Pharm., 1932, 167, 224—236).—Aq. HCl of concn. up to 0.045% causes a marked corrosion of the mucous lining of the rat's stomach to an extent not exceeded by that due to normal human gastric juice containing 5—6 times this HCl concn. F. O. H.

Colorimetric determination of hydrogen-ion concentration in milk. A. C. GALLETTI (Arch. Farm. sperim., 1932, 54, 229—236).—The p_H of milk can be determined rapidly and simply by dialysis into indicator solutions. The non-dialysable portion of the milk does not affect its reaction. R. N. C.

Milk of the American buffalo. F. T. SHUTT (Analyst, 1932, 57, 454).—Analyses of the milk of *Bison americanus* are given. W. J. B.

Human milk. IX. Variations in composition. B. NIMS, I. G. MACY, M. BROWN, and H. A. HUNSCHER (Amer. J. Dis. Children, 1932, 43, 828—844).—Variations are independent of diet, activity, climate, and stage of lactation. The fat and total solids are max. at 10 a.m. and decrease until 2 p.m. Total ash, Ca, and P are min. at 6—10 a.m. and max. at 2 p.m. Cl' is highest in the early morning; N is max. at 2 and 6 p.m. CH. ABS.

Dietary of the human mother with respect to the nutrients secreted into breast milk. C. F. SHUKERS, I. C. MACY, B. NIMS, E. DONELSON, and H. A. HUNSCHER (J. Nutrition, 1932, 5, 127—139).—The intake in food and the output in milk of protein, fat, carbohydrate, Ca, and P for 3 lactating women are recorded and discussed. A. G. P.

Influence of certain balanced rations on chemical and physical properties of milk-fat. O. R. OVERMAN and O. F. GARRETT (J. Agric. Res., 1932, 45, 51—58).—Cotton-seed, linseed, and soya-bean meals produce slight variations in the physical consts. of the corresponding milk-fats when fed to dairy cows. These are too small to be of practical interest. H. G. R.

Determination of bile acids with the help of the step-photometer. H. SULLMANN and L. SCHAUB (Biochem. Z., 1932, 251, 369—383).—Investigation of the absorption by the step-photometer of the colours obtained by carrying out the Pettenkofer reaction with bile acids leads to a method for their determination, the ratio of the concns. of the unknown to a known solution of bile acid being directly as their extinction coeffs. The purification of the bile acid becomes extremely important when the method is adapted for determinations in organs, blood, urine, etc. P. W. C.

Anion-cation studies in liver and gall-bladder bile. I. S. RAYDIN, C. G. JOHNSTON, C. RIEGEL, and J. H. AUSTIN (Amer. J. Med. Sci., 1932, 183, 148—150).—The hepatic bile of different animals and of the same animal at different times is more variable than serum in its electrolyte content. The base, total anion, Ca, and usually HCO_3' are higher, and Cl' is lower. The bile salt varies from 15.6 to 66 milliequiv. per litre, and the p_H is 7.1—8.6. Unknown anions account for about 12 milliequiv. per litre. The composition of bile after a period in the gall bladder is the resultant of absorption of H_2O , some bile salts, and much Cl' and HCO_3' . CH. ABS.

Determination of cholesterol in the bile. R. ELMAN and J. B. TAUSSIG (J. Lab. Clin. Med., 1931, 17, 274—279).—The production of a green colour by non-cholesterol substances is avoided by saponification with KOH before extraction with light petroleum. CH. ABS.

Stalagmometric determination of bile acids in urine. M. TAKEDA, T. OHO, and T. YOSHINARE (J. Biochem. Japan, 1932, 15, 413—425).—The urine is filtered, the sp. gr. adjusted to 1.010, and

the p_H to 9.0, 7.0, or 4.0. For each reaction the "drop no." is determined by the stalagmometer, the vals. obtained forming a criterion of the amount of bile acids present. F. O. H.

Is blood-protein amide-nitrogen a source of urinary ammonia? II. T. P. NASH, jun., and E. F. WILLIAMS, jun. (J. Pharm. Exp. Ther., 1932, 45, 487—492).—A reply to criticisms by Bliss (this vol., 635) of previous work by the authors (*ibid.*, 1925). A. L.

Effect of grapes and grape products on urinary acidity. L. G. SAYWELL (J. Nutrition, 1932, 5, 103—120).—Addition of grapes, grape-juice, raisins, etc. to a basal diet resulted in a decrease in NH_3 excreted and a corresponding decrease in total acidity and a rise in p_H (0.8—1.2 units) in the urine. The alkalinity of the ash of the grape is correlated with the physiological reaction. The increased excretion of org. acids is attributed to the presence of incompletely oxidised tartaric acid. Approx. 94% of the ingested org. acids were oxidised. A. G. P.

Determination of magnesium in urine by the step-photometer. II. C. URBACH (Biochem. Z., 1932, 252, 74—80; cf. A., 1931, 1444).—An improved micro-method is described. W. McC.

Relation of neutral sulphur content and of "iodic acid value" to the appearance of ether-insoluble phenols in urine. O. FURTH, R. SCHOLL, and H. HERRMANN (Biochem. Z., 1932, 251, 148—161; cf. this vol., 186).—The neutral S (total S—total sulphate S) in urine (and in other body-fluids) is best determined iodometrically by a modification of Lang's method (A., 1929, 1500). Increased excretion of neutral S in (pathological) urine is usually accompanied by increased excretion of the phenols which are found in the Morner and Sjoquist fraction. The "iodic acid val." (Chikano, A., 1929, 474) of this fraction of the urine is probably a measure of the amount of easily oxidised substances, and these are related to polyphenols. In the Morner and Sjoquist fraction about half of the N is loosely bound and can be eliminated as NH_3 by hydrolysis and almost all of the N can be converted by energetic hydrolysis into free NH_2 -groups. Possibly the fraction contains carbamido-acids in addition to NH_2 -acids and polypeptides. W. McC.

Microphotometric method for determination of chlorine. Rapid determination of chlorine in biological media. E. OBERMER and R. MILTON (Biochem. Z., 1932, 251, 329—342).—The method is described and adapted to determination of Cl in urine. P. W. C.

Causes of errors in investigations of urine. K. BECHER (Pharm. Ztg., 1932, 77, 784—785).—An account is given of the precautions necessary in the collection of urine, and examination of its sediment. Photomicrographs of different types of foreign matter are given. A. C.

Acid-base balance in sweat. E. H. FISHBERG and W. BIERNAN (J. Biol. Chem., 1932, 97, 433—441).—In diseased man a rise of body temp. to approx. 41° induced by radiothermal treatment

causes a loss of sweat almost equal to the blood-vol. The skin exerts a base-sparing function by excreting the sweat at a much lower p_H than that of the plasma and by a part of the excreted lactate being non-ionised. The presence of lactic acid (which possibly functions as a stimulus to the sweat glands) and lactates prevents, by their buffering action, a p_H of < 4 and hence protects the skin from damage. F. O. H.

Azotæmia. II—IV. R. A. IZZO (Semana med., 1932, i, 387—398, 522—551, 619—654).—Blood-urea is normally 0.036—0.0398%. The distribution of blood-N in relation to disease is discussed. CH. ABS.

Value of some vegetables in nutritional anæmia. H. LEVINE, F. P. CULP, and C. B. ANDERSON (J. Nutrition, 1932, 5, 295—306).—Lettuce, lettuce and tomato, asparagus, spinach, and broccoli supplied in amounts to produce the same Fe intake induced blood regeneration in periods varying inversely with the Cu contents. Solutions of inorg. salts of Cu alone or of Fe alone permitted only partial regeneration, but mixed solutions effected a rapid recovery of hæmoglobin. A. G. P.

Plasma-catalase in artificially induced anæmia of rabbits and the origin of normal plasma-catalase. Y. TAKIZAWA (Tohoku J. Exp. Med., 1932, 18, 512—525).—There is no definite relationship between the state of the blood and the amount of plasma-catalase. CH. ABS.

Is tissue respiration depressed in beriberi? H. G. K. WESTENBRINK (Arch. Néerl. Physiol., 1932, 17, 239—256).—On statistical examination only 2 out of 15 investigations on the cell metabolism of normal and beriberi animals point to a significant difference. W. O. K.

Influence of the geological nature of the soil and of the mineral content of the drinking water on the frequency of cancer in man. F. BLANCHET and L. BETHOUX (Compt. rend., 1932, 195, 469—472).—In France the rate of mortality from cancer is higher in those districts in which the rocks are chiefly cryst. (granite, schists, etc.) than in those in which sedimentary rocks predominate. In the former regions the drinking H_2O is relatively pure and low in mineral content. W. O. K.

Action of glutathione on the Pasteur reaction. E. BUMM and H. APPEL (Z. physiol. Chem., 1932, 210, 79—86).—Neither oxidised (I) nor reduced glutathione (II) has any effect on the respiration or anaerobic glycolysis of rat sarcoma tissue. Under aerobic conditions, glycolysis (lactic acid formation) is reversibly increased by (II) and almost reaches the normal anaerobic val., whilst (I) has no action. J. H. B.

Anaerobic activation of glycolysis in tumour tissue. F. DICKENS and G. D. GREVILLE (Nature, 1932, 130, 206).—A spontaneous increase occurs in the anaerobic conversion of glucose into lactic acid by the Jensen rat sarcoma, but the pre-activation period is shorter than is the case with fructose. 0.001M-AcCO₂Na (I) abolishes the pre-activation period in both cases. Mill Hill fowl tumour attacks

fructose with the same vigour as the Jensen sarcoma, but without the spontaneous increase in lactic acid formation; (I) has no effect in this case. (I) may be able to replace the anaerobic activator in partly activated tissues, but has no effect when activation is complete. L. S. T.

Failure to produce dental caries in the white rat with high-carbohydrate diet and *B. acidophilus* or with vitamin-D deficiency. C. A. LILLY (J. Nutrition, 1932, 5, 175—181).—Administration of these abnormal diets for a year failed to induce experimental caries. A. G. P.

Muscle-creatine in nutritional muscular dystrophy of the rabbit. M. GOETTSCH and E. F. BROWN (J. Biol. Chem., 1932, 97, 549—561).—The abs. and relative creatine contents of the skeletal muscle, but not of the heart or brain, decrease. Both white muscle (which normally contains 0.42—0.50%) and red muscle (normally 0.26—0.36%), at the final stages of degeneration, contain 0.11—0.25%, the normal level of the cardiac muscle-creatine. The content of the degenerated muscle is independent of the fat content (0.5—48.0%). Degeneration is accompanied by an increase in H₂O content. The extent of pathological lesion appears to be parallel with the degree of diminution in creatine. F. O. H.

Glucose-tolerance curve in epilepsy. G. W. J. MACKAY and H. BARBASH (J. Mental Sci., 1931, 77, 83—85).—A high percentage of epileptic patients present a glucose-tolerance curve of a subnormal type. J. H. Q.

Metabolism of fats during experimental yellow fever in monkeys. P. GERARD, (MLLE.) MOISSONIER, and (MLLE.) WELTI (Bull. Soc. Chim. biol., 1932, 14, 916—928).—Lipin fractions have been determined in various organs of monkeys after death from yellow fever. Vals. for one healthy animal serve as normals. The disease is marked by decreases in lipid P, lipocytic coeff., and in the unsaponifiable matter of the heart, suprarenals, kidney, and ganglions. The proportion of fatty acids to total lipins is increased. There is little or no change in the content of phosphate-fatty acids and their I vals. A. C.

Carbohydrate metabolism in a case of hæmochromatosis. R. P. STETSON and J. P. PETERS (Arch. Int. Med., 1932, 50, 226—231). J. B. B.

Cholesterol of the blood-plasma in hepatic and biliary diseases. E. Z. EPSTEIN (Arch. Int. Med., 1932, 50, 203—222).—Hypercholesterolaemia generally occurs in obstructive jaundice, but in degenerative liver diseases jaundice is accompanied by a decrease in cholesterol. In atrophic cirrhosis of the liver and in cholecystitis and cholelithiasis without bile duct obstruction the cholesterol figures are practically normal. J. B. B.

Influence on carbohydrate metabolism of experimentally-induced hepatic changes. III. Chloroform poisoning. T. L. ALTHAUSEN and E. THOENES (Arch. Int. Med., 1932, 50, 257—268).—Rabbits were injected with a large dose of CHCl₃ and the effects of the resulting injury to the liver were studied. Blood-sugar and glucose tolerance were reduced. Adrenaline caused no hyperglycemia. Recovery was associated with increased utilisation of glucose. That injury to the pancreas was not involved was shown by glucose injections without insulin. J. B. B.

Malarial pigment (hæmozoin) in the spleen. R. C. WATTS and W. J. WHITE (Indian J. Med. Res., 1932, 19, 945—950).—The pigment is bleached by conc. H₂O₂. The alkaline solution has no sp. absorption bands, nor does it yield hæmatin. An alkaline extract of minced spleen does not give flocculation or complement fixation with malarial sera. CH. ABS.

Determination of the isoelectric point of crystalline Bence-Jones protein. O. JERVELL and R. NICOLAYSEN (Biochem. Z., 1932, 250, 308—311).—Crystallisation occurs only in acid reaction and the isoelectric point of the cryst. material as determined by electrometric titration is at p_H 4.0—4.25. P. W. C.

Organic acids of the cerebrospinal fluid [in general paralysis]. R. H. HURST (J. Mental Sci., 1931, 77, 119—126).—There is no increase in lactic acid of the cerebrospinal fluid in general paralysis, but a definite increase in "total org. acids." J. H. Q.

Boltz acetic anhydride test [in general paralysis]. J. E. NICOLE and E. J. FITZGERALD (J. Mental Sci., 1931, 77, 321—331).—The Boltz test (carried out with Ac₂O and H₂SO₄ on cerebrospinal fluid) is rarely positive in nonparetic cases except in certain conditions of meningeal involvement. It is usually positive in general paralysis and becomes negative after malarial treatment, especially after some years have elapsed since the first malarial attack. The test appears to be associated with, if it is not identical with, the glyoxylic acid test for tryptophan. J. H. Q.

Parallel study of the psycho-galvanic reflex and the hyperglycæmic index in psychotics. M. R. LOCKWOOD (J. Mental Sci., 1932, 78, 288—301).—A close parallelism exists, in psychotics, between the hyperglycæmic index (cf. McCowan and Quastel, *ibid.*, 1931, 77, 525) and the psychogalvanic reflex. J. H. Q.

Solvent action of the blood-serum of healthy and rachitic young pigs on the bone salts. J. MAREK, O. WELLMANN, and L. URBANEK (Biochem. Z., 1932, 252, 131—144).—Blood-serum from healthy young pigs deposits salts when shaken with bone-powder, bone ash, Ca₃(PO₄)₂, or CaCO₃ (or mixtures of these salts), whereas that from young pigs suffering from experimental rickets due to acidosis or alkalosis produced by appropriately unsuitable or unbalanced mineral content in the diet dissolves these materials. The nature of the deposition or dissolution depends on the prevailing composition of the serum and of the bone; acidosis in the bone causes deposition chiefly of CaCO₃, alkalosis causes deposition chiefly of Ca₃(PO₄)₂. Ca and P contents and also the Ca/P quotient are greatly affected by the digestive processes. W. McC.

Phosphorus partition in the blood of rachitic and non-rachitic calves. F. J. STARE and C. A. ELVEHJEM (J. Biol. Chem., 1932, 97, 511—524).—Experimental rickets in calves is accompanied by a decrease in inorg., acid-sol., and total P. The

decrease in total P is slightly greater than that in the inorg. P, indicating small decreases in ester-P and possibly in lipin-P. The distribution of the fractions between corpuscles and plasma also appears to be affected by the disease, and for this reason, together with the possible change in P distribution during separation, the plasma-inorg. P is not truly indicative of the total change in the inorg. P fraction during rickets. F. O. H.

Sodium iodobismuthite for use in the treatment of syphilis. C. GURCHOT, P. J. HANZLIK, and J. SPAULDING (*J. Pharm. Exp. Ther.*, 1932, 45, 427—467).—The prep. of cryst. Na iodobismuthite (I), $\text{Na}_2\text{BiI}_5 \cdot 4\text{H}_2\text{O}$, and its properties are described. In aq. and glycol solutions the Bi is combined with I as electronegative complex. Glycol and especially NaI inhibit the hydrolysis of (I) by H_2O and its pptn. by horse and ox sera and ovalbumin. (I) dialyses slowly through celloidin and frog's skin. Serum-proteins increase, whilst NaI has no effect on, the rate of dialysis. A 6% solution of (I) in glycol containing 12% NaI is recommended for the treatment of syphilis. A. L.

Standardisation of colloidal gold sols in the Lange test. W. A. KREIDLER and J. C. SMALL (*J. Lab. Clin. Med.*, 1931, 17, 259—268).—The sols are standardised against a cerebrospinal fluid with a val. of 4 and the required sensitiveness is obtained by adjustment of the η_{H} . CH. ABS.

Standardisation of colloidal gold sols by utilising a standard solution of globulin. W. A. KREIDLER and J. C. SMALL (*J. Lab. Clin. Med.*, 1931, 17, 269—271).—A solution of edestin is employed. CH. ABS.

Animal calorimetry. XLII. Respiratory metabolism of exercise and recovery in depancreatized dogs. W. H. CHAMBERS, M. A. KENNARD, H. POLLACK, and M. DANN (*J. Biol. Chem.*, 1932, 97, 525—547).—The elevation of the R.Q. occurring in depancreatized dogs during exercise is followed by a compensatory fall during rest such that the combined periods of activity and recovery show no increase over the basal level. The recovery process is slightly slower in the diabetic than in the normal fasting dog. No significant differences occur in the contents of glycogen, sugar, and lactic acid of the tissues of diabetic dogs before and after work. The data indicate that the rise in R.Q. is due to changes in the CO_2 equilibrium in the body rather than to carbohydrate oxidation and favour the theory that fat is the fuel utilised in the depancreatized dog during exercise. F. O. H.

Effects of low environmental temperature on metabolism. I. Technique and respiratory quotient. II. Influence of shivering, subcutaneous fat, and skin temperature on heat production. R. W. SWIFT (*J. Nutrition*, 1932, 5, 213—225, 227—249).—I. Exposure to cold does not favour any preferential oxidation of carbohydrate in man. Depletion of glycogen stores is proportional to the increased total metabolism.

II. Exposure at 2° for 1 hr. resulted in no change in protein metabolism or blood-sugar level. In general

reaction to cold varied inversely to the amount of subcutaneous fat. A. G. P.

Analysis of the curve of heat production in relation to the plane of nutrition. E. B. FORBES and M. KRISS (*J. Nutrition*, 1932, 5, 183—197).—The heat derived from body substance and from nutrient constituents at various levels of intake from fasting up to thrice the maintenance ratio is examined. The heat contribution from protein has approx. the same proportion of the total heat at all levels of feeding. The fat contribution is approx. 83—86% of the total at fasting and falls to zero at the maintenance level. Between fasting and maintenance the carbohydrate contribution is the complement of that of the fat, and above the maintenance level does not vary greatly. A. G. P.

Manometric measurement of the metabolism of growing tissue cultures. H. LASER (*Biochem. Z.*, 1932, 251, 2—9).—A method and apparatus for measuring the gaseous metabolism are described. The respiration of the cultures (osteoblast) increases with time. The initially very extensive anaerobic glycolysis decreases and the aerobic glycolysis is not always const. W. McC.

Alleged evidence for an α -oxidation of fatty acids [in muscle]. F. KNOOP (*Z. physiol. Chem.*, 1932, 209, 277—279).—The figures of Hahn (A., 1930, 1064), from which he concludes conversion of EtCO_2H into AcCO_2H , are within the limits of experimental error. J. H. B.

α -Oxidation of fatty acids. A. HAHN (*Z. physiol. Chem.*, 1932, 209, 279—280).—A reply to Knoop (see preceding abstract). J. H. B.

Behaviour of the phosphatides and cholesterol of whole blood, plasma, and erythrocytes in normal men after taking olive oil with and without previous administration of phosphate. H. WENDT (*Biochem. Z.*, 1932, 250, 212—219).—Administration of olive oil to healthy man and animals causes, 4 hr. later, an increase in blood-phosphatide and -cholesterol, the increase occurring only in the serum and plasma and not in the corpuscles. Previous administration of PO_4''' or addition of PO_4''' to the olive oil has no influence on the result. Prolonged administration of PO_4''' increases the plasma-phosphatide val. P. W. C.

Destruction of cholesterol by the animal organism. I. H. PAGE and W. MENSCHICK (*J. Biol. Chem.*, 1932, 97, 359—368).—Rabbits were fed on large amounts of cholesterol and the faecal cholesterol and, after death, the body distribution of the sterol were determined. Deposition of cholesterol occurred in all organs except the brain. A deficiency in the balance indicated a destruction of cholesterol of 0.8—1.8 g. per week. The bearing of the results on cholesterol arteriosclerosis is discussed. F. O. H.

Fate of orally administered cholesterol in the human intestine. H. SALOMON (*Z. physiol. Chem.*, 1932, 209, 276).—Polemical in reply to Bürger and Winterseel (this vol., 85). J. H. B.

Fate of orally administered cholesterol in the human intestine. M. BURGER (Z. physiol. Chem., 1932, 209, 276).—A reply to Salomon (cf. preceding abstract). J. H. B.

Carbohydrate metabolism of resting and active mammary glands. H. K. BARRENSCHEEN and N. ALDERS (Biochem. Z., 1932, 252, 97—112).—The phosphate content of the lactating mammary gland (I) (guinea-pig, rabbit) is considerably higher than that of the resting gland (II), the increase being chiefly in the org. acid-insol. fraction. The acid-sol. org. P (hexosephosphoric ester) of (I) also is greater than that of (II). Since the glands contain a pyrophosphate fraction (adenosinetriphosphoric acid), and since added hexosediphosphate is converted into methylglyoxal when glycolysis in them is inhibited with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$, it seems that the hexosephosphoric ester is an intermediate product in the production of lactose in the glands. (I) and (II) contain the same (very small) amount of glycogen, but the glycolytic power of (I), which seems necessarily to involve intermediary phosphorylation, is much greater than that of (II). (I) produces lactic acid from added lactose and galactose [(II) does not] and only (I) can produce the acid in pure O_2 . Glucose, glycogen, lactose, galactose, and hexosediphosphate are decomposed to equal extents by (I). W. McC.

Bile acids and carbohydrate metabolism. XXII. Influence of loss of bile on sugar tolerance in dogs with biliary fistulae. T. TANAKA (J. Biochem. Japan, 1932, 15, 381—398).—The tolerance is increased on parenteral administration of cholic acid and decreased on withdrawal of bile, the two effects being mutually dependent. On the other hand, the tolerance of such dogs injected with very small amounts of adrenaline together with glucose is greater when accompanied by withdrawal of bile. F. O. H.

Changes in colloidal condition of muscle-proteins in muscle activity. H. J. DEUTICKE (Z. physiol. Chem., 1932, 210, 97—124).—Changes in solubility of the proteins were determined by extraction with buffer solutions, after electrical stimulation of the isolated frog's muscle. The decreases run parallel with the development of tension. The solubility changes are reversed after keeping the isolated muscle in O_2 , but not in N_2 . Resting muscle, on keeping in O_2 , develops only a slight increase in protein solubility. The reversion shown by fatigued muscle in O_2 is a relatively slow process. Neither a high degree of tension nor a subminimal stimulus produces a measurable change in protein solubility. The colloidal changes probably occur at the moment of muscle contraction, and are an important cause of fatigue. J. H. B.

Influence of the sympathetics on the biochemical processes of fatigued muscle. P. JACKY (Biochem. Z., 1932, 250, 178—192).—With fresh frog's muscle and with muscle fatigued by stimulation of the sciatic and curarised, stimulation of the sympathetics on one side did not increase the creatinephosphoric acid content of that side, but when the muscle was severely fatigued by stimulation

of the anterior roots, stimulation of the sympathetics always gave an increase of creatinephosphoric acid.

P. W. C.

Elimination of purines in fatigue of isolated frog's muscle. S. E. KERR (Z. physiol. Chem., 1932, 210, 181—193).—Small amounts of purines, apparently not in the form of nucleotides, are present in fresh frog's muscle. The purine fraction is considerably increased by fatigue induced by electrical stimulation. J. H. B.

Urea formation in the animal body. H. A. KREBS and K. HENSELEIT (Z. physiol. Chem., 1932, 210, 33—66).—The rate of synthesis of urea from CO_2 and NH_3 in surviving tissue sections of rat's organs was measured under varying conditions. The liver is the only organ in which urea is synthesised. The synthesis is greatly accelerated by ornithine, which acts like a catalyst in that it is not used up, and small amounts can effect a large conversion. No other substance examined had a similar action. Citrulline accelerates urea formation from NH_3 , but is consumed in the process, furnishing 1 atom of N per mol. of urea. Urea formation is intimately linked with respiration; its object is apparently to detoxicate NH_3 in the body. Urea is not formed by liver pulp, in which the cell structure is destroyed. The reactions are explained as follows: ornithine takes up CO_2 and NH_3 to form citrulline, which reacts with NH_3 to give arginine. The latter is decomposed by arginase into ornithine and urea:

$$\text{R}\cdot\text{CH}_2\cdot\text{NH}_2 + \text{CO}_2 + \text{NH}_3 \longrightarrow \text{R}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \longrightarrow$$

$$\text{R}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2 \longrightarrow \text{R}\cdot\text{CH}_2\cdot\text{NH}_2 + \text{CO}(\text{NH}_2)_2$$

[$\text{R}=\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$]. J. H. B.

Ammonia in human brain. H. SCHWARZ and H. DIBOLD (Biochem. Z., 1932, 251, 187—189).—Fresh diseased (tumours) human brain-tissue (5 cases examined) contains, on the average, 0.204 mg. of NH_3 per 100 g. and there may be a relation between pathological (or physiological) condition and NH_3 content. At room temp. the tissue produces NH_3 rapidly. W. McC.

Production of ammonia in brain. Effect of alteration of the circulation and of administration of insulin on this production. H. SCHWARZ and H. DIBOLD (Biochem. Z., 1932, 251, 190—198; cf. preceding abstract).—Fresh rabbit's brain contains, on the average, 0.4 mg. of NH_3 per 100 g. and produces NH_3 rapidly at room temp. Ligature of the carotid frequently leads to increase in the NH_3 content of the brain, especially when there is accompanying section of the vagus nerves. Administration of insulin irreversibly reduces the NH_3 content of brain, since counteraction of the hypoglycæmia by administration of sugar is not accompanied by restoration of the original NH_3 val. W. McC.

Protein metabolism in men and animals. E. VOIT (Z. Biol., 1932, 93, 15—41).—Cell wear and tear, physiological protein decomp., and min. requirements are related to each other and have separate vals. Min. protein requirements acquire significance in the dieting of men and animals only when measured during an exact diet, in which case the val. obtained

is higher than when measured on animals fed on excessive diets. H. D.

Determination of the biological value of protein in the study of avian nutrition. J. L. ST. JOHN, O. JOHNSON, J. S. CARVER, and S. A. MOORE (J. Nutrition, 1932, 5, 267—276).—During 12 weeks following the hatching of chickens the % of total N and uric acid eliminated varied from day to day, but the total quantity per day remained practically the same throughout. The total faecal N was comparatively small. No relationship was observed between either faecal or urinary N and the age of the chicks. A. G. P.

Changes in the weights of various organs and systems of young rats maintained on a low-protein diet. M. LIMSON and C. M. JACKSON (J. Nutrition, 1932, 5, 163—174).—Low-protein diets fed to rats increased the wt. of some organs and decreased that of others. The effect is ascribed to deficiency of sp. nutrients for certain organs the growth of which is suppressed while other organs develop more or less normally. A. G. P.

Effects of restricted protein intake on the oestrous cycle and gestation in the rat. H. R. GUILBERT and H. GOSS (J. Nutrition, 1932, 5, 251—265).—Protein-deficient diets produced either a cessation of oestrus or long and irregular cycles together with infertility. A. G. P.

Feeding experiments with decomposition products of proteins. U. SUZUKI and N. HASHIMOTO (Proc. Imp. Acad. Tokyo, 1932, 8, 292—295).—Mayeda's experiment (this vol., 643) is repeated and the results are confirmed. The mixed acid and alkaline hydrolysis products of the horse-meat protein of a rat's diet can replace the protein entirely without affecting growth, but the acid products alone require addition of 3% *L*-tryptophan. P. W. C.

Feeding experiments with decomposition products of proteins. II. S. MAYEDA (Proc. Imp. Acad. Tokyo, 1932, 8, 296—299).—The protein of a rat's diet can be replaced completely by either a mixture of alkaline and acid hydrolysis products or by acid hydrolysis products with 3% of tryptophan, but cannot be replaced by either acid or alkaline hydrolysis products separately. The baryta hydrolysis product was fractionated with HgSO_4 into the tryptophan-containing ppt. and the tryptophan-free filtrate. The baryta filtrate has no supplementary effect on the acid hydrolysis product, and omission of the filtrate from a sufficient diet of acid hydrolysis product + tryptophan + filtrate did not effect growth. P. W. C.

Utilisation by human subjects of the nitrogen, calcium, and phosphorus of the navy bean (*Phaseolus vulgaris*), with and without a supplement of cystine. M. A. PITTMAN (J. Nutrition, 1932, 5, 277—294).—With diets of which navy bean formed the chief source of N the balance became increasingly negative. Addition of cystine slightly increased N retention. The Ca and P of the beans were insufficient to maintain the normal balance. There was better utilisation of P than of Ca. Improvement in the utilisation of P corresponded with greater retention of N. A. G. P.

Calcium retention on a diet containing American cheddar cheese. M. G. MALLON, L. M. JOHNSON, and C. R. DARBY (J. Nutrition, 1932, 5, 121—126).—The Ca of this cheese is as well utilised as that from pasteurised whole milk. A. G. P.

Iron requirement of the pre-school child. J. M. LEICHSENREING and I. H. FLOR (J. Nutrition, 1932, 5, 141—146).—The maintenance requirement of Fe for children was similar to that for adults (average 0.12 mg. per kg.) and the growth requirement was approx. 0.2 mg. per kg. A. G. P.

Corrosive action of hydrofluoric acid [on the skin etc.]. K. FREDENHAGEN and M. WELLMANN (Angew. Chem., 1932, 45, 537—538).—The action of HF on the skin is due to the rapid diffusion of F⁻ into the underlying tissue. Application of a paste of MgO and glycerol, or, in severe cases, subcutaneous injection of 20% aq. MgSO_4 or of certain non-toxic Ca compounds, is recommended. H. F. G.

Physiological action of aluminium. J. H. BURN (Analyst, 1932, 57, 428—440).—From a review of the literature it is concluded that when Al compounds are given by mouth, only traces of Al are absorbed from the intestine and that no effect other than mild catharsis follows the feeding of Al salts to man even when this is continued for 6 months. W. J. B.

Influence of industrial poisons on antibody formation. I. Lead. II. Benzene and turpentine. F. W. BICKERT (Arch. Hyg., 1931, 106, 271—298; 107, 1—10).—Subcutaneous administration to rabbits of $\text{Pb}(\text{OAc})_2$ or other Pb salts stimulates the production of haemolysins for sheep erythrocytes, of agglutinins for typhus bacilli, and of an antitoxin for diphtheria toxin. Administration of $\text{Pb}(\text{OAc})_2$ inhibits the formation of precipitins for sheep serum. Haemolysin production appears to be inhibited by subcutaneous injections of C_6H_6 and to be stimulated by injections of turpentine. CH. ABS.

Zinc content of internal organs in two cases of poisoning by zinc phosphide. A. MONTEFREDINE (Arch. Farm. sperim., 1932, 54, 223—228).—The organs analysed showed high Zn contents, ranging from 10 to 60 times the normal val. The kidney was an exception, showing only a slight increase, owing to its excretory activity. The livers showed a high fat content, due to fatty degeneration. R. N. C.

Action of thorium on the metabolism [of rabbits]. J. Z. DOMINGUEZ (Biochem. Z., 1932, 251, 141—147).—In rabbits parenteral administration of small amounts (0.1—0.2 g. per kg.) of ThCl_4 has slight irregular effects on the metabolism (oxidations, excretion of C, O, and N), but larger doses (0.2—0.6 g. per kg.) stimulate oxidations. W. McC.

Biochemical action of arsenic acids of the pyridine series. VI. Excretion of organic halogen compounds in the urine. A. BINZ and H. MAIER-BODE (Biochem. Z., 1932, 252, 16—21; cf. A., 1931, 1454).—The max. urinary concn. of combined Br or I which can be attained as a result of injection of aliphatic or aromatic I or Br compounds is not proportional to the amount of halogen injected. The diuretic effect, the time required for attaining this

max., and the long time which elapses before excretion of halogen ceases, vary greatly from substance to substance, and no relationship can be traced between these factors and the halogen content of the substances. Within the observed time $\text{CHI}(\text{SO}_3\text{Na})_2$ was almost quantitatively excreted and the excretion of other I compounds exceeded 80%, but $\text{CHBr}(\text{SO}_3\text{Na})_2$ and $\text{CH}_2\text{Br}\cdot\text{SO}_3\text{Na}$ as well as certain I compounds were excreted less completely (or more slowly).

W. McC.

Relationship between chemical structure and physiological response. II. Conjugation of hydroxy- and methoxy-benzoic acids. A. J. QUICK [with M. A. COOPER] (J. Biol. Chem., 1932, 97, 403—419).—The principal conjugated product excreted in the urine of dogs fed with $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (I) is the *diglycuronic acid* derivative, m.p. 200—201° (decomp.), $[\alpha]_D^{20}$ -15° to -16° (1% aq. solution), exhibiting mutarotation in alkaline solution. Conjugation with 2 mols. of glycuronic acid also occurs in dogs with *o*- and *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. Ingestion of (I)-diglycuronic acid by man is not followed by excretion of this compound, only (I) and its glycine derivative appearing in the urine. *m*- and *p*-Hydroxy- and -methoxy-hippuric acids were isolated from human urine following ingestion of the corresponding benzoic acids, which, however, are also excreted free or, in some cases, combined with glycuronic acid. In man *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is excreted as the free acid. The theory is advanced that, in a conjugation process of detoxication, a weak acid is converted into a strong acid which can be eliminated through the kidney.

F. O. H.

Ethyl alcohol. III. Combustion of ethyl alcohol by a homeotherm (mouse) at the neutral temperature. M. NICLOUX (Bull. Soc. Chim. biol., 1932, 14, 861—872; cf. A., 1931, 1327).—The combustion of EtOH in mice at 30° after subcutaneous injection of quantities varying between 0.18 and 4.9 mg. per g. of mouse is proportional to time, and is almost complete in 3 hr. The amount of EtOH oxidised per g. of body-wt. per hr. is approx. const. This "coeff. of ethyloxydation" has a mean val. of 0.65 mg. for the mouse at 30°.

A. C.

Esters of dialkylaminomethanols as local anaesthetics. E. V. LYNN and F. V. LOFGREN (J. Amer. Pharm. Assoc., 1932, 21, 761—764).—Of 16 cinnamyl, *m*- and *p*-aminobenzoyl, and Bz esters of a series of dialkylaminomethyl alcohols together with their salts, all the sol. salts possessed local anaesthetic properties. Some of the bases showed local anaesthetic properties. The sol. salts, especially those of high mol. wt., were readily hydrolysed and very irritating when applied to the cornea of a rabbit.

E. H. S.

Conditions for novocaine action. A. WEISS (Arch. exp. Path. Pharm., 1932, 167, 177—190).—The anaesthetic action of novocaine on the rabbit's cornea is increased by parenteral administration of CaCl_2 or morphine and is accelerated by that of KCl. With morphine the duration of anaesthesia can be increased eightfold and this phenomenon is used as a method of assay of morphine preps. Other opium alkaloids also possess this synergising action, but generally to a smaller extent. Heroin and

dilaudid, however, increase the anaesthesia to the extent of, respectively, 280 and 500% of that of morphine.

F. O. H.

Effect of phloridzin on the rate of absorption from the gastro-intestinal tract of the white rat. R. H. WILSON (J. Biol. Chem., 1932, 97, 497—502).—Rats continuously subcutaneously injected with phloridzin absorb glucose, glycine, and alanine at 70, 137, and 134% of the normal rate, respectively. These changes afford an explanation of the equal rates of glucose excretion in phloridzin glycosuria of dogs after the ingestion of these substances.

F. O. H.

Variations of alkaline reserve in organisms stimulated by pharmacodynamic substances. —R. MESSINA (Arch. Farm. sperim., 1932, 54, 207—213).—Subcutaneous injection of morphine and pilocarpine in the dog caused a marked fall in alkaline reserve, the effect lasting several hr. Atropine had the same effect to a smaller degree. With all three alkaloids, small doses caused a greater fall than larger doses. It is suggested that the rise in blood-Ca following the injections results in an increased production of H^+ .

R. N. C.

Influence of pharmacodynamic substances on calcium-potassium equilibrium. R. MESSINA (Arch. Farm. sperim., 1932, 54, 214—222).—Subcutaneous injection of small quantities of morphine, pilocarpine, and atropine in the dog resulted in a rise of blood-Ca together with a corresponding fall in blood-K. Results obtained with larger quantities were irregular. These variations are attributed to secondary effects following the disturbance of the sympatheticotonic state by morphine and pilocarpine, or vagal paralysis by atropine.

R. N. C.

Colloid chemistry of nervous systems. V. W. D. BANCROFT, R. S. GUTSELL, and J. E. RUTZLER, jun. (J. Physical Chem., 1932, 36, 2011—2082).—Administration of large amounts of NaCNS to four morphine addicts during morphine withdrawal alleviated withdrawal symptoms, and mental rehabilitation was accomplished in three cases. Overdosage of NaCNS can be counteracted by Na amytal, an agglomerating agent.

C. T. S. (b)

New class of choline esters (carbamylcholine chloride or "lentine"). II. Action on the blood-pressure, intestine, digestive glands, and its fate in the organism. H. NOLL (Arch. exp. Path. Pharm., 1932, 167, 158—170; cf. this vol., 301).—Carbamylcholine chloride (I) is 1000 times as powerful as acetylcholine (II) in its action on the blood-pressure of the decapitated cat, whilst in their action on the isolated small intestine both the two substances are approx. equal. In contrast to (II), intravenous injection of (I) results in a contraction of the intestine *in situ*. (I) excites salivation, approaches histamine in its promotion of the flow of gastric juice, does not influence the excretion of bile, and, unlike choline or (II), is stable in the body.

F. O. H.

Depressor substances of yeast. U. S. VON EULER (Arch. exp. Path. Pharm., 1932, 167, 171—176).—The depressor substance obtained by von

Euler and Gaddum (*J. Physiol.*, 1931, 72, 74) is not present in EtOH extracts of fresh, frozen, or heated yeast. The depressor substances of yeast fall into two groups, choline-like substances and adenyl compounds. Acetylcholine does not occur in yeast. The actions of adenylythiomethylpentose and of a vitamin-*B*₁ prep. on the blood-pressure and on the isolated intestine of the rabbit are similar to, but much weaker than, those of yeast-adenylic acid.

F. O. H.

Protective action of optical desensitisers towards photo-biological processes. E. SZORENYI (*Biochem. Z.*, 1932, 252, 113—125).—Photographic desensitisers (dyes) protect sensitised blood-corpuscles and *Paramecia* from the detrimental action of light, the protective effect being much greater than that of resorcinol or of serum. The toxicity of hæmatoporphyrin as an optical sensitiser is greater at acid than at alkaline reaction, that of rose-Bengal 3B (tetrachlorotetraiodofluorescein) is greater at alkaline than at acid. White mice sensitised to light are protected against its harmful effects by subcutaneous injection of serum.

W. McC.

Mitogenetic radiation. III. Induction in onion roots with yeast and blood. M. MOISEJEVA (*Biochem. Z.*, 1932, 251, 133—140; cf. this vol., 201).—Since no mitogenetic effects can be produced in onion roots by induction with yeast, blood from healthy or tuberculous persons, or rat's blood, such roots cannot serve as detectors of mitogenetic radiation and the results of all investigations in which the roots were so used are erroneous.

W. McC.

Mitogenetic radiation from white blood-cells. J. KLENITZKY (*Biochem. Z.*, 1932, 252, 126—130).—Mitogenetic radiation characteristic of glycolysis (I), oxidation, and phosphatase action is emitted by white polynuclear blood-corpuscles and such rays, characteristic of proteolytic processes (II), are probably also emitted. Most of the rays are of intra-cellular origin. The cell-free liquid emits only the rays characteristic of (I) and possibly also those of (II).

W. McC.

Catalase. III. Types of inhibition and mechanism of the catalase reaction. K. G. STERN (*Z. physiol. Chem.*, 1932, 209, 176—206; cf. this vol., 775).—The mechanism of the inhibition of catalase by various methods is discussed. EtO₂H has an affinity for catalase and hence acts as inhibitor; Et₂O₂ has no such affinity and shows no inhibition. The comparative activity of a no. of inhibitors is given. The theory of action of catalase is based on the assumption of the breakdown of the H₂O₂ into two OH groups, yielding O₂ and H₂O as end-products.

Biological reduction. I. Active hydrogen-donor from heart-muscle. K. KODAMA. II. Distribution of "biosugar"-dehydrogenase in various tissues and the co-enzymic action of extract of suprarenal cortex. M. TSUKANO. III. Oxidation-reduction potential of "biosugar" with its dehydrogenase. M. TSUKANO. IV. Biological reduction of cystine. M. TSUKANO (*J. Biochem. Japan*, 1932, 15, 473—476, 477—485, 487—490, 491—496).—I. Ox heart-muscle was ex-

tracted with boiling 70% aq. EtOH, the extract pptd. by HgCl₂, and the filtrate treated with Ba(OH)₂, followed by pptn. with EtOH. The salt thus obtained corresponded with a Ba hexosemonophosphate, $[\alpha]_D^{20}$ +7.82° (phenylhydrazone, m.p. 138°). The identity of the ester with that of Embden (A., 1927, 749) or that of Robison (A., 1923, i, 86) was doubtful and it was therefore designated "biosugar." "Biosugar" acts as a H-donor to a dehydrogenase.

II. The distribution of the dehydrogenase in various ox and rabbit tissues was determined. Suprarenal cortex has an outstanding activity due to the presence of a "co-donor" which resembles adenylypyrophosphate and does not itself reduce methylene-blue but promotes the action of the dehydrogenase as donor.

III. The reduction potentials of systems containing "biosugar" and heart-muscle, suprarenal cortex, or suprarenal cortex + heart-muscle + hexosediphosphate were determined. The vals. obtained were in agreement with the biochemical behaviour of such systems.

IV. The system "biosugar"—heart-muscle emulsion can reduce cystine to cysteine to an extent greater than succinate-dehydrogenase can, the optimum pH being approx. 7.4.

F. O. H.

Hexosediphosphatedehydrogenase and carb-oxylase in plant seeds. B. ANDERSSON (*Z. physiol. Chem.*, 1932, 210, 15—29).—A hexosediphosphatedehydrogenase occurs in several plant seeds from which Thunberg reported its absence. The inactivity of these seeds is not due to lack of enzyme, but to the absence in sufficient amount of cozymase. The activity of certain seeds (oats, rye, wheat) is much increased during the first days of germination. This is due not to an increase in enzyme but to the production of cozymase. The enzyme of peas fermenting AcCO₂H requires a co-enzyme identical in its action with cocarboxylase. Mg also activates this fermentation.

J. H. B.

Asymmetric catalysis with organic fibres (a new enzyme model). G. BREDIG and F. GERSTNER (*Biochem. Z.*, 1932, 250, 414—429).—Cotton fibres are converted by introduction of a NEt₂ group into a very active catalyst, which is able to decarboxylate β -keto-acids and to catalyse the formation of mandelonitrile from HCN and PhCHO, a considerable amount of the product being lævorotatory.

P. W. C.

Specificity of polysaccharide-splitting enzymes. W. GRASSMANN, L. ZECHMEISTER, G. TÓTH, and R. STADLER (*Naturwiss.*, 1932, 20, 639).

W. R. A.

Specificity of amylases. I. Separation and properties of the two malt amylases. G. A. VAN KLINKENBERG (*Z. physiol. Chem.*, 1932, 209, 253—268).—The Wijsman diffusion experiment (A., 1890, 998) offers a good method for studying amylases. Dry preps. of α - and β -amylase were obtained each free from the other form. β -Amylase shows optimal activity at 4.55—5.15, α -amylase at 5.65—5.85 with citrate buffer. The I reaction disappears completely with α -amylase, but changes to purple with β -amylase, corresponding with the formation of

erythrogranulose. The reaction of α -amylase is inhibited more by α -maltose, that of β -amylase by β -maltose. J. H. B.

Effect of the colloidal condition of starch and of amylase solution on the rate of the enzymic hydrolysis. E. A. SYM (Biochem. Z., 1932, 251, 116—132).—The colloidal condition of starch has no effect on its reaction with amylase, but that of the amylase influences its activity and is affected by such factors as the protective action of starch against inactivation by H^+ or by salts and the high temp. coeff. of the inactivating process. The lower is the concn. of the starch the greater is the degree of hydrolysis by amylase. Free amylase is much less stable than amylase-starch compound. The inactivation of amylase by salts ($NaCl$, $CaCl_2$, Na_2SO_4) is partly an ionic phenomenon (at optimum acid reaction anions act, at optimum alkaline reaction, cations), but also partly dependent on the colloidal condition of the enzyme. In acid solutions amylase is very labile and very readily affected by all inactivating factors. The way in which hydrolysis proceeds is probably determined by the intermediate products in the reaction. Amylase apparently does not combine with the end-products. W. McC.

Activity of the amylase in the leaves of the sugar-beet. A. OPARIN and S. RISSKINA (Biochem. Z., 1932, 252, 8—15; cf. A., 1929, 1106).—When the fresh or dried leaves of the sugar-beet are mixed with H_2O (or with buffer solutions) part of the amylase present dissolves and part remains bound to (or adsorbed on) the leaves in an inactive state. The amount of active (dissolved) amylase attains an equilibrium with that of the bound. Most of the latter can be extracted gradually from the leaves by repeated washing with H_2O , and extraction with McIlvaine's buffer solution removes most of the amylase from the leaves in the active (dissolved) state. Autolysis in the leaves is accompanied by rapid inactivation of the amylase. W. McC.

Glutathione as a complement of amylases. H. PRINGSHEIM, H. BORCHARDT, and H. HUPFER (Biochem. Z., 1932, 250, 109—124).—Glutathione behaves very similarly to yeast-complement in the activation of pancreatic amylase. The complement action of solutions containing equimol. amounts of oxidised and reduced glutathione and of cysteine are approx. the same. Dithioglycolic acid has no complement action. The action of glutathione is the same with and without the addition of $NaCl$. Glutathione and yeast-complement do not activate yeast-amylase. Whereas addition of glutathione and yeast-complement to the starch-pancreatic amylase mixture after attainment of equilibrium takes the amylolysis further, no such action is obtained with yeast-amylase. Salivary amylase behaves like pancreatic amylase. P. W. C.

Separation of α -glucosidase and β -*h*-fructosidase in yeast autolysates, and the hydrolysis of sucrose. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1932, 82, 503—519).—The author restates his theory of the sp. action of sugar enzymes (A., 1928, 1157, 1281; 1929, 352, 722) and describes the separation of the two sucrose-splitting enzymes, which are

both present in yeast, by preferential adsorption of α -glucosidase (maltase) on β - $Al(OH)_3$ (cf. A., 1930, 1065; 1931, 653). α -Glucosidase hydrolyses sucrose about twice as rapidly as it does maltose. J. H. L.

Emulsin. VIII. B. HELFERICH and S. WINKLER (Z. physiol. Chim., 1932, 209, 269—275).—*Phenol- α -d-mannoside*, m.p. 132—133°, $[\alpha]_D^{25} +113.5^\circ$, is hydrolysed by preps. of emulsin at substantially the same rate ratios as the β -*d*-glucoside and β -*d*-mannoside whereas *phenol- β -d-mannoside*, m.p. 175—176.5°, $[\alpha]_D^{25} -71.6^\circ$, is not attacked. The decisive factor in hydrolysis by β -*d*-glucosidase is probably the *trans*-position of the O atoms at C_1 and C_2 . J. H. B.

Pectolase. I. F. EHRLICH (Biochem. Z., 1932, 250, 525—534).—A theoretical paper announcing the prep. of a highly-active enzymic system, pectolase, from mould cultures which is able to hydrolyse the complex tetragalacturonic acid of pectin to unimol. *d*-galacturonic acid. P. W. C.

Pectolase. II. F. EHRLICH (Biochem. Z., 1932, 251, 204—222).—Examples of the action of samples of pectolase from various sources (takadiastase, emulsin, moulds) are given. W. McC.

Enzymic hydrolysis and synthesis of aspartic acid. A. I. VIRTANEN and J. TARNANEN (Biochem. Z., 1932, 250, 193—211).—A very sp. enzyme, *aspartase*, is isolated from cultures of *B. fluorescens liquefaciens* which effects the interconversion *l*-aspartic acid \rightleftharpoons fumaric acid $+ NH_3$ at pH 7, but not below pH 6. The reaction follows the mass law; the synthetic action is increased by addition of NH_3 , and the equilibrium is reached from both sides. The enzyme solution also contains fumarase and asparaginase. It does not cause addition of NH_3 to fumaric acid diamide, nor to mesaconic, aconitic, and sorbic acids. It does not cause deamination of NH_2 -acids (except asparagine). Aspartase is much more sensitive to acids and $EtOH$ than is asparaginase. Its pH optimum is 7—7.5. It occurs widely in plants (pea seedlings, young grass), but was not detected either in yeast or in animal organs. P. W. C.

Activation and inhibition of arginase preparations by oxygen, carbon dioxide, cysteine, and salts of heavy metals. II. S. SALASKIN and L. SOLOVIEV (Biochem. Z., 1932, 250, 503—518).—Arginase prepared by different methods is differently affected by gases. The $COMe_2$ prep. is affected most strongly with O_2 and the glycerol prep. with CO_2 . The glycerol prep. after partial loss of activity by the action of gases is completely reactivated by addition of cysteine, whereas the $COMe_2$ prep. and the $AcOH$ prep. under the same conditions are inhibited. After treatment with salts of heavy metals (Fe , Cu) all the arginase preps. are activated by cysteine. P. W. C.

Liver autolysis. W. LAVES and E. SCHADEN-DORFF (Z. physiol. Chem., 1932, 210, 168—180).—In progressive autolysis of cell and tissue structures, the morphological changes are accompanied by a displacement of the isoelectric point of the colloids to the alkaline side. These changes in liver tissue extracted with $EtOH$ correspond with an increase

of protein degradation products and a higher acidity in the extracts. J. H. B.

Quinones as enzyme models. V. Comparison of the deamination of di- and tri-peptides with that of glycine. B. KISCH (Biochem. Z., 1932, 250, 135—148).—Catalytic oxidative deamination of glycylglycine (I) and glycyl-leucine by hydroxyquinol is not preceded by splitting of the substrate. Leucylglycylglycine is not deaminised at p_H 6—12. Whereas deamination at p_H 7—9 of (I) by a series of quinones and resorcinol occurs less readily than with glycine, insertion of a p -OH group in the catalyst enables deamination to occur more readily than with glycine. The reverse is the case at p_H 9—11. The p_H optimum for deamination of (I) is much lower than for glycine and serine (cf. this vol., 578). P. W. C.

Proteases of insectivorous plants. K. G. STERN and E. STERN (Biochem. Z., 1932, 252, 81—96).—The secretion in the trap and the extract from its glandular tissue of *Nepenthes Hibberdii* and of *N. mixta* contain a catheptic (I) (optimum activity at p_H 4—5) and a tryptic (II) (optimum activity at about p_H 7) protease. Since the p_H of the secretion is about 7 (II) is more active under natural conditions than is (I). The action of (I) on gelatin is not stimulated by HCN, H₂S, or cysteine nor that of (II) by enterokinase. W. McC.

Tyndallometric determination of pepsin. E. HERZFELD (Biochem. Z., 1932, 251, 384—393).—A method is described for the rapid determination of small amounts of pepsin in terms of the turbidity of the protein degradation products, obtained under standard conditions. P. W. C.

Action of pancreatin on gelatin surfaces. M. BERGMANN and F. FOHR (Biochem. Z., 1932, 250, 568—576).—The gelatin with which is incorporated some black material is spread in layers of known thickness on glass and the extent of digestion by pancreatin is measured optically in terms of decrease in blackness by comparison with a standard wedge made of the same substances. Curves showing the dissolution of gelatin as a function of the digestion time closely approximate to straight lines. P. W. C.

Enzymic fission of proline peptides. II. W. GRASSMANN, O. VON SCHOENEBECK, and G. AUERBACH (Z. physiol. Chem., 1932, 210, 1—14; cf. A., 1929, 848).—The new substrates were prepared by treating the corresponding α -dibromovaleryl compounds with 25% aq. NH₃, avoiding the use of Ag. The following were employed: dl-prolylglycine, m.p. 225—227° (decomp.), dl-prolylglycylglycine, m.p. 217° (from α -dibromovalerylglucylglycylglycine, m.p. 153°), prolylalanine, and prolyl-leucylglycine. In confirmation of previous work all the proline peptides were hydrolysed by crude erepsin solutions, also by peptidase solutions from spleen, liver, kidney, lung, and yeast. Dried preps. of amino- and poly-peptidase were inactive towards the proline peptides. The divergent results of Abderhalden and Zumstein (A., 1931, 767) may be due to traces of Ag in their poly-peptides, since the metal is a powerful inhibitor. Prolinase was obtained almost free from poly-peptidase, but not from dipeptidase. It differs

from dipeptidase in being less sensitive to HCN and more readily adsorbed by kaolin and Al(OH)₃ Cy. J. H. B.

Formation of lysolecithin from egg-yolk lecithin by pancreas extract. Z. NIKUNI (Proc. Imp. Acad. Tokyo, 1932, 8, 300—303).—When egg-yolk lecithin is digested with pancreas extract a powerful hæmolytic substance identical with the lysolecithin formed from lecithin by the action of snake venom is obtained. P. W. C.

Nuclein metabolism. XXIX. Enzymic fission of pus-nucleic acid with nucleotidase from intestinal mucosa and a new carbohydrate from animal nucleic acid. F. BIELSCHOVSKY (Z. physiol. Chem., 1932, 210, 134—138; cf. this vol., 776).—From the products of enzymic hydrolysis of pus-nucleic acid were isolated guanosine, inosine, thymosine, cytidine (as picrate), and a carbohydrate, darkens at 150°, m.p. 204° (decomp.), giving negative NHPH₂, Kiliani, fuchsin-H₂SO₄, and Angeli-Rimini tests. J. H. B.

Urea formation in the animal body. VI. A.4. **Urea formation in surviving organs and in their press-juice.** L. SOLOVIEV and S. MARDASCHEV (Z. physiol. Chem., 1932, 209, 239—246; cf. this vol., 544).—In liver autolysis neither NH₄ salts nor NH₂-acids give rise to urea, the only source of which is arginine. J. H. B.

Urease. II. Action of neutral chlorides on urease. A. RUCHELMANN (Biochem. Z., 1932, 251, 51—59; cf. this vol., 777).—At p_H 7.1 (7.4 for LiCl) the activity of urease and the rate at which it decomposes urea are affected by the presence of the chloride of Na, K, Rb, or Li usually according to the amount of buffer present. The salts diminish the activity of the enzyme to some extent in proportion to their concn., but other factors (accumulation of NH₃, effects on the two phases of the reaction, binding of the enzyme or of the substrate) are also involved. W. McC.

Influence of hydrogen-ion concentration on the phosphorylation and lactic acid formation in muscle. B. TANKÓ (Biochem. Z., 1932, 250, 7—17). In fresh muscle-pulp the p_H optimum of OH·CHMe·CO₂H formation, using PO₄''' + glycogen + pulp at room temp., is 7.6 (corrected for phosphatase action 7.3), whilst in muscle-powder the vals. are 7.3—7.4 (corr. 7.2). The displacement of p_H with muscle-powder is probably related to the action of glycogenase. The p_H optima for phosphatase are with fresh pulp 7.2—7.3 and with muscle-powder 7.1. P. W. C.

Co-enzyme action. II. Adenosinetriphosphoric acid. H. K. BARRENSCHEEN and W. FILZ (Biochem. Z., 1932, 250, 281—304).—A method for the prep. of adenosinetriphosphoric acid by pptn. with alkaline CaCl₂ or Ca(OAc)₂·NaOAc is described. The Ag salt from mammalian muscle has the formula C₁₀H₁₃O₁₃N₅P₃Ag₃. The carbohydrate component on distillation with HCl gave only traces of furfuraldehyde and no levulic acid. The velocity of hydrolysis as followed by Van Slyke's method was much smaller than for Embden's muscle-adenylic acid and in the hydrolysate inorg. PO₄''' and inosic acid were detected.

whilst inosinepyrophosphoric acid was not found. After 4 hr. hydrolysis, an *adenosinetriphosphoric acid* was also isolated which differed from the original material in that it was much more sol., it contained 6 OH groups titratable potentiometrically (the original substance contained only 5), and it gave a Ag salt containing Ag_4 . Muscle-deaminase did not separate NH_3 from either of these acids, but a mixture of adenylic acid deaminase and pyrophosphatase separated both P and N in the ratio 2:1. Liver-nucleo-phosphatase did not separate P from these acids. The structural formula is discussed. P. W. C.

Effect of phosphatases in lactic and alcoholic fermentations and on the relationship of cozymase. C. ARNAUDI and M. FRANCIOLI (Biochem. Z., 1932, 250, 125—134).—Small amounts of the phosphatases of *Aspergillus niger*, *A. oryzae*, of yeast, and of phytase accelerate alcoholic fermentation. These phosphatases are not all able to protect pigeons fed on rice from polyneuritis. The enzymic power of *B. bulgaricus* can be increased by addition of phytase and by the phosphatase of *A. oryzae*, the increase being pronounced in presence of inorg. PO_4''' . Fermentation of glucose can be effected by an enzymic system in which the cozymase is replaced by the phosphatases of *A. oryzae* or *A. niger*, and by phytase. P. W. C.

Zygosaccharomyces. M. SACCHETTI (Atti R. Accad. Lincei, 1932, [vi], 15, 762—765).—Various conjugating yeasts were isolated from Italian products, two new species being named *Zygosaccharomyces gracilis italicus* and *Z. felsineus*. T. H. P.

Biological action of arsenate. II. Influence of arsenate on phosphorylation by muscular tissue. L. R. SUBKOVA and A. E. BRAUNSTEIN (Biochem. Z., 1932, 250, 496—502).—Tables show the extent of inhibition by arsenate of phosphorylation by pigeon's breast muscle (pulp and dried powder preps.) with and without addition of NaF and of glycogen and the mechanism of the inhibition is discussed. P. W. C.

Biological action of arsenate. III. Biochemical esterification of arsenic acid by yeast. A. E. BRAUNSTEIN and M. M. LEVITOV (Biochem. Z., 1932, 252, 56—63; cf. this vol., 882).—During the esterification of H_3AsO_4 by yeast labile hexose-arsenic esters are very probably produced. $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{H}$ inhibits the production of the esters. W. McC.

Action of halogenoacetic acids on hydrolysis and oxidative metabolism. E. LUNDSGAARD (Biochem. Z., 1932, 250, 61—88).—In experiments of short duration at p_{H} 4.5—5, fermentation by yeast is completely inhibited, but respiration is unaffected by 0.001M solutions of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$. $\text{CHBr}_2\cdot\text{CO}_2\text{H}$ has some, $\text{CBr}_3\cdot\text{CO}_2\text{H}$, $\text{CHMeI}\cdot\text{CO}_2\text{H}$, $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{CHMeBr}\cdot\text{CO}_2\text{H}$, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ have only a fleeting or no effect on fermentation. The conditions for maintaining respiration (R.Q. about 1) for a long time are given, fermentation being excluded. EtOH and AcCO_2H are more readily oxidised by poisoned yeast than is carbo-

hydrate. Synthesis of carbohydrate from EtOH does not occur with poisoned yeast. Oxidation with poisoned yeast in glucose solution is essentially similar to that in EtOH solution, but the CO_2 development is about twice as great as that obtainable from the EtOH formed in fermentation and the R.Q. is much greater than when EtOH is oxidised. It appears that a direct oxidation of glucose occurs. P. W. C.

Is the nutritive for "Gebrüde Mayer" yeast of universal biological importance? R. J. WILLIAMS, C. M. LYMAN, G. H. GOODYEAR, and J. H. TRUESDAIL (J. Amer. Chem. Soc., 1932, 54, 3462—3463).—An unknown hydroxy-acid, *M* about 200, is the responsible agent for a remarkable growth stimulation of "Gebrüde Mayer" yeast. It is found in a great variety of living tissues; its esters are not basic, it contains several OH groups, is not olefinic, and does not contain CHO, CO, or aromatic groups. C. J. W. (b)

Biochemical conversion of ethyl alcohol into citric acid by moulds. T. CHRZASZCZ, D. TIUKOV, and M. ZAKOMORNY (Biochem. Z., 1932, 250, 254—269).—During the conversion by various species of *Penicillium* of EtOH into citric acid, the following products arise: acetic, succinic, fumaric, *l*-malic, glycollic, oxalic, and other acids. These products arise also from sugar, but only after the sugar is completely degraded to EtOH. The mechanism suggested is, therefore, $\text{sugar} \rightarrow \text{EtOH} \rightarrow \text{AcOH} \rightarrow \text{glycollic} \rightarrow \text{l-malic} \rightarrow \text{citric acids}$. The influence of the medium and of the particular strain determines the relative amounts of these products and the extent of the conversion of glycollic into oxalic acid. P. W. C.

Ergosterol and mannitol from *Aspergillus fischeri*. L. M. PRUESS, W. H. PETERSON, and E. B. FRED (J. Biol. Chem., 1932, 97, 483—489).—The dried mycelium of *A. fischeri* (Thom 5041) on extraction with 96% EtOH yields mannitol (0.4%) and ergosterol (0.1%). These substances are also produced by *A. oryzae*. F. O. H.

Formation and biological significance of a growth regulator by *Aspergillus niger*. P. BOYSEN-JENSEN (Biochem. Z., 1932, 250, 270—280).—A method is described for the prep. of a metabolic product of *A. niger*, which, although unnecessary for the growth of the organism itself, is able to accelerate the growth of *Avena coleoptile*. The formation of this substance occurs only when certain NH_4 -acids of high mol. wt. are present in the medium. P. W. C.

Biochemistry of luminous bacteria. II. Influence of sugars with sodium chloride on luminosity. F. FUHRMANN (Monatsh., 1932, 60, 414—430).—Under the experimental conditions, glucose, fructose, and galactose do not cause appreciable increase of luminosity; the two first-named sugars are generally restrictive whether the NaCl content is optimal or less. With 0.5M-NaCl in the initial stages up to 24 hr., galactose and fructose in particular exercise a marked impulse on the luminosity if the amounts used are small. In these small amounts, glucose has an appreciably

slower action, since, as when other hexoses are employed in larger amount, the max. luminosity is attained only after 36 hr. When judged by the amount of acid produced, galactose is least attacked, although it produces the greatest luminosity. Generally, in presence of the hexoses larger amounts of NaCl lead to greater light max. followed by rapid decline. In the initial stages of growth sucrose and lactose in all amounts employed strongly excite the luminous process, the max. being lower with lactose. In 0.25*M*-NaCl lactose restricts the luminosity more or less, since the max. attained are lower than in the sugar-free controls. In 0.5*M*-NaCl additions of sucrose are without marked effect on the luminescence, whereas analogous additions of medium amounts of lactose have a favouring action. Development of acidity is not marked with the disaccharides and is absent at the optimal NaCl content. Very small additions of maltose facilitate the development of light. Small amounts, in solutions of much less than the optimal NaCl concn., cause a very rapid increase of the luminosity to a high max. in the first 24 hr., followed by an extremely rapid decline.

H. W.

Hemicellulose-decomposing bacteria. A. G. NORMAN (J. Bact., 1932, 23, 72—73; cf. this vol., 1955).—Soil bacteria fermenting hemicellulose at 65°, but more rapidly at 25—35°, were examined. Lactobionic acid was utilised by all strains and maltobionic acid by many. Gum arabic, mesquite gum, and tetragalacturonic acid were fermented. In liquid media the fermentation of complex hemicelluloses proceeded slowly.

A. G. P.

Thermophilic fermentation of beet pulp. C. H. WERKMAN and J. STRITAR (J. Bact., 1932, 23, 70—71).—Soil organisms ferment pulp at 56—58°. Sugars, pentosans, pectins, and, later, cellulose are decomposed. Lignin is very resistant. CH₄ is among the products from cellulose. Small amounts of HCO₂H are produced.

A. G. P.

Bacterial decomposition of glucose, fructose, and glucosamine. F. LIEBEN and L. LOWE (Biochem. Z., 1932, 252, 70—73; cf. A., 1930, 251).—Fructose by itself is more extensively decomposed by *B. proteus vulgaris* (I), and by *B. prodigiosus* (II) than is glucose by itself, but (I) decomposes the two sugars to the same extent and (II) decomposes glucose to a much greater extent than fructose in a mixture of equal parts of the two sugars. (II) decomposes glucosamine to the same extent as it does glucose.

W. McC.

***Lactobacillus acidophilus*.** I. Occurrence of free, optically active, dihydroxystearic acid in the fatty extract. J. A. CROWDER and R. J. ANDERSON (J. Biol. Chem., 1932, 97, 393—401).—Treatment of the fat, extracted from the bacteria by Et₂O+EtOH, with Et₂O leaves an insol. residue (2.6%) which, on crystallisation from suitable solvents, yields dihydroxystearic acid, m.p. 108° (softening at 105°), $[\alpha]_D^{25} +7.78^\circ$ in MeOH (recrystallisation from EtOAc gives m.p. 106—107°, but $[\alpha]_D^{25} +2.92^\circ$, indicating racemisation by contact with hot solvents); Ac derivative, an oil at 0°; Ba salt, m.p. 208—209°.

F. O. H.

Effect of associated growth on the forms of lactic acid produced by certain bacteria. E. L. TATUM, E. B. FRED, and W. H. PETERSON (J. Bact., 1932, 23, 73—74).—Many organisms normally producing specifically *d*- or *l*-lactic acid when grown in association with *Cl. acetobutylicum* yield inactive forms. This effect is due to the production of a heat-labile substance by the latter organism. A disarrangement of the normal enzymic system of the lactic organisms is suggested.

A. G. P.

Propionic acid bacteria. E. R. HITCHNER (J. Bact., 1932, 23, 40—41).—Variations in the characteristics of numerous cultures are recorded. Pigmentation occurred in certain cases in which a neutral reaction was maintained throughout growth. Stimulated growth occurring in association with other organisms is ascribed to modification of the oxidation-reduction potential of the medium. Catalase activity of cultures varied considerably and was extremely low in many cases. All cultures fermented hexoses and glycerol but not inulin or dulcitol. EtCO₂H, AcOH, and CO₂ were the chief fermentation products of glucose. Small amounts of succinic acid were also formed.

A. G. P.

Factors involved in the biological production of acetone and butyl alcohol. L. WEINSTEIN and L. F. RETTGER (J. Bact., 1932, 23, 74—75).—The presence of EtOH-sol. protein in the medium is essential for the normal production of BuOH by *Cl. acetobutylicum*. Acid hydrolysates of sawdust, cottonseed hulls, maize cobs, etc. yielded normal amounts of COMe₂ but no BuOH. The latter was formed only after the addition of prolamine.

A. G. P.

Activity of the enzyme dismuting acetaldehyde in aerobic cell metabolism. F. WINDISCH (Biochem. Z., 1932, 250, 466—486).—The conversion of MeCHO into AcOH and EtOH by bacteria (*B. ascensens*, *B. pasteurianum*, *B. aceti*, Hansen) under aerobic conditions is examined and methods for the macro-determination of O₂ utilisation and AcOH and EtOH production are described. The results are discussed from the viewpoint of mechanism of reaction.

P. W. C.

Nitrogen metabolism of bacteria as affected by colloids and replaceable bases in soil. H. J. CONN (J. Bact., 1932, 23, 77).—Certain non-sporing, humifying soil bacteria fail to develop in soils rich in total N, without the addition of N compounds, or salts or hydroxides of strong bases. This apparent deficiency of available N is characteristic of soils having high ratios of colloids to Ca. The presence of much adsorbed N liberated by the addition of strong bases is suggested.

A. G. P.

Synthesis of amino-acid by animal tissue and bacteria *in vitro*. T. ISHIHARA (Fukuoka-Ikwad.-Zasshi, 1931, 24, 1231—1304).—Aspartic acid was synthesised by many bacteria from a mixture of fumaric acid and NH₄ salt. The fumaric acid could not be replaced by crotonic, β-hydroxybutyric, or pyruvic acid. No animal tissues, even embryonic or neoplastic, synthesised NH₂-acid *in vitro*.

CH. ABS.

Growth of *Rhizobia* on rich nitrogenous media. A. W. HOFER and I. L. BALDWIN (J.

Bact., 1932, 23, 65—66).—In high-N media marked physiological differences between *R. meliloti* and other nodule organisms are apparent. A. G. P.

Dependence of the respiration of nitrogen bacteria on the oxygen tension. O. MEYERHOF and W. SCHULZ (Biochem. Z., 1932, 250, 35—49).—Curves show the variation of the respiration of cultures of *Azotobacter chroococcum* in N-free salt solutions with the Q_{O_2} vals. at O_2 concns. of 0.3, 1, and 4%. Corresponding with the incomplete saturation of the respiratory enzyme at lower O_2 tensions, the CO inhibition decreases with decreasing O_2 tension. P. W. C.

Effect of lecithin and cholesterol on the biology of the human tubercle bacillus. I. LOMINSKY (Ann. Inst. Pasteur, 1932, 49, 194—219).—A comparison of the development of the bacilli grown on potato media containing (a) 0.07% cholesterol, (b) without addition, (c) 0.1% lecithin, (d) 0.07% cholesterol and 0.1% lecithin showed that the rate of growth increased in this order. The order of toxicity of such cultures for white mice was (c), (b), (d), (a), and for guinea-pigs, (d), (c), (b), (a), (c) and (d) being the most toxic, respectively. A. L.

Chemical, microscopical, and serological properties of filtrates of *B. tuberculosis* and *B. phlei*. C. NINNI (Ann. Inst. Pasteur, 1932, 49, 186—193).—The filtrates from the bacilli grown on Sauton medium contain protein and lipins, the amount of ultra-virus present depending on the amount of protein and colloidal material. The fats and lipins which will not pass through the Chamberland L_2 filter are present as complex lipo-proteins and are pptd. from the filtrates dried at 38° by EtOH at 96°. Filtrates after such treatment are antigenic. A. L.

Presence of bacteria in coal seams. R. LIESKE (Biochem. Z., 1932, 250, 339—351).—The bacterial content of seams of coal does not vary inversely with the density of the coal, anthracite often giving a large and porous coal a small count. The natural flora is not the same as that of the air of the mine. Very frequently gas-rich coal contains a greater no. of bacteria than gas-poor coal. P. W. C.

Occurrence of micro-organisms in peat bogs and their role in peat formation. S. A. WAKSMAN and E. R. PURVIS (J. Bact., 1932, 23, 76).—Profiles of forest and sedge peats contain high bacterial nos. irrespective of the age of the various layers. Cellulose-decomposing bacteria are more concerned in peat formation than is usually supposed and are active in transformation processes long after the peat is laid down. Many organisms concerned are facultative anaerobes capable of developing at fairly high acidity. A. G. P.

Microflora of old volcanic ash with special reference to nitrogen-fixing bacteria. N. R. SMITH (J. Bact., 1932, 23, 75—76).—No evidence of N fixation by *B. radiobacter* in volcanic ash was obtained, although the organism was present. *Azotobacter* was not observed. A. G. P.

Influence of dyes on the formation of catalase in certain bacteria. I. A. VOLFSO (Arch. sci.

biol., Russia, 1931, 31, 161—172).—The production of catalase by Gram-positive bacteria was affected much more than that by Gram-negative bacteria on treatment of the medium with methylene-blue, neutral-red, gentian-violet, acid-fuchsin, or eosin. The basic dyes were more effective than the acid dyes. The presence of dyes had no appreciable effect on the decomp. of H_2O_2 . CH. ABS.

Use of reduced iron in the cultivation of anaerobic bacteria. E. G. HASTINGS and E. MCCOY (J. Bact., 1932, 23, 54—56).—Addition of reduced Fe to milk prior to routine tests for anaerobic organisms renders these tests much more definite. A. G. P.

Soya-bean culture media. E. T. H. TSEN and S. SUNG (Chinese Med. J., 1932, 46, 603—606).—The soya-bean media described give as good bacterial growth, with the same morphological and antigenic properties, as meat-peptone agar. H. G. R.

Relation of temperature to the germicidal efficiency of lye solutions. E. C. MCCULLOCH (J. Bact., 1932, 23, 50—51).—A high-grade household lye effectively destroyed *B. abortus* and *E. coli*, a 1:800 solution having PhOH coeff. 8. Between 2° and 25° temp. had little influence on toxicity, which is associated with the activity of OH^- . A. G. P.

Oligodynamic action of metals. H. LANGWELL (Chem. and Ind., 1932, 701—702).—The oligodynamic action of metals may inactivate extracellular enzymes without causing injury to the organisms. Where fermentation is unaffected by oligodynamic action no extracellular enzymes are present. T. McL.

Oligodynamic action of silver. F. L. HAHN (Biochem. Z., 1932, 251, 101—104; cf. Egg and Jung, A., 1929, 1494).—Although the bactericidal effect of solutions of normal Ag salts depends on $[Ag^+]$, solutions of complex Ag salts need contain, initially, only sufficient of the ions to permit adsorption of them by the bacteria. Subsequent decomp. of complex ions and repetition of the process carry on the reaction. W. McC.

Perfusion fluid for rabbit-ear vessels in determining blood-adrenaline. Z. KANOWOKA (Tohoku J. Exp. Med., 1932, 18, 553—558).—Na citrate (10 g.) and old serum (100 c.c.) are diluted with "Tyrode" or "normosal" to 1000 c.c. CH. ABS.

Threshold sensitivity of the rabbit ear method for determining adrenaline. H. SATO (Tohoku J. Exp. Med., 1932, 18, 475—481).—Poor results were obtained with Schlossmann's perfusion fluid. CH. ABS.

Standardisation of secretin. O. WILANDER and G. AGREN (Biochem. Z., 1932, 250, 489—495).—The method is described. The active substance behaves like a base; it does not contain histamine and has no influence on the secretion of bile. P. W. C.

Protection of insulin by antiproteases and its absorption from the intestine. B. K. HARNED and T. P. NASH, jun. (J. Biol. Chem., 1932, 97, 443—456).—From *Ascaris lumbricoides* was obtained an antitryptic prep. which almost entirely prevented the

action of trypsin on insulin *in vitro*. Small amounts of the prep., however, did not afford protection against very large amounts of trypsin, indicating a stoichiometric relation between trypsin and antitrypsin. The introduction of antitrypsin-insulin mixtures into the duodenum of normal dogs had no influence on the blood-sugar, whereas introduction into the stomach (where the antitrypsin functions as antipepsin) or duodenum of depancreatized dogs abolished the sugar excretion for short periods and produced an increase in the D:N ratio sufficient to indicate a temporary storage of glycogen. The relation between dosage and effect, however, indicated that the absorption of insulin from the intestine is small.
F. O. H.

Physiology of glands. CXXVI. Relationship of the spleen and thyroid to iron metabolism. L. ASHER and H. TSCHUMI (Biochem. Z., 1932, 251, 418—431).—The excretion of Fe by normal rabbits is investigated under const. conditions. After injection of thyroxine a considerable increase, and after splenectomy a decrease, of excretion of Fe occurs, but injection of thyroxine into splenectomized animals causes an even greater increase of Fe excretion than in the case of normal animals.
P. W. C.

Effect of thyroid administration on blood-cholesterol. A. G. DUNCAN (J. Mental Sci., 1931, 77, 332—340).—The administration of thyroid to patients suffering from a wide variety of mental disorders results in a rapid lowering of blood-cholesterol. After cessation of the thyroid administration the blood-cholesterol rises gradually to a figure considerably above the former resting val. This phenomenon probably applies also to normal individuals.
J. H. Q.

Direct measurements of the oxygen consumption of isolated, beating auricles from normal and thyrotoxic guinea-pigs. D. McEACHERN (Bull. Johns Hopkins Hosp., 1932, 50, 287—294).—The O_2 consumption is (7—20%) higher in the latter.
CH. ABS.

Respiratory metabolism in infancy and in childhood. XIII. Calorigenic action of thyroid extracts in normal infants. T. C. WYATT, L. E. WEYMULLER, and S. Z. LEVINE (Amer. J. Dis. Children, 1932, 43, 845—864).
CH. ABS.

Relation of the blood-silica to the parathyroid gland and to the blood-calcium. J. GURSCHING and H. KRAUT (Arch. exp. Path. Pharm., 1932, 167, 146—157).—The ash of normal dog's blood contains 1—6.1% SiO_2 . During tetany due to parathyroidectomy the Si contents of whole blood and serum decrease. Introduction of parathyroid hormone in such dogs and also in normal dogs effects an increase in the blood-Si. Hence the parathyroid gland regulates both the Ca and Si levels of the blood. Both Ca and Si are increased by administration of calcinosis factor. On subcutaneous injection of the one substance the blood level of the other also increases, both levels subsequently decreasing at approx. the same rate.
F. O. H.

Comparative pharmacology of calcinosis factor and parathyroid hormone. T. VON BRAND,

F. HOLTZ, and W. PUTSCHAR (Arch. exp. Path. Pharm., 1932, 167, 113—145).—Whilst the injection of calcinosis factor (irradiated ergosterol in which vitamin-D is either left intact or destroyed by heat or hydrogenation) is attended by symptoms resembling those due to injection of parathyroid hormone, differences occur in the type of calcification, in the changes in the serum-Ca, and in the relative sensitivity of different animals. Hence the mechanism of the action of the two substances must be different, despite the fact that, in the alleviation of tetany due to parathyroidectomy, the hormone may be completely replaced by the calcinosis factor.
F. O. H.

Carotenoids and sex hormones. I. H. VON EULER and E. KLUSMANN (Biochem. Z., 1932, 250, 1—6).—The presence of β -carotene in cows' corpus luteum and placenta, and of xanthophyll in human placenta, is detected.
P. W. C.

Detection of sex hormones in totally castrated animals. S. LOEWE, W. RAUDENBUSCH, H. E. VOSS, and F. LANGE (Biochem. Z., 1932, 250, 50—52).—Sex hormones are detected in the excretions of castrated animals (ox and cock).
P. W. C.

Androkinin content of the faeces. S. LOEWE, F. ROTHSCHILD, and H. E. VOSS (Biochem. Z., 1932, 251, 246—247).—The faeces of young men contain 2 mouse units of androkinin per kg.
P. W. C.

Concentration-action curve for the follicular hormone (menformon). S. E. DE JONGH, E. LAQUEUR, and P. DE FREMERY (Biochem. Z., 1932, 250, 448—465).—A more accurate method using the morphological examination of vaginal smears in the determination of the degree of action is employed for the construction of concn.-action curves for menformon, six concns. of the prep. being injected into 1200 mice in two different laboratories. The importance of the curves for evaluation of the prep. is indicated.
P. W. C.

Action of the follicular hormone on plants. II. Action of crystalline β -follicular hormone. W. SCHOELLER and H. GOEBEL (Biochem. Z., 1932, 251, 223—228; cf. A., 1931, 1337).—The flowering of plants (*Calla aethiopica*) is accelerated by treatment with cryst. β -follicular hormone (Butenandt, this vol., 781) (300 mouse units per week) which also causes the growth of a second crop of flowers. The cryst. hormone, however, has none of the effects on the coleoptile of *Avena* which both the "auxin" of Went and Kogl (cf. this vol., 661) and commercial progynon solutions have. These solutions therefore contain "auxin."
W. McC.

Magnesium content of blood-corpuscles after injection of prolan. L. CANNAVÒ and R. INDOVINA (Biochem. Z., 1932, 250, 405—407).—When prolan is subcutaneously injected into man, a considerable increase in serum-Mg occurs (cf. this vol., 432) without any corresponding decrease in the corpuscle-Mg and the excess Mg must be derived from reserves in the tissues. Intramuscular injection of $MgCl_2$ solution causes a large increase of serum-Mg which is of only short duration and is not comparable with the effect of prolan.
P. W. C.

Recent researches on the nature and function of vitamins. J. C. DRUMMOND (J. Roy. Soc. Arts, 1932, 80, 949—957, 959—965, 974—980, 983—990).—Cantor lectures.

Carotene and vitamin-A. H. VON EULER (Bull. Soc. Chim. biol., 1932, 14, 838—860).—A lecture.

Carotene and vitamin-A. H. VON EULER and E. KLUSSMANN (Svensk Kem. Tidskr., 1932, 44, 223—224).—In cow-liver extracts (physiological salt solution) to which colloidal carotene has been added the characteristic absorption at 328 $m\mu$ is three times as strong as in those to which only H_2O has been added, but with blood extracts there is no such increase in strength. The content of carotenoid substances of the livers of rats to which carotene and thyroxine are administered is $<$ that of the livers of rats receiving carotene alone. Spectroscopic examination shows that although the vitamin-A contents are the same, there is less carotene in extracts from the livers of rats which receive thyroxine than in those from the livers of rats which receive only carotene. W. McC.

Prophylactic dose of vitamin-A in the form of carotene. A. POLAK and J. A. STOKVIS (Arch. Néerl. Physiol., 1932, 17, 299—306).—0.5—1.0 $\times 10^{-6}$ g. of carotene per day (dissolved in arachis oil) administered to young rats on a diet otherwise lacking vitamin-A prevents xerophthalmia and ensures normal growth. W. O. K.

Specific effect of vitamin-B on growth. B. SURE, M. C. KIK, and M. E. SMITH (J. Nutrition, 1932, 5, 155—162).—The sp. effect of vitamin-B on growth is produced by raising the level of nutrition by a stimulation of the appetite. A. G. P.

Dietary requirements for fertility and lactation. XXIV. Specific effect of vitamin-B on lactation. B. SURE and M. E. SMITH (J. Nutrition, 1932, 5, 147—153; cf. A., 1931, 772).—Data from experiments with rats indicate that vitamin-B, in addition to stimulating the appetite, exerts a sp. influence on lactation unrelated to the food and H_2O intake. A. G. P.

Is the vitamin-B content of milk under physiological control? F. L. GUNDERSON and H. STEENBOCK (J. Nutrition, 1932, 5, 199—212).—No essential differences were apparent in the vitamin-B content of milk from cows or goats of different breeds, or in different stages of lactation, or receiving rations in which the vitamin-B content was varied in relation to the amount of milk produced. A. G. P.

Vitamin-B₁. H. MISAWA (J. Biochem. Japan, 1932, 15, 439—471).—The prep. of vitamin-B₁ by a method based on that of Jansen and Donath (A., 1927, 382) yielded 13.38—23.0 mg. of cryst. material from 10 kg. of rice germ. The purest prep. had a protective dose against polyneuritis in pigeons of 0.007 mg. per day, whilst 0.02 mg. per day maintained normal growth in rats on a vitamin-B₁-free diet. Aq. extraction of these preps. yielded a cryst. substance and a less active amorphous substance. The cryst. preps. contained no P, were optically inactive, gave positive Jendrassik (A., 1923, ii, 892), Pauly, and Folin-Denis (phenol) tests, and in EtOH solution showed absorption bands at 250—280 and 310—360 $m\mu$. F. O. H.

Antineuritic vitamin. III. Removal of impurities by fractional precipitation. R. J. BLOCK and G. R. COWGILL (J. Biol. Chem., 1932, 97, 421—431).—Extracts of rice polishings with cold H_2O or of yeast with hot aq. HCl were conc. and treated by the CCl_4 technique (this vol., 309, 657). Treatment of the solutions thus obtained with HNO_2 did not reduce the total N content, but considerably decreased the potency. Fractionation by addition of picric, flavianic, or rufanic acid followed by BuOH-Et₂O (1:1) extraction was not satisfactory. More favourable was fractional pptn. by org. solvents. The vitamin was destroyed by AcOH and Ac₂O. Of 50 inorg. salts only $CuCl_2$ and $Hg(NO_3)_2$ gave ppts. which contained the vitamin in a conc. form without considerable loss of potency. $SnCl_2$ caused extensive destruction. Animal tests indicated that the preps. lacked some substance other than the antidermatitis factor which was supplied in the diet by crude yeast and by liver-preps. F. O. H.

Influence of vitamin-B, on carbohydrate metabolism. J. A. COLLAZO and C. PI-SUNER BAYO (Biochem. Z., 1932, 250, 89—108).—When natural fluids rich in the B group of vitamins are heated for 3 hr. at 100—120°, vitamin-B₁ and various enzymes are destroyed but vitamin-B₂ is unaffected. The glycogen and glutathione contents of muscle and liver and the sugar, uric and lactic acid, and glutathione contents of the blood of pigeons are investigated under varying conditions of B-avitaminosis. Vitamin-B₂ is the carrier of the enzyme complex responsible for glycogen formation and disappearance of sugar and lactic acid and increases the oxido-reduction power of the tissues. P. W. C.

Vitamin-C. E. OTT and K. PACKENDORFF (Z. physiol. Chem., 1932, 210, 94—96).—A review. J. H. B.

Vitamin-C. J. TILLMANS and P. HIRSCH (Biochem. Z., 1932, 250, 312—320).—A discussion. P. W. C.

Narcotine and vitamin-C. O. DALMER and T. MOLL (Z. physiol. Chem., 1932, 209, 211—230; 211, 284).—Methylnornarcotine (I) prepared from the natural alkaloid was not cryst. and had no antiscorbutic action (cf. this vol., 310). Attempts to synthesise (I) by condensation of cotarnine and normeconine failed. Narcotine could not be isolated from unripe orange juice or from potatoes. The Et₂O extract of ripe orange juice was not antiscorbutic and the extracted juice was as active as the original material. Hexuronic acid concentrates prepared by the method of Szent-Gyorgyi (A., 1929, 98) had definite antiscorbutic action. J. H. B.

Vitamin-C. V. Vitamin-C in seeds germinating in a dark place. T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1931, 7, 1070—1081).—Vitamin-C was not produced until the third day of germination; after 10 days the quantity was $<50\%$ of that of seeds germinated in (artificial) light. CH. ABS.

Vitamin-C in cranberries. O. M. BOGOLIOBOVA (Arch. sci. biol., Russia, 1931, 31, 322—329).—Preservation, at a low temp. without freezing, for 4 months did not impair the vitamin-C content;

fermentation, freezing, and drying destroy the vitamin-C. Vitamin-A is probably present.

CH. ABS.

Vitasterol-D. IV. Activation of ergosterol by irradiation with natural light. A. JENDRASSIK (Biochem. Z., 1932, 252, 205—211).—Antirachitic activity (equal to 0.02 or more of that produced by ultra-violet rays) is developed in ergosterol solutions on irradiation with direct or diffuse sunlight at 3450 m. and also at much lower altitudes. Although the absorption decreases continuously as the irradiation continues, no relation between the former and vitamin-D production can be traced.

W. McC.

Chemical nature of vitamin-D. I. REMESOV (Biochem. Z., 1932, 250, 560—563).—It is suggested that cholesterol exists in keto- and enol forms, the enol form being provitamin-D, which on irradiation passes to the keto-form, vitamin-D. Identity of ergosterol and provitamin-D is discredited.

P. W. C.

Irradiated cholesterol. R. G. GUSTAVSON (J. Colo. Wyo. Acad. Sci., 1929, 1, No. 1, 23).—Extraction of irradiated cholesterol with liquid NH_3 gives a yellow, resinous, antirachitic material.

CH. ABS.

Toxicity of irradiated ergosterol. G. TIXIER (Bull. Soc. Chim. biol., 1932, 14, 896—899).—No abnormal calcification was observed in the viscera of rats which received in addition to a normal diet daily doses of 5, 10, or 20 mg. of a commercial prep. of irradiated ergosterol for 90 days, corresponding with 750, 1500, and 3000 times the therapeutic dose, respectively. The highest of these doses was fatal in 87 days to 1 of 2 rats which showed only hæmorrhage of the renal parenchyma. Any toxicity of antirachitic preps. is due to incorrect irradiation or contaminated ergosterol.

A. C.

(A) Reduction in the blood-calcium content of parathyroidectomised dogs to which irradiated ergosterol has previously been administered. (B) Reduction in the calcium content resulting from subcutaneous injection of turpentine with production of abscesses. J. CHEYMOL and A. QUINQUAUD (J. Pharm. Chim., 1932, [viii], 16, 185—190, 190—194).—A. The life of parathyroidectomised dogs is prolonged, sometimes very greatly, by administration of irradiated ergosterol in doses of about 0.005—0.01 g. per kg. for periods of 17 days to one month prior to the operation. At the same time the Ca content of their blood is reduced by amounts up to 50%.

B. Subcutaneous injection of turpentine (2—4 c.c.) (with production of abscesses) into dogs treated as in A sometimes produces further small reductions in the Ca content of the blood-serum.

W. McC.

Physiology of apples. XII. Ripening processes in the apple and the relation of time of gathering to chemical changes in cold storage. H. K. ARCHBOLD. **XIII. Starch and hemicellulose content of developing apples.** E. M. WIDDOWSON (Ann. Bot., 1932, 46, 407—459, 597—631;

cf. A., 1929, 362).—XII. The total growth rate of apples increased during the first 3 weeks of development and subsequently remained practically const. In the first 3 weeks no starch was present and 53% of the dry matter consisted of EtOH-insol. material and acids, together with 15% of sugars. During the period of starch synthesis the proportion of insol. matter and acids fell to 17% and that of total sugars rose to 55%. During the final ripening stages starch was hydrolysed, the sugar content rose to approx. 80%, and the acids and insol. matter declined to 14%. The rate of N intake reached a max. after 2 weeks of development and subsequently decreased steadily. During the storage of packed fruit any remaining starch is hydrolysed and sucrose inverted. Oxidation of sugars and the inversion of sucrose did not always occur at corresponding rates and differences were manifest by variations in the proportion of fructose. The glucose content remained practically const. throughout. Acid and a portion of the insol. matter were lost continuously during storage. Only a portion of the products of hydrolysis of the insol. matter was oxidised and the balance accumulated as (undetermined) non-reducing substances. Late gathering is associated with a low rate of loss of total sugars, a high rate of sugar inversion, a higher level of concn. at which sucrose inversion ceases, greater changes in reducing sugar contents, and low initial acidity.

XIII. Starch in the EtOH-insol. residue from apple tissue is determined by hydrolysis with taka-diastase after the partial removal of pectins by extraction with $\text{K}_2\text{C}_2\text{O}_4$ solution. Starch formation begins about mid-June and reaches a max. (1.5—2% of green wt.) in July—August, disappearing by the end of October. Apple tissue contains a readily hydrolysable polysaccharide other than starch or pectin. From the residue not hydrolysed by taka-diastase two H_2O -sol. substances, a polyuronide and a polysaccharide, were isolated. Both yield arabinose on hydrolysis and are classed as hemicelluloses. Both the hemicellulose and pectin contents of the growing apple increase steadily to a const. val. which persists during storage. Hemicelluloses do not act as reserve carbohydrates, but in structure and function are closely related to pectins.

A. G. P.

Determination of lipin-soluble bismuth in oil solutions. F. ROTHEA (J. Pharm. Chim., 1932, [viii], 16, 110—112).—2 c.c. of the solution are heated, finally in a muffle furnace, and the residue is treated with HNO_3 and re-ignited. The residual Bi_2O_3 is weighed.

R. S. C.

Colorimetric determination of sulphate in biological fluids. S. MORGULIS and M. G. HEMP-HILL (Biochem. Z., 1932, 249, 409—411).—Lang's technique (A., 1929, 1500) is unsatisfactory, but if the H_2CrO_4 is determined by titration with I after addition of KI and H_2SO_4 results which differ by only 0.6% from gravimetric are obtained provided that phosphates are first removed with $\text{Ca}(\text{OH})_2$ and reducing substances destroyed with H_2O_2 and FeCl_3 .

W. McC.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1932.

General, Physical, and Inorganic Chemistry.

Pressure effects in the secondary spectrum of hydrogen. W. G. GUTHRIE (Proc. Roy. Soc. Edin., 1931—1932, 52, 315—322).—The secondary spectrum of H₂ has been investigated at pressures between 30 cm. and 1 atm. The relative intensities of the lines are only slightly affected. W. R. A.

Absorption measurements for Balmer lines in a neon-hydrogen mixture subjected to condensed discharge. T. TAKAMINE, L. S. ORNSTEIN, and J. M. W. MILATZ (Z. Physik, 1932, 78, 169—176).—A Ne discharge tube with traces of H₂ gives intensity of absorption measurements in agreement with Schrödinger's theory. A. B. D. C.

Excitation of continuous and line spectra in helium. J. S. TOWNSEND and M. H. PAKKALA (Phil. Mag., 1932, [vii], 14, 418—431).—The change in intensity of the yellow line and of the continuous spectrum with pressure and current in the high-frequency discharge in He has been measured. H. J. E.

Infra-red spectra of helium. W. F. MEGGERS and G. H. DIEKE (Bur. Stand. J. Res., 1932, 9, 121—130).—Using xenocyanine-sensitised plates, 120 new lines from the infra-red spectrum of He, emitted by a Geissler tube, are recorded in the spectral range 8361—11,045 Å.; 32 belong to He I and 88 to the band spectrum of the He₂ mol. W. R. A.

Perturbations and rotation constants of some first negative nitrogen bands. W. H. J. CHILDS (Proc. Roy. Soc., 1932, A, 137, 641—661).—The 0,0 and 0,1 first negative N bands emitted from an arc have been examined under high dispersion. Vals. for the spin-doubling const. have been obtained. The bands were excited to such high rotational levels that a no. of large, hitherto unobserved perturbations were revealed. These are discussed in detail. L. L. B.

Recombination spectra in the positive column of metal vapours with doublet series. H. KREFFT (Z. Physik, 1932, 77, 752—773).—Recombination spectra were observed in positive columns of Na, K, Rb, Cs, In, and Tl. A. B. D. C.

Spectra of Na II, III, and IV in the extreme ultra-violet. B. B. VANCE (Physical Rev., 1932, [ii], 41, 480—485).—New lines in the region 434,000—242,000 cm.⁻¹ are reported and classified. N. M. B.

New lines in the absorption spectra of the alkalis. S. DATTA and B. CHAKRAVARTY (Indian J. Physics, 1932, 7, 273—282).—Data for K, Na, and

Rb are reported. New lines were found on both sides of the absorption lines of the principal series. N. M. B.

Wood's method of separating the D-lines. E. GAVIOLA and P. PRINGSHEIM (Z. Physik, 1932, 78, 211—219).—An investigation of the separation of the D-lines by means of interference bands due to a quartz plate. A. B. D. C.

Selective light absorption in thin layers of alkali metals. R. FLEISCHMANN (Nachr. Ges. Wiss. Gottingen, 1931, 252—256; Chem. Zentr., 1932, i, 2293).—Experiments with Na, K, Rb, and Cs are described, and the conditions responsible for the selective absorption are discussed. A. A. E.

Nuclear moments of lighter elements. S. TOLANSKY (Z. Physik, 1932, 78, 71—73).—The curve giving $g(I)$ factors against at. no. for odd elements passes through a min. between the at. nos. 23 and 55. A relation between nuclear spin and mass defect is shown; protons contributing most to a positive mass defect possess nuclear spin. A. B. D. C.

Nuclear spin of arsenic. S. TOLANSKY (Proc. Roy. Soc., 1932, A, 137, 541—558).—The spectrum of As II has been observed in the region 6400—4300 Å., and the fine structures of the majority of the strong visible lines have been analysed. Most of the lines involve the $4p \times 5s$ and $4p \times 5p$ electron configurations. The structures can be explained by taking the nuclear spin as $3/2$. The fine structure observations confirm the gross structure multiplet analysis (cf. Rao, this vol., 668). L. L. B.

Further investigation of the arc spectrum of arsenic. A. S. RAO (Proc. Physical Soc., 1932, 44, 594—607).—The spectrum of As obtained by the hollow-cathode discharge method in He and Ne has been investigated and about 100 new lines have been recorded. A new analysis of As I has been made. The first ionisation potential is approx. 10.5 volts. A. J. M.

Extinction of fluorescence of iodine vapour by intense magnetic fields. J. GENARD (Z. Physik, 1932, 77, 791—794).—Study of the influence of magnetic fields on the rotation doublets and on the distribution of intensity in the resonance series indicates that only the excited state of the I₂ mol. is perturbed by a magnetic field. A. B. D. C.

Wave-lengths and Zeeman effects in lanthanum spectra. W. F. MEGGERS (Bur. Stand. J. Res., 1932, 9, 239—268).—Wave-length measurements and estim.

ated relative intensities for 1535 lines of the arc and spark spectra of La between 2100 and 11,000 Å. are recorded. Zeeman effects for 476 lines between 2800 and 7500 Å. are also given. A new sequence for LaO (8423—9729 Å.) is appended. W. R. A.

Emission of glowing platinum in gases, especially in iodine vapour and chlorine. E. MÜLLER (Ann. Physik, 1932, [v], 14, 831—855).—The emission of glowing Pt in O₂, N₂, H₂, I, and Cl₂ has been investigated. The vals. for O₂, N₂, and H₂ agree with those obtained by Richardson and Wilson. The emission in H₂, I, and Cl₂ decreases with time, and shows a decreasing sensitivity towards pressure changes. The high emission in these gases is therefore probably due to chemical processes. The carriers in I and Cl₂ are electrons. A. J. M.

Hyperfine structure and nuclear moment of mercury. K. MURAKAWA (Z. Physik, 1932, 77, 699—700).—Polemical, against Schüller and Jones (this vol., 440). A. B. D. C.

Hyperfine structure and nuclear moment of mercury. H. SCHÜLER and E. G. JONES (Z. Physik, 1932, 77, 701—702).—A reply (cf. preceding abstract). A. B. D. C.

Perturbation of hyperfine structure terms of mercury. H. SCHÜLER and E. G. JONES (Z. Physik, 1932, 77, 801—810).—Anomalies in the hyperfine structure of odd Hg isotopes are due to repulsion of levels with the same *I* and *F* vals., and the perturbation is dependent on these vals. A. B. D. C.

Isotope shift in hyperfine structure. (Miss) J. E. ROSENTHAL and G. BREIT (Physical Rev., 1932, [ii], 41, 459—470).—The effect of deviations of the nuclear field from the inverse square law is calc., and considered in relation to the spectrum of Tl, Pb I, and Pb II. N. M. B.

Nuclear magnetic moments. S. TOLANSKY (Nature, 1932, 130, 402—403).—It is possible that both neutrons and protons contribute to the production of nuclear spin and if the spin *g* factors differ considerably, then anomalous *g(I)* factors will arise (cf. A., 1931, 1345). Orbital motion and variable *g* factor may both be responsible in the case of the lighter elements (this vol., 439). L. S. T.

Characteristics of ultimate lines. A. T. WILLIAMS (Nature, 1932, 130, 313). L. S. T.

Multiplet splitting and intensities of inter-combination lines. I. H. C. WOLFE (Physical Rev., 1932, [ii], 41, 443—458).—Mathematical. N. M. B.

Sum rules for atomic transition probabilities. J. P. VINTI (Physical Rev., 1932, [ii], 41, 432—442).—Mathematical. General rules, applicable to any discrete state of any atom, are deduced (cf. Dirac, this vol., 553). N. M. B.

Magneto-rotation between Zeeman components. W. SCHÜTZ (Z. Physik, 1932, 77, 437—445). A. B. D. C.

Optical investigation of spark ignition in air at atmospheric pressure by means of suppressed breakdown. W. HOLZER (Z. Physik, 1932, 77, 676—694).—A study of the formation of electric arcs

indicates that the primary mechanism is electron collision. A. B. D. C.

Electric discharges in gases at low pressures. I. LANGMUIR (J. Franklin Inst., 1932, 214, 275—298).—A review of published work on the properties of the plasma, and anode and cathode sheaths of discharge tubes. A. B. D. C.

Intensities of certain nebular lines and the mean lives of atoms emitting them. A. F. STEVENSON (Proc. Roy. Soc., 1932, A, 137, 298—325).—Mathematical. The intensities and mean lives have been calc. for O III and N II. L. L. B.

Intensity of cosmic radiation in the high atmosphere. E. REGENER (Nature, 1932, 130, 364).—There appears to be no γ -radiation from common radioactive bodies in outer space. L. S. T.

Effect of a secondary structure on the interference of X-rays. H. M. EVJEN (Physical Rev., 1932, [ii], 41, 265—273). N. M. B.

Emission series in the ultra-soft X-ray region. J. A. PRINS and A. J. TAKENS (Z. Physik, 1932, 77, 795—800).—New vals. are given for *L*, *M*, and *N* series of Ir, Zr, Y, and S. An unsuccessful attempt was made to obtain Li (*K*), Al (*L*), Fe (*M*), Cu (*M*), Zn (*M*), Au (*N*), and Bi (*O*). Available results for this region are given as a Moseley diagram. A. B. D. C.

X-Ray emission spectra and chemical binding. I. Fluorescence excitation of the $K\alpha_{1,2}$ doublets of sulphur. O. LUNDQUIST (Z. Physik, 1932, 77, 778—787).—Displacement of the $K\alpha_{1,2}$ lines of S by chemical combination was studied for Cr₂S₃, CuS, ZnS, Ag₂S, Na₂SO₃, CaSO₃, CuSO₃, BaSO₃, Na₂SO₄, CaSO₄, NiSO₄, and CuSO₄. A. B. D. C.

Scattering of X-rays from solids. A. W. COVEN (Physical Rev., 1932, [ii], 41, 422—431).—For Mo $K\alpha$ radiation the scattering from NaF and MgO and from KCl was approx. the same as that from Ne and Ar, respectively. The intensities of the diffracted part of the scattered ray and the sum of the diffracted and diffuse intensities are in agreement with theoretical relations for gases. N. M. B.

Scattering of X-rays by diatomic gases. Y. H. Woo (Sci. Rep. Tsing Hua Univ., 1932, 1, 177—180; cf. this vol., 892).—The Raman-Compton-Jauncey formula leads to an equation for electron scattering which is compared with the experimental results of Wollan (cf. A., 1931, 781). N. M. B.

Thermionic emission of metals in iodine vapour. S. KALANDYK (Spraw. Prace Polsk Towarz. Ficyz., 1930, 5, 141—156; Chem. Zentr., 1932, i, 3039).

Glow in photo-electric cells. (LORD) RAYLEIGH (Nature, 1932, 130, 365—366).—A "Mazda" thin-film Cs cell begins to glow at 15.8 volts, near the lower ionisation potential of Ar. L. S. T.

Normal gradient in gases. (Super-conductivity in inert gases.) A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 77, 703—712).—A discharge tube eliminating the influence of walls indicated that there is no potential gradient in the anode column of

the gases He, Ne, and A; H_2 has a gradient 2.4 volts/cm. per mm. pressure. A. B. D. C.

Breakdown potential of nitrogen in the "restricted" discharge region for potentials up to 70 kv. H. FRICKE (Z. Physik, 1932, 78, 59—70).—The breakdown potential of N_2 was studied for pressures near 0.01 mm., where this potential rises rapidly with decreasing pressure and electrode separation.

A. B. D. C.

Discharge potential of helium, neon, and argon in presence of mercury vapour. B. KLARFELD (Z. Physik, 1932, 78, 111—122).—The presence of Hg vapour lowers the discharge potential, but addition of small quantities of non-inert gases greatly increases the discharge potential in A, and to a smaller extent in Ne and He; the effect might be used as a measure of the purity of A. A. B. D. C.

Effect of oxygen on thermal electron emission from platinum. H. CASSEL and E. GLÜCKAUF (Z. physikal. Chem., 1932, B, 18, 347—359).—The electron emission voltage, E , into O_2 from glowing Pt previously treated with O_2 is const. for O_2 pressures of 10^{-5} mm. downwards at 8.46 volts. Treatment of the Pt with Hg vapour does not alter this val. If the Pt is heated in H_2 , E falls below 5 volts, but as the H_2 is pumped off E rises and approaches a limiting val. of 6.45 volts. The theoretical implications of these results are discussed. R. C.

Surface potential for electrons emitted from metals. I. TAMM and D. BLOCHINZEF (Z. Physik, 1932, 77, 774—777).—The work required to remove an electron from a metal surface is due to an image force rather than to a surface potential barrier.

A. B. D. C.

Diffraction of electrons in mercury vapour. F. L. ARNOT (Nature, 1932, 130, 438). L. S. T.

Pliable electron rays. E. BRÜCHE (Z. Physik, 1932, 78, 177—195).—An electron beam in a discharge tube at 0.5 mm. H_2 pressure will follow a metal tube through 90° without loss of intensity; the pliability is due to space-charge effects, and the focussing of electron beams by residual gas is discussed.

A. B. D. C.

Method of amplifying the energy of canal rays and its use in atomic disruption. C. GERTHSEN (Naturwiss., 1932, 20, 743—744). W. R. A.

Experiments on potassium ions in potassium vapour. H. J. J. BRADDICK (Phil. Mag., 1932, [vii], 14, 450—464).—No K_2^+ ions are formed on leading K^+ ions into K vapour (cf. A., 1929, 735).

H. J. E.

Slow mercury ion-rays. F. BEYERLEIN (Z. Physik, 1932, 77, 632—643).—Low-velocity rays of Hg ions were obtained by evaporating Hg through nozzles; the rays were electromagnetically analysed.

A. B. D. C.

Energy distribution among the positive ions at the cathode of the glow discharge through gases. R. M. CHAUDRHI and M. L. OLIPHANT (Proc. Roy. Soc., 1932, A, 137, 662—676).—The energy distribution among the positive ions which strike the cathode of the glow discharge through gases (air, H_2 , and A) is independent of the current and the

voltage across the dark space, and is, for any one gas, a function of pressure alone. The max. energy of the positive ions corresponds with the full potential on the discharge tube. At any given pressure the no. of ions possessing any one energy is proportional to the discharge current, but if the voltage is kept const. and the current varied by varying the pressure, then the no. of slow ions increases with the current more rapidly than the fast.

L. L. B.

Diffraction of gas atoms. H. S. W. MASSEY and C. B. O. MOHR (Nature, 1932, 130, 276—277).

L. S. T.

Dissociation by collision with positive ions. A. C. G. MITCHELL (Z. Physik, 1932, 78, 138—140).—Polemical, against Schechter (this vol., 670).

A. B. D. C.

Ionisation by positive ions. J. S. TOWNSEND and F. L. JONES (Nature, 1932, 130, 398).—The energies of the positive ions in the collisions in which mols. of H_2 are ionised are of the same order as that of the electrons.

L. S. T.

Reflexion of molecular beams. R. FRISCH and O. STERN (Naturwiss., 1932, 20, 721).—Mol. beams of He and H_2 are reflected at cleavage surfaces of LiF and NaF with intensities which vary sharply as the reflecting surface is rotated in its own plane. A. C.

Existence of element 85. G. VON HEVESY and R. HOBBIIE (Z. anorg. Chem., 1932, 208, 107—112).—X-Ray analysis of concentrates from pitchblende failed to reveal any lines due to element 85. It is inferred that, if the reactions of this element are similar to those of I, its concn. in pitchblende is < 1 in 10^9 .

E. S. H.

Fundamental at. wts. XI. At. wt. of iodine. II. O. HONIGSCHEID and H. STRIEBEL (Z. anorg. Chem., 1932, 208, 53—58; cf. A., 1931, 1208).—Using AgI pptd. from aq. solution, the val. 126.917 is obtained for the at. wt. of I (from the ratio AgI:AgCl), in agreement with that obtained with synthetic AgI.

E. S. H.

Radioactivity of potassium. D. BOCCIARELLI (Atti R. Accad. Lincei, 1932, [vi], 15, 686—693).—Further details are given showing the existence of a less intense, hard component of the β -radiation of K (cf. A., 1931, 1208). The radiation is more heterogeneous and harder than that of Rb.

O. J. W.

Absorption of boron neutrons by lead. M. DE BROGLIE and L. LEPRINCE-RINGUET (Nature, 1932, 130, 315).—Neutrons emitted from B bombarded by α -rays from radon appear to possess less energy than neutrons from Be, and are more absorbed by Cu and paraffin wax than by Pb. Pb is transparent to neutrons from B, 5 cm. showing little or no absorption.

L. S. T.

Excitation of neutrons in beryllium. F. RASETTI (Z. Physik, 1932, 78, 165—168).—The intensity of neutrons emitted from Be bombarded by Po α -rays was determined for various ranges of the α -rays.

A. B. D. C.

Wave-mechanical classical model of the neutron. H. K. KUDAR (Z. Physik, 1932, 78, 279—282).—Theoretical.

A. B. D. C.

Range and total ionisation of α -rays in gases. M. MÄDER (Z. Physik, 1932, 77, 601—615).—Ionisation in air, CO₂, and N₂ was determined for α -rays from Po; the half val. period for Po is 138 days.

A. B. D. C.

Scattering of α -particles at small angle by helium. P. WRIGHT (Proc. Roy. Soc., 1932, A, 137, 677—688).—The agreement between the observed scattering at 10°, 15°, and 27°, and that predicted by Taylor's theory (this vol., 106) is close enough to support the general explanation advanced by Taylor, i.e., that the anomalous scattering is a consequence of the wave-mechanical scattering by the non-coulombian fields of force.

L. L. B.

α -Rays of ionium. F. SODDY (Nature, 1932, 130, 364—365).—Curves for the α -rays of ionium correlating differential ionisation current with distance show irregularities at present unexplained.

L. S. T.

Scattering of fast β -particles by electrons. F. C. CHAMPION (Proc. Roy. Soc., 1932, A, 137, 688—695).—In 650 m. of track of fast β -particles in N₂, photographed by the expansion method, 250 collisions with electrons have been obtained with angles of scattering >10° and with β varying from 0.82 to 0.92. The abs. no. scattered and the distribution with angle were in good agreement with Moller's formula based on quantum mechanics (Z. Physik, 1931, 70, 786).

L. L. B.

Absorption and scattering of hard γ -rays. C. Y. CHAO (Sci. Rep. Tsing Hua Univ., 1932, 1, 159—176).—A detailed account of work previously reported (cf. A., 1931, 142).

N. M. B.

Selective transmission of γ -radiation by lead. F. L. HOPWOOD, T. E. BANKS, and T. A. CHALMERS (Nature, 1932, 130, 506).—Experiments indicate that a substance is selectively transparent to some of the radiations emitted by its radioactive isotope.

L. S. T.

Energy exchange between inert gas atoms and a solid surface. J. M. JACKSON and N. F. MOTT (Proc. Roy. Soc., 1932, A, 137, 703—717).—Theoretical. A theory of the accommodation coeff. for He on W is given, using an exponential field between the gas atom and a surface atom of the solid. Good agreement is obtained with the experimental results of Roberts (A., 1930, 1340).

L. L. B.

Conception of the chemical elements. F. PANETH (Schr. Königsberg Gelehr. Ges. Nat.-Wiss. Kl., 1931, 8, 101—125; Chem. Zentr., 1932, i, 3025).

Structure of nuclei. II. W. HEISENBERG (Z. Physik, 1932, 78, 156—164).—The hypotheses previously advanced (this vol., 894) are applied to the stability of nuclei on β -ray disintegration and to the scattering of γ -radiation. An attempt to determine the "binding energy" of the electron in a neutron indicates that the neutron does not follow the laws of quantum mechanics.

A. B. D. C.

Nuclear structure. H. C. UREY (Nature, 1932, 130, 403).—A claim for priority (cf. this vol., 894).

L. S. T.

Absorption of Debye-Falkenhagen relaxation power in a neutral, partly-ionised gas (plasma, Kennelly-Heaviside layer). K. F. NIESSEN (Physikal. Z., 1932, 33, 705—718).—Mathematical.

W. R. A.

Molecular spectra and spectroscopic analysis. IV. Scandium. G. PICCARDI and A. SBERNA (Atti R. Accad. Lincei, 1932, [vi], 15, 577—579; cf. this vol., 673).—As in the case of La and Y, Sc can be detected conveniently by means of the band spectrum of ScO.

O. J. W.

Play of colours in leucite. F. BAIER (Z. Krist., 1932, 83, 141—144; cf. this vol., 359).

C. A. S.

Intensity distributions in molecular spectra: Swan system (C₂). R. C. JOHNSON and N. R. TAWDE (Proc. Roy. Soc., 1932, A, 137, 575—591).—The difficulties of obtaining accurate measurements of the relative intensities of spectral lines or bands when these cover a wide wave-length range are discussed. The Swan system has been produced and studied from five sources, differing widely in temp. and in electrical conditions, and the peak intensities have been measured.

L. L. B.

Absorption spectrum of photochemically coloured alkali halide crystals at various temperatures. E. MOLLWO (Nachr. Ges. Wiss. Göttingen, 1931, 236—239; Chem. Zentr., 1932, i, 2137).—With rise of temp. the spectra are displaced towards longer wave-lengths.

A. A. E.

Absorption spectra of chromium ammine hydrates. R. I. COLMAR and F. W. SCHWARTZ (J. Amer. Chem. Soc., 1932, 54, 3204—3212).—Measurements in the visible spectrum have been made. On substitution of a H₂O mol. for an NH₃ mol. in either a Cr or Co complex (up to 4 substitutions) n , the wave no. at which max. absorption occurs, decreases by 610 mm.⁻¹ On substitution of a H₂O for an NH₃ mol. in a Cr complex the val. of the mol. extinction coeff., k , at the absorption max. decreases successively by 4.9 units. In Co complexes a decrease in k occurs with substitution of the first H₂O mol., but is followed by an increase for the second mol. entering. Substitution of a Co for a Cr atom in a complex reduces n by 510 mm.⁻¹ At the max. k is higher for Co than for the corresponding Cr compounds. Substitution of Cl for an NH₃ mol. reduces n by 1970 mm.⁻¹

C. C. K. (c)

Ultra-violet absorption of the ethylenic hydrocarbons Ph·[CH₂] _{n} ·CH:CH₂. (MME.) RAMART-LUCAS and (MLLE.) P. AMAGAT (Bull. Soc. chim., 1932, [iv], 51, 965—968).—Data are given for the compounds with $n=0-5$, and for Ph·CH:CH·[CH₂] _{n} ·Me, PhEt, and CH₃·CH·[CH₂] _{n} ·CH:CH₂ (I). Compounds with the double linking adjacent to Ph give characteristic intense absorption bands. The other Ph compounds have absorption spectra similar to PhEt. (I) gives no bands. Compounds Ph·[CH₂] _{n} ·CH:CH₂ were prepared by the action of allyl bromide on Ph·[CH₂] _{$n-1$} ·MgX in Et₂O at 0°. η -Phenyl- Δ^a -heptene has b.p. 236°/760 mm., 123°/24 mm. α -Phenylnonan- α -ol, prepared from C₉H₁₉·MgBr and PhCHO, gave α -phenyl- Δ^a -decene, b.p. 162—163°/14 mm., on warming with kieselguhr.

D. R. D.

Spectral changes on ageing of mineral oils. II. Validity of Beer's law in the visible spectrum. E. VELLINGER (Ann. Off. Nat. Combust. liq., 1931, 6, 225—228; Chem. Zentr., 1932, i, 2794).

A. A. E.

Absorption spectra of carbon dioxide, carbon monoxide, and water vapour in the range 600—900 Å. H. J. HENNING (Ann. Physik, 1932, [v], 14, 856).—Corrections to an earlier paper (this vol., 673).

Change in the infra-red reflecting power of bismuth in a magnetic field. J. C. McLENNAN, E. J. ALLIN, and A. C. BURTON (Phil. Mag., 1932, [vii], 14, 508—512).—For cast Bi no change was observed between 5 μ and 8 μ .

H. J. E.

New infra-red bands photographed in the absorption spectrum of acetylene. W. LOCHTE-HOLTGREVEN and E. EASTWOOD (Nature, 1932, 130, 403).—Details of new bands at 10,164.8 and 10,369.8 Å. are recorded.

L. S. T.

Molecular spectra and the effect on them of intermolecular forces. I. Strength of NH linking in gaseous, liquid, and dissolved ammonia. G. JUNG and H. GÜDE (Z. physikal. Chem., 1932, B, 18, 380—400).—The fourth and fifth harmonics of a series of rotation-vibration bands starting from 3 μ for gaseous NH₃ are at 6474.0 and 5526.1 Å. The rotational fine structure of the fourth harmonic has been determined. In liquid NH₃ and solutions of NH₃ the third and fourth harmonics are displaced towards longer wave-lengths. With solutions the displacement, Δ , increases in a linear manner with the vol. concn., and is greater for the fourth than the third harmonic. There is no connexion between Δ and the dielectric const. of the solvent. Δ is attributed to a loosening of the N·H linking, which is most pronounced in liquid NH₃ and least in aq. NH₃.

R. C.

Infra-red region of the spectrum. VI. Absorption spectra of the dioxides of chlorine and sulphur. C. R. BAILEY and A. B. D. CASSIE (Proc. Roy. Soc., 1932, A, 137, 622—640).—The infra-red absorption spectrum of ClO₂ is found to be very similar to that of SO₂. The two substances are also physically alike and have similar structures. Two structures are possible, with vertices angles of approx. 60° and 120°; the available evidence is slightly in favour of the acute-angled form. The mol. characteristics for the acute-angled form are: SO₂: ν_1 1361, ν_2 524, ν_3 1152 cm.⁻¹ (fundamental frequencies); K_1 9.6 (S—O), K_2 1.7 (O—O) $\times 10^{-5}$ dynes/cm. (force consts.); ClO₂: ν_1 1109, ν_2 527, ν_3 946 cm.⁻¹; K_1 6.7 (Cl—O), K_2 1.8 (O—O) $\times 10^{-5}$ dynes/cm.;

OSO 60°; S—O and O—O 1.37 Å.; OClO 60°; Cl—O and O—O 1.4 Å. For the obtuse-angled structure: SO₂: ν_1 1152, ν_2 524, ν_3 1361 cm.⁻¹; 9.6 (S—O), K_2 3.3 (O—O) $\times 10^{-5}$ dynes/cm.; ClO₂: 946, ν_2 527, ν_3 1109 cm.⁻¹; K_1 6.7 (Cl—O), K_2 3.6

(O—O) $\times 10^{-5}$ dynes/cm.; OSO 122°; S—O 2.3 Å.; O—O 3.9 Å.; OClO 140°; Cl—O 2.4 Å., O—O 4.2 Å.

L. L. B.

Isotope separations in the infra-red absorption spectrum of HCl and the possible existence of a chlorine isotope of mass 39. J. D. HARDY and G. B. B. M. SUTHERLAND (Physical Rev., 1932, [ii], 41, 471—479).—No trace of a Cl³⁹ isotope was found (cf. Hettner, A., 1931, 1348); the relative abundance Cl³⁵ to Cl³⁹ cannot exceed 1—500. Accurate measurements of the isotope separations due to Cl³⁵ and Cl³⁷ are compared with theory.

N. M. B.

A double band of solid hydrogen chloride. G. HETTNER (Z. Physik, 1932, 78, 141—155).—The ordinary rotation-vibration doublet of HCl near 3.65 μ was investigated for the solid at 87° and 20° abs. At the lower temp. the longer wave-length branch almost vanishes; the actual shape of the doublet and sp. heat data fit neither the hypothesis of a rotating mol. in the solid, nor that of a mol. vibrating about some fixed direction, but suggest that the actual system is one intermediate between the two.

A. B. D. C.

Absorption spectrum of benzene in the region of 6.75 μ . S. SILVERMAN (Physical Rev., 1932, [ii], 41, 486—488).—The spectrum of the vapour showed three branches with evidence of unresolved fine structure. The liquid showed a less regular spectrum with a shift towards longer wave-lengths. New H₂O vapour lines in the 6.26 μ band are also reported.

N. M. B.

Significance of infra-red characteristic vibrations for dielectric loss. M. CZERNY and W. SCHOTTKY (Z. Physik, 1932, 78, 220—229).—The damping of infra-red characteristic vibrations (beyond 40 μ) can account quantitatively for the dielectric loss observed for very short electric waves.

A. B. D. C.

Are argon and methane molecules optically anisotropic? S. PARTHASARATHY (Indian J. Physics, 1932, 7, 243—249).—Transversely scattered radiations from A and CH₄ excited by polarised light were unpolarised, suggesting that the mols. oscillate as anisotropic electric dipoles in the field of the light wave.

N. M. B.

Raman effect in salt solutions. A. DA SILVEIRA (Compt. rend., 1932, 195, 521—523; cf. this vol., 983).—In similar conditions the Raman spectra of saturated solutions of (NH₄)₂SO₄, NH₄NO₃, and NH₄Cl have been measured. New lines attributed to SO₄²⁻ (possibly suppression of degeneration) are 553 and 683 cm.⁻¹, whilst three lines at or near 1116, 1300, and 1460 (1116 and 1351 only in the nitrate) are due to NH₄⁺.

C. A. S.

Raman effect in aqueous nitrate solutions. P. GRASSMANN (Z. Physik, 1932, 77, 616—631).—A study of the Raman displacement near 1050 cm.⁻¹ due to aq. solutions of H, Li, Na, NH₄, K, Ag, Mg, Ca, Cu, Zn, Cd, Ba, and Pb nitrates, and of the displacement near 720 cm.⁻¹ due to Li, NH₄, Na, Ag, Mg, Ca, Cd, and Pb nitrates.

A. B. D. C.

Spectroscopic evidence for the existence of the hydroxonium ion (H₃O)⁺. Raman effect for perchloric acid and perchlorates. Z. OLLANO (Z. Physik, 1932, 77, 818—822).—Raman displacements were obtained for NaClO₄, KClO₄, NH₄ClO₄, and HClO₄. The displacements 1118, 936, 627, and

461 cm^{-1} are ascribed to ClO_4^- . Displacements near 3580 cm^{-1} are ascribed to the ions $(\text{H}_3\text{O})^+$ and $[\text{H}(\text{H}_2\text{O})_n]^+$ in the aq. solutions. A. B. D. C.

Raman spectra of dimethyl ether, diethyl ether, and heptane. S. C. SIKKAR (Indian J. Physics, 1932, 7, 257—272).—Full data and comparisons with infra-red absorption curves are reported. Me_2O shows new lines at 333 and 416 cm^{-1} .

N. M. B.

Raman spectrum of some aniline derivatives. G. B. BONINO and P. CELLA (Atti R. Accad. Lincei, 1932, [vi], 15, 568—572).—The Raman spectra of benzylidene-, *p*-chlorobenzylidene-, and benzylidene-*p*-chloro-aniline, and of benz-anilide and -*p*-toluidide have been measured. The presence of a C:N linking in the mol. corresponds with the appearance of one or two lines between 1400 and 1500 cm^{-1} .

O. J. W.

Raman spectrum of Δ^2 -dihydronaphthalene. G. B. BONINO and P. CELLA (Atti R. Accad. Lincei, 1932, [vi], 15, 572—576).—The lines found in the Raman spectrum of the above substance are in complete accordance with its structural formula (cf. deca- and tetra-hydronaphthalene, this vol., 7).

O. J. W.

Raman spectra of naphthalene derivatives. S. ZIEMECKI (Z. Physik, 1932, 78, 123—132).—The Raman spectra of naphthalene, 1- and 2-methyl-, -chloro-, and -bromo-naphthalene all show the characteristic displacement 1377 cm^{-1} ; they also show displacements 3058 and 1575 cm^{-1} , although these vary in position with the derivative. A. B. D. C.

Raman effect with terpenes. II. Monocyclic terpenes. G. DUPONT, P. DAURE, and J. LEVY (Bull. Soc. chim., 1932, [iv], 51, 921—932).—Data are given for *p*-cymene, limonene, carvomenthene, menthane, sylvestrene, Δ^1 -*m*-menthene, and α - and β -phellandrene.

D. R. D.

[Ionic] emission of glasses of the composition $\text{B}_2\text{O}_3 + \text{Na}_2\text{O}$. H. BOLLING (Physikal. Z., 1932, 33, 625—632).—The emission of these glasses at 160—230° decreases at first with time, reaching finally an almost const. val. This variation is dependent on an internal lattice change and on a surface phenomenon which is modified by moisture, the latter increasing the emission. The emission rises with temp., but preheating to a higher temp. lowers the subsequent emission at a lower temp. Recovery is observed on keeping. Increased Na content raises the emission.

J. W. S.

Line emission and absorption of chromium phosphors. I, II. O. DEUTSCHBEIN (Ann. Physik, 1932, [v], 14, 712—728, 729—754).—I. The prep. of several phosphors is described. Their spectra were investigated. As a phosphor, Cr acts differently from the rare-earth elements, for emission and absorption spectra agree.

II. The light emission from many substances containing Cr, and the phosphorescence of some artificial and natural minerals were studied. Cr causes emission only if Cr_2O_3 is isomorphous with the principal substance, or if it occurs as a large mol. in the lattice. The emission and absorption

spectra were determined at 20° and -195°. The Raman spectrum of a synthetic, colourless corundum was investigated. A. J. M.

Influence of carbon tetrachloride and of phosphorus oxychloride on the maximum oxygen pressure at which the chemiluminescence of white phosphorus commences. F. SCHACHERL (Gazzetta, 1932, 62, 610—621).— CCl_4 lowers, POCl_3 raises, the max. O_2 pressure (*p*) at which chemiluminescence of P begins. In presence of POCl_3 vapour alone, there is no chemiluminescence. The variation of *p* with the concn. of the added substance, *x*, is given by $p_{15} = 533 - 835x$ and $p_{20} = 678 - 1245x$ for CCl_4 , and $p_{20} = 16.5/(0.021 - x)$ for POCl_3 . The formation of P_4O by the action of P on POCl_3 may explain the favourable action of the latter.

O. J. W.

Fluorescence. A. KUTZELNIGG (Z. anorg. Chem., 1932, 208, 29—32).—Under the influence of ultra-violet light (with visible rays excluded) solid CO_2 has a bright bluish-violet fluorescence. A feeble effect is observed with MgO, but the MgO obtained by heating a solution in molten NH_4NO_3 (cf. this vol., 1099) gives a strong scarlet fluorescence. CuI in contact with the pptn. liquid fluoresces with a violet colour, but after washing the effect is red. Films of CuI on a Cu surface give a dark red fluorescence after a time or after mechanical working. Hydrosols of anthracene, prepared by pouring an EtOH solution into H_2O , show the fluorescence of massive anthracene. ZnMe_2 and ZnEt_2 have a weak bluish fluorescence. No effect was observed with pure As_2O_3 or Al_2O_3 .

E. S. H.

Necrobiotic rays. W. W. LEPESCHKIN (Science, 1932, 76, 168).—Ultra-violet rays emitted by dying cells are designated necrobiotic rays. Some of these rays, which are observed by means of a suspension of AgBr, have a wave-length shorter than that of any known ultra-violet rays.

L. S. T.

Hallwachs effect in compounds of elements with double valency. A. POCHETTINO (Atti R. Accad. Lincei, 1932, [vi], 15, 505—509).—Measurement of the Hallwachs effect in many pairs of compounds containing an element with a variable valency shows that the effect is always greater, for a given pair of compounds, in that one in which the variable valency is lower, irrespective of the sign of the radical in which the element with variable valency is present, e.g., $\text{K}_4\text{Fe}(\text{CN})_6 > \text{K}_3\text{Fe}(\text{CN})_6$, $\text{FeCl}_2 > \text{FeCl}_3$. The direct connexion between the Hallwachs effect and photo-chemical oxidation is not certain. O. J. W.

Life of excited NO_2 . O. HEIL (Z. Physik, 1932, 77, 563—566).—Excited NO_2 is shown to have a life period of 10^{-5} sec.

A. B. D. C.

Photo-ionisation of the vapours of anthracene and diphenylamine. E. C. ALLBERRY (Phil. Mag., 1932, [vii], 14, 400—404).—No evidence of photo-ionisation was found (cf. A., 1909, ii, 778).

H. J. E.

Conditions necessary for production of an independent photo-electric potential. H. TEICHMANN (Z. Physik, 1932, 78, 21—25).—Becquerel, Hallwachs, internal photo-electric, barrier layer photo-

electric, and crystal photo-electric potentials are ascribed to the potential barrier existing at an interface separating media with different distributions of possible electronic levels.

A. B. D. C.

Influence of humidity and temperature on the characteristics of discharges in an electro-filter. S. P. ŻEBROWSKI (Physikal. Z., 1932, 33, 727—729).

W. R. A.

Use for the titanium photo-electric cell. J. W. MARDEN and K. O. SMITH (Trans. Electrochem. Soc., 1932, 62, 237—244).—Erythemogenic strengths of Hg discharge lamps can be closely estimated by means of the Ti photo-electric cell.

H. J. T. E.

Chromium-selenium photo-voltaic cells. C. G. FINK and D. K. ALPERN (Trans. Electrochem. Soc., 1932, 62, 305—313).—A sensitivity of 150 micro-amp. per lumen has been obtained with commercial forms of the cells. The max. colour response depends somewhat on conditions of prep., but a typical val. is 5100 Å. The relationship between photo-voltaic cells and vac. and gas photo-electric cells is discussed.

H. J. T. E.

Effect of a superimposed magnetic field on the dielectric properties of some solid, liquid, and gaseous bodies. R. SCHMID (Ann. Physik, 1932, [v], 14, 809—830).—The effect of a superimposed magnetic field on the dielectric current in liquids, the disappearance angle for solid insulators, and the breakdown potential of air at atm. pressure were investigated.

A. J. M.

Electrolytic valve action. V. Properties of sparks. A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1932, 78, 196—210; cf. A., 1931, 546, 1130).—The size, duration, and spectral properties of the minute sparks formed with Al and Ta in borax solutions were studied, and estimates are given of the quantity of electricity transported by these sparks.

A. B. D. C.

Electrical conductivity of barium oxide in relation to electron emission. W. MEYER and A. SCHMIDT (Z. tech. Physik, 1932, 13, 137—144; Chem. Zentr., 1932, i, 2934).

Electric dipole moment of nickel carbonyl. L. E. SUTTON and J. B. BENTLEY (Nature, 1932, 130, 314).—The total and the electron polarisations of Ni(CO)_4 in CCl_4 at 0° are 39.5 and 37.3 c.c., respectively. The apparent orientation polarisation of 2.2 c.c. gives a max. val. of 0.3×10^{-18} e.s.u. for the electric dipole moment. As this is of the order expected for the atom polarisation of such a mol., the moment is taken to be zero. The structure, which must be symmetrical and not cyclic, is discussed.

L. S. T.

Electric moments of acetone, acetaldehyde, acetyl chloride, chloroacetone, and chloroacetyl chloride. C. T. ZAHN (Physikal. Z., 1932, 33, 686—687).—Observed vals. for COMe_2 , MeCHO , and AcCl are compared with vals. calc. by the method of Eucken and Meyer. Discrepancies are explained as arising from deformation of the tetrahedral symmetry. The val. obtained for CH_2ClAc is intermediate between the calc. vals. for a mol. with free rotation and a *trans* mol., and the val. depends on the temp.

$\text{CH}_2\text{Cl-COCl}$ gives a val. in good agreement with the theoretical val. Measurements were made on the vapours of these compounds at different temp.; except for CH_2ClAc , μ is independent of temp.

W. R. A.

Dipole moments of unsaturated compounds. I. I. M. A. BRUYNE, R. M. DAVIS, and P. M. GROSS (Physikal. Z., 1932, 33, 719—724).—Dipole moments of dichloropropylene, dichloroisobutylene, and trichloroethylene are 1.73, 2.01, and 0.94×10^{-18} , respectively. Vals. calc. by a new method are compared with observed vals. and with vals. calc. by the method of Eucken and Meyer for 28 unsaturated hydrocarbon derivatives.

W. R. A.

Electric moments of certain fatty acid esters. C. T. ZAHN (Physikal. Z., 1932, 33, 730—731).—Electric moments of the vapours of HCO_2Et , EtOAc , MeOAc , and amyl formate and acetate are uninfluenced by temp. Vals. calc. by different methods are compared with experimental results.

W. R. A.

Dependence of measured dipole moments on the solution media. H. MÜLLER (Physikal. Z., 1932, 33, 731—732).—The polarisation at infinite dilution of PhCl for seven different solvents is given. Vals. of P_2 vary from 86.5 to 76.

W. R. A.

Magnetic rotation dispersion of nickel tetracarbonyl. J. VERHAEGHE (Bull. Acad. roy. Belg., 1932, [v], 18, 532—539).—The variation of refractive index and magnetic rotation of Ni(CO)_4 between 4000 and 7000 Å. have been determined; the results indicate that the electrons effective in the magneto-optical rotation are the valency electrons of Ni.

A. B. D. C.

Faraday effect in molecules. R. SERBER (Physical Rev., 1932, [ii], 41, 489—506).—Mathematical. The effect when the frequency of the incident light is near resonance or well removed from resonance with absorption lines of the mol. is examined. In the former case the mol. rotation, independence of spin, and magnitude of rotation and comparison with experiment, and in the latter case perturbation of energies by the magnetic field, with special reference to I vapour and the alkali metals, are considered.

N. M. B.

Diamagnetic susceptibility of inorganic compounds. II. Cu^+ , Ag^+ , Au^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Hg_2^{2+} ions. K. KIDO (Sci. Rep. Tôhoku, 1932, 21, 288—297).—The vals. found for the ionic susceptibilities ($-\chi_{\text{ion}} \times 10^6$) are: Cu^+ 16.0, Ag^+ 26.2, Au^+ 44.8, Zn^{2+} 12.8, Cd^{2+} 20.3, Hg^{2+} 36.6, Hg_2^{2+} 2×40.3 and CN^+ 16.6. The relation between χ_{ion} and the no. of electrons in the ion (n) is $\chi_{\text{ion}} = -c \cdot n \times 10^6$; the const. c is 0.6 for the Cu group and 0.46 for the Zn group. The difference in the susceptibilities of Hg_2^{2+} and Hg^{2+} is attributed to a diamagnetic effect of the shared electrons in Hg_2^{2+} .

A. R. P.

Nature of ferromagnetism. F. BITTER (Physical Rev., 1932, [ii], 41, 507—515).—Irregularities in the magnetisation of ferromagnetic crystals were studied by means of magnetic Fe_2O_3 particles suspended in EtOAc . The patterns of the particles on Fe, Ni, and Co crystals were observed.

N. M. B.

Magnetic analysis of molecular orientations in crystals. K. S. KRISHNAN (Nature, 1932, 130, 313).—Correlation of magnetic consts. of a diamagnetic crystal with those of the individual mols. gives the mol. orientations in the crystal. This method is applied to diphenyl and dibenzyl.

L. S. T.

Theory of induced polarity in benzene. A. LAPWORTH and R. ROBINSON (Nature, 1932, 130, 273).—A further discussion (cf. this vol., 795).

L. S. T.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1932, [v], 18, 578—595; cf. A., 1930, 277, 853; 1931, 685, 1106, 1127, 1215, 1356).—Mathematical.

J. W. S.

Surface tensions of ethyl ether, acetone, toluene, and methyl alcohol at low temperatures. T. TONOMURA and K. CHUJO (Bull. Chem. Soc. Japan, 1932, 7, 259—264).—The surface tensions between 30° and —100° of Et₂O, COMe₂, and PhMe were measured in a capillary tube. Results fit formulæ of the Eotvos type, $\gamma(M/d)^{2/3} - A(-+B)$. The surface tension of MeOH does not fit this expression, probably on account of association.

A. G.

Quantitative measurements with the multiple interference spectroscope. P. GORLICH and E. LAU (Z. Physik, 1932, 77, 746—751). A. B. D. C.

Asterisms in X-ray diagrams. W. BERG (Z. Krist., 1932, 83, 318—322; cf. A., 1931, 782).—A qual. explanation of how these are caused in Laue diagrams by distortion of the crystals. C. A. S.

Influence of divergence [of radiation], thickness of substance examined, and depth of penetration on precision of lattice dimensions [determined] by the Debye-Scherrer method. F. LIHL (Z. Krist., 1932, 83, 193—221).—Corrections due to these causes in the localisation of the centre of the lines are calc. and practical applications given (cf. A., 1931, 1217). C. A. S.

Structure of polished solids. L. HAMBURGER (Nature, 1932, 130, 435—436).—A discussion.

L. S. T.

Scattering of X-rays and cathode rays in free molecules. L. BEWILGUA (Physikal. Z., 1932, 33, 688—692).—Theoretical. Experimental data on C₆H₆ and CCl₄ are discussed. W. R. A.

Method for deducing accurate values of the lattice spacing from X-ray powder photographs taken by the Debye-Scherrer method. A. J. BRADLEY and A. H. JAY (Proc. Physical Soc., 1932, 44, 563—579).—By the use of a calibration and an extrapolation process it is possible to eliminate many errors in deducing lattice spacing from X-ray photographs. A. J. M.

Closest spherical packing of higher orders. E. K. BROCH (Z. Physik, 1932, 78, 257—270).—Lattices of closest spherical packing with layer periodicities greater than the hexagonal 2, or cubic 3, and their possible interference patterns, are discussed. A. B. D. C.

Crystals as continuous media. A. V. SCHUBNIKOV (Bull. Acad. Sci. U.R.S.S., 1932, No. 6, 799—

815).—An exposition of the theories of the author (Z. Krist., 1929, 72, 271; 1930, 73, 430). R. T.

Crystallisation of thin films of salol and of benzophenone. I. V. KROTOV (Bull. Acad. Sci. U.R.S.S., 1932, No. 6, 817—828).—The stability of supercooled liquid films of salol or CPh₂ is proportional to the smoothness of the supporting surface, but is independent of its nature (Cu, Ni, glass, wood, paper). The velocity of crystallisation of seeded films is independent of both the nature and the smoothness of the surface. R. T.

Applicability of the statistical method to ionic lattices. W. LENZ (Z. Physik, 1932, 77, 713—721).—Theoretical. The Thomas-Fermi method is applied to lattices of ions with many electrons. A. B. D. C.

Separation of the α -phase in β -brass. M. STRAUMANIS and J. WEERTS (Z. Physik, 1932, 78, 1—17).—The formation of the face-centred cubic α -phase from the body-centred β -phase subjected to various heat-treatments has been examined by X-ray and microscopical methods. A. B. D. C.

Determination of molecular structure by means of electron diffraction. III. Formaldehyde. IV, and V. Dimethyl ether and diethyl ether. L. BRU (Anal. Fis. Quim., 1932, 30, 483—485, 486—491).—III. The distance between the C and O atoms of the CO group of CH₃O is 1.15 ± 0.05 Å.

IV, V. The distance between the C and O atoms is 1.34 ± 0.06 Å. for Me₂O, and 1.33 ± 0.08 Å. for Et₂O. The angle formed by the two alkyl groups and the O atom is 100°. H. F. G.

X-Ray determination of size and form of crystals of carbon. U. HOFMANN and D. WILM (Z. physikal. Chem., 1932, B, 18, 401—416).—Examination of various forms of C, including technical activated C, has shown that each has the graphite lattice without essential modification. For a given variety the crystal size rises with the temp. of formation. The CO crystals of C obtained by decomp. of Fe carbide are, however, considerably greater even at 400° than C crystals formed by dissociation of benzene vapour at 950°. The crystals of highly active C are comparable in size with single large org. mols., so that the no. of mols. which can be adsorbed on a single crystal will often be small. With activated C, in which the surfaces of almost all the crystals are available for adsorption, the adsorbing surface calc. from the dimensions of the crystals agrees with the val. deduced from observations on the adsorption of dissolved substances. R. C.

Crystal structure of yttrium. L. L. QUILL (Z. anorg. Chem., 1932, 208, 59—64).—The following data have been determined: a 3.663 ± 0.008 , c 5.814 ± 0.012 Å., c/a 1.588, d (calc.) 4.34. E. S. H.

Determination of lattice constant of titanium carbide. M. VON SCHWARZ and O. SUMMA (Z. Elektrochem., 1932, 38, 743—744).—TiC crystallises in the rock-salt type of the cubic system; the lattice const. is 4.311 Å. E. S. H.

Transformation of magnetite at a low temperature. T. OKAMURA (Sci. Rep. Tôhoku, 1932,

21, 231—241).—Sudden changes which occur in the thermal expansion, electric resistance, and magnetic properties of magnetite at -158° to -166° are attributed to an allotropic transformation. No change in the lattice structure can be detected.

A. R. P.

Lattice constants of $\alpha\text{-Fe}_2\text{O}_3$ and of $\gamma\text{-Al}_2\text{O}_3$. R. BRILL (Z. Krist., 1932, 83, 323—325).— $\alpha\text{-Fe}_2\text{O}_3$ [from $\text{Fe}(\text{CO})_5$] has a 5.429 Å., α $54^\circ 58'$ (cf. A., 1930, 1361). $\gamma\text{-Al}_2\text{O}_3$ has a 7.91 Å., and like $\gamma\text{-Fe}_2\text{O}_3$ has the spinel structure (cf. this vol., 113).

C. A. S.

Structure of hydroxides and hydrates. IV. Strontium peroxide octahydrate. G. NATTA (Gazzetta, 1932, 62, 444—456; cf. A., 1929, 244).—X-Ray analysis by the powder method shows that $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$ crystallises in the tetragonal system with a unit cell containing 1 mol. (a 6.32, c 5.56 Å., c/a 0.88), and belongs to the space-group D_{2h}^{10} . The co-ordinates of the ions are: Sr^{++} (0,0,0), O_2^{--} of peroxide ($\frac{1}{2}, \frac{1}{2}, u'$)

O'' of H_2O (u, u, v) (u, u, v) (u, u, v) (u, u, v) (u, u, v), where $u' = 0.10$, $u = 0.20$, $v = 0.25$. The radius of the O'' ion in H_2O mols. is calc. to be 1.30 Å. In the O_2^{--} ion of the peroxide the distance between the two O atoms is less than the diameter of the neutral atom.

O. J. W.

Structure of lead chloride. H. BRÆKKEN (Z. Krist., 1932, 83, 222—226; cf. A., 1929, 631).—Revised results are: for the unit cell a 4.525, b 7.608, c 9.030 Å.; each Pb atom is surrounded by 9Cl, which form a kind of double octahedron; $\text{Cl—Cl} = 3.4\text{—}4.1$; $\text{Pb—Cl} = 2.8\text{—}3.5$ Å.

C. A. S.

Structures of potassium and rubidium dithionates. G. HAGG (Z. Krist., 1932, 83, 265—273).— $\text{K}_2\text{S}_2\text{O}_6$ and $\text{Rb}_2\text{S}_2\text{O}_6$ crystallise in space-group D_{2h}^{10} with 3 mols. in the unit cell and, respectively, a 9.756, c 6.274, and a 10.144, c 6.409 Å. (cf. A., 1931, 1113); $\text{Rb}_2\text{S}_2\text{O}_6$ has d 2.89. The S_2O_6 group has a trigonal axis of symmetry, but the three such groups in the unit cell are not structurally equiv. $\text{K}_2\text{S}_2\text{O}_6$ and $\text{Tl}_2\text{S}_2\text{O}_6$ do not form mixed crystals (cf. A., 1905, ii, 390), nor was it possible partly to replace Rb by Cs in $\text{Rb}_2\text{S}_2\text{O}_6$. Huggins and Frank's proposed structure (cf. Amer. Min., 1931, 16, 580) is not confirmed.

C. A. S.

Crystal structure of double salts with different anions. H. SEIFERT (Z. Krist., 1932, 83, 274—300).—A discussion on the structure and growth of crystals of such salts with special reference to the layer structure as found in compounds such as the humite, staurolite, chlorite, and parisite groups (cf. A., 1930, 280, 528, 1396; 1931, 1218); also on types transitional between these and the zeolites, e.g., apatite, apophyllite, etc. (cf. A., 1931, 671; this vol., 494).

C. A. S.

Structures of calcium chromate and its mono- and di-hydrates. J. H. CLOUSE (Z. Krist., 1932, 83, 161—171).— CaCrO_4 is tetragonal, and not isomorphous with CaSO_4 , but is so with ZrSiO_4 and YPO_4 (cf. A., 1881, 352). Its unit cell has a 7.25, b 6.34 Å., and contains 4 mols., space-group D_{2h}^{10} ($I4/amd$); d^{20} 3.12. Each Cr is surrounded tetrahedrally by 4O at 1.64 Å., and each Ca by 8O at 2.45

Å. $\text{CaCrO}_4 \cdot \text{H}_2\text{O}$ is rhombic, a 7.99, b 12.77, c 8.11 Å., with 8 mols. in the unit cell, space-group V_h^{10} ($Pcab$). $\beta\text{-CaCrO}_4 \cdot 2\text{H}_2\text{O}$ (prepared by evaporating at room temp. conc. aq. Na_2CrO_4 to which a little CaCl_2 has been added) is rhombic, a 16.02, b 11.39, c 5.60 Å., with 8 mols. in the unit cell, space-group V_h^{10} ($Pcmb$), d 2.50.

C. A. S.

Isomorphism of borates and carbonates. V. M. GOLDSCHMIDT and H. HAUPTMANN (Nachr. Ges. Wiss. Göttingen, 1932, 53—72; Chem. Zentr., 1932, i, 2678).— ScBO_3 , InBO_3 , and YBO_3 , space-group D_{2h}^{10} , have 2 mols. in the rhombohedral cell, and 12 in a larger (non-unit) hexagonal cell. Vals. of a (hexag.), c (hexag.), a (rhombohedral), α , d_{calc} , and H are, respectively: 4.747±0.01, 4.766±0.01, 5.06±0.05 Å.; 15.274±0.04, 15.455±0.04, 17.21±0.15 Å.; 5.782±0.015, 5.841±0.015, 6.44±0.06 Å.; $48^\circ 28'$, $48^\circ 10'$, $46^\circ 17'$; 3.451, 5.576, —; 7, 6.5, —. LaBO_3 is rhombic; space-group V_h^{10} , with 4 mols. in the unit cell: a 5.10±0.01, b 8.22±0.02, c 5.83±0.01 Å.; d_{calc} 5.339, H 5. The structure of orthoborates of trivalent metals is very similar to that of carbonates of bivalent metals.

A. A. E.

Structure of sillimanite and related materials. W. H. TAYLOR (J. Soc. Glass Tech., 1932, 16, 111—120T).—The co-ordination no. of corresponding Al atoms is 4, 5, and 6 in sillimanite, andalusite, and cyanite, respectively. The close resemblance of sillimanite and mullite is due to the fact that one SiO_4 group per unit cell of sillimanite is replaceable by one AlO_4 group in mullite. The fibrous component of porcelain, "porcelainite," is distinct from mullite and sillimanite.

J. A. S.

Crystal structure of bronzite from Chichi-jima in the Bonin islands. K. TAKANE (Proc. Imp. Acad. Tokyo, 1932, 8, 308—311).—The dimensions of the unit cell are a_0 18.16, b_0 8.84, c_0 5.19 Å.; $a:b:c = 2.0543:1:0.5871$; the unit cell contains 16 mols. of $15.5\text{FeSiO}_3 + 84.5\text{MgSiO}_3$.

P. W. C.

Equiline and folliculine. C. GAUDEFRY (Compt. rend., 1932, 195, 523—524; cf. this vol., 547).—The unit cell of equiline has a 6.42, b 9.06, c 23.5 Å., for folliculine a 7.84, b 10.0, c 10.2 Å. Corrected axial ratios (goniometric) are 0.720:1:2.61, and 0.776:1:1.826, respectively.

C. A. S.

X-Ray study of prehnite and lawsonite. B. GOSSNER and F. MUSSGUG (Zentr. Min. Geol., 1931, A, 419—423; Chem. Zentr., 1932, i, 1874).—Prehnite has a 4.65, b 5.52, c 18.53 Å.; d 2.925; the unit cell contains 2 mols. of $\text{Ca}_2(\text{SiO}_3)_3(\text{AlOH})\cdot\text{AlO}_2\text{H}$; space-group V_h^7 or C_{2v} . Lawsonite has a 5.87, b 8.85, c 13.22 Å.; the unit cell contains 4 mols. of $\text{Ca}(\text{SiO}_3)_2(\text{AlO}_2\text{H})_2$; space-group probably V_h^7 .

A. A. E.

Crystal structure of pyrrhite. F. MACHATSCHKE (Zentr. Min. Geol., 1932, 33—37; Chem. Zentr., 1932, i, 2702).—Pyrrhite has a 10.41±0.02 or 10.37 Å.; it is classed with the pyrochlores, and its composition corresponds with $(\text{Ca}, \text{Na}, \text{Fe})_2(\text{Nb}, \text{Ta}, \text{Ti})_2(\text{O}, \text{OH}, \text{F})_7$.

A. A. E.

Crystal structure of iodoform. M. L. HUGGINS and B. A. NOBLE (Amer. Min., 1931, 16, 519—525).—The hexagonal unit cell has a 6.81, c 7.52 Å., and contains 2 mols.; space-group C_6 .

CH. ABS.

[Crystal structure of] triphenylbismuthine dichloride. G. GREENWOOD (Amer. Min., 1931, 16, 473—483).—Holoaxial symmetry is confirmed; $a:b:c=0.7743:1:0.4115$; d 1.908; space-group V^2 . The unit cell contains 8 mols. CH. ABS.

X-Ray investigation of colour dimorphism among stilbene derivatives. E. HERTEL and K. SCHNEIDER (Z. physikal. Chem., 1932, B, 18, 436—440; cf. A., 1916, i, 24).—The unit cell of the stable red form of *o*-nitro-*p*-cyano-*p'*-methoxystilbene has I_a 8.50, I_b 7.45, and I_c 13.35 Å., and contains 2 mols. This form is to be regarded as a unimol. mol. compound without dipole association. The metastable yellow form has I_a 14.2, I_b 27.8, and I_c 7.6 Å., the constituent units of the lattice being double mols. formed by dipole association at the OMe groups.

R. C.

Highly polymerised compounds. LXXI. X-Ray examination of polyoxymethylenes of high mol. wt. E. SAUTER (Z. physikal. Chem., 1932, B, 18, 417—435).—Results previously reported for β -polyoxymethylene are confirmed (A., 1927, 647). The most probable space-groups are C_3^{2-} . Examination of a γ -polyoxymethylene with an average degree of polymerisation of 100 has shown that it is impossible to determine the degree of polymerisation by X-ray examination. Polyoxymethylene glass, obtained by polymerisation of liquid CH_2O in O_2 at -80° , has a macromol. lattice (cf. A., 1930, 1241).

R. C.

Paracrystalline and crystalline 1-anisylidene-amino-4-benzeneazophthalene. F. RINNE (Z. Krist., 1932, 83, 227—242).—This compound melts to an isotropic fluid at 150° ; on slow cooling it passes into a paracryst. phase at 110° , and then into α - and (below 75°) into β -spherulites, the individual crystals of which show respectively oblique and straight extinction. X-Rays show the α - and β -spherulites (m.p. 150.5 — 151°) to have identical structures, their relationship being that of mimetic isomerism, as boracite. The paracryst. phase has the ordinary nematic structure. The changes are well shown by reason of the different colours of the phases.

C. A. S.

X-Ray interpretation of the molecular structure of feather keratin. W. T. ASTBURY and T. C. MARWICK (Nature, 1932, 130, 309—310).—Details of the mol. interpretation of feather keratin are given and its bearing on protein analysis is discussed. L. S. T.

X-Ray investigation of subcrystalline materials. R. D. MILES (J.S.C.I., 1932, 51, 247—255t).—Suitable types of X-ray tubes are described and their efficient operation is discussed. An account is given of the various types of X-ray diagram which are yielded by the organised fibres, crystal powders, glasses, and liquids. The significance of these diagrams is indicated. Investigation has shown that the spiral structure of the cotton fibre is present in the fibre in the boll, before the convolutions are formed. Mercerisation of ordinary cotton under tension yields a fibre of which the X-ray diagram shows no sign of spiral structure. The main results of the X-ray examination of cellulose nitrate and rubber are reviewed.

Theory of association in dielectric liquids. M. WOLKE (Spraw. Prace Polsk. Towarz. Fizy., 1930, 5, 157—167; Chem. Zentr., 1932, i, 3038).—A statistical theory is developed. Association of two dipolar mols. may occur with resulting zero moment, or with doubling of the electric moment. A. A. E.

Internal Barkhausen effect. S. PROCOPIU (Bull. Acad. Sci. Roumaine, 1932, 15, 84—86).—An explanation of the observations of von Hippel and Stierstadt (A., 1931, 790) is offered.

Hall effect in beryllium. A. CICCONE (Nature, 1932, 130, 315).—99.5% Be gave a val. $+0.0024 \pm 0.0001$ for the Hall coeff. L. S. T.

Influence of plastic deformation on the susceptibility of dia- and para-magnetic metals. A. KUSSMANN and H. J. SEEMANN (Z. Physik, 1932, 77, 567—580).—Plastic deformation influences the susceptibility of Cu, Ag, Bi, and Pb, but not that of Al, Au, Zn, W, Mo, and Cu-Zn-Ni alloys; the observed effects are due entirely to ferromagnetic impurities, which in the first series of metals can separate out as ferromagnetic particles.

A. B. D. C.

Anomalous behaviour of the magnetic permeability of iron in high frequencies. G. R. WAIT (Z. Physik, 1932, 77, 695—698).—Eddy currents may apparently change the permeability of Fe with frequency, but no real effect has been observed (cf. Malov, this vol., 449; Arkadiev, *ibid.*).

A. B. D. C.

Change in electrical resistance of magnetostrictive metals in magnetic fields. II. T. GNESSOTTO (Atti R. Ist. Veneto Sci. Lett. Art., 1931, 90, 1153—1163).

Slipping and consolidation in single zinc crystals. M. STRAUMANIS (Z. Krist., 1932, 83, 29—34).

C. A. S.

Plasticity of rock-salt and sylvite. F. RINNE and W. HOFMANN (Z. Krist., 1932, 93, 56—74; cf. A., 1930, 1243).

C. A. S.

Relaxation period of the vibrational energies of CO_2 and N_2O . H. O. KNESE and J. ZÜHLKE (Z. Physik, 1932, 77, 649—652).—The dispersion of sound waves in N_2O was measured, the relaxation period being 10^{-6} sec.; the dispersion curves indicate that the transverse vibration is the principal factor in the vibrational sp. heat.

A. B. D. C.

Thermo-electric power of single-crystal bismuth near the m.p. A. SOROOS (Physical Rev., 1932, [ii], 41, 516—522).—In the region from the m.p. to about 8° above it the thermo-electric power gradually changes from that characteristic of the solid to that characteristic of the final liquid state, indicating a persistence of a crystal structure into the liquid state.

N. M. B.

Viscosity of molten sodium chloride. E. VAN AUBEL (Bull. Acad. roy. Belg., 1932, [v], 18, 692—695).—Using the viscosity data of Dantuma, the internal friction of molten NaCl has been estimated between 816° and 997° . The crit. density is 0.509.

W. R. A.

Viscosity of nitrobenzene. A. VAN ITTERBEEK (*Nature*, 1932, 130, 399—400; cf. this vol., 899, 905).—Viscosity curves for pure PhNO_2 , determined by the oscillating-disc method, are linear with no discontinuous transition point. PhNO_2 containing H_2O as impurity gives 2 linear curves which intersect at approx. 9.6° , indicating that the results obtained by Mazur (A., 1931, 148) must be attributed to insufficient drying. Compared with other methods the oscillating-disc method provides, for relative measurements, very accurate results. L. S. T.

Influence of a magnetic field on the viscosity of oxygen. H. ENGELHARDT and H. SACK (*Physikal. Z.*, 1932, 33, 724—727).—With the help of an "aerodynamic Wheatstone bridge" the influence of a magnetic field between 0 and 2000 gauss on the viscosity of O_2 , air, and N_2 was studied. The viscosity of O_2 is influenced considerably by the pressure, of air only slightly, and of N_2 not at all. W. R. A.

Limiting values of physical observations. F. EHRENHAFT (*Physikal. Z.*, 1932, 33, 673—682).—The determination of the wt. and charge of some sub-microscopic bodies and experiments on photophoresis are discussed. W. R. A.

Precipitated sulphur. A. NIELSEN (*Dansk Tidsskr. Farm.*, 1932, 6, 177—181).—The solubility of pptd. S in C_6H_6 , olive oil, and other org. solvents is identical with that of rhombic S; hence the particles in pptd. S consist of rhombic S in a microcryst. state. H. F. H.

Vapour pressure of rhenium heptoxide and vapour pressure and dissociation pressure of rhenium octoxide. E. OGAWA (*Bull. Chem. Soc. Japan*, 1932, 7, 265—273).—The following data have been obtained for Re_2O_7 and Re_2O_8 . V.p. of solids: $\log P = -7217.95/T + 14.83866$; $\log P = -1738.74/T + 5.48512$. V.p. of liquids: $\log P = -3920.13/T + 9.04668$; $\log P = -924.18/T + 3.54384$. M.p. 297° and 145° , b.p. of Re_2O_7 363° . Heats of sublimation 33,050 g.-cal. (230 — 295°) and 7960 g.-cal. (100 — 140°). Heats of evaporation 17,950 g.-cal. (300 — 360°) and 4230 g.-cal. (160 — 220°). Heats of fusion 14,610 and 2500 g.-cal. Dissociation pressure of Re_2O_8 , $\log P = -416.08/T + 1.73877$. A. G.

F.p. of "isooctane" ($\beta\beta\delta$ -trimethylpentane). J. H. BRUUN and M. M. HICKS-BRUUN (*Bur. Stand. J. Res.*, 1932, 9, 269—270).—The f.p. of pure isooctane is -107.41° ; the purity of a commercial sample is given by $3.86t_f + 514.8$, where t_f is the initial f.p. in $^\circ\text{C}$. W. R. A.

Latent heats and heat conductivities of some aqua-crystalline compounds. K. R. STURLEY (*J.S.C.I.*, 1932, 51, 271—273r).—The latent and sp. heats of $\text{Na}_2\text{S}_2\text{O}_3$, NaOAc , and K alum are given and the methods of obtaining them described.

Specific heats of ammonium salts. J. L. CRENSHAW and I. RITTER (*Z. physikal. Chem.*, 1932, B, 19, 84).—In a previous paper (this vol., 453) the data given for NH_4CN refer to NH_4CNS .

M.p. of benzene. A. W. MENZIES and D. A. LACOSS (*J. Physical Chem.*, 1932, 36, 1967—1968).—The val. $5.49 \pm 0.02^\circ$ has been obtained (cf. A., 1920, i, 152; 1931, 1361; this vol., 452). Saturation

with H_2 , N_2 , or air depresses the f.p. by 0.017° . The f.p. is not dependent on the rate of cooling.

J. H. R. (c)

Equation for representation of high-temperature heat content data. C. G. MAIER and K. K. KELLEY (*J. Amer. Chem. Soc.*, 1932, 54, 3243—3246). The equation $-Q_{773.1}^T - [aT + \frac{1}{2}bT^2 + c/T]_{773.1}^T$ appears to represent such data better than the usual power-series expression.

L. P. H. (c)

Constants of the higher aliphatic alcohols. C. H. KAO and S. MA (*Sci. Rep. Nat. Tsing Hua Univ.*, 1932, 1, 181—183).—The b.p., d_4 , and n_D at 15° , 20° , and 25° are recorded for the Et esters of the n -acids from valeric to decic acid and for the primary n -alcohols from amyl to decyl alcohol.

R. S. C.

Diffusion coefficients of bromine-hydrogen, bromine-nitrogen, bromine-oxygen, and bromine-carbon dioxide. J. E. MACKENZIE and H. W. MELVILLE (*Proc. Roy. Soc. Edin.*, 1931—1932, 52, 337—344).—The observed diffusion coeffs. for Br are lower than the theoretical vals. and usually increase with time of diffusion.

W. R. A.

Diffusion of alcohols. G. FRANKE (*Ann. Physik*, 1932, [v], 14, 675—682).—The diffusion coeffs. of EtOH and MeOH in H_2O and of C_6H_6 in CCl_4 have been determined by an optical method. A. J. M.

Diffusion of particles and the energy loss resulting from collision. W. DE GROOT (*Physica*, 1931, 11, 337—342; *Chem. Zentr.*, 1932, i, 2299).

Humidity diagram for water vapour-air mixture. S. KAMEI (*Chem. Fabr.*, 1932, 337—339).

E. S. H.

Formation of amalgams: its physico-chemical aspect. B. N. SEN (*Chem. News*, 1932, 145, 93).—Metals and metalloids form amalgams with Hg when the distance of closest approach of their atoms exceeds 2.5 \AA .

E. S. H.

X-Ray study of alloys of the iron-tungsten system and their carbides. A. ŌSAWA and S. TADEKA (*Kinzoku-no-Kenk.*, 1931, 8, 181—196).—The system is distinguished by the compound Fe_3W_2 (ϵ -phase), trigonal, a 4.738, c 25.726 \AA , the unit cell containing 8 mols. In the Fe-rich region of the system Fe-W-C there are three phases: WC, Fe_3C (η), and $\text{Fe}_3\text{W}_2\text{C}$ (η). WC is hexagonal, a 2.910, c 2.838 \AA ; Fe_3C is orthorhombic, a 4.626, b 5.107, c 6.633 \AA . The double carbide is face-centred cubic with a 10.97—11.08 \AA , according to the composition and heat treatment. CH. ABS.

Structure of some copper-zinc phases. O. CARLSSON and G. HAGG (*Z. Krist.*, 1932, 83, 308—317).—The ϵ -phase (prepared by very slow cooling of an alloy containing 60 at.-% Sn) is rhombic, a 5.510, b 38.18, c 4.319 \AA . The η -phase (about 45.5 at.-% Sn) is hexagonal, a 20.95, c 25.43 \AA . The unit cells of these phases contain 32 and 500 atoms, and are hyperstructures of a hexagonal lattice, and of a NiAs structure with $a \times 2$, $b \times 8$, and $a \times 5$ and $c \times 5$, respectively (cf. A., 1928, 822). The γ' -phase (prepared by chilling an alloy of 21.8 at.-% Sn after 15 hr. annealing at 595°), is hexagonal, a 7.316, c 7.854 \AA , with 26 atoms in the unit cell. The space-group is D_{3d}^4 .

but one atom of each group is absent, so that the lacunæ form a hexagonal lattice (cf. A., 1931, 1900, where the phase is denoted by ϵ). C. A. S.

Constitution of lead-tin alloys. D. STOCKDALE (Inst. Metals, Sept., 1932. Advance copy, 16 pp.).—The system has been re-examined by micrographic, electrical resistance, and two thermal methods. The eutectic point is placed at 61.86% Sn, and the solid solubility of Sn in Pb is 19.5% and of Pb in Sn 2.5% at the eutectic temp.; at room temp. the solubility of each metal in the other is very small. The evolution of heat which is observed at about 150° on cooling Pb-rich alloys varies in magnitude according to the previous history of the specimen; the temp. also varies somewhat with the composition and previous heat treatment. It is suggested that the phenomenon may be due to the separation of Sn from supersaturated solid solution in a form other than the ordinary white form, which is then converted into this form with the evolution of heat. A. R. P.

Hall effect and grating constants of alloys. E. VAN AUBEL (Bull. Acad. roy. Belg., 1932, [v], 18, 696—699).—Cu-Ni alloys do not show the relation between the Hall effect and grating constns. which Ornstein and van Geel found for Ag-Au alloys. Au-Pd, Ag-Pd, and Au-Cu alloys are also discussed. W. R. A.

Magnetic properties of solid solutions. S. S. BHATNAGAR and P. L. KAPUR (J. Indian Chem. Soc., 1932, 9, 347—356).—Magnetic susceptibilities have been determined for $\text{KMnO}_4\text{-KClO}_4$, KCl-NaCl , KBr-KCl , and KBr-NaBr . In the first case, where the salts are true isomorphs, the mixture rule is obeyed and the susceptibility-composition graph is linear. For the three remaining systems curves are obtained, the max. deviation being at 50% for KCl-NaCl and KBr-NaBr and at 70% KBr for KBr-KCl , corresponding in each case with the min. m.p. In the last case the deviation from a straight line is slight. The solid solutions $\text{KMnO}_4\text{-KClO}_4$ have no heat of formation. The heat of formation of the 70% KBr solution in KBr-KCl is 220 g.-cal., whilst for the 50% KBr-NaBr and KCl-NaCl solutions, where the deviation is large, the heats of formation are 1400 and 2100 g.-cal. M. S. B.

Magnetic susceptibility and electrical resistance of the series of mixed crystals Pd-Ag and Pd-Cu. B. SVENSSON (Ann. Physik, 1932, [v], 14, 699—711).—The susceptibility of Ag-Pd and Cu-Pd alloys has been determined; in the Cu-Pd series the susceptibility changes on passing from the disordered to the ordered at. state. Electrical resistance determinations were also made with the alloys. These new observations afford further knowledge of the equilibrium states in their dependence on the previous heat treatment. A comparison of the resistance-concn. and susceptibility-concn. diagrams shows certain deviations that would not be expected for binary systems. A. J. M.

Electrical properties of dilute mixed-crystal alloys. II. Resistance of silver alloys. J. D. LINDE (Ann. Physik, 1932, [v], 14, 353—366).—The effect of adding elements of at. no. 29—33, 46—51,

and 78—83 to Ag on the electrical resistance has been determined. Some preliminary results on the effect of temp. on the resistance are given. The increase in resistance varies with the square of the horizontal distance of the element added from the chief metal of the alloy in the periodic table. A. J. M.

Magnetic moment and the chemical linking in alloys. J. DOREMAN (Nature, 1932, 130, 506).—A re-interpretation of previously recorded data (cf. this vol., 679, 901) for Ni alloys. Calc. effective moments per atom are $\text{Ni}^+ 1$, $\text{Cu}^+ 0$, Zn^{+1} , Al^{+2} , Sn^{+3} (M_B). L. S. T.

Aluminium-antimony alloys. J. VESZELKA (Mitt. berg.-hüttenmann. Abt. Hochschule Sopron, 1931, 193—201; Chem. Zentr., 1932, i, 2230).—Equilibrium is reached very slowly in a mixture of fused Al and Sb. The liquidus has a max. at 1080°, corresponding with AlSb , which was present in all the alloys (Al 99 to <1.2%). AlSb is decomposed in moist air with formation of Al(OH)_3 . A. A. E.

Equilibrium diagram of the copper-silicon system. K. IOKIBE (Kinzoku-no-Kenk., 1931, 8, 433—456).—A homogeneous phase, X (Cu 89.4—89.3%), is formed at 800° by the peritectoid reaction $\delta + \epsilon \rightleftharpoons X$. The δ - γ transformation occurs only in the alloys which contain a smaller amount of Si than X; the ϵ - ϵ' transformation occurs only in alloys of higher Si content than X. The ϵ -phase shows a transformation ϵ - ϵ'' (558—442°) besides ϵ - ϵ' (626—556°). CH. ABS.

Liquation or "inverse segregation" in the silver-copper alloys. J. H. WATSON (Inst. Metals, Sept., 1932. Advance copy, 12 pp.).—Chilling experiments with alloys having a wide solidification range have been made after soaking them for several hr. within this range; analyses of samples from various parts of the specimens and micrographic examination of the structure indicate that the primary crystals, whether Ag or Cu, are free to move under the influence of gravity while the metal is within the freezing range and may be repelled from their positions by severe local chilling in their vicinity. All liquation and segregation phenomena observed in these alloys can be explained by the formation of primary Ag- or Cu-rich crystals at the chilling surface of the mould during transition of the metal through the freezing range and their subsequent repulsion towards the hotter metal in the centre of the ingot. A. R. P.

Equilibrium of the ternary system tin-lead-antimony. K. IWASE and N. AOKI (Kinzoku-no-Kenk., 1931, 8, 253—267).—The diagram, determined by means of total and differential thermal analyses and by microscopical examination, has three non-variant points corresponding with (1) $\beta \rightleftharpoons \beta'$ transformation of Sb-Sn, (2) eutectic crystallisation of α , β , and δ , (3) the peritecto-eutectic reaction $L + \beta \rightleftharpoons \gamma + \beta$. The solubilities of 4 solid solutions at each non-variant point have been accurately determined. CH. ABS.

Intermetallic compounds formed in mercury. IV. Summary of work on the Sn-Cu, Sn-Fe,

Zn-Cu, Zn-Fe, Cd-Cu, Hg-Cu, Mn-Cu, and Zn-Mn systems. A. S. RUSSELL, T. R. KENNEDY, J. HOWITT, and H. A. M. LYONS (J.C.S., 1932, 2340—2342).—In addition to those described previously (this vol., 456), evidence has been obtained for a large no. of further binary and ternary compounds.

D. R. D.

Specific gravity and vapour pressure of concentrated sea-water at 0—175°. R. HARA, K. NAKAMURA, and K. HIGASHI (Tech. Rep. Tohoku, 1932, 9, 99—118).—Measurements at concns. ranging from the normal to approx. saturation with respect to NaCl have been made. The stable modification of CaSO_4 which is in equilibrium with the brine under varying conditions, and the effect of saturation with this salt on the sp. gr. are discussed. A graphic method is described whereby the v.p. of sea- H_2O may be readily obtained for any concn. and temp. within the range considered.

M. S. B.

Vapour pressure of binary liquid mixtures. Benzene toluene and benzene-*m*-xylene. W. VON HUHN (Forsch. Gebiet Ingenieurwesens, 1931, A, 2, 109—113, 129—138; Chem. Zentr., 1932, i, 1502).—Equilibrium data for 20° intervals between 100° and 300° have been obtained. Empirical relations connecting pressure, temp., and composition are given for each mixture.

L. S. T.

Vapour pressures of aqueous solutions of lithium nitrate and activity coefficients of some alkali salts in solutions of high concentration at 25°. J. N. PEARCE and A. F. NELSON (J. Amer. Chem. Soc., 1932, 54, 3544—3555).—The v.p. of aq. solutions of LiNO_3 and of five alkali halides have been determined for concns. from 0.1*M* to saturation by Pearce and Snow's method (A., 1927, 302). The activity of the solvent, the mean activity coeffs. of the ions, and the free energy changes accompanying the transfer of solute and solvent are tabulated.

CH. ABS. (c)

Calculation of the affinity of vaporisation on the plates of a rectifying column. (MLLE.) G. SCHOOLS (Bull. Acad. roy. Belg., 1932, [v], 18, 730—736).—Mathematical; an extension of de Donder's theory of affinity to the problem of distillation. Calculations have been made for a mixture of PhCl and PhBr.

W. R. A.

Formation of molecular additive compounds from observations of ultra-violet absorption spectra. N. G. RUIZ (Anal. Fís. Quím., 1932, 30, 561—563).—The displacement of the absorption bands for solutions of COPh_2 , camphor, PhOH, and resorcinol in CHCl_3 , as compared with solutions in H_2O or EtOH, indicates that additive compounds are formed between the solute and CHCl_3 .

H. F. G.

Solvent influence. V. Dipole moment of solvents and rotatory power of dissolved menthyl dialkylmalonates. H. G. RULE and J. T. R. RITCHIE (J.C.S., 1932, 2332—2340).—Measurements have been made of the rotatory powers, $M[\alpha]$, of *l*-menthyl oxalate, phthalate, acetate, and malonates of the type $\text{C}_{10}\text{H}_{19}\text{O}_2\text{C}\cdot\text{CR}_2\cdot\text{CO}_2\text{R}'$, where $\text{R}=\text{H}$, Me, Et, Pr, or Bu, and $\text{R}'=\text{C}_{10}\text{H}_{19}\text{O}_2\text{C}$ or H, in 12 org. solvents, and of the Na salts ($\text{R}'=\text{Na}$) in EtOH.

For the dimethyl esters ($\text{R}'=\text{C}_{10}\text{H}_{19}\text{O}_2\text{C}$), $M[\alpha]$ falls as the alkyl chain R becomes longer, except when $\text{R}=\text{Pr}$, in which case exceptionally high vals. are obtained in liquids of low polarity. The variation of $M[\alpha]$ with change in the solvent is greatest when R is large. In the case of the phthalate, acetate, and dipropyl- and dibutyl-malonates, $M[\alpha]$ falls regularly with increase in the polarity of the solvent, but no such regularity is observed with the other compounds. Cryoscopic measurements of the mol. wt. of the oxalate and dibutylmalonate in C_6H_6 indicate that no association occurs. Di-*l*-menthyl oxalate was obtained in two forms. On cooling the molten substance in $\text{CO}_2\text{-Et}_2\text{O}$, an unstable form, m.p. 39°, separates. This form can be recryst. from light petroleum, but on keeping for 2 months reverts to the normal form, m.p. 68°, b.p. 222—224°/11 mm. Both forms give the same val. for $M[\alpha]$, so that the difference is attributed to dimorphism. The following compounds were prepared by the methods previously employed for their lower homologues (A., 1930, 1558): di-*l*-menthyl dipropylmalonate, m.p. 94°; *l*-menthyl hydrogen dipropylmalonate, m.p. 41—42°; di-*l*-menthyl dibutylmalonate, m.p. 58°; and *l*-menthyl hydrogen dibutylmalonate, a syrup.

D. R. D.

Magnetic susceptibility of mixtures of acetone and chloroform and of trichlorobutyl alcohol. B. CABRERA and A. MADINAVEITIA (Anal. Fís. Quím., 1932, 30, 528—539).—The susceptibility of mixtures of COMe_2 and CHCl_3 is a linear function of the composition. Vals. are also recorded for trichlorobutyl alcohol, COMeEt , Bu^nOH , *sec.*- and *tert.*- BuOH , and Pr^nOH . For the first-named, the susceptibility is somewhat greater than that of an equimol. mixture of COMe_2 and CHCl_3 ; the cause of this difference is discussed.

H. F. G.

Magnetic study of colour changes in cobalt chloride. S. S. BHATNAGAR and A. N. KAPUR (J. Indian Chem. Soc., 1932, 9, 341—346).—The val. of the Weiss magneton no. for the red Co^{++} in H_2O solution is 25, confirming Chatillon's conclusion (A., 1928, 454). When $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ is dissolved in EtOH the no. varies between 22 and 23, according to the concn. of the solution. Vals. below 25 are also found in MeOH and $\text{C}_5\text{H}_{11}\text{OH}$. These changes are probably related to the colour changes in Co solutions and indicate the presence of different ions. In HCl solutions the val. lies between 22 and 24. This is not due to the production of anhyd. CoCl_2 or $\text{CoCl}_2\cdot 2\text{H}_2\text{O}$, as the no. for these salts is practically 25 and is also high for CoCl_2 in H_2SO_4 (A., 1929, 862). The effect is attributed, therefore, to the formation of $(\text{CoCl}_3)'$ and $(\text{CoCl}_4)''$.

M. S. B.

Solubility of praseodymium selenate in water. J. N. FRIEND (J.C.S., 1932, 2410—2413).—The solubility is almost const. up to 60°, above which temp. it falls abruptly, the dodecahydrate, $\text{Pr}_2(\text{SeO}_4)_3\cdot 12\text{H}_2\text{O}$, being formed. The existence of the octa- and pentahydrates has been confirmed. Addition of H_2SeO_4 has only a slight influence on the solubility. The solubility curve is closely similar to those of $\text{La}_2(\text{SeO}_4)_3$ and $\text{Nd}_2(\text{SeO}_4)_3$, and recrystallisation of the selenates cannot be recommended as a method for separating Pr, La, and Nd.

D. R. D.

Solubility of the mixed crystals $m(\text{NH}_4)_2\text{SO}_4 + n(\text{NH}_4)_2\text{CrO}_4$ and $m\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + n\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. J. MARKOWSKA (Arch. Min. Soc. Sci. Varsovie, 1930, 6, 11—28).—The diagrams are of Roozeboom's types V and IV, respectively.

CH. ABS.

Solubility of calcium gluconate in presence of sodium phosphate and arsenious acid. F. DE CARLI (Atti R. Accad. Lincei, 1932, [vi], 15, 579—583; cf. this vol., 16).—Data for 20° show that NaH_2PO_4 increases the solubility of Ca gluconate; the double salt $(\text{C}_6\text{H}_{11}\text{O}_7)_2\text{Ca} \cdot \text{NaH}_2\text{PO}_4$ is formed. The solubility of the gluconate is also increased by As_2O_3 .

O. J. W.

Solubilities of amino-acids and proteins. E. J. COHN (Naturwiss., 1932, 20, 663—672).—The solubility of NH_2 -acids and proteins in various solvents is considered with reference to the nature of the ions.

A. J. M.

Micro-determination of reciprocal solubilities. System phenol-water. R. A. SMITH (Mikrochem., 1932, 11, 227—236).—Homogeneous mixtures of the two components are sealed within capillary tubes and the temp. at which turbidity appears on cooling are observed. Measurement of the temp. at which a heterogeneous mixture becomes clear is not recommended, owing to the difficulty of mixing in narrow tubes. Results are given for the system $\text{PhOH-H}_2\text{O}$.

H. F. G.

Distribution of acids between water and several immiscible solvents. R. C. ARCHIBALD (J. Amer. Chem. Soc., 1932, 54, 3178—3185).—The distribution ratios at 25° of the normal fatty acids from HCO_2H to hexoic acid, and of HCl , HClO_4 , H_2SO_4 , and HNO_3 between H_2O and COMeEt or an aliphatic alcohol have been determined.

B. E. T. (c)

Static adsorption isotherms. Adsorption of carbon dioxide by charcoal. L. J. BURRAGE (J. Physical Chem., 1932, 36, 2272—2283; cf. A., 1931, 558).—The isotherm at 25° has been determined between 0.04 and 81 mm.

P. H. E. (c)

Modification of Freundlich adsorption isotherm. W. ROGERS, jun., and M. SCLAR (J. Physical Chem., 1932, 36, 2284—2291).—A form of equation is derived which is particularly suitable for the calculation of equilibrium concns. and pressures and the amount of adsorbent required for total adsorption.

P. H. E. (c)

Adsorption of gases by glass. IX. Nitrous oxide. M. CRESPI (Anal. Fis. Quím., 1932, 30, 520—527).—The adsorption of N_2O on glass at 16° between 253 and 760 mm. has been measured. The correction to be applied to v.d. measurements in a 1-litre vessel is about 6×10^{-5} g. The adsorbed film is probably unimol.

H. F. G.

Pressure to which adsorbed air is subjected on the surface of an adsorbent (charcoal or soil). M. V. CHAPEK (Pedology, Russia, 1931, 26, No. 3, 57—66).—The adsorbed air and H_2O form a multimol. layer on the surface of the adsorbent. The lower layers of the air adsorbed by C are under a pressure equiv. to 64.5 atm., whereas those of the soil are

under a pressure of 5—18 atm. Adsorbed air is similar in composition to atm. air.

CH. ABS.

Adsorption isotherm? S. CASPE (J. Chem. Educ., 1932, 9, 907—909).—Adsorption experiments with animal C before and after prolonged treatment with HCl are recorded.

CH. ABS.

Sorption of alcohol vapours by cellulose and cellulose acetate. S. E. SHEPPARD and P. T. NEW-SOME (J. Physical Chem., 1932, 36, 2306—2318).—The amount of alcohol adsorbed under the saturated v.p. at 30° increases, in general, with the Ac content of the primary acetates, which have a smaller adsorption capacity than *sec.* acetates. Higher alcohols are usually adsorbed and desorbed more slowly than lower alcohols. The no. of mols. adsorbed per g. of adsorbent decreases with the mol. wt. of the alcohol, but is practically const. from BuOH to octyl alcohol.

P. H. E. (c)

Adsorption of cations from ammoniacal solution by silica gel. I. M. KOLTHOFF and C. A. STENGER (J. Physical Chem., 1932, 36, 2113—2126).—With increase in the NH_3 concn. the adsorption of Ca^{++} and Cu^{++} passes through a max. NH_4^+ , Na^+ , and K^+ tend to reduce the adsorption of Ca^{++} and Cu^{++} . The adsorption of aq. Ca ions is similar in character to the adsorption of ammoniacal Cu ions. The ratio NH_3 : Cu in the adsorption of the latter is < 4 .

P. H. E. (c)

Selective adsorption of metallic oxides and their auto-reduction in presence of glycogen. L. HUGOUNENQ and J. LOISELEUR (Bull. Soc. Chim. biol., 1932, 14, 1011—1016; cf. A., 1931, 1091).—The auto-reduction in alkaline solution of "pseudo-colloidal" metallic oxides in presence of glycogen is due to the hydrolysis of a minute part of the glycogen providing reducing sugars. In some cases (e.g., Au) this takes place at room temp., whilst in others warming is necessary, the metal remaining in colloidal solution.

A. A. L.

Adsorption and capillary condensation. G. LINDAU (Kolloid-Z., 1932, 60, 253—263).—The equiv. pressure curves of two vapours or of a vapour at two temp. are linear and independent of the adsorbent. The slope of the curves is not in accordance with the requirements of the capillary condensation theory, but agrees better with that calc. from the potential theory. As saturation is approached, systematic deviations from linearity appear, the curve eventually satisfying the Thomson equation. The deviations mark the beginning of capillary condensation.

E. S. H.

Film which adsorbs atomic hydrogen and does not adsorb molecular hydrogen. K. B. BLODGETT and I. LANGMUIR (J. Amer. Chem. Soc., 1932, 54, 3781—3782).—Discussion of the behaviour of tungsten and Elinvar filaments towards H .

C. J. W. (c)

Effect of X- and γ -radiation on adsorption. G. HARKER (J.S.C.I., 1932, 51, 314—316r).—X-Radiation has no effect on the direct union of C_2H_4 and H_2 , but accelerates the reaction in presence of a Cu catalyst. The amount of H_2 adsorbed by Cu is increased by about 2% under the influence of

X-rays; a similar effect occurs with Pd. These effects are intelligible in the light of Nyrop's views (A., 1931, 1375). The adsorption of Congo-red and methylene-blue by filter paper is retarded by γ -radiation from Ra; in presence of electrolytes the retardation is increased with Congo-red and diminished with methylene-blue. E. S. H.

Adsorptive power of protein-cellulose membranes. J. LOISELEUR and P. MOREL (Compt. rend. Soc. Biol., 1931, 108, 484—486; Chem. Zentr., 1932, i, 1885).—The presence of casein or ovalbumin endows a cellulose acetate membrane with marked adsorptive power for dyes from dil. H_2SO_4 solution; the effect runs parallel with the ratio protein : cellulose. A similar phenomenon is observed with cellulose acetate-casein membranes in $BiCl_3$ solution. A. A. E.

Inhibition of chemical reactions. V. Influence of pyridine and other substances on the absorption of ethylene by sulphuric acid and on the surface tension of sulphuric acid. W. S. E. HICKSON and K. C. BAILEY (Sci. Proc. Roy. Dublin Soc., 1932, 20, 267—279; cf. A., 1928, 718; 1929, 151; 1930, 429; 1931, 438).—The absorption of C_2H_4 by H_2SO_4 is inhibited by $C_{10}H_8$, $PhOH$, piperidine, $m-C_6H_4Me_2$, C_5H_5N , $COMe_2$, $(NH_4)_2SO_4$, quinoline, NH_2Ac , C_6H_6 , NH_2Ph , and H_2O , and is accelerated by $CHCl_3$ and SO_3 . The effects of C_5H_5N , H_2O , and SO_3 , which have been studied in detail, show no discontinuities, and the surface tensions of H_2SO_4 solutions of these compounds are consistent with the view that inhibition takes place in the surface layer of the liquid. J. W. S.

Interfacial tensions between hexane and aqueous salt solutions. M. KIDOKORO (Bull. Chem. Soc. Japan, 1932, 7, 280—286).—Measurements by the capillary-tube and drop-no. methods show that the interfacial tension between H_2O and n -hexane from petroleum (b.p. 68.5° , d 0.6691) is raised by the addition of $BaCl_2$, $BaBr_2$, $NaCl$, KCl , KBr , KI , $CuCl_2$, $AgNO_3$, $Ba(NO_3)_2$, or $[Co(NH_3)_6]Cl_3$. A. G.

Gum surfaces. II. F. V. VON HAHN (Kolloid-Z., 1932, 60, 247—253; cf. this vol., 691).—The spreading of a drop of aq. dye solution containing a surface-active substance increases with the available area of the gum surface on which it is placed up to a crit. val., beyond which increase in the gum surface has no effect. The crit. val. varies with the gum. The spreading is least when the contour of the surface is circular. E. S. H.

Theory of flotation. P. SIEDLER, A. MOELLER, and T. REDDEHASE (Kolloid-Z., 1932, 60, 318—324).—Photomicrographs of the flotation of various minerals show that the particles are held at the surface of the air bubbles, not by edges or points, and do not penetrate the bubble. Ostwald's theory (this vol., 333) is criticised; flotation is not a linear, but a laminar, effect, and the ideal flotation agent is not tri-, but di-affine; it has essentially metallophilic and aerophilic groups, which serve as a union between the solid and gaseous phases. Reduction of surface tension aids the process by providing a large liquid-gas interface. E. S. H.

Theory of flotation. II. W. OSTWALD (Kolloid-Z., 1932, 60, 324—340).—The theory of linear flotation formerly advanced (this vol., 333) is amplified. A reply is made to criticisms (cf. preceding abstract). E. S. H.

Properties of protein films. W. Y. LEE and H. WU (Chinese J. Physiol., 1932, 6, 307—320).—The rate of spreading of films of protein over the surface of aq. solutions varies with the protein. Whilst haemoglobin and serum-albumin spread to their max. areas on 0.1N-HCl in a few min., ovalbumin requires 8 hr. The protein remains entirely on the surface. The max. area occupied by carbamide-denatured ovalbumin is 10,400 sq. Å. per mol., whilst that of natural ovalbumin is 8400 sq. Å., the film thicknesses being 4.1 and 4.8 Å., respectively. For natural ovalbumin, the film area is a max. at p_H 4.8, the isoelectric point; that for carbamide-denatured ovalbumin is a max. at p_H 7.0, which would therefore seem to be the isoelectric point. The compressibility of the albumin film varies with p_H , being a max. at the isoelectric point, at which also the "film viscosity" is a min. The "film tension" of ovalbumin films, measured at varying p_H and pressure, is a linear function of the pressure. The slope $-\Delta\sigma/\Delta P$ varies with p_H , with a max. at the isoelectric point. The significance of these observations is discussed. R. N. C.

Rhythmic crystallisation of melts. I. Factors influencing the phenomenon. J. F. J. DIRRY (J. Physical Chem., 1932, 36, 2354—2361).—Rhythmic crystallisation of thin films has been observed with various aromatic compounds. When supercooling is prevented rhythmic crystallisation stops. Unless an air interface is present, crystallisation is continuous. The thinner is the layer of melt, the more rapid are the pulsations of crystal growth; thick films crystallise continuously. 3:5-Dichloromethyldiphenyl crystallises rhythmically when a thin layer of an Et_2O solution evaporates at room temp. E. J. R. (c)

Method of counting particles. L. H. C. TIPPETT (Proc. Roy. Soc., 1932, A, 137, 434—446).—Counts are made only on zones with few particles, those zones with more than a certain no. of particles being classed together. The mean is estimated from the modified frequency distribution so formed. L. L. B.

True specific gravity of colloid-containing materials such as the bentonites. R. M. WOODMAN (J.S.C.I., 1932, 51, 327—328t).—An attempt is made to determine the true sp. gr. of the bentonites by submersion in liquids causing no swelling. The alkaline bentonites have the greatest densities.

Structure of colloidal particles. S. M. LIEPATOV (J. Appl. Chem., Russia, 1931, 4, 1023—1029).—Pauli's theory is criticised. CH. ABS.

Dispersion of gases in liquids. H. RUDOLPH (Kolloid-Z., 1932, 60, 308—317).—The bubbles formed when air is passed into water through a porous diaphragm have been photographed. As the size of the pores decreases, the bubbles decrease in size, but increase in no. per unit vol., whilst the velocity of rise in the liquid decreases and the rotation and screw-like

motion increase. With increasing pressure of gas the bubbles increase in size up to a const. max. val., whilst the velocity and rotation increase by reason of the expansion on release. The size of the bubbles increases with the height of the liquid column. Reduction of surface tension of the liquid leads to a decrease in size and an increase in the no. of bubbles per unit vol. Quant. relations between these effects are worked out. E. S. H.

Preparation of colloidal silver and gold by means of a continuous high-frequency electrical discharge. A. N. FRASER and J. GIBBARD (Canad. J. Res., 1932, 7, 133—136).—Metal sols may be prepared by passing a high-frequency discharge, of sufficient intensity to produce a continuous spark, between electrodes of the metal under H_2O ; the electrodes are preferably knife-edges 5 mm. long and 1—2 mm. apart. A high-frequency continuous-wave thermionic valve generator circuit is described. Stable yellow (2 mg. per litre) and black (16 mg. per litre) Ag sols free from Ag^+ , and purplish-red Au sols have been prepared by this method, without addition of a protective colloid. H. F. G.

Preparation and properties of highly concentrated sols. I. R. N. MITTRA and N. R. DHAR (J. Indian Chem. Soc., 1932, 9, 315—327).—Highly conc. sols of Fe, Al, and Cr hydroxides, containing 0.5063, 0.5255, and 0.8356 mol. of the respective oxides per litre, have been prepared. The sols cannot be freed completely from peptising substances, even by hot dialysis, and when purification is carried beyond a certain point they set to a firm gel. The undialysed sol is more stable towards pptg. agents than the dialysed sol of the same concn., and the ratio of the pptg. concns. of uni- to bi-valent ions decreases as the purity of the sol increases. The viscosity is very high for conc. sols and increases with purity (cf. A., 1929, 506, 1234). The viscosity-concn. curves are very steep and resemble those obtained for lyophilic sols. The vals. of the surface tension of Fe and Cr sols are only slightly less than for H_2O , but for Al sol the val. is considerably less. The conc. sols of Al and Cr are reversible colloids, since the air-dried solids swell and pass into the colloidal condition again in contact with H_2O . The empirical formulæ for the solids are respectively, $Al(OH)_3 \cdot H_2O \cdot AcOH$ and $Cr_5(OH)_{12}Cl_3 \cdot 28H_2O$. M. S. B.

Emulsification. J. B. SPEAKMAN and N. H. CHAMBERLAIN (Nature, 1932, 130, 274).—Theoretical. In ordinary emulsification the cybotactic condition of an oil is as important as the magnitude of the interfacial tension and the adsorption at the interface; in scouring processes adhesion phenomena are exceptionally significant. L. S. T.

Mercury emulsions prepared by means of ultrasonic waves. H. B. BULL and K. SOLLNER (Kolloid-Z., 1932, 60, 263—268).—By the action of ultrasonic waves on Hg under H_2O or aq. solutions, emulsions having a particle size 0.5—1.0 μ are formed. The process is aided by multivalent and strongly adsorbable ions, such as citrate. The charge on the particles is positive in pure H_2O ; the positive charge is increased by adding the effective cations, but the

effective anions produce a negatively-charged emulsion. Dispersion also takes place in non-aq. media, the tendency to emulsify being very weak in C_6H_6 , PhMe, and CCl_4 , but strong in viscous liquids containing O, such as olive oil and turpentine. Ga is also dispersed in H_2O under the action of ultrasonic waves, forming positively-charged sols, which are more stable than those of Hg. It is not necessary to melt the Ga, for heat is developed at the surface of the metal under the influence of the waves. E. S. H.

Emulsions. IV. Systems of sodium oleate, phenol, and water. II. J. WEICHHERZ and H. SÄCHTLING (Kolloid-Z., 1932, 60, 298—306).—The viscosities and d of binary and ternary mixtures between 20° and 80° are tabulated. E. S. H.

Conductivity of sodium myristate solutions at various temperatures. P. EKWALL [with B. OTTERSTROM] (Z. physikal. Chem., 1932, 161, 195—210).—The equiv. conductivity, λ , of 0.0008—0.19N aq. solutions has been measured at 17—80°. The λ -concn. curves are anomalous between 0.0015N and 0.006N and between 0.08N and 0.19N. The former anomaly, which becomes less pronounced and shifts towards higher concns. as the temp., T , rises, is attributed to the variation with concn. of the proportions of acid soap and neutral colloid in the solution. As T rises the tendency to form acid soap and the formation of colloid by supersaturation diminish. The second anomaly, which is that investigated by MacBain, does not become less marked as T rises. It is suggested that the formation of neutral colloid in soap solutions may be caused either by supersaturation, which depends on T , or, in the more conc. solutions, by associative forces, which are independent of T . R. C.

Cryolysis of lyophilic colloids. H. B. BULL (Z. physikal. Chem., 1932, 161, 192—194).—Application of Einstein and von Smoluchowski's viscosity equations to existing data (this vol., 337) shows that the freezing of a homogeneous ovalbumin sol causes an increase in the total vol. of the suspended particles, presumably by increase in the amount of bound H_2O consequent on disaggregation of the particles. With a gelatin sol freezing seems to favour aggregation. R. C.

Viscosity of cellulose glycollate. T. NAKASHIMA (J. Soc. Chem. Ind. Japan, 1932, 35, 352—355B).—Cellulose glycollate, prepared according to the method of Sakurada (A., 1929, 430), was rendered ash-free by dialysis, repptd. several times from EtOH, and neutralised with NaOH. The viscosity of an aq. solution of this ester with the addition of NaOH and/or neutral salts has been determined. The relationship between viscosity and concn. is represented by $\eta_s/\eta_0 = 1 + ac$. The influence of the electrolyte on the viscosity is discussed. V. E. Y.

Variation of the rigidity of colloids with temperature. M. M. S. VENCOV and O. TEODORESCU (Bull. Acad. Sci., Roumaine, 1932, 15, 91—94).—A mathematical discussion. A. G. P.

Colloidal, ferromagnetic ferric oxide as a biological indicator. O. BAUDISCH and W. H.

ALBRECHT (Naturwiss., 1932, 20, 639).—Magnetic susceptibility measurements for colloidal H_2O solutions of $\gamma\text{-Fe}_2\text{O}_3$ have been made. The magnetisation varies linearly with Fe content. The ferromagnetism of the oxide is influenced by dilution. W. R. A.

Stability of negative and positive silver halide and thiocyanate sols. A. BASINSKI (Kolloid-Beih., 1932, 36, 257—349).—Sols of AgCl , AgBr , AgI , and AgCNS have been prepared by the interaction of aq. AgNO_3 and the corresponding K salt. Negative sols are formed when the K salt is in slight excess, and positive sols when AgNO_3 is in slight excess. The order of stability of both positive and negative sols is $\text{AgI} > \text{AgBr} > \text{AgCl} > \text{AgCNS}$. Positive AgCl sols are more stable than the negative AgCl sols at all concns. of electrolyte, but negative AgI sols are more stable than positive AgI sols. Negative AgI and AgBr sols are also stabilised by K salts having the anions Cl' , Br' , I' , CN' , CNS' , $\text{Fe}(\text{CN})_6'''$, $\text{Fe}(\text{CN})_6''''$, but not by those containing HF_2' , NO_3' , ClO_4' , MnO_4' , $\text{C}_2\text{O}_4''$, CO_3'' , SO_4'' , CrO_4'' , or $\text{Cr}_2\text{O}_7''$. The amount of Ag salt dispersed increases with increasing concn. of stabilising K salt up to a max., KCNS being the most effective. At higher concns. the K salts have a coagulating effect. The amount of sedimentation of the Ag salt is related to the time by an S-shaped curve; the rate of sedimentation is low at first, then increases rapidly, and again falls. As the excess of K salt present is increased, the sedimentation velocity rises in a short time to a max. The charge on the particles of positive Ag halide sols in excess of AgNO_3 falls gradually to 0 when the sol is diluted, and at great dilutions a const. negative val. is reached. The charge on the particles of both positive and negative sols is lowered by diluting the sol with the ultrafiltrate. In all the sols examined, the charge decreases with time, indicating the formation of secondary from the primary particles. E. S. H.

Lyophilic colloids. XV. Influence of high concentrations of electrolyte on sols of amylum and gum arabic. H. R. KRUYT and H. J. EDELMAN (Kolloid-Beih., 1932, 36, 350—384; cf. A., 1931, 796).—When progressively-increasing, small concns. of electrolyte are added to a sol of amylum, the viscosity of the sol is rapidly reduced. As more electrolyte is added, the viscosity generally passes through a min. and then rises at a rate which depends on the ions present. In the case of Li_2SO_4 , MgSO_4 , and BeSO_4 (which salt out the colloid) the viscosity continues to fall slowly, probably in consequence of dehydration. The increase of viscosity due to higher concns. of other electrolytes follows the lyotropic series and is apparently due to increasing hydration of the amylum particles. With gum arabic sols the addition of increasing quantities of electrolytes causes the viscosity to fall at first rapidly and then slowly to a const. val. E. S. H.

Influence of temperature on the coagulation of sols of silver halides and of arsenic trisulphide. T. KATSURAI (Bull. Chem. Soc. Japan, 1932, 7, 257—259).—Sols of Ag halides are most stable to heat when prepared from an excess of halide, and increase in stability in the order AgCl , AgBr , AgI ; the last is fully coagulated only at 200° . Sols of As_2S_3 freed

from H_2S coagulate almost completely at 200° , whereas in presence of H_2S dissolution occurs at 180° . A. G.

Electrolyte coagulation of colloids. XII. Second phase of the coagulation of arsenious sulphide sols. A. J. RABINOVITSCH and D. T. VASSILIEV (Kolloid-Z., 1932, 60, 268—273; cf. A., 1929, 1143).—The first stage of coagulation of As_2S_3 sols consists of exchange of added cations with the H' of the sol particles; the second stage is the visible clotting of particles. The action of dil. solutions of KCl , BaCl_2 , and AlCl_3 on As_2S_3 sols was observed over periods of 4—9 months. The concn. of electrolyte required to coagulate the sols is not equiv. to $[\text{H}']$ liberated from the sol; in the case of KCl this is due to feeble displacement of adsorbed H' , and with AlCl_3 it is due to hydrolysis. The second stage of coagulation is traced to an electrostatic compression. E. S. H.

Physico-chemical properties of sulphite-chromium complexes. E. PREIS (Vestn. Kozhev. Prom. Torgov., 1929, 692—695).—The complex obtained by adding Na_2SO_3 to $\text{Cr}(\text{OH})\text{SO}_4$ is most stable at p_{H} 7. Migration to the anode starts at 1.3 mols. SO_3 per mol. at p_{H} 8.4, or 2.0 at p_{H} 7. The point of change to negative charge corresponds with that of max. Cr fixation by hide powder; this max. is also shown by a solution 2 days old. SiO_2 gel and cellulose do not fix Cr, but reversibly adsorb a little; gluten adsorbs it irreversibly. Activated C gives a characteristic adsorption curve without max. Cr solutions containing 0.25—100 mols. SO_3'' give characteristic absorption spectra; at least two Na_2SO_3 -Cr complexes are formed. CH. ABS.

Volume relations in the system cellulose-water. E. FILBY and O. MAASS (Canad. J. Res., 1932, 7, 162—177).—The sp. vol. of cellulose has been determined by allowing He to expand into, or from, a vessel containing the specimen, the pressure changes being measured. The method is more accurate than gas injection methods and allows a correction to be made for adsorption of the gas. The sp. vol. of cellulose is 0.64 c.c. The sp. vol. of the system cellulose- H_2O vapour is much smaller than that calc. additively when the H_2O content is $<4\%$; with further increase of the H_2O content the apparent density of the H_2O falls, becoming normal at about 8% . It is suggested that the first H_2O adsorbed combines chemically, with contraction of the system, and that further addition of H_2O increases the cellulose surface and consequently the contraction, until finally normal liquid H_2O begins to fill the capillaries of the cellulose. The relation of the results to the difference between the adsorption and desorption isotherms, and to the process of paper-making, is discussed. H. F. G.

Heat capacity measurements in gelatin gels. I. W. F. HAMPTON and J. H. MENNIE (Canad. J. Res., 1932, 7, 187—197).—The heat capacities of dry gelatin and of gelatin containing 12.5 and 24% H_2O have been determined. The problem of calculating from such data the amount of bound H_2O is discussed, and a new equation for this purpose is derived. In an 87.5% gel probably all the H_2O is bound, but in a

24% gel the bound H_2O (g. per g. of dry gelatin) falls continuously from 0.69 at -3° to 0.24 at -78.5° .

H. F. G.

Changes caused in isoelectric gelatin by the action of neutral salts. A. SCALA (*Annali Igiene*, 1931, 41, 325—336; *Chem. Zentr.*, 1932, i, 1639).—Changes in p_H caused by the addition of acids, bases, and neutral salts to isoelectric gelatin are recorded; the changes in swelling power are also described.

A. A. E.

Diffusion velocity in gelatin gels as a function of the viscosity of the dispersion medium. E. HATSCHEK (*Kolloid-Z.*, 1932, 60, 273—276).—The velocity of diffusion of K_2CrO_4 in gelatin gels with aq. glycerol as dispersion medium deviates a little from the inverse sq. root viscosity relation and the deviation increases with the concn. of glycerol. It is suggested that the "solid" phase is hydrated to a smaller degree in presence of increasing amounts of glycerol, causing a widening of the channels for diffusion and a reduction of the viscosity of the original dispersion medium.

E. S. H.

Reversible sol-gel transformation, "crystallisation" of gelatin, and the fine structure of elastic gels, especially of gelatin and caoutchouc, in the light of Röntgen optics. O. GERNGROSS, K. HERRMANN, and R. LINDEMANN (*Kolloid-Z.*, 1932, 60, 276—288).—An apparatus is described by means of which X-ray interference photographs of gelatin can be taken during the sol-gel transformation. As the swelling and H_2O content increase the interference lines gradually disappear. This is due to distortion of the lattice by the H_2O taken up, for interference rings reappear when the swollen gelatin is stretched. The particles of gelatin are regarded as long polypeptide chains, three-dimensional in the middle and unidimensional towards the ends. When the gelatin is stretched the particles are brought into parallel positions and partial valency linkings come into operation, thus explaining the development of heat. An X-ray diagram can be obtained from the sol just above its setting point, showing that the three-dimensional micelles still exist, but at higher temp. these break up into single polypeptide chains. This state of disaggregation of the particles can be fixed by pouring the hot sol into a plate kept at 100° , so that H_2O evaporates; the dried gelatin then gives no interference figures. On the addition of H_2O a rearrangement takes place and X-ray interference is again obtained. The crystallinity of gels of gelatin and caoutchouc increases with the age of the gel consistently with the increase in solidity; the crystallinity is destroyed by vigorous stirring. The caoutchouc micelle is regarded as similar to that of gelatin, but the three-dimensional kernel is much smaller and accounts for the greater elasticity. When unstretched, the caoutchouc cannot give an interference diagram, by reason of its small kernel, but in the stretched condition the parallel orientation of micelles causes interference.

E. S. H.

Formation and decomposition of urate gels. E. G. YOUNG and F. F. MUSGRAVE (*Biochem. J.*, 1932, 26, 941—953).—The optimal temp. for supersaturation is $80-90^\circ$. The degree of cooling required to produce

gelation varies with the concn. of urate between 0° and 40° . The limiting concns. have been determined for different urates: for Na urate gels between p_H 5 and 8.5, K urate between p_H 6 and 11.5, and Li urate between p_H 6 and 12. There is a shift to the basic side in the formation of gels. The dissociation consts. for uric acid are $K_a=8 \times 10^{-6}$, $K_a=7 \times 10^{-10}$ and a possible $K_a=6 \times 10^{-11}$. Some org. bases form supersaturated solutions with uric acid which ultimately undergo gelation under the usual conditions; others form gels only in the presence of traces of NaCl or KCl. These gels crystallise, with one exception, in the course of a few min. to several weeks, depending on the nature of the base and the concn. of uric acid used. The cryst. deposits consist of 2 mols. of acid and 1 mol. of base.

S. S. Z.

Properties of proteins in organic solution. J. LOISELEUR (*Bull. Soc. Chim. biol.*, 1932, 14, 1088—1100).—Lipins, proteins, and some carbohydrates form true solutions in HCO_2H , $AcOH$ (less effective), lactic and pyruvic acids either alone, or with the addition of certain auxiliary substances (NH_2 -acids, simple aromatic compounds, HCl , etc.). Dissolution in some cases may also be obtained under sp. conditions with other solvents. Colloidal properties reappear on addition of H_2O . The solubility and stability of the solutions appear to depend on the hydrophilic nature of the solute. Dissolution is due to the formation of sol. complexes with the solvent. Proteins dissolved in anhyd. HCO_2H give a violet coloration on warming, and similar solutions of caseinogen and keratin give "nitro"-derivatives with HNO_3 and HCl at 40° .

A. A. L.

Denaturation of proteins. III. Reversibility of the changes which occur when serum-proteins are adsorbed and eluted. M. SPIEGEL-ADOLF (*Biochem. Z.*, 1932, 252, 37—55; cf. A., 1930, 101).—Complete adsorption of the proteins [serum-albumin (I), pseudoglobulin (II), euglobulin (III)] in 0.2—1.1% solution by $Al(OH)_3$ occurs only when 0.17 g. of the latter is produced from $AlCl_3$ in 10 c.c. of the protein solution by addition of alkali. As regards their adsorbability, the proteins form the ascending series (I), (II), (III). (I) and (II) entirely lose their H_2O -solubility on adsorption by $Al(OH)_3$ or mastic. For removal of the adsorbed proteins by elution 0.01N-NaOH is most suitable. (I) in concns. up to 1.6% can be almost completely removed by elution and (II) can be removed somewhat less completely. Only about 34% of (III) can be removed thus. For (I) and (II) part of the material removed by elution is H_2O -sol. and heat-coagulable, the amount depending on the ratio protein: alkali prevailing during elution. The partly reversible changes which occur on adsorption are similar to those caused by heat or treatment with $EtOH$.

W. McC.

Mobility of protein ions. P. KÖNIG and W. PAULI (*Biochem. Z.*, 1932, 252, 325—342).—The velocity of migration of protein ions (egg- and serum-albumin and pseudoglobulin) in electrolyte-free aq. solution on addition of varying amounts of strong acid and alkali has been measured and a series of curves indicates the variation of mobility with the amounts of combined acid and alkali.

P. W. C.

Physical chemistry of lipins. I. Swelling and specific anion action. M. SPIEGEL-ADOLF (Klin. Woch., 1932, 11, 185—186; Chem. Zentr., 1932, i, 2190).—Bromides reduce the viscosity of 1% lecithin and lecithin-protein (serum-albumin and -pseudoglobulin), but not of protein, sols; the effect exceeds that of Cl⁻, I⁻, CNS⁻, K *d*-tartrate, and K₂B₄O₇. The result is not a sp. ionic effect of Br, but appears to be associated with ease of oxidisability. A. A. E.

Colloidal pectin. S. A. GLIKMAN (J. Appl. Chem., Russia, 1931, 4, 1041—1059).—Pectin has no chemical action on sugar; the influence of sugar on the formation of pectin gels is due to the weakening of the association characteristics of H₂O mols. Cations have a considerable effect on the gel-forming properties of pectin. The dimensions of the micelles remain unchanged, and the differences must be due to changes in the composition of the dissolved pectin. The *p*_H is important; when the *p*_H is high the properties of different acids need separate investigation.

CH. ABS.

Union of biocolloids. VII. Protein and nucleic acid and their degradation products. S. J. VON PRZYLECKI and M. Z. GRYNBERG (Biochem. Z., 1932, 251, 248—265).—The combination between albumin and yeast-nucleic (Na salt), guanylic, adenylic, xanthylic, and cytidinic acids, adenosine, guanosine, guanine, xanthine, and KH₂PO₄ has been investigated. The formation of a salt (union of NH₃⁺ and PO⁻) with albumin and nucleic acid and phosphorylated nucleotides occurs at a *p*_H lower than the isoelectric point of the albumin. At the isoelectric point union with nucleic, adenylic, and cytidinic acids occurs only by double salt formation (union of CO₂H of albumin with NH₂ group of adenine and cytosine), the NH₃ group being still dissociated at *p*_H 5.6. All other combinations, e.g., between protein and the free purines, nucleosides, and phosphorylated substances at a *p*_H greater than the isoelectric point of albumin, are non-chemical in nature. P. W. C.

Isoprene and caoutchouc. XL. Elasticity of caoutchouc. H. STAUDINGER (Kolloid-Z., 1932, 60, 296—298).—The double linking plays no part in the elasticity of caoutchouc, for hydrocaoutchouc is also elastic. The length of the mol. is probably the determining factor. E. S. H.

Free energy of water, carbon monoxide, carbon dioxide, and methane. Their metallurgical significance. J. CHIPMAN (Ind. Eng. Chem., 1932, 24, 1013—1017).—The following expressions are derived for the mol. heat capacities of substances over the range 300—2300° abs.: H₂ 6.70 + 0.0007*T*, N₂, O₂, and CO 6.50 + 0.0010*T*, H₂O 7.20 + 0.0027*T*, CO₂ 7.40 + 0.0066*T* - 1.50 × 10⁻⁶*T*², CH₄ 3.60 + 0.0180*T* - 4.20 × 10⁻⁶*T*². The free energies obtained are: (1) H₂ + 0.5O₂ = H₂O (gas) - 57,120 + 2.75*T* log *T* - 0.00075*T*² - 6.65*T*, (2) C (graphite) + 0.5O₂ = CO - 27,070 - 2.05*T* log *T* + 0.00225*T*² - 0.20 × 10⁻⁶*T*³ - 7.92*T*, (3) C (graphite) + O₂ = CO₂ - 94,210 + 0.30*T* log *T* - 0.0003*T*² + 0.05 × 10⁻⁶*T*³ - 0.94*T*, (4) C (graphite) + 2H₂ = CH₄ - 15,320 + 11.00*T* log *T* - 0.0058*T*² + 0.50 × 10⁻⁶*T*³ - 50.94*T*. E. S. H.

Dissociation constant of acetic acid. C. W. DAVIES (J. Amer. Chem. Soc., 1932, 54, 3776—3777).

—Correction of MacInnes and Shedlovsky's conductivity data (this vol., 695) for viscosity gives nos. which agree with the "theoretical" vals.

C. J. W. (c)

Limiting mobilities of some univalent ions and the dissociation constant of acetic acid at 25°. A. I. VOGEL and G. H. JEFFERY (Nature, 1932, 130, 435).—The mobility of AcO⁻ is found to be 37.85. Conductivity measurements in SiO₂ cells with 0.0001—0.01*N*-AcOH give a val. of 1.776 × 10⁻⁵ for the thermodynamic dissociation const. of this acid (cf. this vol., 695). L. S. T.

Activity coefficients of barium chloride. R. F. NEWTON and E. A. TIPPETTS (J. Amer. Chem. Soc., 1932, 54, 3779).—E.m.f. data show that the activity coeff., *γ*, of BaCl₂ passes through a max. as the temp. rises (cf. this vol., 467). For a given concn. *γ* is about the same at 45° as at 0°, but at 25° is appreciably greater. C. J. W. (c)

Relations between structure and strength of certain organic bases in aqueous solution. N. F. HALL and M. R. SPRINKLE (J. Amer. Chem. Soc., 1932, 54, 3469—3485).—The ionisation consts. of 38 org. derivatives of NH₃ have been determined by H electrode measurements. The temp. coeff. of *K*_a/*K*_B varies regularly with the basic strength. The effect of substituents on the strength of bases is comparable with their effects on the strength of acids. Attention is directed to the effect of two Et groups in enhancing basic strength. CH. ABS. (c)

Affinity between asymmetric acids and bases. H. ERLÉNMEYER and K. G. HOFFMANN (Helv. Chim. Acta, 1932, 15, 1140—1157).—At 31.5° the solubilities in EtOH of *l*-strychnine *d*-α,β-dibromocinnamate (*l*BdA) and *l*-strychnine *l*-α,β-dibromocinnamate (*l*BIA) are equal, whilst at temp. above or below 31.5° *l*BdA is more sol. The separation of the latter from a mixture, sometimes observed at room. temp., is due to infection with cryst. nuclei and does not represent a true equilibrium. No resolution is effected by adsorption on animal C. It is concluded that in solution there are no forces affecting asymmetrically the affinity between asymmetric acids and bases. Solubility and conductivity data are given. *l*BdA has *d*₄²⁰ 1.536 ± 0.01 and *l*BIA 1.589 ± 0.01. F. L. U.

Hydrolysis of mercurous sulphate. C. B. HAGER and G. A. HULETT (J. Physical Chem., 1932, 36, 2095—2098; cf. A., 1900, ii, 481; 1902, ii, 74; 1904, ii, 563).—A saturated solution of Hg₂SO₄ in pure H₂O at 25° contains 0.002 mol. per litre of HgHSO₄. The solubility curve of Hg₂SO₄ in aq. H₂SO₄ exhibits slight discontinuities at 0.27 and 0.025 and a marked discontinuity at 1*M*-H₂SO₄. This last corresponds with the disappearance of Hg(OH)₂.Hg₂SO₄ from the solid phase, pure Hg₂SO₄ remaining. The e.m.f. of a Cd cell containing saturated Hg₂SO₄ in 0.1*M*-H₂SO₄ as a depolariser decreases slowly; this is attributed to slow hydrolysis of Hg₂SO₄. J. H. R. (c)

Metastability of elements and compounds as a consequence of enantiotropy or monotropy. XVI, XVII. Precipitation reactions. I, II. E.

COHEN and J. W. A. VAN HENGEL (Z. physikal. Chem., 1932, 161, 161—178, 179—191).—I. The heat of the reaction $\text{AgNO}_3 + \text{KI} \rightarrow \text{AgI} + \text{KNO}_3$ in aq. solution is the same whether the AgNO_3 is added to the KI or the KI to the AgNO_3 , and this is true even if impurities are present. Hence there is no evidence that metastable forms of AgI are pptd.

II. Calorimetric and dilatometric measurements and X-ray examination show that the BaCO_3 pptd. from a mixture of BaCl_2 and Na_2CO_3 is heterogeneous; the proportion of the metastable form diminishes on keeping. R. C.

Effect of pressure on the liberation of gases from metals, with special reference to silver and oxygen. N. P. ALLEN (Inst. Metals, Sept. 1932. Advance copy, 24 pp.).—When Ag saturated with O is allowed to cool in air two arrest points occur on the cooling curve, the first at 951° and the second at $930\text{--}940^\circ$; the latter coincides with the temp. at which "spitting" occurs. During solidification comparatively pure Ag separates at first and the liquid becomes enriched in O until the pressure of O which would be in equilibrium with it is \leq the external pressure; at this stage bubbles of O_2 are evolved, but prior to this there is practically no loss of O_2 . Escape of O_2 can therefore be prevented by the application of sufficient external pressure, in which case the liquid solidifies as a $\text{Ag-Ag}_2\text{O}$ eutectic. The rate of cooling has no effect on the temp. at which spitting occurs, but more O_2 is liberated at slow rates of cooling. The m.p. of Ag is lowered by the presence of O according to the expression $T^\circ = 961 - 22.31P^1$, where P = pressure in atm. The $\text{Ag-Ag}_2\text{O}$ eutectic forms at $500\text{--}600^\circ$; by extrapolation of the m.-p. curve the eutectic point is 507° and 414 atm. Mathematical expressions are derived for calculating the pressure necessary to prevent gas evolution from liquid metals when the evolution is due to solubility changes and when it is due to reactions. For tough-pitch Cu this pressure is 0.5 ton per sq. in. A. R. P.

Irregularities in the behaviour of the systems CaO-SO_2 and CaO-CO_2 . S. BRETSZNAJDER (Rocz. Chem., 1932, 12, 551—556).—At partial CO_2 or SO_2 pressures which are relatively high or low in comparison with the equilibrium pressure, it is found that false equilibria supervene, in which the pressures are respectively $>$ or $<$ theoretical. This effect is ascribed to formation of systems possessing greater surface energy than at true equilibrium. R. T.

Equilibrium diagram of the system PbO-SiO_2 . K. A. KRAKAU and N. A. VAKHRAMEEV (Keram. i Steklo, 1932, 8, no. 1, 42—43).—The system has been examined up to 72 mol.-% SiO_2 . 2PbO.SiO_2 and PbO.SiO_2 are definite compounds, the temp. of crystallisation being 746° and 765° , respectively. The former undergoes polymorphic conversion at 600° . The orthosilicate-metasilicate eutectic temp. is 700° . 3PbO.SiO_2 is metastable below 690° , and forms eutectics also. The $\text{PbO.SiO}_2\text{-SiO}_2$ eutectic is at about 700° . Tridymite and cristobalite are produced during crystallisation of silicates from glasses containing 60—70% SiO_2 . CH. ABS.

Influence of gaseous thermal diffusion on equilibrium measurements on iron-oxygen-hydrogen system. P. H. EMMETT and J. F. SHULTZ (J. Amer. Chem. Soc., 1932, 54, 3780—3781).—Preliminary data are presented to show that the principal cause of discrepancy between the various steam equilibrium consts. for this system is thermal diffusion. This also applies to the Sn-H-O system. C. J. W. (c)

System iron-cobalt-carbon. R. VOGEL and W. SUNDERMANN (Arch. Eisenhüttenw., 1932—1933, 6, 35—38).—The system has been investigated by thermal analysis, magnetic measurements, and micrographic examination of alloys containing up to 5% C. Primary crystals which separate from the liquid may consist of ternary α , ternary γ , or graphite. The eutectic consists of ternary solid solution and either cementite or graphite; the fields in which the cementitic and graphitic eutectics solidify are separated by a narrow field in which both eutectics separate together in proportions which vary according to the rate of cooling and the pressure. In alloys containing up to 80% Co the γ -phase decomposes on cooling into pearlite composed of binary α and graphite or cementite; in alloys with 80—94% Co the γ -phase is stable at room temp. The magnetic transformation occurs in all alloys with $>$ 70% Co at a temp. which rises with increasing Co content and eventually with high C or $>$ 12% Co coincides with the A3 point. With a rate of cooling of 65° per sec. a martensitic structure is obtained in alloys containing $<$ 1.7% C, 2% Co; 1.5% C, 4% Co; 0.9% C, 8% Co, and 0.01% C, 9.5% Co; all alloys containing C and Co above these limits retain a pearlitic structure and none of the alloys shows an austenitic, sorbitic, or troostitic structure. A. R. P.

Equilibrium diagram of the $\text{Fe-Fe}_3\text{C-FeS}$ system. T. SATO (Tech. Rep. Tohoku, 1932, 9, 119—159).—Primary crystallisation and transformation points have been determined by thermal analysis for 75 alloys containing 0—62.1% Fe_3C and 0—89.0% FeS. Isothermal diagrams for the primary crystallisation surfaces of the space model of the ternary system have been constructed. The results, combined with microscopical investigation, have confirmed the existence of the two liquid phases observed by Hanemann and Schildkötter (B., 1930, 242), the upper layer being rich in FeS, whilst the lower layer is rich in Fe and Fe_3C . A binary monotectic reaction takes place in the range covering the primary crystallisation surfaces of $\gamma\text{-Fe}$ and cementite and a monotectoeutectic reaction takes place at 1103° . Thermal analysis indicates two polymorphic transformations in FeS at 135° and 308° , and also in the alloys Fe-FeS and Fe- $\text{Fe}_3\text{C-FeS}$. The crit. points Acl, Ac3, Ar3, Ar1, A2, and A0 have been determined. These are practically the same as for plain C steel, indicating that FeS can be only slightly sol. in γ - and α -Fe. The binary equilibrium diagram for the system Fe-FeS is similar to that found by other investigators. Section diagrams for const. FeS or Fe_3C content and also a projection diagram of the space model of the ternary system have been constructed. A qual. binary diagram for the system $\text{Fe}_3\text{C-FeS}$ has been

deduced from the diagrams of the ternary system. The process of crystallisation for a no. of alloys belonging to the respective fields in the projection diagram has been deduced and changes in alloys have been confirmed by microscopic examination. S appears to be almost insol. in solid Fe. M. S. B.

Equilibria between potassium chloride, sodium chloride, and water from -23° to 190° . E. CORNEC and H. KROMBACH (Ann. Chim., 1932, [x], 18, 5—31; cf. this vol., 339).—There is no evidence of the existence of mixed crystals. E. S. H.

Solubility of the carnallite system. N. S. KURNAKOV, D. P. MANOEY, and N. A. OSOKOREVA (Kali, Russia, 1932, No. 2, 25).—Solubility tables and diagrams are given for $\text{KCl-NaCl-MgCl}_2\text{-H}_2\text{O}$ (25° and 100°), $\text{KCl-NaCl-H}_2\text{O}$, $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$, $\text{KCl-MgCl}_2\text{-H}_2\text{O}$ (25° and 100°), $\text{KCl-H}_2\text{O}$, $\text{NaCl-H}_2\text{O}$, and $\text{MgCl}_2\text{-H}_2\text{O}$ ($10-110^{\circ}$). CH. ABS.

System calcium chloride-magnesium chloride-water at 0° , -15° , and -30° . C. F. PRUTTON and O. F. TOWER (J. Amer. Chem. Soc., 1932, 54, 3040—3047).—Solubility data give no indication of double-salt formation. Only one form of $\text{MgCl}_2\cdot 8\text{H}_2\text{O}$ has been observed. B. E. T. (c)

Equilibrium in the system $(\text{NH}_4)_2\text{SO}_4\text{-Th}(\text{SO}_4)_2\text{-H}_2\text{O}$. A. ROSENHEIM and J. ZICKERMANN (Z. anorg. Chem., 1932, 208, 95—99).—The data for 25° reveal the existence of 3 double salts: $(\text{NH}_4)_6[\text{Th}(\text{SO}_4)_5]\cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_4[\text{Th}(\text{SO}_4)_4]\cdot 3\cdot 5\text{H}_2\text{O}$, and $(\text{NH}_4)_2[\text{Th}(\text{SO}_4)_3]\cdot 5\text{H}_2\text{O}$. The stability increases with increasing proportion of $(\text{NH}_4)_2\text{SO}_4$. E. S. H.

System manganese sulphate-thorium sulphate-water at 30° . New type of double salt. R. M. CAVEN (J.C.S., 1932, 2417—2420).—The stable solid phases are $\text{Th}(\text{SO}_4)_2$, $\text{MnSO}_4\cdot 5\text{H}_2\text{O}$, and the double salt $\text{MnSO}_4\cdot \text{Th}(\text{SO}_4)_2\cdot 7\text{H}_2\text{O}$; the last separates only from solutions containing a large excess of $\text{Th}(\text{SO}_4)_2$ and cannot be recryst. from H_2O . D. R. D.

Phase-rule studies on metallic thiocyanates. II. Systems $\text{AgNCS-NaNCS-H}_2\text{O}$, $\text{AgNCS-KNCS-H}_2\text{O}$, and $\text{AgNCS-NH}_4\text{NCS-H}_2\text{O}$ at 25° . V. J. OCCLESIAW (J.C.S., 1932, 2404—2410).—The following double salts are recorded: $3\text{NaNCS}\cdot \text{AgNCS}$; $\text{NaNCS}\cdot \text{AgNCS}\cdot 2\text{H}_2\text{O}$ (new); $\text{KNCS}\cdot \text{AgNCS}$; $2\text{KNCS}\cdot \text{AgNCS}$; $\text{NH}_4\text{NCS}\cdot \text{AgNCS}$; $5\text{NH}_4\text{NCS}\cdot \text{AgNCS}$ (I). Only (I) can be recryst. from H_2O . The rate of dehydration of $\text{NaNCS}\cdot 2\text{H}_2\text{O}$ (the stable phase at 25°) over CaCl_2 or H_2SO_4 affords no indication of the existence of a lower hydrate at this temp. D. R. D.

Ternary systems. W. F. EHRET (J. Amer. Chem. Soc., 1932, 54, 3126—3134).—The stable double salt $\text{CaCl}_2\cdot \text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ occurs in the system $\text{CaCl}_2\text{-Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ at 25° . There are no double salts in the systems $\text{CaCl}_2\text{-Ca}(\text{ClO}_3)_2\text{-H}_2\text{O}$ and $\text{SrCl}_2\text{-Sr}(\text{NO}_3)_2\text{-H}_2\text{O}$ at 25° or in the system $\text{KNO}_3\text{-Pb}(\text{NO}_3)_2\text{-H}_2\text{O}$ at 0° . B. E. T. (c)

Properties of solutions of calcium chloride and carbamide. F. DE CARLI (Atti R. Accad. Lincei, 1932, [vi], 15, 584—590).—Solubility data at 11° and 25° are recorded. The cryst. compound $\text{CaCl}_2\cdot 4\text{CO}(\text{NH}_2)_2\cdot 2\text{H}_2\text{O}$ can be obtained by slow

evaporation of the corresponding solution. Viscosity and refractivity data indicate that there is no association between CaCl_2 and $\text{CO}(\text{NH}_2)_2$ in solution. O. J. W.

Specific heats of aqueous solutions of formic, acetic, propionic, and *n*-butyric acids. C. R. BURY and D. G. DAVIES (J.C.S., 1932, 2413—2417).—Data are given for concns. up to approx. 30%. For aq. HCO_2H , AcOH , and EtCO_2H the sp. heat falls regularly with increase in concn., but with $\text{Pr}^n\text{CO}_2\text{H}$ there is an abrupt change in slope at a concn. of 13%, due to the formation of micelles. The form of the curve indicates that the heat of micelle formation is small. D. R. D.

Heats of formation of [ternary] water-alcohol mixtures. P. BRUN (J. Chim. phys., 1932, 29, 362—366; cf. A., 1928, 844).—Sp. heats and heats of mixing are recorded for $\text{H}_2\text{O-EtOH-isoamyl alcohol}$ mixtures in the range of complete miscibility. The results are at variance with those of Mondain-Monval (*ibid.*, 1084) in the zone of crit. miscibility. J. G. A. G.

Heats of combustion and formation of carbon monoxide and methane. W. A. ROTH and H. BANSE (Arch. Eisenhüttenw., 1932—1933, 6, 43—46).—Combustion of CO and CH_4 in a brass bomb with an insulated ignition device gave the following results: $\text{CO} + 0\cdot 5\text{O}_2 = \text{CO}_2 + 67\cdot 70 \text{ kg.-cal. at } 20^{\circ}$ and $\text{CH}_4 + 3\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O (liq.)} + 213\cdot 0 \text{ kg.-cal.}$ From these results it follows that the heat of formation of CO from graphite at 20° is $26\cdot 57 \text{ kg.-cal.}$ and that of CH_4 $17\cdot 97 \text{ kg.-cal.}$ A. R. P.

Thermal calculations for determining the reactivity of carbon monoxide. I. A. TREFILIEV and S. A. KOSTRO (Gorni Zhur., 1930, 13, No. 10—11, 11—17).—The "thermal difference" (heat of combustion—sum of heat effects of components) $\times 100/\text{sum of heat effects of components}$, is: C_2H_6 $-7\cdot 07\%$ ($-28\cdot 18 \text{ kg.-cal.}$), C_2H_4 $+4\cdot 72\%$ ($+15\cdot 60 \text{ kg.-cal.}$), C_2H_2 $+19\cdot 32\%$ ($+50\cdot 58 \text{ kg.-cal.}$), CO $+19\cdot 69\%$. It is shown that the expected similarity in the reactivities of C_2H_2 and CO exists. On raising the temp. of distillation of hard coal the CO content of the gases decreases. When cellulose is heated with CO_2 at 30 atm. the pressure progressively decreases, the cellulose becoming extensively oxidised. CH. ABS.

Heat of combustion of methylglyoxal. C. NEUBERG and E. HOFMANN (Biochem. Z., 1932, 252, 440—450).—The heats of combustion of AcCHO , its oxime, $\text{BzCHO}\cdot \text{H}_2\text{O}$, its oxime and BzCO_2H are $345\cdot 7$, $402\cdot 9$, 905 , $970\cdot 4$, and $843\cdot 5 \text{ kg.-cal. per mol.}$ and the heats of dissolution $+10\cdot 3$, $-3\cdot 9$, $-4\cdot 8$, $-?$, and $-2\cdot 44 \text{ kg.-cal. per mol.}$, respectively. The bearing of these vals. on the mechanism of the degradation of sugar is discussed. P. W. C.

Heat of combustion of some mixtures of organic compounds. M. MILONE and P. ROSSIGNOLI (Gazzetta, 1932, 62, 644—655).—Data are given for C_{10}H_8 -phenanthrene, $\text{C}_{10}\text{H}_8\text{-}\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$, salicylic acid- α - and β - $\text{C}_{10}\text{H}_7\text{-NH}_2$, $\text{BzOH-}\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$, C_{10}H_8 -picric acid, anthracene-picric acid. In general, when the equilibrium diagram shows the absence of compound formation, the heat of combustion of the mix-

tures is a linear function of the composition. Cases of compound formation are indicated by corresponding points of inflexion in the heat of combustion-composition curves. O. J. W.

Heat of formation of calcium metasilicate (wollastonite) and ferrous orthosilicate (fayalite). W. A. ROTH and H. TROITZSCH (Arch. Eisenhüttenw., 1932—1933, 6, 79—83).—A calorimeter is described by the aid of which the constituents of slags and cements can be readily dissolved in a mixture of 20% HCl and HF at 77°. From the vals. obtained for CaO, FeO, SiO₂ (α -quartz and amorphous SiO₂), CaSiO₃, and Fe₂SiO₄ the heats of formation of CaSiO₃ and Fe₂SiO₄ from the oxides and α -quartz are, respectively, +21.0 and +10.3 kg.-cal. at 77°, and +20.96 and +9.6 kg.-cal. at 500°. The heat of dissolution of amorphous SiO₂ in 20% HF is 36.44 and of α -quartz 32.93 kg.-cal., whence the heat of transformation of the former into the latter at 77° is 3.51 kg.-cal. A. R. P.

Thermochemistry of metasilicates of calcium and magnesium and of diopside. H. WAGNER (Z. anorg. Chem., 1932, 208, 1—22).—The true sp. heats of α - and β -wollastonite have been determined from 10° to 300° abs., and the mean sp. beats of α -wollastonite, β -wollastonite, clinoenstatite, and diopside from 273° to 1600° abs. At room temp. the heat of dissolution of α -wollastonite in 2N-HCl is 21,270 g.-cal.; that of β -wollastonite is 20,010 g.-cal. No anomalies are shown by the sp. heat-temp. curves. The transformation of α - into β -wollastonite has been examined with reference to Nernst's heat theorem. E. S. H.

Transport number of gold in a gold amalgam. K. SCHWARZ (Z. physikal. Chem., 1932, 161, 231—232).—In 0.1% Au amalgam the Au migrates to the cathode, its transport no. at 25° being 2.7×10^{-7} . R. C.

Transference of water. II. Its dependence on concentration and temperature in the electrolysis of sodium chloride solutions. G. DAVIES, N. J. HASSID, and M. TAYLOR (J.C.S., 1932, 2497—2503).—The transference of H₂O to the cathode during the electrolysis of aq. NaCl has been measured, using CO(NH₂)₂ as non-electrolytic reference substance. The quantity transferred increases with increasing dilution and with falling temp., the variation being too great to be due solely to changes in transport no. or degree of hydration. It is inferred that the ions transport a considerable quantity of H₂O which is not chemically combined. D. R. D.

Conductivity of alkali metal hydroxides in water, and the mobility of the hydroxyl ion. J. GOWORECKA and M. HŁASKO (Rocz. Chem., 1932, 12, 403—415).—At 25° the limiting mol. conductivities are 239.55 for LiOH, 251.0 for NaOH, and 274.9 for KOH. The conductivity coeffs. (λ_v/λ_∞) of these hydroxides are for dil. solutions 1% smaller than the vals. given by Onsager's formula (cf. A., 1927, 517), and increase in the order Li < Na < K (cf. A., 1926, 906). R. T.

Conductivity of alkylated ammonium picrates in aqueous solution at 0°, 25°, and 90°. I. P.

EKWALL (Z. physikal. Chem., 1932, 161, 211—226).—Measurements have been made over a wide concn. range. R. C.

Variation of the potential of a hydrogen electrode with pressure, in the low-pressure region. R. ROMANN and W. CHANG (Bull. Soc. chim., 1932, [iv], 51, 932—938).—The e.m.f. of the cell +Hg|0.1N-KCl saturated with HgCl|0.1N-HCl|(H₂+xN₂)⁻ at 1 atm. and 25° has been measured for partial pressures of H₂ from 1 to 0.001 atm. Down to 0.005 atm. the observed results agree well with theory. D. R. D.

Electrode potentials of iron-manganese alloys. C. WELLS and J. C. WARNER (Trans. Electrochem. Soc., 1932, 62, 233—236).—The electrode potential of Fe-Mn alloys in 0.1M-MnSO₄ when plotted against alloy composition gives a smooth curve over the whole range from 1.8 to 100% Mn. This result is discussed in relation to X-ray and metallographic data. H. J. T. E.

Electrometric studies of the precipitation of hydroxides. V. Tervalent gold chloride solutions. H. T. S. BRITTON and N. E. DODD. VI. Sexavalent uranium chloride solutions. H. T. S. BRITTON and A. E. YOUNG (J.C.S., 1932, 2464—2467, 2467—2469).—V. Measurements of p_H (by means of a glass electrode) and of conductivity during the titration of aq. HAuCl₄ with NaOH indicate that the former behaves as a mixture of HCl and partly hydrolysed AuCl₃. The HCl is neutralised immediately, whilst the AuCl₃ reacts slowly with NaOH, forming NaAuO₂.

VI. Similar data for a solution of U(OH)₆ in aq. HCl, using both glass and quinhydrone electrodes, indicate that the original solution contains UO₂Cl₂, which does not react appreciably with HCl, and that the ppt. produced by NaOH is U(OH)₆. D. R. D.

Deposition potential of some complex oxalates. A. MAZZUCHELLI and U. BACCI (Gazzetta, 1932, 62, 764—774).—Measurements have been made of the deposition potential and of the static potential of the deposited metal for Cr, Fe, Co, Ni, and Cu deposited electrolytically from solutions of their complex NH₄ oxalates. The deposition potentials show a considerable overvoltage, decreasing from Cr to Cu; passivity phenomena are associated with the static potential. O. J. W.

Kinetics of electrode processes. I. Depolarisation effects by hydrogen and oxygen at platinum electrodes. J. A. V. BUTLER and G. ARMSTRONG (Proc. Roy. Soc., 1932, A, 137, 604—621).—On anodic polarisation of a Pt electrode, which has previously been cathodically polarised in a solution saturated with H₂, using c.d. between 0.5 and 30 $\times 10^{-3}$ amp. per sq. cm., two depolarisation processes are observed at potentials more negative than that at which steady liberation of O₂ occurs. They are attributed respectively to electrolytic dissolution of adsorbed or dissolved H₂ and to the formation of a layer of adsorbed O₂. Only one such process, which marks the disappearance of a layer of adsorbed O₂, is observed in the cathodic polarisation of an electrode which has previously been anodically polarised. L. L. B.

Polarographic studies with the dropping mercury cathode. I. Determination of decomposition potential. G. SEMERANO (*Gazzetta*, 1932, 62, 518—538).—A theoretical discussion of the polarisation curves, obtained by the method of Heyrovsky and Shikata, at a dropping Hg cathode. The decomp. potential is taken to be the point of max. curvature on the curve. A method for calculating the resistance of the polarised circuit and the order of the electrolytic process from the polarisation curve is described. O. J. W.

Polarographic studies with the dropping mercury cathode. XXV. Solutions of Ga, Ti, V, Nb, and Ta. S. ZELTZER (*Coll. Czech. Chem. Comm.*, 1932, 4, 319—334).—Current-voltage curves with a dropping Hg cathode show that reduction occurs at the following voltages compared with the normal HgCl electrode. Ga^{III} to metal at -1.08 volts in acid solutions and at -1.5 volts in aq. NH_3 ; no reduction in aq. alkali hydroxides. Ti^{IV} to Ti^{III} at -0.8 volt in acidic, no reduction in alkaline, solutions. V^{IV} or V^{III} to V^{II} at -0.84 volt in acid solutions, at -1.50 volts in aq. NH_3 , and at -1.80 volts in aq. alkali hydroxides; V^{V} oxidises Hg. Nb^{V} at -0.83 volt in aq. HNO_3 but not in aq. HCl or in alkaline solutions. Ta^{V} is not reduced. Ga can be detected in the presence of excess of Al and of equal amounts of In or Zn. Ti can be approx. determined in the presence of Cr, Fe, and Al. V is distinguished from Ti in alkaline solutions. By examination in aq. HCl, aq. HNO_3 , and aq. NH_3 mixtures of Ti, V, Nb, and Ta can be approx. analysed. A. G.

Polarographic studies with the dropping mercury cathode. XXVI. Decrease of hydrogen over-potential effected by traces of platinum. I. ŠLENDYK (*Coll. Czech. Chem. Comm.*, 1932, 4, 335—349).—Current-voltage curves with a dropping Hg cathode show a current increase at -1.0 volt compared with the normal HgCl electrode in aq. HCl containing traces of PtCl_4 . For this purpose a cell is used in which the Hg anode is in a separate compartment. That the current increase is not due to Pt deposition is shown by the voltage at which it occurs, by its excessive amount, and by its increase with increasing $[\text{H}^+]$. It is ascribed to catalysed H_2 deposition, and this large effect of traces of Pt is said to be the cause of irregular results in measurements of H_2 over-potential. In $2N\text{-HCl}$ a concn. of $10^{-7}M\text{-PtCl}_4$ can be detected. Many commercially "pure" salts are shown to contain traces of Pt not present in the natural crude compounds. A. G.

Anodic behaviour of nickel. II. K. GEORGI (*Z. Elektrochem.*, 1932, 38, 714—731; cf. this vol., 1000).—The p.d.-time curves in aq. salt solutions have been determined. Three states of the Ni anode are recognised. The active state is favoured by a low c.d., a small anion, high $[\text{H}^+]$, and temp.; the reverse conditions favour an impoverished diffusion layer next to the anode and cause a transition to a state of higher p.d. At the lowest c.d. the change $\text{Ni} \rightarrow \text{Ni}^{\text{II}}$ takes place at certain active centres on the electrode, whilst H collects on the greater (passive) portion and may be removed by oxidation or other depolarising influences. The second state is charac-

terised by an invisible film of $\text{Ni}(\text{OH})_3$ and the third state by a porous diaphragm of $\text{Ni}(\text{OH})_3$. The effect of the easily-penetrating ions Cl^- and Br^- on the transition from one state to another has been examined; in some cases periodic effects are noted.

E. S. H.

Passivity of metals. VII. Specific function of chromates. T. P. HOAR and U. R. EVANS (*J.C.S.*, 1932, 2476—2481).—The inhibiting effects of different oxidising agents on the corrosion of Fe in H_2O or aq. KCl have been compared. $\text{K}_2\text{CrO}_4 > \text{NaVO}_3 > \text{KMnO}_4 > \text{H}_2\text{O}_2$; the last-mentioned accelerates corrosion under certain conditions. The sp. inhibiting action of CrO_4^{II} is due to the fact that it ppt. Fe completely, the ppt. consisting of hydrated Fe_2O_3 and Cr_2O_3 , which has considerable protective action owing to its gelatinous nature, high sp. vol., close adhesion to the Fe, etc. The sp. protective action of Cr in steel and of Cr pigments is due to the formation of similar films.

D. R. D.

Relation between the two constants of the Arrhenius equation. M. J. POLISSAR (*J. Amer. Chem. Soc.*, 1932, 54, 3105—3111).—The simple collision hypothesis cannot account for all known bimol. reactions. Gas-collision formulae probably do not apply to reactions in liquid solution. An explanation of the linear relation between the consts. in Arrhenius' equation for bimol. reactions in solution is given.

S. L. (c)

Spontaneous inflammability and chemical constitution. C. ZERBE and F. ECKERT (*Angew. Chem.*, 1932, 45, 593—598).—The temp. of spontaneous ignition have been determined for hydrocarbons and compounds containing O in the aromatic, aliphatic, and naphthene series. For each ignition temp. there is a crit. concn. of O_2 and for a given concn. of O_2 there is a min. temp. required. The rule breaks down above the spontaneous inflammability temp. in the case of aliphatic compounds and naphthenes which contain no conjugated double linking. This linking definitely reduces the tendency to spontaneous inflammability. The no. of H atoms is unimportant, except in so far as the general constitution is altered, but the presence of O lowers the temp. of spontaneous ignition of aromatic compounds and raises that of aliphatic compounds.

E. S. H.

Inflammation of air-hydrocarbon mixtures by heated substances. M. AUBERT and A. PIGNOT (*Ann. Off. Nat. Combust. liq.*, 1931, 6, 819—828; *Chem. Zentr.*, 1932, i, 2435).—In contact with Pt heated at a sufficiently high temp., mixtures of 400 c.c. of air with 0.02—0.09 c.c. of hydrocarbon (hexane, cyclohexane, C_6H_6) explode. The lowest ignition temp. of hexane- and heptane-air mixtures is about 300° . The time taken by a mixture to reach the max. temp. depends on the temp. of the Pt wire and on the composition of the mixture.

A. A. E.

Influence of foreign gases on the lower critical oxidation pressure of carbon disulphide. A. RITCHIE, R. R. H. BROWN, and J. J. MUIR (*Proc. Roy. Soc.*, 1932, A, 137, 511—519).—The lower crit. oxidation pressure for $\text{CS}_2 : 3\text{O}_2$ mixtures in presence of A, N_2 , CO_2 , and SO_2 is given by the expression

$p_{CS_2} p_{O_2} [1 + (f D_x^{-1} p_x) / (p_{CS_2} + p_{O_2})] = \text{const.}$, where p_{CS_2} and p_{O_2} are the lower crit. explosion pressures in the presence of pressure p_x of inert gas. D_x is the diffusion coeff. of the chain propagator into the foreign gas. H_2 , CCl_4 , and C_6H_6 do not behave as inert gases and give abnormal results. With H_2 , the main reaction appears to be the $H_2 : O_2$ explosion, with CS_2 acting as an explosion sensitizer.

L. L. B.

Decomposition of diethyl ether at low pressures. O. K. RICE and D. V. SICKMAN (J. Amer. Chem. Soc., 1932, 54, 3778—3779).—In the decomp. at 525° and 462°, with initial pressures of 0.15—200 and 0.8—450 mm., respectively, the graph of the logarithm of the velocity coeff., k , against the logarithm of the pressure falls much less rapidly in the region of the lower pressure than would be expected from the usual theory; the very slight concavity upwards suggests that a second unimol. region is approached at low pressures. The increase in k by H_2 has been verified.

C. J. W. (c)

Homogeneous first-order gas reactions. III. Decomposition of paraldehyde. C. C. COFFIN (Canad. J. Res., 1932, 7, 75—80).—The decomp. of paraldehyde to $MeCHO$ is a homogeneous gas reaction of the first order. Between 209° and 270° and initial pressures of 1.18 and 52.0 cm. the velocity is unaffected by the pressure and only slightly by the presence of Hg , H_2O , or tap grease or by the area of glass surface. The influence of temp. is given by the equation $\log_e k = 34.83 - (44,160/RT)$, the energy of activation being thus 44,160 g.-cal. per mol.

A. G.

Kinetics of reaction between hydrogen peroxide and potassium permanganate in acid solutions. I. W. LIMANOWSKI (Rocz. Chem., 1932, 12, 519—535).—The velocity of reduction of $KMnO_4$ by excess of H_2O_2 in acid solution is $dx/dt = k_1 b(1-x) + k_2 ax(1-x)$, where a and b are the initial concn. of $KMnO_4$ and H_2O_2 , and x is the relative concn. of Mn^{++} .

R. T.

Differing velocity of esterification of the optical antipodes of a racemate using optically active catalysts. R. WEGLER (Annalen, 1932, 498, 62—76).—Treatment of dl - α -phenylethyl alcohol (I) with Ac_2O in presence of CCl_4 and brucine gives an optically active acetate. The rotation of the ester increases with the reaction time to a max. and then decreases (to approx. 0), is always smaller at higher temp., is max. when approx. 0.25 mol. of brucine per mol. of (I) is used, and varies with the solvent and the order of addition of the reagents. The velocity of esterification of (I) is 20 times as great in presence of brucine as in its absence. The results are ascribed to the more rapid esterification of one antipode of (I). The use of $AcCl$ (for Ac_2O) leads to a product which has a final rotation; in this case, one antipode is esterified, whilst the other is partly converted into styrene and α -phenylethyl chloride. (+)- α -Phenylethyl alcohol is esterified more readily with $AcOH$ in presence of CCl_4 and brucine than the (—)-form. dl - α -Phenylpropyl alcohol and "brucine acetate" (from brucine hydrate and Ac_2O in CCl_4) in pyridine or CCl_4 give dextrorotatory esters. dl - α -

Phenylethylamine (II) and $ClCO_2Et$ in CCl_4 containing brucine afford a urethane ($\alpha +3.64^\circ$); the unreacted amine had $\alpha -3.1^\circ$. The unreacted amine from (II) and $PhNCO$ in pinene ($\alpha -33.25^\circ$) had $\alpha +0.25^\circ$.

H. B.

Phenomena accompanying the hydrolysis of sucrose. S. BEZZI (Gazzetta, 1932, 62, 745—755).—In HCl solutions $[H^+]$ increases with the amount of added glucose or invert-sugar, and also during the hydrolysis of sucrose. The increase, therefore, of the velocity not only during the inversion of sucrose but also with increasing sugar concn. is explained by the increase in the catalyst concn., which can be attributed to hydration of H^+ and of the sugars. The calc. degree of hydration of the latter agrees well with the vals. obtained in other ways.

O. J. W.

Rate of decomposition of the normal diazotates. Z. E. JOLLES and W. CAMIGLIERI (Gazzetta, 1932, 62, 720—726).—Curves are given showing the rate of evolution of N_2 at 20° in the decomp. of diazotates of the following bases: NH_2Ph , o -, m -, and p - $C_6H_4Me \cdot NH_2$, o - and p - $NH_2 \cdot C_6H_4 \cdot OMe$, o - and p - $NH_2 \cdot C_6H_4 \cdot OEt$, α - $C_{10}H_7 \cdot NH_2$, and phenylazoxycarbonamide. The rate of decomp. is increased by the presence of alkoxy-groups in the o - and p -positions and of Me in the p -position with respect to the diazo-group, whereas the opposite is the case with diazonium salts.

O. J. W.

Oxidation rates of silicon carbide and graphite powders. A. H. BALLARD and R. R. RIDGWAY—See B., 1932, 841.

Mass rate of reactions in solids. R. S. BRADLEY, J. COLVIN, and J. HUME (Proc. Roy. Soc., 1932, A, 137, 531—541).—An attempt is made to evaluate the effect of progressive nucleation in the reactions $CaCO_3 \cdot 6H_2O \rightarrow CaCO_3 + 6H_2O$ and $KHC_2O_4 \cdot 0.5H_2O \rightarrow KHC_2O_4 + 0.5H_2O$ by means of an analysis of the form of the mass decomp. curves.

L. L. B.

Temperature increment of reaction velocity in heterogeneous reactions. IV. Reactions of cadmium carbonate. K. FISCHBECK and K. SCHNAIDT (Z. Elektrochem., 1932, 38, 731—737; cf. this vol., 577).—The temp. increments of the reactions of $CdCO_3$ with H_2 and with liquid S are each 20 kg.-cal. This val. is < that obtained for CdO , which is more reactive.

E. S. H.

Velocity of dissolution of metals in bromine water. A. BASINSKI (Rocz. Chem., 1932, 12, 536—550).—The velocities of dissolution of Cd , Zn , and Ni in aq. Br are, under similar conditions of temp. and stirring, identical; the temp. coeff. for the interval 15—25° is in all cases 1.43. In the case of Sn and Cu the reactions are: $Sn + Br_2 \xrightarrow{Br_2} SnBr_2 \xrightarrow{Br_2} SnBr_4 \xrightarrow{Sn} SnBr_2$ and $Cu + Br \xrightarrow{Br} CuBr \xrightarrow{Br} CuBr_2 \xrightarrow{Br} CuBr$, the first and third reactions taking place at the metal surface, and the second in solution. Assuming the velocity of the second reaction to be great relatively to that of the first and third, the velocity of the process is given by $K_1 - K_2 = 2.303V \log \{K_1 a - (K_1 - K_2) / S(t_2 - t_1) \times \log \{K_1 a - (K_1 - K_2)x\}$, where K_1 and K_2 are the velocity coeffs. of the first and third reactions, respectively, V is the vol. of aq. Br , S

the area of the metal surface, a the initial Br concn., and x is the concn. of reaction products after t min.

R. T.

Reactions between gas and solid. V. Azotation of calcium carbide and the effect of size of grain on its velocity. T. AONO (Bull. Chem. Soc. Japan, 1932, 7, 274—280).—At 1140° the rate of nitrogenation of grains of CaC_2 is proportional to the surface area of the unchanged part and is unaffected by the outer layer of nitride; at 950° and below the rate is also inversely proportional to the thickness of this layer.

A. G.

Kinetics of reaction $\text{NH}_3(\text{gas}) \rightleftharpoons \text{N}$ (dissolved in $\alpha\text{-Fe}$) + $1.5\text{H}_2(\text{gas})$. G. ENGELHARDT and C. WAGNER (Z. physikal. Chem., 1932, B, 18, 369—379).—The rate is given by $dc/dt = kp(c_e - c)$, where c is the N concn. in the Fe at time t , and c_e the equilibrium concn. when the partial pressure of H_2 in the gas phase is p . Both forward and backward reactions seem to occur in stages, the rate of nitriding probably being determined by the rate of decomp. of NH_3 formed as an intermediate product in the adsorbed film, and the rate of denitriding by the rate of formation of NH_3 .

R. C.

Corrosion and Tammann's resistance limits. X-Ray study of gold-copper single crystals. L. GRAF (Metallwirt., 1932, 11, 77—82, 91—96; Chem. Zentr., 1932, i, 2379).—Strongly oxidising reagents produce a corrosion pattern of pure Au; slightly oxidising, S-containing, or gaseous reagents produce one of mixed crystals rich in Au. The mechanism of the process is discussed.

A. A. E.

Kinetics of the acetylation of cellulose. II. I. SAKURADA.—See B., 1932, 880.

Kinetics of the nitration of cellulose. I. SAKURADA and M. SHOJINO.—See B., 1932, 880.

Dynamics and catalysis of the thermal decomposition of hydrogen carbonates in aqueous solution. VI. Hydrogen carbonate decomposition in the gas stream. VII. Hydrogen carbonate decomposition in boiling calcium, strontium, and barium hydrogen carbonate solutions. R. STUMPER (Z. anorg. Chem., 1932, 208, 33—45, 46—52; cf. this vol., 234, 703).—VI. The velocity of decomp. of $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ in aq. solution depends partly on the rate at which the CO_2 can be removed. Experiments on passing various gases through 0.005*N* and 0.01*N* solutions at 100° show that the acceleration of the decomp. increases with increasing streaming velocity for all the gases and also increases specifically in the order $\text{H}_2 < \text{O}_2 < \text{air}$. The sp. effect is related to various physical properties of the gases. In a stream of CO_2 the decomp. is retarded in the case of $\text{Ca}(\text{HCO}_3)_2$, whilst $\text{Mg}(\text{HCO}_3)_2$ does not decompose even at 100°. A sufficient stream of CO_2 serves to separate a boiling mixed solution of $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$, CaCO_3 being pptd. and $\text{Mg}(\text{HCO}_3)_2$ remaining in solution. When CO_2 is removed by a stream of indifferent gas, the decomp. of $\text{Ca}(\text{HCO}_3)_2$ is bimol.; the decomp. of $\text{Mg}(\text{HCO}_3)_2$ is complicated by hydrolysis of MgCO_3 .

VII. The decomp. of boiling 0.0025, 0.005, and 0.010*N*- $\text{Ca}(\text{HCO}_3)_2$, - $\text{Sr}(\text{HCO}_3)_2$, and - $\text{Ba}(\text{HCO}_3)_2$ with

or without the aid of a gas stream decreases in the order $\text{Sr} > \text{Ca} > \text{Ba}$, bearing a relation to the solubilities of the carbonates. The general course can be represented by $dx/dt = k_2[\text{HCO}_3']^2 - k_1C$, in which the second term is practically negligible. E. S. H.

Ozone as an oxidation catalyst; ozonation of benzaldehyde. E. BRINER, A. DEMOLIS, and H. PAILLARD (J. Chim. phys., 1932, 29, 339—361; cf. A., 1931, 1016; this vol., 235).—The oxidation of PhCHO and its solutions in hexane, petrol, CCl_4 , and C_2HCl_5 by O_3 containing 0.9—8% O_3 and 0—90% N_2 has been investigated by a dynamic and a static method at temp. between -20° and 60°. The additional yield of BzOH produced in a fixed time by a const. gas flow due to catalysis by the O_3 : (a) increases rapidly with O_3 concn. to a max. and then decreases slowly, (b) decreases regularly with falling O_2 concn. (but O_3 consumption increases), and (c) passes through a max. with increasing concn. of PhCHO . O_3 lowers the temp. at which autoxidation of PhCHO becomes appreciable. The yield of BzO_2H increases rapidly during an experiment and tends to a const. val. which, in general, varies concomitantly with that of BzOH . The catalysis is explained on the basis of reaction chains initiated by the interaction of O_3 with PhCHO , and not BzOH , to produce activated BzO_2H capable of reacting with PhCHO , and O atoms which propagate the chains by regenerating O_3 from O_2 .

J. G. A. G.

Spontaneous oxidation of cysteine. E. G. GERWE (Science, 1932, 76, 100).—A reply to criticism (this vol., 129). The autoxidation of cysteine is not due to the presence of Cu, which was shown to be absent by means of Yoe's $\text{K}_4\text{Fe}(\text{CN})_6$ test and by the failure of cyanide to reduce the rate of oxidation. Oxidation is also unaffected by the addition of pyrophosphate, which inhibits the catalytic activity of Fe and Mn, but not of Cu.

L. S. T.

Autoxidation of fatty acids. I. W. FRANKE.—See this vol., 1112.

Relation of adsorption to catalysis. Catalytic union of ethylene and hydrogen. G. HARKER (J.S.C.I., 1932, 51, 323—326t).—Experiments on the adsorption of C_2H_4 and H_2 and catalysis of their union at a surface of Cu distributed on diatomaceous earth show that the activity of the catalyst is promoted by the adsorption of H_2 and degraded by adsorption of C_2H_4 . The reaction occurs at active centres, representing about 1/2000 of the total metal. The active centres are more readily oxidised than the bulk of the metal; admission of a trace of air destroys the activity of the catalyst.

E. S. H.

Catalytic properties of rhenium. H. TROPSCH and R. KASSLER (Mitt. Kohlenforsch.-Inst. Prag, 1931, 13—15; Chem. Zentr., 1932, i, 2420).—Re catalyses the hydrogenation of ethylenic linkings.

A. A. E.

Non-metallic catalysts for hydrogenation and dehydrogenation. II. Catalytic properties of chromium oxide. W. A. LAZIER and J. V. VAUGHEN (J. Amer. Chem. Soc., 1932, 54, 3080—3095).—Amorphous Cr_2O_3 , prepared by pptn. as $\text{Cr}(\text{OH})_3$ or by igniting $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in a vac. or in thin layers

in air, is an active catalyst for the hydrogenation of C_2H_4 , C_3H_6 , and C_8H_{16} and the dehydrogenation of C_6H_{12} (cf. A., 1931, 1376). Cr_2O_3 prepared by igniting the nitrate or oxalate or by reducing higher oxides yields an X-ray diffraction pattern and is inactive. Any treatment inducing the glow phenomenon results in crystallisation of Cr_2O_3 , and destroys its activity towards hydrocarbons, but not to the same extent for MeOH synthesis or alcohol decomp. The capacity of amorphous Cr_2O_3 for activating hydrocarbons is not in harmony with Balandin's mechanism of hydrogenation and dehydrogenation (A., 1929, 519).

J. V. V. (c)

Catalytic oxidation of *n*-propyl alcohol. A. R. DAY and A. EISNER (J. Physical Chem., 1932, 36, 1912—1915).—In the oxidation by air at 350—500°, using mixtures of Ag and Sm_2O_3 as catalysts, the max. yield of EtCHO (76.4%) is obtained with a small rate of flow of the gas mixture and a catalyst containing 0.25% Sm_2O_3 .

J. H. R. (c)

Electrolytic oxidation. I. Electrolytic oxidation of sodium thiosulphate at a platinum anode. S. GLASSTONE and A. HICKLING (J.C.S., 1932, 2345—2356).—The main product of the electrolytic oxidation of $S_2O_3^{2-}$ at a Pt anode in buffered solutions is $S_4O_6^{2-}$. A small amount of SO_4^{2-} is also formed, and this increases with the p_H of the solution. The curve obtained by plotting anode potential against amount of electricity passed indicates that the oxidation apparently takes place at two different potentials, but, although the relative amounts of electricity passing at the two stages can be altered by varying the current, the nature and amounts of the products remain practically const. The addition to the electrolyte of catalysts for the decomp. of H_2O_2 results in a marked decrease in current efficiency for the oxidation and in the quantity of electricity passing at the initial lower potential stage. $Hg(CN)_2$, which is not a catalyst for H_2O_2 decomp., suppresses the lower potential stage, but does not affect the oxidation efficiency. The results may be explained by supposing that OH^- discharged at the anode forms H_2O_2 and part of this is decomposed spontaneously, the rate determining the relative extent of the two potential stages, whilst part reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ and SO_4^{2-} . The anodic oxidation of $S_2O_3^{2-}$ thus appears to be a secondary chemical reaction and not an electrochemical process involving the discharge of $S_2O_3^{2-}$.

M. S. B.

Avoidance of the loss of anodic platinum in the electrolysis of alkaline, especially ammoniacal, solutions. E. REICHEL (Z. anal. Chem., 1932, 89, 411—421).—Loss in wt. of a Pt-Ir gauze anode, observed in solutions containing aq. NH_3 with or without $(NH_4)_2SO_4$, KOH, or KCN, is due to transference of Pt to the cathode. This is prevented by the addition of $N_2H_4 \cdot H_2SO_4$ or $NH_2OH \cdot H_2SO_4$. More accurate results were obtained by adding these substances in the electrolytic determination of Zn, Ni, or Ga in presence of aq. NH_3 and its salts.

M. S. B.

Electrochemical production of sodium hyposulphite. I. M. A. RABINOVITSCH and A. S. FOKIN. II. P. B. SHIVOTINSKI, A. P. MASCHOVETZ,

and A. S. FOKIN. III. P. B. SHIVOTINSKI.—See B., 1932, 840.

Electrolytic oxidation of iodine and of iodic acid. H. H. WILLARD and R. R. RALSTON (Trans. Electrochem. Soc., 1932, 62, 249—263).—Well-stirred suspensions of I in dil. HCl were electrolysed in a diaphragm cell with a Pt anode in the suspension, and a H_2O -cooled Au-plated Cu coil as cathode in 2*N*- HNO_3 , until the anolyte was free from I. HIO_3 was produced with current efficiencies >90%, but to avoid loss through reduction by HCl it is advantageous to continue electrolysis until anodic evolution of Cl_2 ceases; the total current efficiency of HIO_3 production was then 75—88% at 0.11 amp. per sq. cm. At this or higher c.d. the HCl concn. must not be <0.3*N* or else I is not dissolved as rapidly as it is oxidised. If, after completion of Cl_2 evolution, the Pt anode is replaced by one of PbO_2 electrodeposited on Pt gauze, further electrolysis converts HIO_3 almost completely into periodic acid at a current efficiency which approaches 50% if the c.d. is below about 0.2 amp. per sq. cm. Anode potential measurements show that although higher polarisations may be obtained at a Pt anode, scarcely any periodic acid is formed, probably because Pt catalyses its decomp. Commercial I may be used for both of the above prep., for the HIO_3 and H_5IO_6 obtained by evaporation of the anolytes are easily recryst. from conc. HNO_3 .

H. J. T. E.

Deposition of copper in presence of gum arabic. R. TAFT and O. R. BINGHAM (J. Physical Chem., 1932, 36, 2338—2353; cf. A., 1931, 1249).—The mass of cathode deposit, both in neutral and acid solutions of $CuSO_4$, increases with the gum concn. to a limiting val. Deposits in neutral solutions contain more Cu than is obtained in the Cu coulometer placed in series, the proportion of excess increasing with rising temp. The results are interpreted as indicating that Cu oxides and gum are simultaneously adsorbed on the newly-deposited Cu crystals obtained on electrolysis of neutral $CuSO_4$ solutions. From acid solutions gum alone is adsorbed.

C. L. R. (c)

Electrodeposited ϵ -brass. H. KERSTEN and J. MAAS (J. Physical Chem., 1932, 36, 2175—2177).—Solutions containing 40 g. $Zn(CN)_2$, 50 g. NaCN, 30 g. Na_2CO_3 , and 1.5—1.7 g. CuCN per litre, electrolysed at 50° using stainless steel electrodes and a c.d. of 2 amp. per sq. dm., give ϵ -brass. The deposit contains 11.4—21.4% Cu. The lines of the X-ray diagram of the electrodeposited material are not as sharp as those for fused ϵ -brass.

C. L. R. (c)

Electrodeposition of cadmium from cadmium sulphate solutions. I. S. WERNICK.—See B., 1932, 846.

Cathodic disintegration of metallic alloys. III, IV. L. BELLADEN (Gazzetta, 1932, 62, 493—496, 497—503; cf. this vol., 237).—III. Data similar to those obtained previously are given for Bi-Sb and Cu-Sn alloys.

IV. The results of previous papers are discussed. If atoms of a second metal, which increases the unit cell of the alloy, are introduced into a given metallic lattice, the ease of disintegration of the resulting

alloy increases, whether mixed crystals or inter-metallic compounds are formed. Alloys which crystallise in the hexagonal system, with $a=2.70$ Å. approx., are not easily disintegrated and correspond with minima in the disintegration-composition curve. Compounds which crystallise in other systems different from those of the constituents give either a max. or a point of inflexion in the curve. The metal which is disintegrated from definite compounds has the same composition as the alloy. A relation is given between the ease of disintegration and the dimensions of the unit cell of pure metals which are of the same lattice type. O. J. W.

Electrodeposition of chromium, molybdenum, and tungsten. L. F. YNTEMA (J. Amer. Chem. Soc., 1932, 54, 3775—3776).—Preliminary note.

C. J. W. (c)

Electrodeposition of chromium from tervalent chromium salt solutions. II. Chromium acetate, oxalate, and tartrate baths. H. T. S. BRITTON and O. B. WESTCOTT.—See B., 1932, 893.

Control of operations in chromium-plating baths. A. WOGGINZ; J. KORECKY.—See B., 1932, 845.

Electrolysis of red ammonium chromioxalate. A. MAZZUCHELLI and U. BACCI (Gazzetta, 1932, 62, 756—763; cf. this vol., 236).—Investigation of the electrolysis of solutions of $[(\text{H}_2\text{O})_2\text{Cr}(\text{C}_2\text{O}_4)_2]\text{NH}_4 \cdot 3\text{H}_2\text{O}$ under varying conditions of temp., c.d., and time of electrolysis show that this compound is not so suitable as the blue complex salt previously described for the deposition of Cr. O. J. W.

Electrochemical oxidation of molybdenum in potassium hydroxide solutions. M. DEK. THOMPSON and A. L. KAYE (Trans. Electrochem. Soc., 1932, 62, 271—281).—KOH solutions of various concn. were electrolysed in a diaphragm cell with Fe cathode and Mo sheet anode at 25° and various c.d. At low c.d. molybdate is formed with 100% current efficiency, but at higher c.d., especially in more dil. KOH solutions, increasing amounts of oxide mud in which the valency of Mo is 4—5.4 are produced. No O_2 is liberated even at 0.4 amp. per sq. cm. C.d.-anode potential curves for the separate anode reactions are recorded. Curves showing the relation between anode potential at given c.d. and KOH concn. resemble those for Fe-Mn anodes, but no min. is obtained when current efficiency is plotted against KOH concn. (cf. B., 1924, 907).

H. J. T. E.

Electrodeposition of tin. J. J. COLLINS.—See B., 1932, 846.

Electrolytic oxidation of leuco-bases of the triphenylmethane series of dyes. G. H. WHITE, jun. [with A. Lowy].—See B., 1932, 848.

Electric discharges in liquids. II. Arc discharge in water (continued). H. D. CARTER and A. N. CAMPBELL (Trans. Faraday Soc., 1932, 28, 634—644; cf. this vol., 580).—The heat evolved by the arc running at known p.d. and current is about 88% of the energy input as determined by the constant-flow calorimeter described. The rate of evolution of gas increased with the current, and the C cathode

was worn away at a rate inappreciable compared with the C anode. Fe or Cu cathodes had little effect, but with Fe or Cu anodes the rate of gas evolution decreased and hydrated metallic compounds were produced. The $\text{CO}:\text{CO}_2$ ratio in the evolved gases decreases with increase of current and rise of temp. of the H_2O surrounding the arc; the concn. of O_2 is diminished by metallic anodes. The results are discussed and are at variance with the "thermal" theory. J. G. A. G.

Chemical action in glow discharge. IX. Reaction in Crookes dark space and negative glow. A. K. BREWER and P. D. KUECK (J. Physical Chem., 1932, 36, 2133—2140; cf. this vol., 130).—The rate of synthesis of NO_2 is practically zero throughout the Crookes dark space, and is a max. at the beginning of the negative glow and decreases exponentially with the distance from the Crookes dark space. Under 1 mm. pressure the average path over which electrons from the cathode are capable of initiating reaction is 0.36 cm., which shows the no. of positive ions formed per electron in the negative glow to be 3.3. P. H. E. (c)

Influence of stirring on the velocity and temperature coefficient of photochemical reactions. W. V. BHAGWAT and N. R. DHAR (J. Indian Chem. Soc., 1932, 9, 335—340).—An expression has been deduced which indicates that when the ratio between the light absorption and velocity of a photochemical reaction deviates appreciably from unity, stirring leads to increased velocity and decreased temp. coeff. When the ratio is 1, stirring should have no effect. M. S. B.

Photochemical fission of metallic salts dissolved in organic solvents. E. PUXEDDU (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 26; Chem. Zentr., 1932, i, 2293—2294).—In abs. EtOH, HgCl_2 dissociates into $\text{HgCl}+\text{Cl}$; in COMe_2 cryst. Hg_2Cl_2 is formed, whilst in $\text{C}_5\text{H}_5\text{N}$ there is no ppt., the cryst. mass which remains after distillation of the solvent containing $2\text{C}_5\text{H}_5\text{N} \cdot 2\text{HgCl}_2$, m.p. 179° , and $2\text{C}_5\text{H}_5\text{N} \cdot 3\text{HgCl}_2$, m.p. 194 — 195° . HgI_2 dissociates in COMe_2 , and CuCl_2 in Et_2O . A. A. E.

Action of oxides on silver nitrate and gold chloride in light. C. RENZ (Helv. Chim. Acta, 1932, 15, 1077—1084; cf. this vol., 821).—Photo-reduction of aq. AgNO_3 is sensitised by oxides of Al, Y, La, Sm, Er, Pr+Nd, Ce, Zr, Ti, Nb, Bi, W, Cd, and, less strongly, by those of Be, Ta, Th, and In. With Sb_2O_3 the AgNO_3 is unchanged, whilst Sb is formed. Aq. AuCl_3 is photolysed in presence of only some of the above, including Sb_2O_3 .

F. L. U.

Destruction of the latent image by monochromatic light from the whole visible spectrum. J. NARBUTT (Z. wiss. Phot., 1932, 31, 146—151; cf. A., 1930, 1385).—The latent image in photographic plates, exposed, and subsequently desensitised with pinacryptol-yellow, is partly destroyed by exposure to blue light, and to a smaller extent by yellow or red light; undesensitised plates also show the effect weakly. If the desensitiser is removed from treated plates by washing, the emulsion regains some of its sensitivity to light. J. L.

Nature of the latent image for physical development. III. H. ARENS (Z. wiss. Phot., 1932, 31, 125—130; cf. this vol., 821).—The amount of Ag developed in unit time on unit surface of Ag nuclei is not const. The rule that the amount of Ag developed is dependent only on the no. of nuclei per sq. cm. is correct only for nuclei of average wt. $<10^{15}$ g. (which is about the size of nuclei of photographic plates). J. L.

Evaluation and production of orthoactinic radiation. H. BERTLING (Z. wiss. Phot., 1932, 31, 107—124).—The energy vals. of the light from various types of discharge tubes are compared. The abs. vals. can be calc. from photometric results using the mechanical equiv. of light according to Brodhun and Hoffmann, or Ives. Suitable combination of different discharge tubes can be used to give a required orthoactinic radiation. J. L.

Action of light on thallos chloride in presence of ammonia or oxalic acid. E. BAUR and C. RENZ (Helv. Chim. Acta, 1932, 15, 1085—1088).—When illuminated by a quartz lamp, TiCl_3 in presence of aq. NH_3 gives a "photochloride" and HNO_3 , and in presence of aq. $\text{H}_2\text{C}_2\text{O}_4$ a similar photochloride and CO_2 . In neither case is any Ti^{III} compound formed. F. L. U.

Degradation of protein by ultra-violet light. J. P. BECKER and P. SZENDRO (Pflüger's Archiv, 1931, 228, 755—763; Chem. Zentr., 1932, i, 2959).—On irradiation of dialysed ovalbumin solutions free from globulin the characteristic max. at 280 μ disappears; the presence of O_2 is necessary. The products do not give pptn. reactions. A. A. E.

Azeotropy and the preparation of pure compounds. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1932, 12, 567—575).—Theoretical. R. T.

"Triatomic" hydrogen. C. NAEGELI and B. LAMBERT (Helv. Chim. Acta, 1932, 15, 1137—1139).—In experiments on the production of active ("triat.") H by electrical discharge under conditions used by previous workers, positive results (formation of H_2S from S) were obtained only when parts of the apparatus adjacent to the S became electrically charged. F. L. U.

Direct preparation of hydrogen peroxide in a high concentration. J. H. WALTON and G. W. FILSON (J. Amer. Chem. Soc., 1932, 54, 3228—3229).—When O_2 is bubbled into an EtOH solution of hydrazobenzene autoxidation occurs, $\text{NPh}\cdot\text{NPh} + \text{O}_2 \rightarrow \text{NPh}\cdot\text{NPh} + \text{H}_2\text{O}_2$. About 97% of the theoretical yield of H_2O_2 can be obtained. E. G. V. B. (c)

New form of H_2O_2 . K. H. GEIB and P. HARTECK (Ber., 1932, 65, [B], 1551—1555).—The action of H atoms on O_2 at low temp. gives a colourless, glassy solid with the at. ratio H : O :: 1 : 1. At -115° it is partly decomposed with production of normal H_2O_2 . It is regarded as a new form of H_2O_2 , possibly H_2O_2 . H. W.

Lithium cyanide. A. PERRET and R. PERROT (Helv. Chim. Acta, 1932, 15, 1165—1171).—Observations previously recorded (cf. this vol., 238) have

been confirmed and extended. Anhyd. LiCN can be prepared by the action of a mixture of HCN and C_6H_6 (1 : 1) on Li foil. LiCN is very hygroscopic and is readily hydrolysed; m.p. 160° , d_4^{25} 1.0755. Conversion of LiCN into Li_2CN_2 above 300° is measurably rapid only in presence of Fe as catalyst. LiCN is formed when a mixture of LiCl , C, and CaCN_2 is heated at 850° . F. L. U.

Metal cyanamides. A. PERRET and A. M. KRAWCZYNSKI (Helv. Chim. Acta, 1932, 15, 1009—1022).— Na_2C_2 reacts with NH_3 at 300° to give Na_2CN_2 , with intermediate formation of NaNH_2 and C_2H_2 . Above 300° the Na_2CN_2 is slowly converted into NaCN . Up to 68% CaCN_2 was obtained by interaction of CaCO_3 and NH_3 (with or without CO_2) for 6 hr. at 750° ; SrCO_3 and BaCO_3 behave similarly, but not MgCO_3 . CaCN_2 was also obtained from CaO by the action of a mixture of NH_3 and CO at 750° . None of these methods offers any advantage over the usual procedure. F. L. U.

Gurwitsch radiation in simple chemical reactions. L. K. WOLFF and G. RAS (Biochem. Z., 1932, 250, 305—307).—The radiation arises during neutralisation of NaOH with HCl . P. W. C.

Carbonates of copper (MLLE.) S. HEMAR (Bull. Soc. chim., 1932, [iv], 51, 969—974).—The products described as $6\text{CuO}\cdot\text{CO}_2$ (J.C.S., 1862, 14, 70) and $8\text{CuO}\cdot\text{CO}_2$ (Ann. Chim. Phys., 1851, [iii], 33, 75) are mixtures of variable composition (cf. J.C.S., 1909, 95, 1409). D. R. D.

Simple and double carbonates of copper. (MME.) E. POULENC-FERRAND (Bull. Soc. chim., 1932, [iv], 51, 883—902).—The existence of the compounds $\text{K}_2\text{Cu}(\text{CO}_3)_2$ and $\text{K}_2\text{Cu}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$ (A., 1907, ii, 620) has been confirmed. The compound described as $\text{K}_2\text{Cu}(\text{CO}_3)_2\cdot 4\text{H}_2\text{O}$ has the formula $2\text{CuCO}_3\cdot 3\text{K}_2\text{CO}_3\cdot 9\text{H}_2\text{O}$, whilst Groger's $\text{K}_6\text{Cu}(\text{CO}_3)_4$ is really $\text{K}_2\text{Cu}(\text{CO}_3)_2$ contaminated with K_2CO_3 . The results obtained by Benrath (A., 1926, 695) could not be confirmed. D. R. D.

Sulpho-salts of copper and iron. L. CAMBI and L. SZEGO (Atti R. Accad. Lincei, 1932, [vi], 15, 599—602).—The substance $\text{K}_2\text{FeCu}_3\text{S}_4$ described by Schneider consists of a series of solid solutions with a tetragonal lattice, c/a 1.182. They are paramagnetic and contain Fe^{III} . The sulpho-salts of Cu, e.g., KC_2S , KC_4S_3 , and KC_6S_4 , are diamagnetic. O. J. W.

Formation of ammines in aqueous solution. IX. R. RIPAN (Bul. Soc. Stiinte Cluj, 1931, 6, 286—298; Chem. Zentr., 1932, i, 2003).—The following hexamethylenetetramine (X) compounds have been prepared: $\text{Cu}_2(\text{OAc})_4\cdot\text{X}$; $\text{Cu}_3(\text{C}_6\text{H}_4\cdot\text{CO}_2)_6\cdot\text{X}$; $\text{Cu}_3(\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}_2)_6\cdot\text{X}$; $\text{Cu}_3(\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_4\cdot\text{X}$; $\text{Cu}_3(\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_6\cdot\text{X}$; $\text{Cu}_2(\text{m-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_4\cdot\text{X}$; $\text{Cu}_2(\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_4\cdot\text{X}$. A. A. E.

Magnesium sulphide and polysulphides. A. TETTAMANZI (Gazzetta, 1932, 62, 597—600).—The labile sulphides of Mg can be fixed by means of hexamethylenetetramine (cf. A., 1914, i, 1125). The latter acts on a solution of $\text{Mg}(\text{OAc})_2$ and $(\text{NH}_4)_2\text{S}$ to give white crystals of the compound $\text{Mg}(\text{SH})\text{OH}\cdot 2\text{C}_6\text{H}_{12}\text{N}_4\cdot 10\text{H}_2\text{O}$. By using solutions of

MgSO_4 and NH_4 polysulphides the orange-yellow compounds $\text{MgS}_4 \cdot 2\text{C}_6\text{H}_5\text{N}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgS}_5 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 10\text{H}_2\text{O}$ are obtained. O. J. W.

Hydrates of magnesium chloride and preparation of the anhydrous salt from the hexahydrate. W. D. TREADWELL and T. ZURRER (Helv. Chim. Acta, 1932, 15, 1271—1280).—When $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is slowly dehydrated in a circulating stream of dry HCl, it loses H_2O in stages corresponding with hydrates containing 5, 4, 3.5 (new), 2, and $1\text{H}_2\text{O}$. Anhyd. MgCl_2 is rapidly formed at 200° in dry HCl. V.p. of the monohydrate between 100° and 170° are given. Heats of hydration are calc. and discussed theoretically. F. L. U.

Preparation of anhydrous magnesium chloride by action of chlorine on magnesium oxide in presence of carbon. J. G. SCHTSCHERBAKOV and A. K. RASPOPIA (Techn. Urals, 1931, 7, No. 5—6, 16—20; Chem. Zentr., 1932, i, 1939).—Reaction begins at 200° and is nearly complete at 300° , when a product containing 1—1.5% MgO may be obtained. At 500° , with a small excess of Cl_2 , the product contains <0.5% $[\text{MgO}]$. The reaction is $2\text{MgO} + 2\text{Cl}_2 + \text{C} = 2\text{MgCl}_2 + \text{CO}_2$, but the gas contains about 12% CO . A. A. E.

Oxidisability of zinc. I. Influence of nickel on the oxidation of zinc. A. OLIVERIO and O. BELFIORE (Annali Chim. Appl., 1932, 22, 484—493).—The Zn—Ni couple, derived from the action of Zn on solutions of NiSO_4 or NiCl_2 , or from contact of the two metals, liberates H_2 from cold H_2O . If the metals are finely divided, and if the temp. is raised to the b.p., the reaction with H_2O is very vigorous. The couple may be of use for the reduction of org. compounds in neutral media. E. W. W.

Brick-red form of zinc oxide. A. KUTZELNIGG (Z. anorg. Chem., 1932, 208, 23—28).— ZnO dissolves in molten NH_4NO_3 , liberating NH_3 and forming basic Zn nitrate. When the product is heated it deflagrates, leaving brick-red ZnO . The colour is not affected by repeated boiling with H_2O , but it becomes cream after ignition. The brick-red form fluoresces under the influence of ultra-violet light; X-ray analysis does not distinguish it from the white form. E. S. H.

Ammines. Simple selenocynoammines. VI. G. SPACU and C. G. MACAROVICI (Bul. Soc. Stiinte Cluj, 1932, 6, 401—410; Chem. Zentr., 1932, i, 3044).—The following compounds of tellurine (T) and $\text{NHPh} \cdot \text{NH}_2$ are described: $[\text{CdT}(\text{C}_6\text{H}_5\text{N})_4](\text{SeCN})_2$, $[\text{ZnT}_2(\text{C}_6\text{H}_5\text{N})_4](\text{SeCN})_2$, $[\text{MnT}_2(\text{C}_6\text{H}_5\text{N})_4](\text{SeCN})_2$, $[\text{X}(\text{NHPh} \cdot \text{NH}_2)_6](\text{SeCN})_2$, where $\text{X} = \text{Co}, \text{Ni}, \text{Cd}, \text{Zn}$, and Mn. A. A. E.

Solid mercury hydride. K. H. GEIB and P. HARTECK (Ber., 1932, 65, [B], 1550—1551).—The interaction of Hg vapour and activated H at the temp. of liquid air and 0.5 mm. yields mercury hydride, HgH . Decomp. commences at -125° and is complete at -100° . H. W.

Solubility of mercuric sulphide in dilute hydrochloric acid. M. DORENFELDT-HOLTAN (Z. anorg. Chem., 1932, 208, 76—80).—Black HgS is

perceptibly attacked by hot or cold 5% HCl. Red HgS is attacked by hot but not by cold dil. HCl.

E. S. H.

Chlorination of aluminium oxide with chlorine and carbon. W. D. TREADWELL and L. TEREBEST (Helv. Chim. Acta, 1932, 15, 1053—1066).—The main reaction in the chlorination of Al_2O_3 at 550 — 980° is: $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 = 2\text{AlCl}_3 + 3\text{CO}$, the concurrent reaction: $\text{Al}_2\text{O}_3 + 3\text{CO} + 3\text{Cl}_2 = 2\text{AlCl}_3 + 3\text{CO}_2$ proceeding much more slowly. A mechanism is suggested. The heat and free energy of the reaction are calc.

F. L. U.

Carbon prepared by thermal decomposition of benzene in the gaseous phase. U. HOFMANN and E. GROLL (Ber., 1932, 65, [B], 1257—1267).—Light petroleum, b.p. 60 — 70° , is allowed to drop slowly through a vertical quartz tube filled with H_2 and electrically heated, so that the temp. of the gas space is 950° . The "liquid benzene soot" is freed from tar by prolonged, successive extractions with C_6H_6 and COMe_2 . The product formed on the walls of the quartz tube is lustre C. The crude "soot" contains appreciable amounts of H which is not removed by heating in tetrahydronaphthalene or at 500° /high vac.; ignition in H_2 at 950° or oxidation with CO_2 at 950° effects removal, but the former process is accompanied by enlargement of the crystals. The adsorptive power of "liquid benzene soot" as freshly prepared is immeasurably small, but after activation in CO_2 at 950° or, preferably, 850° , it becomes more than half as potent as the best specimens of technical active C. The catalytic activity also approximates to that of the technical product. Controlled degradation accompanied by measurement of absorptive power and size of crystals proves the material to consist uniformly of cryst. particles, so that adsorption is not conditioned by admixed amorphous C. The adsorptive power of lustre C is too small to be measured, but becomes appreciable after grinding with quartz powder and subsequent activation in CO_2 ; retort graphite behaves similarly. Adsorptive power is regarded as a surface property of C, and the differences shown by "liquid benzene soot" and lustre C are attributed to the production of the former in minute, independent crystals, whereas the lustre C crystals are deposited closely together and grow to thick plates. H. W.

Simple and complex iodates of titanium. P. R. RAY and H. SAHA (Z. anorg. Chem., 1932, 208, 100—106).—The prep. and properties of the following compounds are described: $\text{H}_2[\text{Ti}(\text{IO}_3)_2(\text{OH})_4]$, $\text{H}_2[\text{Ti}(\text{IO}_3)_4(\text{OH})_2]$, $\text{H}_2[\text{Ti}(\text{IO}_3)_6] \cdot 2\text{H}_2\text{O}$, and $\text{X}_2[\text{Ti}(\text{IO}_3)_6]$, where $\text{X} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{NHMe}_3$, or NMe_4 . These are analogous to the corresponding compounds of Sn (cf. A., 1926, 1015). d has been measured at 32° in each case. The mol. vols. are in general smaller than the sum of the mol. vols. of the components, the contraction being 8.4% in the K compound. The contraction is smallest in $\text{Na}_2[\text{Ti}(\text{IO}_3)_6]$, but $\text{Li}_2[\text{Ti}(\text{IO}_3)_6]$ shows a slight increase of mol. vol. E. S. H.

Germanium. X. Aluminium germanates. R. SCHWARZ and G. TRAGESER (Z. anorg. Chem., 1932, 208, 65—75; cf. this vol., 584).—Neutral aq. AlCl_3

and Na_2GeO_3 react with pptn. of $\text{Al}_2\text{O}_3 \cdot 2\text{GeO}_2 \cdot x\text{H}_2\text{O}$. The composition of the ppt. is independent of the ratio of the reactants, and its properties are analogous to those of the corresponding Si compound. The nature of binding of the H_2O is zeolitic. At 100° the compound $\text{Al}_2\text{O}_3 \cdot 2\text{GeO}_2 \cdot 3\text{H}_2\text{O}$ is formed. Permutitic compounds are formed by treatment with NaOH . Ge permutites are also formed by reaction between the solutions or melts of Na_2GeO_3 and Na aluminates. In these the H_2O is zeolitic; the cation can be exchanged for Ag^+ .
E. S. H.

Hydrated stannic oxides and sulphides [and basic chlorides]. P. SISLEY and L. MEUNIER (Bull. Soc. chim., 1932, [iv], 51, 939—946).—The formula $\text{Sn}_5\text{O}_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ for parastannyl chloride (A., 1898, ii, 29) is correct, but metastannyl chloride is $\text{Sn}_5\text{O}_8\text{Cl}_4 \cdot 3\text{H}_2\text{O}$, confirming Weber's results (Pogg. Ann., 122, 358). Structural formulæ are suggested. The conditions of pptn. and redissolution of SnS_2 have been investigated, and the existence of $\text{SnS}_2 \cdot \text{H}_2\text{O}$ and H_2SnS_3 has been confirmed. On passing H_2S into aq. $\text{Sn}_5\text{O}_8\text{Cl}_4 \cdot 3\text{H}_2\text{O}$ and leaving for 12 hr., a ppt. is formed of metastannyl sulphide, of approx. composition $\text{Sn}_5\text{O}_8\text{S}_4 \cdot 6\text{H}_2\text{O}$, which is probably a mixture. Parastannyl sulphide, prepared similarly, is a definite compound, $\text{Sn}_5\text{O}_8\text{S}_2 \cdot 9\text{H}_2\text{O}$, which at 120° is converted into the hexahydrate.
D. R. D.

Action of hydriodic acid on stannic oxide. E. R. CALEY (J. Amer. Chem. Soc., 1932, 54, 3240—3243).—With conc. HI the reaction is $\text{SnO}_2 + 4\text{HI} \rightarrow \text{SnI}_4 + 2\text{H}_2\text{O}$. It commences at about 90 – 95° and is rapid at the b.p. Under similar conditions HBr does not react.
E. G. V. B. (c)

Ammonolysis of tin and lead tetrachloride. R. SCHWARZ and A. JEANMAIRE (Ber., 1932, 65, [B], 1443—1448).— SnCl_4 is converted by liquid NH_3 into a compact, colourless substance and thence into a white powder, whereby somewhat more than 8 mols. of NH_3 are absorbed without production of definite ammonates. Exhaustive extraction with liquid NH_3 leaves a compound, $2\text{Sn}(\text{NH}_2)_3\text{Cl} \cdot \text{NH}_4\text{Cl}$, which, when heated at 100° and again washed with liquid NH_3 , passes into the triaminochloride, $\text{Sn}(\text{NH}_2)_3\text{Cl}$, readily hydrolysed by H_2O . It darkens when heated, becoming brown at 270° and yielding a white sublimate, $\text{SnCl}_4 \cdot 2\text{NH}_3$, and the nitrilochloride, SnNCl . The small amount of gas evolved at 360° is almost exclusively N_2 , which continues to be slowly evolved to 600° . At this temp. the residue consists of globules of Sn mixed with the unstable tin nitride, Sn_3N_4 , which commences to decompose as soon as formed.

$(\text{NH}_4)_2\text{PbCl}_6$ is converted by liquid NH_3 into Pb nitrilochloride, PbNCl , obtained, mixed with NH_4Cl , as a spongy, brown powder. Prolonged extraction of this product with liquid NH_3 gives PbCl_2 and a very explosive powder regarded as derived from the hexameric nitrilochloride by loss of PbCl_2 , and thus having

the constitution $\text{N}:\text{PbCl}-\text{N}:\text{PbCl}-\text{N} \gg \text{Pb}$ H. W.

Existence of lead suboxide, Pb_2O . R. FRICKE and P. ACKERMANN (Z. physikal. Chem., 1932, 161, 227—230).—X-Ray examination has shown that the

supposed Pb suboxide is not Pb_2O , but a mixture of Pb with other Pb compounds (cf. this vol., 823).

R. C.

Reaction between phosphorus pentachloride and metallic fluorides. W. LANGE and G. VON KRUEGER (Ber., 1932, 65, [B], 1253—1257).— NH_4F and PCl_5 react violently at 80 – 110° , yielding NH_4PF_6 in max. yield of 67% calc. on PCl_5 used. The product is dissolved in cold H_2O and the nitron salt is pptd. by nitron acetate and converted into the NH_4 salt by addition of aq. NH_3 and extraction of the org. base with CHCl_3 . The alkali salts resemble the perchlorates chemically and the chlorides crystallographically. NH_4Cl and PCl_5 afford the compound $(\text{PNCl}_2)_x$. Anhyd. KF reacts with PCl_5 more quietly than NH_4Cl ; reaction is never quant., but by use of a large excess of KF , the yield of KPF_6 is raised to 80% (calc. on PCl_5 used). The salt is isolable by fractional crystallisation. With NaF reaction is much slower and, in consequence of loss of PCl_5 by sublimation, the yield of NaPF_6 is only 5–6%. With CaF_2 , BaF_2 , ZnF_2 , or PbF_2 reaction proceeds slowly, leading to evolution of PF_5 without production of salts of HPF_6 .
H. W.

Selenium and selenium dioxide and the oxides of nitrogen. E. BARNES (J. Indian Chem. Soc., 1932, 9, 329—333).— SeO_2 and NO do not react between 30° and 315° nor Se and NO below 330° . Se slowly reacts with gaseous NO_2 at 30° forming SeO_2 and NO , and with liquid N_2O_4 at 0° forming SeO_2 and N_2O_3 . SeO_2 is insol. in liquid N_2O_4 . Pure HNO_3 reacts rapidly with Se and does not appear to require the presence of NO_2 as a catalyst.
M. S. B.

Fourth degree of oxidation of molybdenum. II. W. F. JAKÓB and C. MICHAŁEWICZ (Rocz. Chem., 1932, 12, 576—588).—Red $[\text{Mo}(\text{CN})_4(\text{OH})_4]^{4-}$ undergoes hydrolysis to $[\text{Mo}(\text{CN})_4(\text{OH})_3]^{3-}$, which is further hydrolysed to blue $[\text{Mo}(\text{CN})_4(\text{OH})_2]^{2-}$, a no. of salts of which are described. Acids convert this ion into $\text{Mo}(\text{CN})_2(\text{OH})_2$, and this is irreversibly converted by alkalis into $\text{Mo}(\text{OH})_4$, which can also be obtained directly by adding alkali to the product of reaction of the red hydroxycyanide with acids. The reduction potential of $\text{Mo}(\text{OH})_4$ solutions is < that of $\text{Mo}(\text{OH})_3$ or $\text{Mo}(\text{OH})_5$ solutions. Mo^{IV} is converted without the intermediate stage of Mo^{V} into Mo^{VI} on treatment with KMnO_4 .
R. T.

Peruranates. A. ROSENHEIM and H. DAEHR (Z. anorg. Chem., 1932, 208, 81—94).—By treating $\text{UO}_2(\text{NO}_3)_2$ with alkali hydroxides and H_2O_2 the following peruranates have been isolated: $\text{Na}_2\text{U}_2\text{O}_{10} \cdot 4\text{H}_2\text{O}$, $\text{Na}_4\text{UO}_8 \cdot 8\text{H}_2\text{O}$, $\text{Na}_4\text{UO}_8 \cdot 9\text{H}_2\text{O}$, $\text{K}_2\text{UO}_6 \cdot 3\text{H}_2\text{O}$, $\text{K}_6\text{U}_2\text{O}_{13} \cdot 10\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{U}_2\text{O}_{10} \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{U}_2\text{O}_{10} \cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{U}_2\text{O}_{13}$. Guanidine gives $(\text{CN}_2\text{H}_5)_4\text{UO}_8$. Structural formulæ are suggested for these compounds.
E. S. H.

Preparation of chemically pure hydrofluoric acid. V. Y. TARTAKOVSKI (Mn. Svir., 1931, 6, 853—869).— HF solution is distilled with NaF (1.5–2 pts. > that required for neutralisation of H_2SiF_6 and H_2SO_4). The solubility of Na_2SiF_6 in HF in

presence of much NaF is negligible. Cl is removed with PbCO_3 as PbFCl , which is insol. in 40% HF.

CH. ABS.

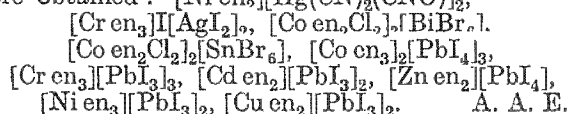
Synthesis of hydrogen chloride. I. G. SCHTSCHERBAKOV and E. A. NIKONOVA (Techn. Urals, 1931, 7, No. 5—6, 20—24; Chem. Zentr., 1932, i, 1939).— Cl_2 (0.4—1.8 pts.) and H_2O vapour (60—100% excess) were passed over C (1 pt.) at temp. up to 350° . The yield of HCl (0.4—0.5% H_2O) varies considerably owing to adsorption of Cl_2 by the C. Experiments were also performed in presence of Fe_2O_3 and at 600° without this catalyst.

A. A. E.

Lower degrees of oxidation of rhenium. E. TURKLEWICZ (Rocz. Chem., 1932, 12, 589—597).— Re^{VII} (KReO_4) is reduced by Cr^{II} to Re^{IV} ; the reaction is catalysed by I^- . $\text{ReO}_2 \cdot x\text{H}_2\text{O}$, pptd. by alkalis from the reduced solutions, yields $\text{K}_3[\text{ReO}(\text{CN})_4\text{OH}]$ on boiling with conc. aq. KCN; in acid solutions this salt yields the ion $[\text{Re}(\text{CN})_4(\text{OH})_2]^-$.

R. T.

Complex salts. IV. G. SPACU and P. SPACU (Bul. Soc. Stiinte Cluj, 1932, 6, 384—395; Chem. Zentr., 1932, i, 3025).—The following compounds were obtained:



A. A. E.

Optically active inorganic salt. F. G. MANN (Naturc, 1932, 130, 368).—Evidence is given for the presence of the *cis*-isomeride in Na diaquorhodium-disulphamide, $\text{Na}[(\text{H}_2\text{O})_2\text{Rh}(\text{NH}_2\text{SO}_2\text{NH}_2)_2]$.

L. S. T.

Behaviour of chelate groupings attached to platinum and palladium. H. D. K. DREW (J.C.S., 1932, 2328—2331).—The diammine, Pt en Cl_2 , and the tetrammines $[\text{Pt en}_2]\text{Cl}_2$ and $[\text{Pt en}(\text{NH}_3)_2]\text{Cl}_2$, are all of the β -types, the chelate grouping being unable to span the α -position, contrary to the behaviour of Pd compounds (this vol., 824). The opening and closing of the chelate group in the Pt compounds by HCl and NaOH, respectively, is in accordance with the theory previously developed, and it can be shown that the positive charges of the cations of the plato-salts and the tetrammines must be located on N atoms in α -positions and not on Pt. Werner's theory of the *trans*-elimination of groups cannot hold for both plato- and pallado-tetrammines at the same time.

M. S. B.

Extraction analysis with two unknowns. H. JESSEN-HANSEN (Z. anal. Chem., 1932, 89, 422—425).—The factors to be taken into account in the determination of a substance by extraction with a solvent from an insol. medium are discussed mathematically.

M. S. B.

Analysis of the anions. F. J. WELCHER and H. T. BRISCOE (Chem. News, 1932, 145, 161—170).—A systematic treatment for the separation of ions is based on a preliminary separation into (a) ions of which the Ba and Ca salts are insol. in H_2O — COMe_2 mixtures; (b) ions with insoluble Zn salts; (c) ions with insoluble Ag salts; (d) the remainder.

J. W. S.

Application of the polarographic method in micro-analysis. J. HEYROVSKÝ (Mikrochem., 1932, 64, 25—64).—A summary of published work.

E. S. H.

Direct titration method on a new principle. I. S. SAITO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 43—48).—A new principle of direct titration takes advantage of two quant. reactions, one producing a less-ionising or insol. two-component compound, the other giving a more stable and much less ionising or more insol. compound of the same two components with a further component.

J. W. S.

Stability of certain volumetric solutions. E. P. HEDLEY (Proc. VI Congr. S. Afr. Sugar Tech. Assoc., 1932, 6—8).—0.1N- KMnO_4 retained its original titre for about 6 months. 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$ showed the same factor for nearly 3 months. 0.1N- As_2O_3 solution, prepared by Kolthoff's directions ("Volumetric Analysis," II, 363), is stable for a long time, and is superior to $\text{Na}_2\text{S}_2\text{O}_3$ as a primary standard.

J. P. O.

Applicability of the antimony electrode. W. BOTTGER and L. VON SZEBELLÉDY (Z. Elektrochem., 1932, 38, 737—742).—Existing forms of Sb electrodes give variable results in measuring the p_{H} of standard buffer solutions. A cast Sb electrode, polished in one direction with emery, and having deposited on it a greyish-black coat of Sb from a solution containing 10% SbCl_3 and 2N-HCl, rapidly acquires its final potential and gives a linear relation with p_{H} . It is suitable for acid-alkali titrations.

E. S. H.

Theory of error of acid-base titration. P. S. ROLLER (J. Amer. Chem. Soc., 1932, 54, 3485—3499).—Equations are formulated by which the accuracy and limiting conditions of titration can be predicted when the end-point is determined colorimetrically or potentiometrically. The error is a simple function of the known error of the colour indicator, or of the potentiometer, and of the concns. and ionisation consts. For an unsymmetrical titration, the error is proportional to the square root of the concn. of the product at the end-point, so that the accuracy may be enhanced by artificially diminishing this concn.

W. T. H. (c)

Poirrier-blue. J. M. OLSEN and F. REIMERS (Dansk Tidsskr. Farm., 1932, 9, 161—177).—The colour change of Poirrier-blue occurs over the p_{H} range about 11—12 in H_2O , 10.0—11.0 in 50% EtOH, and 10.3—11.3 in 75% EtOH. The absorption curves in various media have been determined with the Pulfrich photometer; those in presence of 0.1N-HCl show a marked change from aq. to EtOH solution. Solutions in different concns. of EtOH containing 0.1N- $\text{Na}_2\text{B}_4\text{O}_7$ show a continuous colour progression. Commercial preps. of Poirrier-blue are very impure, but the change occurs at the same p_{H} val.; there is no relation between colour strength and content of ash, H_2O , S, or N. Poirrier-blue can be used as an indicator in the titration of several alkaloid salts in EtOH with 0.1N-NaOH, but it cannot be used for strychnine nitrate.

E. S. H.

Determination of alkalinity in boiler waters. F. G. STRAUB.—See B., 1932, 819.

Determination of hydroxide and carbonate in boiler waters. I, II. E. P. PARTRIDGE and W. C. SCHROEDER. III. L. F. COLLINS and W. C. SCHROEDER.—See B., 1932, 819.

Detection and determination of hydrochloric acid in presence of hydrobromic acid as perchromic acid, chromic oxide, and barium chromate. G. G. LONGINESCU and I. I. PRUNDEANU (Bul. Chim. Soc. Romane, 1931, 34; 5 pp.).—Distillation of the sample with conc. H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ and subsequent oxidation of the CrO_2Cl_2 to the blue perchromic acid provides a very sensitive test for Cl' even in presence of Br' . Determination of the CrO_2Cl_2 as Cr_2O_3 or BaCrO_4 or iodometrically leads to rather high vals. of Cl' content. J. W. S.

Volumetric assay of chlorates. I. Reduction by hydriodic acid in presence of ferrous sulphate. II. Reduction by hydriodic acid in presence of concentrated hydrochloric acid. G. J. W. FERREY (Pharm. J., 1932, 129, 242—243).—I. Contrary to Harvey (A., 1925, ii, 1197), the method (B.P., 1932) gives theoretical results. Either the time or temp. of the reaction may be reduced if the FeSO_4 solution is made more conc. and more strongly acid.

II. Chlorates can be quantitatively reduced by a min. excess of HI in the presence of conc. HCl. Under suitable conditions the action of air on HI is inappreciable. W. S.

Determination of chlorate in nitrates. K. LESNICKENKO.—See B., 1932, 840.

Determination of the oxygen evolved by certain peroxides. R. POGGI (Annali Chim. Appl., 1932, 22, 493—496).—A single vessel contains a tap funnel of dil. H_2SO_4 , a chamber for peroxide, and a trap of conc. H_2SO_4 through which the O_2 evolved can pass. The whole is weighed full of air, the peroxide decomposed, and the O_2 displaced by dry CO_2 -free air; the loss in wt. is the wt. of $\text{O}_2 + \text{CO}_2$ evolved. The CO_2 is trapped and weighed in a second vessel. For testing respirator fillings this method is more suitable than that involving titration by KMnO_4 (cf. A., 1924, ii, 568), which reacts with per-salts.

E. W. W.

Automatic apparatus for the determination of small concentrations of sulphur dioxide in air. III. M. D. THOMAS.—See B., 1932, 841.

Determination of sulphur dioxide when present in low concentration in air. S. W. GRIFFIN and W. W. SKINNER.—See B., 1932, 914.

Reduction indicator. L. MICHAELIS (Biochem. Z., 1932, 250, 564—567).—1:1-Dimethyl-4:4'-dipyridylum chloride, from 4:4'-dipyridyl and Me_2SO_4 by way of the picrate, is normally colourless, but becomes deep blue on reduction, and on titration in alkaline solution with $\text{Na}_2\text{S}_2\text{O}_4$ gives readily reproducible potential curves. The normal potential is sufficiently negative to enable the measurement of reduction intensity of cells to be made under anaerobic conditions. P. W. C.

Determination of selenium in selenious compounds by means of hydrazine and its salts. V. HOVORKA (Coll. Czech. Chem. Comm., 1932, 4, 300—

318).—When H_2SeO_3 is reduced to Se by N_2H_4 in acid solution there is always a small loss, partly as H_2Se and partly mechanical. The amount of H_2Se is min. in the presence of citric acid; in the presence of mineral acids the reaction is faster and the loss greater. A. G.

Detection of nitric acid as fuschin. G. G. LONGINESCU and T. I. PIRTEA (Bul. Chim. Soc. Romane, 1931, 34; 3 pp.).—The PhNO_2 method of detecting HNO_3 is extended by reducing the PhNO_2 to NH_2Ph and converting the latter into fuschin. J. W. S.

Micro-determination of phosphoric acid by means of strychnine molybdate. E. RAUTENBERG (Mikrochem., 1932, 12, 116—117).—Polemical (cf. this vol., 354, 587). E. S. H.

[Micro-determination of phosphoric acid by means of strychnine molybdate.] H. KLEINMANN (Mikrochem., 1932, 12, 118).—A reply (cf. preceding abstract). E. S. H.

Separation of phosphoric acid from calcium and magnesium by means of ammonium molybdate. Z. PERKOWSKI (Przemysł Chem., 1932, 16, 160—161).— PO_4''' is pptd. by Woy's method, and excess of Mo is removed from the filtrate by addition of excess of aq. NH_3 and 3—5 c.c. of $(\text{NH}_4)_2\text{S}_x$. The solution is then made acid with HCl, when MoS is quantitatively pptd. R. T.

Detection of arsenate and phosphate ions. A. I. SHEINKMAN and N. A. GALETZKI (Farm. Zhur., 1932, No. 3—4, 120—121).—The NH_4 molybdate ppt. is boiled until colourless with aq. NH_4OAc ; arsenate produces a white ppt. or turbidity on cooling, and phosphate is tested for in the filtrate.

CH. ABS.

Rapid determination of boron. W. W. SCOTT and others.—See B., 1932, 841.

Determination of silicon in aluminium. L. H. CALLENDAR.—See B., 1932, 844.

Volumetric determination of silica in presence of aluminium and iron compounds. V. TARTAKOVSKI (Min. Svir., 1931, 6, No. 12, 1075—1087).—(1) The silicate or quartz (0.02—0.2 g. SiO_2) is evaporated to dryness with 2N-NaOH (10—20 c.c.) and HF (5—6 c.c.); 1 g. HCO_2Na is added for every 5 c.c. NaOH (to decompose NaHF_2), the solution is evaporated, and the residue dried at 120—130°, and the Na_2SiF_6 titrated hot with 0.5N-NaOH (phenolphthalein). Alkali or alkaline-earth metals, Th, and Pb do not interfere. (2) If other metals (Ce, Ta, Zr, W) or Ti are present the Na_2SiF_6 must first be separated from the residue by adding KCl to 20% concn., then aq. 20% KCl, filtering, and washing the residue with 20% KCl before titration. In presence of Al and Fe, neutral NaF (3—4 g.) is added to the solution (100 c.c.), whereby the action of NaOH on the cryolite-like compounds formed by AlF_3 and FeF_3 is checked. CH. ABS.

Determination of argon. H. COPAUX (Bull. Soc. chim., 1932, [iv], 51, 989—992).—A method is described for the rapid determination of A in mixtures

with O_2 , N_2 , H_2 , etc., these gases being absorbed by means of Li. D. R. D.

Volumetric determination of potassium by the sodium cobaltinitrite method. C. B. MAW and K. R. MILLER (Proc. Utah Acad. Sci., 1931, 8, 61—64).—To obtain a ppt. of uniform composition for treatment with $KMnO_4$ followed by $H_2C_2O_4$ a 3% aq. solution of the reagent should be used and the solution saturated with NaCl. CH. ABS.

Determination of sodium in aluminium. I. Chemical analysis. R. W. BRIDGES and M. F. LEE. **II. Spectrographic analysis.** A. W. PETREY.—See B., 1932, 844.

Direct gravimetric determination of sodium in commercial aluminium. E. R. CALEY.—See B., 1932, 844.

Determination of sodium in aluminium. K. STEINHÄUSER and J. STADLER.—See B., 1932, 892.

Distinction between lithium and strontium by means of their flame colorations. E. MACCIOTTA (Rend. Sem. Fac. Sci. Cagliari, 1931, 1, 55—56; Chem. Zentr., 1932, i, 3324).—A small quantity of the substance on a Pt wire is introduced into the lower part of a Bunsen flame; in presence of Li the whole flame immediately assumes an intense red coloration. If the substance is then moistened with HCl and again heated in the lower part of the flame, in presence of Sr a red spray is produced. Na and Ba must be absent. A. A. E.

Application of spectrum analysis to the determination of alkali and alkaline-earth metals. I. W. H. JANSEN and J. HEYES (Z. physiol. Chem., 1932, 241, 75—87).—The solution is placed in a special form of atomiser whence the vapour passes into a non-luminous C_2H_2 flame. The spectra are photographed and by photometric comparison of the blackening due to the appropriate spectral lines with those obtained from standard solutions, the metal is determined. The results for Na, Li, K, and Ca in a mineral spring water agree well with those obtained by chemical analysis. J. H. B.

Separation and identification of the alkaline-earth metals. P. E. WILLIAMS and H. T. BRISCOE (Chem. News, 1932, 145, 177—184).—The alkaline-earth metals, including Mg, can be separated from the alkali metals as carbonates by addition of $COMe_2$ instead of EtOH. Sr can be separated from Ca and Mg as $SrCrO_4$ or $(p-C_6H_4MeCO_2)_2Sr$ in presence of $COMe_2$. $Ca(NO_3)_2$ is much more sol. in $COMe_2-H_2O$ mixtures than are $Ba(NO_3)_2$ and $Sr(NO_3)_2$.

Gravimetric determination of beryllium and its separation from Fe^{+++} , UO_2^{++} , Th^{+++} , Zr^{+++} , Ti^{+++} , CrO_4^{--} , MoO_4^{--} , Cu^{++} , AsO_3^{--} , SbO_3^{--} , VO_4^{--} , and WO_4^{--} by means of guanidine carbonate. A. JILEK and J. KOŤA (Z. anal. Chem., 1932, 89, 345—354).—The method is similar to that used in the separation of Be from Al except that when VO_4^{--} and WO_4^{--} are present the solution must be made exactly neutral (Me-red) before adding the guanidine (cf. A., 1931, 1024). A. R. P.

4 E

Colorimetric determination of small amounts of magnesium in pure magnesium salt solutions and in presence of calcium. J. TISCHER (Mikrochem., 1932, 12, 65—86).—Mg is pptd. as $MgNH_4PO_4$ and the PO_4 content of the ppt. is determined colorimetrically by a suitable modification of Parker and Fudge's method (B., 1927, 758). The procedure allows the determination of $1-5000 \times 10^{-6}$ g. Mg in 1 c.c. with a max. error of $\pm 2\%$. When Ca^{++} is also present, its pptn. is prevented by adding NH_4 citrate. The amount of NH_4 citrate required to form a stable complex with Ca^{++} increases with the amount of both Ca^{++} and Mg^{++} and it is necessary to allow more time for complete pptn. of $MgNH_4PO_4$. E. S. H.

Titration of zinc salts by means of ferrocyanide solution, and a sensitive reaction for iron. J. GUERON (Ann. Chim. Analyt., 1932, [ii], 14, 393—397).—The slightly acid Zn^{++} solution, containing a trace of $Fe_2(SO_4)_3$, is titrated at $60-70^\circ$ with aq. $K_4Fe(CN)_6$ until the blue colour disappears. The results agree with those obtained potentiometrically, and are less affected by the presence of salts of alkali metals, except acetates. Addition of $ZnSO_4$ makes the $Fe(CN)_6^{--}$ test for Fe^{+++} more sensitive; 1 mg. of Fe^{+++} per litre produces a transient blue colour. The solubility products of $K_2Zn_3[Fe(CN)_6]_2$ and $K_2Cd[Fe(CN)_6]$ are approx. 10^{-14} ; that of $Mn_2[Fe(CN)_6]$ is $2-3 \times 10^{-13}$.

D. R. D.

Rapid determination of volatile constituents in small samples of copper-zinc alloys by a distillation method. L. I. WEINSTEIN and A. A. BENEDETTI-PICHLER.—See B., 1932, 892.

Determination of traces of lead and copper in presence of iron, with special reference to iron ammonium citrate. N. L. ALLPORT and G. H. SKRIMSHIRE (Pharm. J., 1932, 129, 248—249).—After destruction of org. matter by oxidation with H_2O_2 , the Cu and Pb are extracted by means of a $CHCl_3$ solution of diphenylthiocarbazon and determined colorimetrically, the Pb in the usual way with Na_2S , and the Cu with dithio-oxamide. W. S.

Application of Spacu's reaction in the micro-determination of copper. J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1931, 69, 247—269; Chem. Zentr., 1932, i, 3090).—Details of the application of this method (A., 1931, 454) to micro-analysis are given.

A. A. E.

Microchemical contributions. VII. L. ROSENTHALER (Mikrochem., 1932, 12, 98—101; cf. A., 1930, 881).—The microscopical appearance of the ppts. formed by $Hg_2(NO_3)_2$ with numerous org. and inorg. substances is described. E. S. H.

Volumetric determination of mercuric chloride by Rupp's method. H. BRINDLE (Pharm. J., 1932, 129, 245).—The sole drawback of the method (B.P., 1932) is the difficulty of dissolving the Hg ppt. in the I solution, and this is overcome by the addition of a small quantity of a mixture of 1 vol. $CHCl_3$ and 2 vols. Et_2O . W. S.

Titrimetric determination of aluminium in presence of iron and free hydrochloric acid. E. ERDHEIM and E. BENESCH (Przemysł Chem., 1932,

16, 128—130).—Fe⁺⁺ is oxidised to Fe⁺⁺⁺ by H₂O₂, and Fe and Al are pptd. as Na₂FeF₆ and Na₃AlF₆ by NaF; free HCl is titrated with 0.5*N*-NaOH. Fe is determined in another portion of solution by titration with KMnO₄. Excess of 0.4*N*-Na₂CO₃ is added to a third portion, which is then boiled and filtered from Fe(OH)₃ and Al(OH)₃, and an aliquot part of the filtrate is titrated with 0.5*N*-HCl. The Al content is calc. from the difference between the amount of alkali used and that necessary for pptn. of Fe and neutralisation of free HCl. R. T.

Determination of manganese as dioxide. E. WOHLTMANN (Z. anal. Chem., 1932, 89, 321—338).—Mn is quantitatively deposited on a gauze anode by electrolysis of aq. MnSO₄ containing (a) EtOH and NaOAc or (b) HCO₂H and HCO₂Na. The deposit in both cases contains H₂O and more or less MnO, but after heating to const. wt. at 250° the true MnO₂ is obtained by the use of the factors (a) 0.9459 and (b) 0.9085. In the volumetric determination of Mn by Fischer's modification of Volhard's method, boiling with AcOH after the first end-point appears is essential for correct results; in this way adsorbed MnO is converted into MnO₂ during the subsequent addition of KMnO₄ to obtain the second and true end-point. A. R. P.

Spectroscopic determination of nickel, manganese, and chromium in steels. F. TWYMAN and A. HARVEY.—See B., 1932, 891.

Analysis of cations of the ammonium sulphide group. A. I. SHEINKMAN (Farm. Zhur., 1932, No. 3—4, 119—120).—The NH₄OH-(NH₄)₂S ppt. is treated with hot AcOH to dissolve Fe, Cr, Al, and Mn. ZnS is extracted from the residue with 2*N*-HCl. CH. ABS.

Determination of small amounts of iron in copper. B. PARK.—See B., 1932, 844.

Use of α -benzoinoxime in the determination of molybdenum. H. B. KNOWLES (Bur. Stand. J. Res., 1932, 9, 1—7).—Mo is completely pptd. from solutions containing 5 vol.-% H₂SO₄, HCl, or HNO₃ by addition of an EtOH solution of α -benzoinoxime at 5—10°, provided that enough aq. Br is added to colour the solution yellow after addition of the reagent. The ppt. on ignition at 500—525° affords MoO₃ for weighing. WO₃ must subsequently be removed by pptn. with cinchonine. V₂O₅ and CrO₃ must first be reduced by boiling with an excess of SO₂ or by addition of FeSO₄. The method provides an accurate separation of Mo from Sb and gives good results in the analysis of steels and Mo ores in a much shorter time than any other procedure. A. R. P.

Microchemical reaction for the detection of molybdenum, vanadium, and tungsten. A. MARTINI (Mikrochem., 1932, 12, 112—113; cf. A., 1928, 387).—Characteristic cryst. ppts. are formed when a drop of CH₂Ph·NH₂ is added to a drop of 1% aq. solution of a compound of Mo, V, or W containing pyrocatechol, and aq. AcOH is then added. The ppts. formed are of the type H₂[(C₆H₄O)₂OMV(OH)OAc, CH₂Ph·NH₂, where M is Mo, V, or W. E. S. H.

Colorimetric determination of vanadium in titanomagnetites. K. BOLSHAKOV (Tzvet. Met., 1931, 487—493).—The finely-ground ore (1 g.) is evaporated to dryness with HNO₃ (15 c.c.) and HCl (45 c.c.); the residue is treated with conc. HNO₃ (20—30 c.c.), evaporated to small vol., diluted with hot dil. HNO₃, and filtered. The filtrate is again evaporated to dryness and then heated with 20 c.c. of 6*N*-HNO₃ until dissolved. The solution is treated with 10% AgNO₃ solution (1—2 c.c.), Cl is removed by boiling, and the solution filtered. The filtrate is diluted to 100 c.c.; 10 c.c. of this, 18 c.c. HNO₃ (*d* 1.2), and 10 c.c. H₃PO₄ are diluted to 80 c.c., 10 c.c. of fresh NH₄ molybdate solution then being added. The solution is then compared colorimetrically with a solution containing 0.002 g. V₂O₅, 20 c.c. HNO₃ (*d* 1.2), 10 c.c. H₃PO₄, and 10 c.c. of NH₄ molybdate solution in 100 c.c. The presence of Ti does not interfere. CH. ABS.

Use of manganese sulphate in the determination of antimony by Low's method. W. G. LEEMANN (J.S.C.I., 1932, 51, 284*r*).—The difficulty of determining the end-point when the method is applied to Sb in white bearing alloys, owing to the rapid disappearance of the colour of KMnO₄, is overcome by adding MnSO₄ solution before titrating with KMnO₄. The solution is prepared by dissolving 110 g. cryst. MnSO₄ in 500—600 c.c. H₂O, adding 138 c.c. H₃PO₄ (*d* 1.7) and 130 c.c. H₂SO₄ (*d* 1.84), and diluting to 1000 c.c. E. S. H.

Potentiometric determination of platinum and gold with cuprous chloride solution. E. MÜLLER and K. H. TÄNZLER (Z. anal. Chem., 1932, 89, 339—344).—The reduction of AuCl₃ to Au and of PtCl₄ to PtCl₂ by Cu₂Cl₂ in dil. HCl at 50° is made the basis of potentiometric titrations for Au and Pt. Simultaneous determinations of both metals in the same solution are not accurate, as the Au end-point is not sharp in the presence of Pt; the sum of Au and Pt may, however, be ascertained accurately in this way. A. R. P.

Precision aperiodic thermostat. O. H. A. SCHMITT and F. O. SCHMITT (Rev. Sci. Instr., 1932, [ii], 3, 467—473).—Constructional details are given. The temp. variation is <0.001°. C. W. G.

Isothermic titration microcalorimeter. I. V. KROTOV (Bull. Acad. Sci. U.R.S.S., 1932, No. 5, 669—680).—The temp. is kept const. by addition of aq. NH₄NO₃ to H₂O, the heat of reaction being proportional to the vol. of NH₄NO₃ added. In the case of endothermic reactions H₂SO₄ is used in place of NH₄NO₃. An accuracy of 1% is obtained. R. T.

Modification of Lewis-Thomson calorimeter. E. CASATI (Annali Chim. Appl., 1932, 22, 566—570).—A tube conveying O₂ runs along the usual vertical tube and the bell, and enters the base of the combustion chamber. Either an oxidising mixture or a current of O₂ may be used. In the latter case the usual cartridge is replaced by the grate and burner designed for the purpose. O. F. L.

Hydrogen discharge tube for the continuous ultra-violet spectrum. H. C. UREY, G. M. MURPHY, and J. A. DUNCAN (Rev. Sci. Instr., 1932,

[ii], 3, 497—498).—A Pyrex tube with SiO_2 windows is cooled sufficiently to permit the use of currents of 2 amp. C. W. G.

Improved Laue camera. H. KERSTEN and W. LANGE (Rev. Sci. Instr., 1932, [ii], 3, 493—496).—A specially shaped rotating disc is fitted to equalise the exposures of different parts of the plate when the crystal-to-film distance is small. C. W. G.

Spectrophotometer for the visible region in the rapid analysis of alloys. G. SCHEIBE and G. LIMMER (Metall-Wirt., 1932, 11, 107—110; Chem. Zentr., 1932, i, 2977).

Device for demonstrating Brownian movement in gases. D. A. WELLS and W. LANGE (Rev. Sci. Instr., 1932, [ii], 3, 474—475).—Three 5/16-in. cavities are drilled in a brass block and are joined by a 1/8-in. hole perpendicular to their axes. Intense light passes through a simple collimator (a pair of slits) in the first cavity, illuminates smoke in the second one, and is absorbed by the blackened walls of the third. A magnification of 100 is desirable. C. W. G.

Control of ultra-violet ray lamps. W. E. HAMMOND (Science, 1932, 76, 125).—The power of the lamp can be judged by the amount of I liberated from "Lipiodol" after 5 min. irradiation. L. S. T.

Simplified minimum deviation method of measuring refractive indices. P. ROSSIER (Arch. Sci. phys. nat., 1932, [v], 14, 226—227).—A small-angle prism-objective is introduced. N. M. B.

Limitations of a blanket calibration chart for reading dispersions on the Abbe refractometer. L. E. DODD (J. Opt. Soc. Amer., 1932, 22, 477—487).—The exact and approx. forms of the basic Abbe formulæ, and their derivation, are given in detail. The errors involved in using the blanket calibration chart in the measurement of dispersions with a refractometer having compensating prisms are checked by direct calculations. The consts. β , N , ΔN , k should be known precisely for each instrument. J. L.

Determination of refractivity temperature coefficients for liquids. J. J. MANLEY (Proc. Physical Soc., 1932, 44, 556—562).—An improved form of the Jamin interferometer is described by means of which the variation of refractive index of a liquid with temp. can be determined with accuracy. A. J. M.

Portable thermionic electrometer for the determination of glass electrode potentials. C. MORTON (J. Sci. Instr., 1932, 9, 289—293).—Potentiometer current, grid bias, filament current, anode voltage, and compensating current are derived from a common source and are standardised in one operation. Within limits the instrument is self-adjusting for fluctuations in the battery voltage. C. W. G.

Automatic control and recording of hydrogen-ion concentration by means of the glass electrode. C. MORTON (J.C.S., 1932, 2469—2475).—A potentiometric regulator has been constructed for automatic recording or control in conjunction with the glass electrode. Its accuracy is of the order of ± 1 mv. and is unaffected by oxidising or reducing agents, suspended ppts., colloids, or any electrode

"poisons." Electric currents up to 10 amp. at 250 volts may be made or broken without the use of an intermediate relay. Thermionic valves are employed for amplification, but the calibration of the instrument is permanent and unaffected by changes in the battery voltages and valve characteristics. It will function continuously for many months without attention. Photo-electric or other minute leakage currents may also be controlled or recorded, the current sensitivity being approx. 10^6 times that of the standard thread recorder. A simple recording cell, suitable for use with a glass electrode in continuously flowing solutions, is also described. M. S. B.

Multiple-unit electrodialysis apparatus. A. LODDESOL (Science, 1932, 76, 83—84). L. S. T.

Simple apparatus for thermoelectric determination of f.p. H. C. S. SNETHLAGE (Chem. Weekblad, 1932, 29, 557—559).—Constructional details and typical results are given. H. F. G.

Vacuum or circulating pump. E. L. HARRINGTON (Rev. Sci. Instr., 1932, [ii], 3, 476—481).—An inclined helical tube, partly immersed in a suitable liquid, is caused to rotate (by direct drive, or electromagnetically). Gas trapped by the lower end of the helix is forced out of the upper end, together with liquid, which is returned to the main supply. C. W. G.

High-speed high-vacuum diffusion pumps. I. ESTERMANN and H. T. BYCK (Rev. Sci. Instr., 1932, [ii], 3, 482—487).—The construction of glass-metal pumps is described. C. W. G.

Mercury vapour pumps for vacuum distillations. R. H. MUNCH (Science, 1932, 76, 170—171).—A Pyrex glass Hg-vapour diffusion pump, designed to work against an aspirator used as a force pump capable of producing a pressure reduction of 30 mm., is described. The apparatus can advantageously replace pumps of the Cenco Hyvac type. L. S. T.

Cryoscopic mol. wt. determination. F. B. STRAUB (Biochem. Z., 1932, 252, 378—379).—A simple apparatus and method are described which permit the determination of the lowering of f.p. of 0.5M aq. solutions with an accuracy of $\pm 4\%$. P. W. C.

Device for adding saturated alkali solution in the Kjeldahl method for nitrogen determination. F. T. ADRIANO (Univ. Philippines Nat. Appl. Sci. Bull., 1932, 2, 27—32).—Alkali is contained in a funnel connected by a rubber tube and pinchcock to a glass tube entering the steam inlet immediately above the stopper of the Kjeldahl flask, and is added during temporary removal of the flame from the boiler. CH. ABS.

Method of constructing slits of fixed width. W. L. BUXTON (J. Sci. Instr., 1932, 9, 297).—The edges of two metal strips are machined straight, and rectangular notches of depth equal to half the required width of the slit are cut in them. The slits are then formed by mounting the two strips with their machined edges touching. C. W. G.

[Laboratory] sieving machine. E. BERL and A. SCHMIDT (Chem. Fabr., 1932, 299).—Shaking

machines of the type in which a spring is given impulses by a rotating pulley loaded on one side can be adapted to screening, the sieves being clamped in the position occupied by the article to be shaken. Comparative tests with hand-screening for 25 min. show slightly smaller residues in the case of machine-screening. C. I.

Standardisation of weights. F. C. EATON (J. Amer. Chem. Soc., 1932, 54, 3261—3263).—Richards' method of calibration gives vals. identical with those found by substituting in algebraic formulæ, such as those of Kohlrausch. E. G. V. B. (c)

Apparatus for filtration at high temperatures. A. STADLER (Mitt. Kohlenforsch.-Inst. Prag, 1931, 80—81; Chem. Zentr., 1932, i, 2488).

Apparatus for filtration at low temperatures, particularly for the determination of paraffin. B. G. SIMKEK (Mitt. Kohlenforsch.-Inst. Prag, 1931, 74—79; Chem. Zentr., 1932, i, 2488).

Adjustable apparatus stand and truck. R. W. SHAW (Science, 1932, 76, 259). L. S. T.

Automatic control for vacuum apparatus. C. I. SWAYZE (Science, 1932, 76, 196—197). L. S. T.

Improved sodium burner. F. L. HUMOLLER and W. C. AUSTIN (Science, 1932, 76, 105—106). L. S. T.

Micro-balances of the Kuhlmann type. L. RAMBERG (Svensk Kem. Tidskr., 1932, 44, 188—191).—The error due to irregularities in the position of the usual type of rider is pointed out, and an improved form of rider is described. H. F. H.

Lubricant insoluble in organic solvents. C. C. MELOCHE and W. G. FREDRICK (J. Amer. Chem. Soc., 1932, 54, 3264—3266).—A mixture of 25 g. anhyd. glycerol, 7 g. dextrin, and 3.5 g. *d*-mannitol is heated until the solid is dissolved and the solution begins to boil. In general, H_2O , alcohols, aliphatic acids, and certain amines and heterocyclic N compounds prevent the use of the lubricant. E. G. V. B. (c)

Combustion of hydrocarbons. Volumetric composition of the gaseous products. J. RIMBAUT (Ann. Off. Nat. Combust. liq., 1931, 6, 835—873; Chem. Zentr., 1932, i, 2491).—Calculations for the construction of two nomograms are given. A. A. E.

History of red phosphorus. R. WEGSCHEIDER (Oesterr. Chem.-Ztg., 1932, 35, 169—171).

Geochemistry.

Natural gases. III. Methane and its homologues in Polish natural gases. K. KLING, E. BECKÓWNA, and K. KIRSCHBAUM (Przemysl Chem., 1932, 16, 97—108).—The CH_4 content of Galician natural gases varies from 74.5 to 89%, that of C_2H_6 from 1.73 to 11.63%, of C_3H_8 from 1.37 to 6.07%, and of higher homologues from 0.83 to 6.97%. R. T.

Iodine in the air. H. CAUER (Umschau, 1931, 35, 991—992; Chem. Zentr., 1932, i, 1506).—The atm. in Bad Kreuznach is rich in I; 50×10^{-6} g. can be inhaled in 24 hr. Mountain air has a normal I content. The incidence of goitre is discussed. A. A. E.

Formaldehyde in rain water. N. R. DHAR and A. RAM (Nature, 1932, 130, 313—314).— CH_2O occurs in distilled and undistilled rain H_2O obtained from high altitudes at Allahabad. It appears to be obtained from the union of CO_2 and H_2O vapour in presence of solar ultra-violet light and not from the decomp. of vegetable matter. L. S. T.

Analysis of Acquarossa mineral water. P. BERTOLO and S. LANZA (Annali Chim. Appl., 1932, 22, 469—478).— H_2O from this spring, in Belpasso (Catania), contains much CO_2 , with Na, K, Ca, Mg, Al, and Fe; these have been determined, also Cl' , SO_4'' , NO_3' , HCO_3' , and SiO_2 . The solid residue (at 105°) is 1.2828 g., and the total dissolved gas 451 c.c. (at 0° and 760 mm.) per litre. E. W. W.

Mineral water from Madesimo. R. MARCONI (Annali Chim. Appl., 1932, 22, 574—577).—The results of the chemical and physico-chemical examination of this H_2O are given. O. F. L.

Genesis of dolomite. O. BAR (Zentr. Min. Geol., 1932, A, 46—62; Chem. Zentr., 1932, i, 2155).—Solubilities of $CaCO_3$ and $MgCO_3$ in H_2O of varying CO_2 content are recorded. The composition of the solution resulting from magnesite+dolomite and from calcite+dolomite in CO_2+H_2O was also determined; other solubilities in CO_2+H_2O determined were those of $FeCO_3$, $ZnCO_3$, and $MnCO_3$. A. A. E.

Beryl from Erythræa. G. LIBERI (Annali Chim. Appl., 1932, 22, 544—554).—From the result of two analyses the formula appears to correspond with $4BeO, Al_2O_3, 7SiO_2$, i.e., $4BeSiO_3, Al_2(SiO_3)_3$. O. F. L.

Microscopical characters of natural manganese oxides and manganite. J. ORCEL and S. PAVLOVITCH (Bull. Soc. Franç. Min., 1931, 54, 108—179; Chem. Zentr., 1932, i, 2444).

Sodalite from Cerro Sapo, Bolivia. W. BRENDLER (Zentr. Min. Geol., 1932, A, 42—46; Chem. Zentr., 1932, i, 2154).—The large, ultramarine-coloured crystals, *d* 2.290, contained Na_2O 24.53, K_2O 1.13, Fe_2O_3 0.70, Al_2O_3 31.17, SiO_2 36.72, Cl 7.22, H_2O (110°) 0.23%; MgO , CaO , BaO , FeO , and SO_3 were absent. A. A. E.

Granite, vesuvianite, ilmenite, and titanite from Monte Roseo di Verra (Monte Rosa group). I. Granite and vesuvianite. II. Ilmenite and titanite. T. CARPANESE (Atti R. Accad. Lincei, 1932, [vi], 15, 591—595, 694—699).—Analysis of the granite gave: SiO_2 37.66; TiO_2 0.77; Al_2O_3 15.50; Fe_2O_3 9.47; FeO 2.00; CaO 34.51; MnO 0.53=100.44%. This agrees well with the general

formula $M^{II}_3M^{III}_2(SiO_4)_3$. Crystallographic data are given for all these minerals. O. J. W.

Geology of the Roundstone district, County Galway. L. R. WAGER (Proc. Roy. Irish Acad., 1932, 41, B, 46—72).—Analyses are given of picrite, altered allivalite, and a completely altered anorthite-rock. The rocks of the area have been altered by a later intrusion of granite. L. J. S.

Composition of meteorites and of the earth. I. I. ŠASLAVSKY (ZASLAWSKY) (Tsch. Min. Petr. Mitt., 1932, 43, 144—155; cf. A., 1931, 1389).—A speculative deduction of the average composition of meteorites and the earth as a whole. The results obtained differ considerably from those of previous estimates. L. J. S.

Dacite in the Börzsony Mts., Hungary. L. JUŠOVICS (Tsch. Min. Petr. Mitt., 1932, 43, 156—174).—Description of the occurrence and petrography of the dacite. A chemical analysis of the rock is compared with analyses of dacites from other parts of Hungary and Transylvania. It was derived from a quartz-dioritic to granitic magma. L. J. S.

Rocks from the Austrian Alps. F. ANGEL and K. METZ (Tsch. Min. Petr. Mitt., 1932, 43, 175—181).—Analyses are given of granite from Carinthia and of spessartite from Styria. L. J. S.

Parasepiolite from magnesite deposits of the Veitsch type. H. MEIXNER (Tsch. Min. Petr. Mitt., 1932, 43, 182—193).—"Mountain leather" occurs with quartz and dolomite in crevices in magnesite deposits at several places in Styria. That from Sunk gave SiO_2 48.93, Al_2O_3 0.43, Fe_2O_3 1.12, FeO 0.24, MnO 0.04, MgO 24.05, CaO 2.96, CO_2 4.21, $H_2O > 110^\circ$ 9.57, $H_2O < 110^\circ$ 8.35=99.90. Deducing dolomite and limonite, this corresponds with parasepiolite. The reactions of sepiolite, parasepiolite, and palygorskite are compared. L. J. S.

Garnet-cordierite-gneiss from Mogok [Burma]. J. A. DUNN (Rec. Geol. Survey, India, 1932, 65, 445—456).—The rock consists of cordierite, biotite, hypersthene, garnet, plæonaste, and sillimanite with quartz and zircon inclusions, the latter surrounded by haloes. It shows arrested metamorphic diffusion, having been formed by the permeation of an original rock high in MgO , Fe , and Al_2O_3 by an acid granite high in Na_2O according to the equations: 4 garnet + 6 SiO_2 = 8 hypersthene + cordierite; 3 biotite + garnet + 3 SiO_2 = 5 hypersthene + cordierite + 3(KH) $_2O$; and 2 garnet + 4 sillimanite = 2 spinel + cordierite; cordierite acting in all cases as a common solid solvent. C. A. S.

Granitic intrusions and associated rocks in Ranchi and Singhbhum, Bihar and Orissa [India]. L. A. N. IYER (Rec. Geol. Survey, India, 1932, 65, 490—533).—The nature and interrelations of these are discussed, and 23 complete analyses of granites, gneisses, aplites, hornblende and mica schists, dolerites, and perknite given. C. A. S.

Green mica. S. K. CHATTERJEE (Rec. Geol. Survey, India, 1932, 65, 536—539).—A green mica occurs in quartzite near Mahalgau (Bhandara district, Central Provinces, India), in clusters up to

$1/4 \times 1/8$ in. It contains SiO_2 47.35, Al_2O_3 30.99, Cr_2O_3 2.74, V_2O_5 0.48, Fe_2O_3 0.94, FeO 0.64, MgO 1.27, CaO 1.16, Na_2O 1.71, K_2O 9.26, $H_2O > 110^\circ$ 3.96, $H_2O < 110^\circ$ 0.62%, with traces of TiO_2 , MnO , BaO , and (from its spectrum) Cs ; d 2.904, n_g 1.612, n_r 1.615. It is strongly pleochroic (bluish- and olive-green), and appears to be intermediate between fuchsite and roscelite. C. A. S.

Osmiridium. O. E. ZVJAGINTSEV and B. K. BRUNOVSKI (Z. Krist., 1932, 83, 172—192).—Previous analyses are discussed. Fresh analyses by a modification of Leidié and Quennessen's method (cf. A., 1903, ii, 576) of eight samples from Newjansk, and one each from Sysstersk, Miass, and Transbaikalia show (in % in this order), respectively, Ir, Os, Pt, Rh, Ru, Au, Fe, and S: 34.7—44.7, 30.6—41.9, 1.8—13.6, 0.1—2.3, 3.0—14.1, 0—1.5, 0—3.5, 0—0.3; 42.2, 24.8, 8.3, 0, 19.1, 0, 0, 0; 44.8, 35.5, 6.6, 0.2, 13.4, 0, 0, 0; and 24.5, 46.0, 7.4, 0, 18.3, trace, 2.6, 0. The samples are classified as newjanskite, Ru-, Rh-, and Pt-newjanskite, syssterskite, and Ru-syssterskite as they contain predominant or at least considerable amounts of Ir (46.8—77.2), Ru (4.7—13.4), Rh (11.25—12.3), Pt (10.1—13.6), Os (67.9), and Os+Ru (46.0+18.3%), respectively. Ru is not present as laurite, nor is there any definite combination between the metals; all are present in solid solution, the transition from newjanskite to syssterskite being continuous. These conclusions are confirmed by X-ray examination, which shows a hexagonal lattice, a 2.620—2.710, c 4.235—4.282 Å., with no connexion between variations and composition. Pure Os has a 2.716, c 4.331 Å. (cf. A., 1926, 664). Low density (17.0—18.6) is due to gaseous inclusions. C. A. S.

Composition of roeblingite. R. BLIX (Amer. Min., 1931, 16, 455—460).—Roeblingite from Franklin Furnace contained SiO_2 , 23.57, CO_2 0.61, SO_3 10.81, PbO 30.04, MnO 2.49, CaO 23.12, SrO 2.79, H_2O + 6.15, H_2O —0.45, total 100.03%, corresponding with $2PbSO_4 \cdot R_7H_{10}(SiO_4)_6$, where $R=Ca, Sr$, or Mn . CH. ABS.

Presence of beryllium in milarite. C. PALACHE (Amer. Min., 1931, 16, 469—470).—Be is an essential constituent of milarite, $K_2Ca_4(Be_4Al_2Si_{24})O_{60} \cdot H_2O$. One sample contained 5.24% BeO ; a complete analysis is given. CH. ABS.

Zinc-bearing chromite. M. DONATH (Amer. Min., 1931, 16, 484—487).—Ramberg chromite, H 6—7, d 4.5, contains ZnO 2.42, Cr_2O_3 41.66%; the ZnO is present as an isomorphous mixture together with MgO , FeO , and Fe_2O_3 . CH. ABS.

Biology and coal. F. FISCHER (Proc. III Int. Conf. Bit. Coal, 1932, 2, 809—819).—Bacterial decomposition of wood cellulose proceeds actively prior to coalification. Bacteria produced CH_4 from brown coal in a H_2 atm. *B. methanicus* produces CO_2 and H_2O from CH_4 ; *B. oligocarbophilus* oxidises CO , and putrefying bacteria, in absence of air, formed CH_4 from $CO_2 + H_2$, $AcOH$ being an intermediate product. Sewage sludge contained bacteria which produce CH_4 from $CO + H_2$. Small amounts of brown coal stimulate the growth of plants. CH. ABS.

Mineral oil and potassium radiation. F. SCHWARZ (Petroleum, 1932, 28, No. 40, 8—10).—A review.

Physical and chemical characteristics of soils from the erosion experiment stations. H. E. MIDDLETON, C. S. SLATER, and H. G. BYERS (U.S. Dept. Agric. Tech. Bull., 1932, No. 316, 50 pp.).—Numerous analyses are recorded and discussed.

A. G. P.

Mechanical composition of podsol soils. A. A. RODE (Trans. Dokuchaiev Soil Inst., 1932, 6, 153—189).—Mechanical and aggregate analyses on five podsol and podsol-gley soils showed a tendency to aggregate formation in the humus horizons. In lower horizons the tendency is weaker. Particles of diam. 0.0063 mm. mark a boundary between larger particles which are relatively accumulated and smaller particles which are removed. The velocity of disintegration of particles of diam. close to 0.0063 mm. is the same as the velocity of disintegration of the rock as a whole.

A. M.

Age and evolution of soils in connexion with the age of the parent rock and the relief. N. N. SOKOLOV (Trans. Dokuchaiev Soil Inst., 1932, 6, 1—55).—A discussion of the abs. and relative age of

soils. Three methods are appropriate for determining the relative age of soils; (a) the stratigraphical (buried soils), (b) the palaeographical (where the soil does not correspond with present-day conditions), (c) the geographical method (for soils corresponding with present-day conditions).

A. M.

Microflora of soil from the delta of the Lena. N. N. SUSHKINA (Trans. Dokuchaiev Soil Inst., 1932, 6, 191—196).—In the profile investigated bacterial activity was very slight. Nitrifying, cellulose-decomposing, and aerobic putrefying bacteria are absent. Microbiological life is concentrated in A horizon (2—5 cm.). Protein decomp. is caused by moulds or anaerobic putrefying bacteria.

A. M.

Classification of soil colours. N. A. ARCHANGELSKAYA (Trans. Dokuchaiev Soil Inst., 1932, 6, 197—306).—A full account of an attempt to determine soil colour using Ostwald's colour disc. Examples are given from all the main soil groups.

A. M.

Soil protozoa in the Austrian Schneeberge. L. VARGA (Zentr. Bakt. Par., 1932, II, 86, 254—259).—The H_2O content of these mountain soils increases and the p_H decreases with height. The no. of active protozoa is greatest at the highest levels.

A. G. P.

Organic Chemistry.

Thermal decomposition of organic compounds from the point of view of free radicals. II. Experimental evidence of decomposition of organic compounds into free radicals. F. O. RICE, W. R. JOHNSTON, and B. L. EVERING (J. Amer. Chem. Soc., 1932, 54, 3529—3543; cf. A., 1931, 819).—Numerous org. compounds decompose into free radicals when heated at 800—1000°, and by chilling the products the free radicals can be combined with metals. From $COMe_2$ Me only is obtained, but C_3H_8 yields 80% Me and 20% Et and C_4H_{10} gives 70% Me and 30% Et. The half-life of the free radicals so obtained is about $1-2 \times 10^{-3}$ sec. The rate of their disappearance does not exactly follow either the uni- or the bi-mol. law. The temp. coeff. of the decomp. into free radicals of $COMe_2$ is practically the same as that of the ordinary thermal decomp. Free radicals in C_4H_{10} at 40—70 mm. pressure do not show the Paneth effect on a metallic mirror a few mm. from their point of origin.

C. J. W. (c)

Hydration of solid and liquid hydrocarbons under pressure in the laboratory. II. Procedure and methods of expressing the results. F. LAUPICHLER (Chem. Fabr., 1932, 327—331).—A general but detailed review of research methods.

H. F. G.

Synthesis of *n*-hexane from *n*-propyl bromide by Wurtz' method. E. ERDHEIM (Rocz. Chem., 1932, 12, 631—634).—*n*-Hexane is obtained in 47.6% yield by the action of Na on Pr^2Br in the presence of MeCN. $\beta\gamma$ -Dimethylbutane cannot be prepared analogously from Pr^2Br .

R. T.

Selenium dioxide, a new oxidising agent. II. Reaction with some unsaturated hydrocarbons.

H. L. RILEY and N. A. C. FRIEND (J.C.S., 1932, 2342—2344).—Oxidation of C_2H_4 or $CHMe:CH_2$ with SeO_2 occurs exothermally at 45—55°, the temp. rising to 200° with the production of $(CHO:CHO)_2$ and $COMe:CHO$, respectively: $3SeO_2 + 2C_2H_4 = 2(CHO)_2 + 3Se + 2H_2O$. When the SeO_2 is mixed with P_2O_5 monomeric $(CHO)_2$ is formed in small yield. Reduction of SeO_2 with C_2H_2 (at 40—50°) occurs less readily than with C_2H_4 , $(CHO)_2$ (6%) and much CO_2 being formed. With C_2H_6 at 350—400°, $AcOH$, CO_2 , and a little $(CHO)_2$ are formed, but no reduction occurs with β -amylene, $CMc:CHMe$, $CHPh:CH_2$, $CHMe:CH:CHO$, or $CHPh:CH:CHO$ at their b.p., complex products being obtained at higher temp. By passage of C_2H_4 or $CHMe:CH_2$ saturated with HCl through a saturated solution of SeO_2 in fuming HCl aq. $\beta\beta'$ -dichloro-diethyl and -dipropyl selenide dichloride, respectively, are obtained, the dibromide being prepared similarly in HBr aq.: $2C_2H_4 + 4HX + SeO_2 = (CH_2X:CH_2)_2SeCl_2 + 2H_2O$.

J. W. B.

Preparation of pure ethylene from ethyl alcohol. H. TROPSCH and R. KASSLER (Mitt. Kohlenforsch.-Inst. Prag, 1931, 43—44; Chem. Zentr., 1932, i, 2159).—Newth's method (J.C.S., 1901, 79, 915) affords C_2H_4 containing varying proportions of hydrocarbons such as hexane; these may be removed at -80° .

A. A. E.

Production of isoprene from rubber. H. L. BASSETT and H. G. WILLIAMS (J.C.S., 1932, 2324—2328).—Max. yields of isoprene (overall yield 23%; cf. below) are obtained by dropping small pieces of solid rubber (smoked sheet or crepe) into an Fe retort (described) at 600°, and rapid cooling of the

distillate (87%). Fractionation gives (1) b.p. up to 60° (19.9% containing 84% of isoprene), (2) b.p. 60—110° (6.5%, C_6H_8 etc. from secondary changes), (3) b.p. 110—200° (27.9%), and (4) residue (32.5%). By cracking (3) using a modification of the isoprene lamp of Harries and Gottlob (A., 1911, i, 798) a further 17.2% of isoprene is obtained. An improved method for the determination of isoprene based on the Diels-Alder reaction with maleic anhydride in C_6H_6 at 100° (cf. this vol., 141) gives accurate results in the absence of other butadienes, and is unaffected by the presence of amylenes. J. W. B.

Isomerides in "diisobutylene." II. C. O. TONGBERG, J. D. PICKENS, M. R. FENSKE, and F. C. WHITMORE. III. Determination of their structure. F. C. WHITMORE and J. M. CHURCH (J. Amer. Chem. Soc., 1932, 54, 3706—3710, 3710—3714; cf. A., 1931, 1148).—II. Diisobutylene is separated into $\beta\delta\delta$ -trimethyl- Δ^a - (I), b.p. 101.2°/760 mm., f.p. $-93.6 \pm 0.1^\circ$, and Δ^b -pentene (II), b.p. 104.5°/760 mm., f.p. $-106.5 \pm 0.1^\circ$ (an isomorphous form, m.p. -108.3° , is sometimes obtained), by a single distillation through the columns described by Fenske *et al.* (B., 1932, 826). The following m.p. are reported: octane, -56.9° ; heptane, -90.7° ; $\beta\delta\delta$ -trimethylpentane, -107.7° .

III. Details are given for the ozonolysis of (I) and (II). (I) gives CH_2O , Me neopentyl ketone, and a trace of $CMe_3 \cdot CH_2 \cdot CO_2H$, whilst (II) affords $CMe_2 \cdot CMe_2 \cdot CHO$, and $CMe_3 \cdot CO_2H$. C. J. W. (b)

Formation of methylene iodide by oxidation of iodoacetic acid and analogous reactions. L. PANIZZON (Helv. Chim. Acta, 1932, 15, 1187—1194).— $CH_2I \cdot CO_2H$ (10 g.) and $K_2S_2O_8$ (I) (1 mol.) give CH_2I_2 (II) (81.9%), succinic acid (0.3 g.), and a little CO_2 and CH_2O , whereas use of less (I) gives less (II) (cf. A., 1930, 735). $CH_2I \cdot COCl$, 3% H_2O_2 , and pyridine at 0° give *iodoacetyl peroxide*, $(CH_2I \cdot CO_2)_2$, m.p. 50—52°, decomp. 70—80°, which in boiling H_2O yields (II) (76.5%), MeOH, CO_2 , and a little CO . $CH_2Cl \cdot CO_2H$ and (I) give CH_2Cl_2 and a little CH_2O and $H_2C_2O_4$. *Chloroacetyl peroxide*, m.p. 35°, decomp. 70—80°, is stable to boiling H_2O , but in 15% HCl gives about 10% of CH_2Cl_2 . $(CH_2Cl \cdot CO_2)_2$, H_2O , and cold, conc. H_2SO_4 give *perchloroacetic acid*, b.p. 33—34°, which on decomp. by HCl gives O_2 and $CH_2Cl \cdot CO_2H$. The peroxides are considered to be an intermediate product in the formation of methylene halides by electrolysis or action of (I). R. S. C.

Substances analogous to graphite. III. F. BELLINO (Gazzetta, 1932, 62, 795—798).—Thermal decomp. of Cl_4 yields C which after being heated at 700° has d 1.46 and a much higher R than $(C_6)_n$ from C_6I_8 (A., 1928, 721). E. W. W.

Preparation of ethylene chlorohydrin from ethylene, chlorine, and water. H. TROPSCH and R. KASSLER (Mitt. Kohlenforsch.-Inst. Prag, 1931, 16—42; Chem. Zentr., 1932; i, 2159).—The $CH_2Cl \cdot CH_2 \cdot OH$ concn., x , obtained when C_2H_4 and Cl_2 are passed into H_2O , is related to the ratio, y , in which $CH_2Cl \cdot CH_2 \cdot OH$ and $(CH_2Cl)_2$ have been formed, by $y = -1.312x + 0.182p + 8.66$, where $p = 100p_{C_2H_4} / (p_{C_2H_4} + p_{Cl_2})$, $p_{C_2H_4}$ and p_{Cl_2} being the partial pressures of the reacting gases. With increasing x more

$(CH_2Cl)_2$ is formed; the greater is the excess of C_2H_4 , the more is the formation of $(CH_2Cl)_2$ repressed. Working conditions and the course of the reaction are discussed. A. A. C.

Catalytic oxidation of *n*-propyl alcohol. A. R. DAY and A. EISNER.—See this vol., 1096.

Halides from Δ' -octadecenol. W. SECK and F. DITTMAR (Chem. Umschau, 1931, 39, 169—171).—Treatment of oleyl alcohol in EtOH with HCl at 0° yielded κ -chloro-octadecanol, from which $\alpha\kappa$ -dichloro-octadecane was prepared by reaction with PCl_5 in the cold. Direct treatment of oleyl alcohol with HBr, in the cold or at 140°, furnished $\alpha\kappa$ -dibromooctadecane; reaction with PBr_3 in $CHCl_3$ gave mixtures of Br- and Br_2 -derivatives. The halides were yellow or brown liquids, which decomposed on distillation at 11 mm. E. L.

Optical properties of derivatives of lower aliphatic alcohols and aldehydes. W. M. D. BRYANT (J. Amer. Chem. Soc., 1932, 54, 3758—3765).—Optical methods can be used to differentiate between closely related substances, particularly when used in conjunction with the m.p. Complete optical data are reported for the 3:5-dinitrobenzoates of MeOH, EtOH, PrOH, Pr^oOH, BuOH, Bu^oOH, *sec.*- and *tert.*-BuOH, and $CMe_2Et \cdot OH$ and for the 2:4-dinitrophenylhydrazones of CH_2O , MeCHO, EtCHO, Pr^oCHO, and Pr^oCHO. C. J. W. (b)

Configuration of methylisopropylcarbinol: racemisation. P. G. STEVENS (J. Amer. Chem. Soc., 1932, 54, 3732—3738).—Correlation of *l*-CHMePr^oOH and *l*-CHMePr^oOH is accomplished by synthesis from Et *d*-lactate, $[\alpha]_D^{25} +0.52^\circ$. The ester with EtI and Ag_2O gives Et *d*- α -ethoxypropionate, b.p. 152.7—152.8°/730 mm. $[\alpha]_D^{25} +1.69^\circ$, converted by MgMeI into *l*- β -ethoxy- γ -methylbutan- γ -ol (I), b.p. 140—140.5°, $[\alpha]_D^{25} -1.84^\circ$; another sample showed $[\alpha]_D^{25} -0.83^\circ$. The carbinol, dehydrated by Tschugaev's xanthate method, affords *d*- β -ethoxy- γ -methyl- Δ^b -butene, b.p. 97.1—98.1°/730 mm., $[\alpha]_D^{25} +1.85^\circ$, reduced catalytically to *l*-ethoxy- γ -methylbutane, b.p. 100°, $[\alpha]_D^{25} -1.19^\circ$. *d*-CHMePr^oOH is ethylated to *d*- β -ethoxy- γ -methylbutane, b.p. 99—99.4°, $[\alpha]_D^{25} +0.60^\circ$. The K derivative of (I) does not racemise when heated at 190° for 10 hr. This supports Huckel's mechanism (A., 1931, 1286) of racemisation and rearrangement of alcoholates. C. J. W. (b)

Dehydration of secondary carbinols containing a neopentyl system. I. *iso*Propyl*tert.*-butylcarbinol. F. C. WHITMORE and A. L. HOUK (J. Amer. Chem. Soc., 1932, 54, 3714—3718).—None of the normal dehydration products is obtained either by dehydration of the carbinol or by thermal decomp. of the Grignard complex from which it is prepared; about 5% of $\beta\delta\delta$ -trimethyl- Δ^a -pentene is isolated. C. J. W.

Properties of pure decatetraenol. T. REICHSTEIN and G. TRIVELLI (Helv. Chim. Acta, 1932, 15, 1074—1076).— $\Delta^{3,5,7,9}$ -Decatetraenal, m.p. 107—108° (corr.) (cf. this vol., 496), and $Al(OPr^o)_3$ in Pr^oOH afford $\Delta^{3,5,7,9}$ -decatetraenol, m.p. 171—172.5° (corr.) (much lower when determined microscopically), hydrogenated (PtO₂) in Et₂O to pure *n*-decyl alcohol.

The alcohol has an absorption band from 2500 to 3300 Å., with max. at 2985 and 3110 Å. R. S. C.

Reduction of glycidic esters of $\alpha\gamma$ -glycols and transformation of the latter into unsaturated primary alcohols. A. S. PFAU and P. PLATTNER (Helv. Chim. Acta, 1932, 15, 1250—1267).—Reduction of glycidic esters with Na and abs. EtOH gives good yields of $\alpha\gamma$ -glycols, some glycidic acid, and (sometimes) a little saturated alcohol, whilst a small amount of the ester undergoes ketonic fission. The stability of the glycols, particularly of $\gamma\zeta$ -dimethyl- Δ^8 -octadiene- $\alpha\gamma$ -diol (I) (geraniol or nerol hydrate), which undergo only partial decomp. when distilled at atm. pressure, is not in agreement with the view that (I) is an intermediate in the geraniol-linalool change, nor is the fact that cautious dehydration of the glycols gives only $\beta\gamma$ -unsaturated alcohols (and, with Ac_2O , 10—25% of hydrocarbon). Substances of the type $\text{R}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ yield mixtures of the isomerides $\text{R}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ and $\text{R}\cdot\text{CH}_2\cdot\text{C}(\cdot\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$. The glycidic ester from Me heptenone (II) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ with Na and EtOH gives some glycidic acid, some (II), and (I) b.p. 149—150°/10 mm. When amyl alcohol is used, (II), (I), and only a trace of citronellol are obtained (cf. A., 1924, i, 865). Distillation of (I) with I, POCl_3 , ZnCl_2 , PBr_3 , $\text{H}_2\text{C}_2\text{O}_4$, Na_2SO_4 , or H_3BO_3 , and of its Ac_2 derivative with pyridine, NH_2Ph , or NPhMe_2 , gives a mixture (III) of $\gamma\eta$ -dimethyl- Δ^8 -octadien- α -ol (IV) and η -methyl- γ -methylene- Δ^8 -octen- α -ol (V), varying amounts of hydrocarbon (probably a mixture of myrcene and ocimene), and an oxido-alcohol (not isolated). With Ac_2O at 120° (I) gives a mixture of Ac and Ac_2 compounds, which, when distilled at atm. pressure, loses AcOH to yield the Ac derivative, b.p. 122—123°/10 mm., hydrolysed to (III), b.p. 109.5—110°/10 mm., unstable (dibromide, m.p. 185—186°). Quant. ozonolysis of (III) yields COMe , (85%), CH_2O (10%), and HCO_2H (40%). Et methyl-nonylglycidate gives similarly some glycidic acid, methyl-nonylcarbinol, and Me nonyl ketone, and (as main product) γ -methyl-dodecane- $\alpha\gamma$ -diol (VI), b.p. 180—182°/10 mm. (benzal, b.p. 157—158°/0.1 mm.). With Ac_2O (VI) gives a mixture of the Ac_2 , b.p. 172°/4 mm., and Ac derivatives of a mixture (VII), b.p. 145°/10 mm., of γ -methylenedodecan- α -ol and γ -methyl- Δ^8 -dodecen- α -ol. Oxidation of (VII) by KMnO_4 - CrO_3 gives nonoic and decoic acids, by O_3 in CHCl_3 CH_2O and nonoic acid, and by O_3 in AcOH nonaldehyde, hydroxynonyl peroxide, m.p. 72°, and a substance, m.p. 43—44°, hydrogenated (Ni) to Et nonyl ketone; Me nonyl ketone was not formed. Quant. ozonolysis of (VII) showed the presence of 48% of the methylene compound. Ozonolysis of the phenylurethane, m.p. 55.5—56°, of (VII) gives CH_2O . With Na_2SO_4 at 220°/15 mm. (VI) gives partly (VII) and a hydrocarbon, $\text{C}_{13}\text{H}_{24}$, b.p. 108°/10 mm., unstable, which, although it gives only nonoic acid when oxidised, is probably a mixture of γ -methylene- Δ^8 -dodecene and γ -methyl- Δ^8 -dodecadiene. Et methyl-ethylglycidate affords similarly γ -methylpentane- $\alpha\gamma$ -diol, b.p. 115°/10 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 43°/10 mm., of γ -methylenepentan- α -ol and γ -methyl- Δ^7 -penten- α -ol. Et methylisohexyl-

glycidate gives $\gamma\eta$ -dimethyloctane- $\alpha\gamma$ -diol, b.p. 155—156°/10 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 109°/10 mm. (diphenylurethane, m.p. 66.5°), of $\gamma\eta$ -dimethyl- Δ^7 -octen- α -ol and η -methyl- γ -methylene-octan- α -ol. Tetrahydro- ψ -ionone gives the glycidic ester, b.p. 184—186°/10 mm., which with Na and EtOH affords $\gamma\eta\lambda$ -trimethyl- Δ^8 -dodecene- $\alpha\gamma$ -diol, b.p. 160—162°/1 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 161—163°/10 mm., of $\eta\lambda$ -dimethyl- γ -methylene- Δ^8 -dodecen- α -ol and $\gamma\eta\lambda$ -trimethyl- Δ^8 -dodecadien- α -ol. Et phenylglycidate affords a little benzyl alcohol, much γ -phenylpropyl alcohol, b.p. 112—113°/10 mm., and γ -phenylpropane- $\alpha\gamma$ -diol, b.p. 165°/10 mm., the di-*p*-nitrobenzoate of which, when distilled, gives BzOH and *trans*-cinnamyl benzoate. Et phenylmethylglycidate gives a little phenylmethylcarbinol and impure γ -phenyl-*n*-butyl alcohol, b.p. 130—133°/10 mm., and much γ -phenyl-*n*-butane- $\alpha\gamma$ -diol, b.p. 130°/1 mm., changed by refluxing with Ac_2O and AcOH and subsequent hydrolysis to γ -phenyl- Δ^7 -buten- α -ol, b.p. 123°/10 mm., which with O_3 in AcOH gives CH_2O , but only traces of COPhMe derived from the $\alpha\beta$ -isomeride. Et (β -phenylethyl)methylglycidate gives a little δ -phenyl-*n*-butan- α -ol and much ϵ -phenyl- γ -methylpentane- $\alpha\gamma$ -diol, b.p. 149—150°/1 mm., dehydrated (Na_2SO_4) to a mixture, b.p. 153°/10 mm. (diphenylurethane, m.p. 82.5—83°), of ϵ -phenyl- γ -methylenepentan- α -ol and ϵ -phenyl- γ -methyl- Δ^7 -penten- α -ol. R. S. C.

Preparation of pure isoamyl ether. P. SCHORIGIN and J. MAKAROV-SEMLANSKI (Ber., 1932, 65, [B], 1293—1295).—Fermentation amyl alcohol is purified by $\text{H}_4\text{FeC}_6\text{N}_6$ and distilled with H_2SO_4 - H_2O ; H_2O is separated from the distillate, which is returned to the flask, the operation being repeated until the temp. of the liquid in the flask is 140°, after which the product is distilled with steam. Further purification is effected by distillation with the calc. amount of H_3BO_3 and use of C_6H_6 to entrain H_2O vapour. The product is distilled under diminished pressure and finally over Na. Alternatively, the alcohol is heated with p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ under a reflux condenser arranged so that the volatilised H_2O can be drawn off, whereas condensed alcohol returns to the flask. After formation of H_2O has ceased, the product is worked up as described above. The respective yields are 65—70% and 70—75%. H. W.

Dehydration of β -hydroxy-esters. G. A. R. KON and K. S. NARGUND (J.C.S., 1932, 2461—2463).—The relative proportions of $\alpha\beta$ - and $\beta\gamma$ -unsaturated esters obtained by dehydration of Et β -hydroxy- β -methyl- and - β -ethyl-valerate, - β -propylhexoate, and - $\alpha\beta$ -dimethylvalerate, Et cyclohexanol- and cyclopentan-ol-acetate with P_2O_5 (39.5, 23.5, 24.0, 28.0, 19.0, and 30.0%), POCl_3 (62.0, 68.0, 45.5, 47.5, 55.5, and 58.5%), SOCl_2 (53.5, 50.0, 31.5, 33.0, 32.0, and 50.0), and KHSO_4 (57.5, 63.5, 51.0, 28.0, 45.0, and 38.0), have been determined by the iodometric method. Best yields (60—80%) of the unsaturated ester are obtained with P_2O_5 and SOCl_2 , the former giving a mixture of max. $\beta\gamma$ -content, whilst POCl_3 affords the min. proportion of this form, the respective proportions of $\alpha\beta$ -ester being given in parentheses. COMeEt , COEt_2 , and COPr_2 readily condense with

$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ in the presence of Mg powder and a trace of I to give 40–48% yields of the OH-ester.

J. W. B.

Chemistry of the three-carbon system.
XXIX. Tautomerism of unsaturated esters.
 G. A. R. KON, R. P. LINSTEAD, and G. W. G. MACLENNAN (J.C.S., 1932, 2454–2461).—The proportions of $\alpha\beta$ -ester and the mobility of the system, on equilibration, under standard conditions, for the following esters are given in parentheses. *Et* β -hydroxy- α -methyl-*n*-hexoate, b.p. $110^\circ/19$ mm. (acid, m.p. 50°), dehydrated by P_2O_5 in boiling C_6H_6 gives, after fractional hydrolysis and esterification, *Et* α -methyl- Δ^8 -hexenoate, b.p. 68 – $69^\circ/16$ mm. (95%; 151) (better prepared as in preceding abstract), whence, after equilibration, the corresponding Δ^8 -ester, b.p. $72^\circ/10$ mm. (acid, b.p. $118^\circ/11$ mm.), is obtained. *Et* $\alpha\beta$ -dimethyl- Δ^8 -pentenoate, b.p. $68^\circ/10$ mm. (94.5%; 2), and the Δ^8 -ester, b.p. $63^\circ/12$ mm., were similarly prepared from the acids (A., 1928, 1218), purified by partial esterification; *Et* cyclopentylidene- (I), b.p. $96^\circ/15$ mm. (60%; 835), and *Et* cyclopentenyl- (II), b.p. $85^\circ/15$ mm., -acetate; *Et* α -methylcyclopentylidene-, b.p. $96^\circ/12$ mm. (88%; 84), and *Et* α -methylcyclopentenyl-, b.p. $79^\circ/6$ mm.; *Et* α -methylcyclohexylidene-, b.p. $109^\circ/10$ mm. (5%; 0.15), and *Et* α -methylcyclohexenyl-, b.p. $104^\circ/13$ mm., -acetate were similarly obtained from the corresponding acids. *Et* Δ^8 - (75%; 26) and Δ^8 - β -methylpentenoate (preceding abstract), and *Et* Δ^8 - (92%; 153) and Δ^8 -hexenoate were similarly equilibrated, but in the last case the equilibrium proportion of $\alpha\beta$ -ester is only approx. owing to the rapid addition of EtOH to this form to give *Et* β -ethoxyhexoate, b.p. $94^\circ/14$ mm. The proportions of $\alpha\beta$ - and $\beta\gamma$ -isomerides were determined by Linstead's iodometric method and checked by determinations of n_D^{20} and d_4^{20} . The results are discussed and it is concluded that they cannot be correlated with structure on any simple electronic theory. Contrary to expectations based on the high mobility of the system (I) (II), no evidence of alkylation of these esters, under conditions effective in the case of cyclohexenylacetone (a system of similar mobility), could be detected.

J. W. B.

α -Methylhexenoic and $\alpha\beta$ -dimethylpentenoic acids. G. A. R. KON, R. P. LINSTEAD, and G. W. G. MACLENNAN (J.C.S., 1932, 2452–2454).—In the equilibration of the pairs of acids $\text{CH}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ (I) (88–90%) $\text{CHEt}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (II), and $\text{CH}_2\text{Me}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ (III) (72–73%) $\text{CHMe}\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (IV) under the standard conditions previously used (A., 1927, 1167) the equilibrium vals. for the $\alpha\beta$ -form are given in parentheses, the mobility of the systems being 18.8 and 0.12, respectively. (II) is obtained by thermal decarboxylation of α -carboxy- α -methyl- Δ^8 -hexenoic acid, m.p. 130° (decomp.), which is obtained by hydrolysis of the ester, b.p. 130 – $140^\circ/18$ mm., resulting from the methylation of *Et* butylidenemalonate: [for (I), (III), and (IV) see preceding abstract]. An α -Me substituent stabilises the $\alpha\beta$ -phase, but greatly depresses the mobility of the system only if there is also a substituent in the β -position (A., 1931, 935, 934).

J. W. B.

Micro-determination of isopropylidene groups.
Constitution of dehydrogeranic acid. R. KUHN and H. ROTH (Ber., 1932, 65, [B], 1285–1292).—The substance (5–10 mg.) is ozonised in 99–100% AcOH at 0° , the solution is diluted, partly neutralised with NaOH, and oxidised by boiling with KMnO_4 under reflux. COMe_2 is removed by distillation. The distillate is rendered alkaline, treated with 0.05*N*-I at room temp. for 10–15 mm., then acidified with conc. HCl and titrated with 0.05*N*- $\text{Na}_2\text{S}_2\text{O}_3$. Very pure H_2O must be used. COMe_2 is scarcely affected by successive treatments with O_3 and KMnO_4 . The no. of mols. of COMe_2 thus obtained from each substance is given in parentheses; acetonephenylhydrazone (0.95); methylheptenone, geraniol, and citral (0.9). Only under exceptional conditions can treatment with O_3 be omitted. Other Me ketones react with KOI to give CHI_3 . COMeEt and COPhMe quantitatively give EtCO_2H and BzOH , respectively, and can thus be determined iodometrically. The presence of the CMeEt or CPhMe groups interferes with the CMe_2 determination, since the corresponding ketones are only slightly decomposed by KMnO_4 . $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ yields no COMe_2 , very small amounts of which are produced from amylene or isovaleraldehyde. COMe_2 is also obtained from compounds containing Pr^β (thymol, terpin hydrate, Pr^βOH).

Dehydrogeranic acid affords 0.61–0.65 mol. of COMe_2 or less if ozonisation is omitted. The conclusion that it contains the forms $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ is not in harmony with its absorption spectrum in hexane or EtOH and that of its Na salt in H_2O , which resembles closely that of octatrienoic acid, $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_3\cdot\text{CO}_2\text{H}$, and indicates that all double linkages are in conjugation. Preference is accorded to the optical evidence and doubts are expressed as to the validity of calculating the relative proportions of α - and β -forms from the quantity of COMe_2 obtained.

H. W.

Interconversion of *cis*- and *trans*-modifications of monoethylenic higher fatty acids by nitrogen trioxide (elaidin reaction). H. N. GRIFFITHS and T. P. HILDITCH (J.C.S., 1932, 2315–2324).—Isomerisation of oleic, petroselic (Δ^8 -octadecenoic), and crucic (Δ^7 -docosenoic) acids with Poutet's reagent (Hg in HNO_3 , d 1.42) or oxides of N from As_2O_3 and HNO_3 , at 10 – 20° , results in the production of an equilibrium mixture of *cis*- and *trans*-acids containing approx. 66, 60, and 60%, respectively, of the latter form. Small amounts of additive products are also obtained, and since the same equilibrium is attained starting from the *trans*-acids, isomerisation probably occurs through the reversible addition of oxides of N. The gases prepared from NaNO_2 and H_2SO_4 are slightly less effective, whilst those from Cu and HNO_3 give only poor yields (about 25%) of the *trans*-acid and a much greater proportion of additive products, the proportion of the latter being increased by rise of temp. or excess of the reagent. Rankoff's method (A., 1930, 65; 1% S at 220°) effects 55–60% conversion into elaidic acid. Me oleate and triolein undergo isomerisation to the same extent as oleic acid in so

far as the total transformation to elaidic groups is concerned, but only 30% of triolein (separated by crystallisation from COMe_2) is formed, the remaining 35% of elaidic acid being in the form of mixed elaidic-oleic glycerides. Thus the reaction is not suitable for the quant. determination of triolein in natural fats, but may be used for the approx. evaluation of oleic acid in its mixtures with linoleic and linolenic acids, and for differentiation and characterisation of some natural fats. The proportion of *cis*- and *trans*-acids was determined by fractional crystallisation of the Pb salts from EtOH-ligroin and determination of the I val. or thermal analysis of the acids so obtained. J. W. B.

Probable non-existence of normal tribasic aluminium soaps such as aluminium tripalmitate. J. W. McBAIN and W. L. McCLATCHIE (J. Amer. Chem. Soc., 1932, 54, 3266—3268).—Normal tribasic Al soaps have never been prepared, even in completely anhyd. media. In the prep. of oleates, stearates, and palmitates nothing more than the dibasic soap is ever obtained. Al soaps are commonly a mixture of free fatty acid with either monobasic or mono- and di-basic soaps. E. G. V. B. (c)

Autoxidation of unsaturated fatty acids. I. W. FRANKE (Annalen, 1932, 498, 129—165).—Autoxidation of linoleic acid (I) occurs more rapidly in basic (NH_2Ph , NPhMe_2 , pyrrole, $\text{C}_5\text{H}_5\text{N}$, piperidine) than in neutral solvents (PhMe , $\text{C}_6\text{H}_4\text{Me}_2$, amyl alcohol and acetate). The catalytic effect of NH_2Ph (in EtOH) is observed at a concn. of 1.2×10^{-7} mol. per c.c. of (I); the effect increases slightly and then decreases (probably owing to the formation of quinonoid oxidation products) with rise in the concn. $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, *m*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, NHPhMe , NPhMe_2 , and NHPh , are less effective, whilst *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ are more effective, than NH_2Ph . Of the heterocyclic bases studied, 2:2'-dipyridyl and pyrazine are the best catalysts; histamine shows a catalytic effect in concns. of 1.2×10^{-5} mol. per c.c. of (I). The catalytic effect of the following substances increases in the order quoted: $\text{CO}(\text{NH}_2)_2$ (small), KOH , NHEt_2 , acetylcholine, NH_3 , lecithin, $\text{C}_2\text{H}_4(\text{NH}_2)_2$. Proline is more effective than any of the above compounds. Autoxidation of oleic acid is catalysed [to a smaller extent than with (I)] by $\text{C}_5\text{H}_5\text{N}$, piperidine, NHEt_2 , $\text{C}_2\text{H}_4(\text{NH}_2)_2$, proline, and 2:2'-dipyridyl, but is inhibited by NH_2Ph , NHPhMe , and NPhMe_2 . The O_2 -uptake of (I) is increased by addition of an equal vol. of aq. 0.2*M*-solutions of the following NH_2 -acids (in the order quoted): glycine (little effect), valine, proline, leucine, tryptophan, lysine, arginine, and histidine. Aq. $(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ has little effect, but cysteine and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ are good catalysts; cysteine is also effective in the homogeneous mixture with (I). Autoxidation of (I) is catalysed by glyceraldehyde (small effect), $\text{CO}(\text{CH}_2\cdot\text{OH})_2$, and AcCHO ; cholic and deoxycholic acids and cholesterol have little or no effect, whilst ergosterol is active. Carotene and related compounds (except bixin) have approx. the same activity as ergosterol. Autoxidation of (I) is inhibited by the following substances (concn. 1.2×10^{-5}

mol.) in the homogeneous state (in the order quoted): *p*-benzoquinone (initial activation), quinol (slight initial activation), $o\text{-C}_6\text{H}_4(\text{OH})_2$ (I has approx. the same effect), PhOH , *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, and adrenaline (max. inhibition).

Of the metal chloride catalysts used [in concns. of 8×10^{-7} and 1.2×10^{-5} mol. per c.c. of (I)], Co^{++} is infinitely more active than Fe^{++} , Fe^{+++} , or Cu^{++} ; smaller concns. are relatively more active. The activity of dihydroxymaleic acid is increased by Cu, Ni, Co, and Fe^{++} (max.); the influence of $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is either not affected or retarded by the above and Mn. The activity of 2:2'-dipyridyl is increased by Cu, Co, Fe^{++} , and Mn (max.) and retarded by Ni. Autoxidation of (I) is accelerated by hæmin, mesohæmin, and deuterohæmin ester [used in $\text{C}_5\text{H}_5\text{N}$ (which also causes an activation by comparison with EtOH-hæmin)]; hæmin is relatively more effective in small concns. Chlorophyll, α -methylchlorophyllide, bilirubin, biliverdin, and ætioporphyrin have little or no effect, but hæmato-, meso-, and deuteroporphyrins show increasing activity. Hæmin (in $\text{C}_5\text{H}_5\text{N}$) is more effective than hæmoglobin (for the same amount of Fe) with (I) + H_2O . H. B.

Cleavage of $\alpha\alpha$ -diacyl and of β -keto- α -monoacyl derivatives of diethyl succinate, glutarate, and adipate. R. N. ISBELL, B. WOJCIK, and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 3678—3687).—The ratio of cleavage products in the alcoholysis and hydrolysis of five $\alpha\alpha$ -diacyl-succinic and -glutaric esters and of two β -keto- α -acetyl- α -alkyladipic esters is not determined by the relative acidity of the acids produced by cleavage; the ratio of AcOH to BzOH is 2:1 for the hydrolysis of Et α -benzoyl- α -acetyl-succinate and 4:1 for the corresponding glutaric ester. Similarly, the ratio of AcOH to PrCO_2H is approx. 2:5 for Et α -acetyl- α -butyrylsuccinate, whilst AcOH is not produced from Et α -acetyl- α -butyrylglutarate. The size of the alkyl group has a pronounced effect, since the Ac cleavage is only two thirds as much with Et β -keto- α -acetyl- α -lauryladipate as with Et β -keto- α -acetyl- α -butyladipate. Various conclusions previously deduced regarding the cleavage of simple $\alpha\gamma$ -diketones also hold for these more complex $\alpha\gamma$ -diketones which are also β -keto-esters. Et α -acetyl- α -butyrylsuccinate, b.p. 144—150°/4 mm., results in 53% yield from Et α -acetylsuccinate, PrCOCl , and Na. Et α -benzoyl- α -acetylsuccinate (I), b.p. 178—182°/1 mm., is formed similarly in 55% yield and in 54% yield from Et α -benzoyl- α -acetylacetate and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$. Et α -benzoyl- α -acetylglutarate (II), b.p. 184—187°/1 mm.; Et α -acetyl- α -butyrylglutarate, b.p. 156—159°/3 mm.; Et α -acetyl- α -trimethylacetylsuccinate, b.p. 143—146°/4—5 mm.; Et α -acetyl- α -trimethylacetylglutarate, b.p. 148—153°/4—5 mm.; Et β -keto- α -acetyl- α -butyladipate (III), b.p. 147—150°/1 mm.; and Et β -keto- α -acetyl- α -lauryladipate (IV), b.p. 234—239°/1 mm., are prepared. Hydrolysis of (I) with H_2O at 200° and 100 atm. for 25 hr. gives 69% of $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, 64% of AcOH, and 31% of BzOH; (II) affords 79% of $\text{CHBzMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, 80% of AcOH, and 21% of BzOH; (III) yields 18% of γ -ketononoic acid, 45% of AcOH, and 59% of heptan- β -one; (IV) gives 33%

of γ -ketomargaric acid, 30% of AcOH, and 66% of tridecan- β -one.

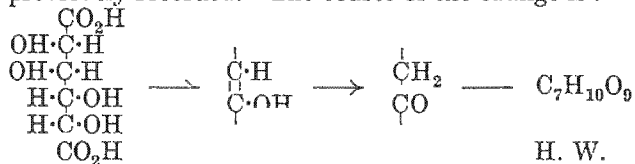
C. J. W. (b)

Electrolytic preparation of *d*-galactonic acid.

H. KILIANI (Ber., 1932, 65, [B], 1269—1272).—Detailed directions are given for the electrolytic oxidation of galactose to Ca *d*-galactonate according to the modified method of Isbell and Frush (A., 1931, 1038).

H. W.

Action of potassium cyanide on potassium mannosaccharate. H. KILIANI (Ber., 1932, 65, [B], 1272—1274).—New analyses of the Ca and Zn salts (A., 1928, 741; 1931, 1274) establish the respective constitutions $C_7H_6O_8Ca$ and $C_7H_6O_8Zn$. They are derived from a monolactone, $C_7H_8O_8$, corresponding with the tribasic acid $C_7H_{10}O_9$ instead of $C_7H_{10}O_{10}$ previously recorded. The course of the change is:



H. W.

Isomerism phenomena of *d*-mannosaccharic acid. K. REHORST (Ber., 1932, 65, [B], 1476—1486).—*d*-Mannosaccharodilactone is converted through the corresponding Na and Ag salts into cryst. *d*-mannosaccharic acid (I), m.p. 128.5°, $[\alpha]_D^{20} +3.6^\circ$ to $+50.0^\circ$ in H_2O (for method, cf. A., 1928, 272). After neutralisation, the solution does not reduce Fehling's solution or react with I and alkali according to Willstätter and Schudel. During the earlier stages of mutarotation, the titratable acidity of the solution diminishes, but reducing products are not formed; after long preservation at room temp., I is absorbed and Fehling's solution reduced to an increasing extent. Neutralisation of cryst. (I) by NaOH or KOH gives the Na salt, $[\alpha]_D -17.2^\circ$, and K salt $[\alpha]_D -14.1^\circ$ (identical with Kiliani's salt from the diamide); the solutions have no reducing properties and do not become discoloured at 100°. If cryst. (I) is kept in aq. solution for 5—6 hr. at 100°, *d*-mannosaccharodilactone (II) is formed with the properties described by Kiliani and Fischer, which can scarcely be attributed to the presence of a $\cdot CHO$ or $\cdot CO$ group. The aq. solution of (II) gradually becomes acid, whereas the consumption of Fehling's solution and of alkaline I diminishes to about 10% of its initial val. (I) is converted instantaneously by a moderate excess of NaOH into (II) and the excess can be titrated accurately after a few min. (I) prepared from (II) through the Na salt and an equiv. amount of acid differs widely from the cryst. acid, since it has $[\alpha]_D -10.8^\circ$ to $+26.4^\circ$, reduces Fehling's solution, and ppts. CHI_3 from alkaline I. Gradual increase of $[\alpha]_D$ is accompanied by diminution of directly titratable acid and of the consumption of I to about 34% of that of the recently liberated acid. Alkali salts derived from (II) by an excess of alkali followed by neutralisation differ from those obtained from cryst. (I) in exhibiting reducing properties. These diminish more rapidly than in the case of the free acid, and at equilibrium the consumption of I is only about 10% of the initial amount. $[\alpha]_D$ changes very rapidly, the vals. recorded

being -32.8° to $+7.5^\circ$ and -31.6° to $+8.5^\circ$ for the K_2 and Na_2 salts, respectively. It is suggested that the valencies of the atoms involved in the formation of the two furan rings and consequently of the C atoms are distorted from their normal position and that, after opening of the rings, the C skeleton, now capable of rotation about a common C-C axis, assumes a labile condition, thus explaining the enhanced reactivity and consequent loosening and readier fission of the C chain. The stable modification of *d*-mannosaccharic acid is coupled with the gradual transition to the normal form of the C chain.

H. W.

Preparation of methyl-*d*-galacturonide. K. P. LINK (Nature, 1932, 130, 402).—When heated with MeOH + HCl commercial polygalacturonide from citrus pectin yields the Me ester of methyl-*d*-galacturonide as $C_6H_{11}O_5 \cdot CO_2Me \cdot H_2O$, m.p. 138—140°, $[\alpha]_D^{25} +124.1^\circ$, no mutarotation. This gives methyl-*d*-galacturonide by way of the Ba salt as $C_6H_{11}O_5 \cdot CO_2H \cdot 2H_2O$, m.p. 112—114°, $[\alpha]_D^{25} +127.6^\circ$, no mutarotation. L. S. T.

Methylation of monocarboxylic acids derived from aldoses. Structure of pentamethyl- α -glucoheptono- γ -lactone. W. N. HAWORTH, E. L. HIRST, and M. STACEY (J.C.S., 1932, 2481—2485).—The OH groups in positions 4 and 5 in galactonic acid, certain hexoses, and α -glucoheptose resist methylation either by $Ag_2O + MeI$ or $Me_2SO_4 + NaOH$, and such methylation of the sugar acid frequently affords the best method for the prep. of the fully methylated γ -lactone. Thus Na α -glucoheptonate with Me_2SO_4 and 30% NaOH in $H_2O - COMe_2$ at 55° (or the γ -lactone with $AgO - MeI$) gives 2:3:5:6:7-pentamethyl- α -glucoheptono- γ -lactone, m.p. 104°, $[\alpha]_D^{20}$ (initial) -13° in H_2O , $+69^\circ$ in Et_2O , hydrolysed extremely slowly in aq. solution and oxidised by HNO_3 (*d* 1.42) to *i*-dimethoxysuccinic acid unaccompanied by trimethoxyglutaric or higher acids. γ -Mannonolactone is similarly methylated to its 2:3:5:6- Me_4 derivative, whilst γ -galactonolactone + H_2O (I) gives 2:3:4:6-tetramethylgalactonolactone and 2:3:5:6-tetramethyl- γ -galactonolactone (II). After dehydration (I) with Ag_2O and MeI (four treatments) and subsequent esterification gives (?) 2:3:6-trimethylgalactonolactone, m.p. 99°, $[\alpha]_D^{25} -40^\circ$ to -28° in H_2O in 14 days, further methylated to (II) and oxidised with HNO_3 (*d* 1.2) to *d*-dimethoxysuccinic acid, no methylated mucic acid being detected. Under the same conditions γ -arabono- and -glucono-lactones give completely methylated products.

J. W. B.

Catalytic hydrogenation of ozonides. F. G. FISCHER, H. DÜLL, and L. ERTEL (Ber., 1932, 65, [B], 1467—1472).—Ozonisation should be effected in dil. solution at a low temp. and an excess of O_3 must be strictly avoided, since oxozonides and perozonides are reduced to acids. To avoid "acid isomerisation" of ozonides, hydrogenation ($Pd - CaCO_3$) is effected with careful cooling. The yields of aldehyde or ketone are 50—90%. Markedly polymerised ozonides are hydrogenated in warm solution under pressure, the use of MeOH or EtOH as solvent also protecting the aldehyde by production of the sluggish acetals. Ozonisation in EtOAc is not accompanied by the production of insol. polymerised ozonides. The fol-

lowing schemes are suggested for the degradation of aldehydes and acids or esters: $\text{CH}_2\text{R}\cdot\text{CHO} \xrightarrow{\text{MgPhBr}} \text{CH}_2\text{R}\cdot\text{CHPh}\cdot\text{OH} \longrightarrow \text{CHR}\cdot\text{CHPh} \xrightarrow{\text{I}_2} \text{R}\cdot\text{CHO} + \text{PhCHO}$; $\text{CH}_2\text{R}\cdot\text{CO}_2\text{H} \xrightarrow{\text{MgPhBr}} \text{CH}_2\text{R}\cdot\text{CPh}_2\cdot\text{OH} \longrightarrow \text{CHR}\cdot\text{CPh}_2 \longrightarrow \text{R}\cdot\text{CHO} + \text{COPh}_2$; MgEtBr may replace MgPhBr. The following examples are recorded: methylheptenone to lœvulaldehyde (yield 70%), mesityl oxide to methylglyoxal, oleic acid to nonaldehyde and azelaic acid semialdehyde; cyclopentene to glutardialdehyde, cyclohexene to adipaldialdehyde (*dioxime*, m.p. 183–184°) and its Me_4 acetal, cycloheptene to pimeldialdehyde (*dioxime*, m.p. 153°), nonoic acid to α -diphenyl- Δ^8 -nonene, b.p. 200–210°/13 mm., and thence to octaldehyde. H. W.

Additive compounds of mercaptans with aldehydes during the formation of mercaptals. T. G. LEVI (Gazzetta, 1932, 62, 775–780).— CH_2O combines in MeOH with EtSH, Pr^nSH , *iso*- $\text{C}_5\text{H}_{11}\text{SH}$, and PhSH to form liquid additive compounds, and with 2-thiolbenzthiazole to a compound (I), m.p. 125–130°. In presence of ZnCl_2 , *di-n-propylthiolmethane*, b.p. 216°, *diisomethylthiolmethane*, b.p. 265°, and $\text{CH}_2(\text{SPh})_2$ are formed. 2-Thiolbenzthiazole is converted by MeI into *methylene dibenzthiazyl sulphide*, m.p. 98°, not obtainable from (I). E. W. W.

Microchemical detection of formaldehyde in presence of hexamethylenetetramine. C. KOLLO and F. POLYCHRONIADE (Pharm. Zentr., 1932, 73, 578–582).—Hexamethylenetetramine (I) is removed from the solution either as the picrate or as the BiCl_3 compound and CH_2O is detected in the residue with dimethyldihydroresorcinol (II) (A., 1928, 1117). (I), which reacts with (II) on heating, is completely pptd. by either reagent and no CH_2O is formed by hydrolysis. E. H. S.

System amino-substance-aldehyde-hydrogen acceptor. F. LIEBEN and V. GETREUER (Biochem. Z., 1932, 252, 420–433).—The hydrogenation of methylen-blue, malachite-green, and cysteine in a system containing an NH_2 -compound, PO_4''' buffer, and an aldehyde is examined. By variation of the NH_2 -compound and the aldehyde, it is shown that introduction of CO_2H and Me groups, especially on the C atom adjacent to the N, decreases, whereas that of Ph and OH groups increases, the rate of hydrogenation. Both a free NH_2 and the NH group of proline and hydroxyproline react in this way. The PO_4''' buffering may be replaced by BO_3''' . EtCHO reacts more slowly than MeCHO. Unsaturated aldehydes (acraldehyde, crotonaldehyde) considerably accelerate the reaction. Decrease of concn. of NH_2 -compound and of aldehyde retards, and increase of concn. accelerates, hydrogenation. P. W. C.

Condensation of bromal with carbamide. F. D. CHATTAWAY and E. J. F. JAMES (Proc. Roy. Soc., 1932, A, 137, 481–488).— $\text{CO}(\text{NH}_2)_2$ condenses with $\text{CBr}_3\cdot\text{CH}(\text{OH})_2$ in H_2O to give α -hydroxy- $\beta\beta\beta$ -tribromoethylcarbamide, m.p. 136° (decomp.) [Ac_2 derivative $\text{CBr}_3\cdot\text{CH}(\text{OAc})\cdot\text{NH}\cdot\text{CO}\cdot\text{NHAc}$, m.p. 184° (decomp.)], which, fused with more $\text{CBr}_3\cdot\text{CH}(\text{OH})_2$, gives *s-di-(α -hydroxy- $\beta\beta\beta$ -tribromoethyl)carbamide*, m.p.

178° (decomp.) [$\text{OO}'\text{-Ac}_2$ derivative, m.p. 180° (decomp.)]. These with N-NaOH and Ac_2O at 0° afford, respectively, bis-(α -carbamido- $\beta\beta\beta$ -tribromoethyl) ether, decomp. 211° [Ac_2 derivative $[\text{NHAc}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CBr}_3)]_2\text{O}$, m.p. 219° (decomp.)], and the anhydro-compound

$\text{O} < \text{CH}(\text{CBr}_3)\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CBr}_3) > \text{O}$ [not pure, m.p. 92° (decomp.)]. Fission of these ethers with NaOR in ROH gives the alkoxy-derivative, $\text{CBr}_3\cdot\text{CHO}$, HCO_2Na , and $\text{CO}(\text{NH}_2)_2$, and thus are obtained: α -methoxy-, m.p. 184° (decomp.), α -ethoxy- (I), m.p. 162° (decomp.) ($\text{N}'\text{-Ac}$ derivative, m.p. 177° (decomp.)], and α -n-propoxy-, m.p. 144° (decomp.), $\beta\beta\beta$ -tribromoethyl-, *s-di-(α -methoxy- $\beta\beta\beta$ -tribromoethyl)-*, m.p. 215° (decomp.), and *s-di-(α -ethoxy- $\beta\beta\beta$ -tribromoethyl)-*, m.p. 196° (decomp.), -carbamide. The mono-alkoxy-compounds also condense with $\text{CBr}_3\cdot\text{CHO}$ or $\text{CCl}_3\cdot\text{CHO}$, and by conversion into the anhydro-derivatives and fission with the appropriate alkoxide, mixed OR-derivatives are obtained. By such methods are prepared: *s-(α -hydroxy- $\beta\beta\beta$ -tribromoethyl)(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)carbamide*, m.p. 186° [$\text{OO}'\text{-Ac}_2$ derivative, m.p. 185° (decomp.)], from the anhydro-derivative of which the corresponding ($\alpha\text{-OEt}$) $_2$ -derivative, m.p. 203° (decomp.), is obtained. (I) and $\text{CCl}_3\cdot\text{CHO}$ give *s-(α -ethoxy- $\beta\beta\beta$ -tribromoethyl)(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)carbamide*, m.p. 144° (decomp.) [O-Ac derivative, m.p. 192° (decomp.)], the anhydro-derivative (not characterised) of which gives *s-(α -ethoxy- $\beta\beta\beta$ -tribromoethyl)(α -ethoxy- $\beta\beta\beta$ -trichloroethyl)carbamide*, m.p. 203° (decomp.). *s-(α -Methoxy- $\beta\beta\beta$ -tribromoethyl)(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-*, m.p. 193° (decomp.), and the isomeric *s-(α -methoxy- $\beta\beta\beta$ -tribromoethyl)(α -ethoxy- $\beta\beta\beta$ -trichloroethyl)-*, m.p. 206° (decomp.), and *s-(α -ethoxy- $\beta\beta\beta$ -tribromoethyl)(α -methoxy- $\beta\beta\beta$ -trichloroethyl)-*, m.p. 197° (decomp.), -carbamide, are similarly obtained. J. W. B.

Alkyl peroxides. IX. Perparaldehyde. A. RIECHE and R. MEISTER (Ber., 1932, 65, [B], 1274–1279).—MeCHO is added to 3% ethereal H_2O_2 at 0° in presence of anhyd. Na_2SO_4 and, after 2 days at 0°, the product is filtered and treated with P_2O_5 . After removal of the solvent at 20°/15 mm., “*synthetic dimeric butylene ozonide*,” $\text{C}_8\text{H}_{16}\text{O}_6$, remains as an unstable, mobile liquid. It is hydrolysed by warm dil. H_2SO_4 to MeCHO and H_2O_2 , slowly by cold H_2O , whereby the active O is slowly utilised in the production of AcOH; utilisation is immediate in the presence of FeSO_4 . When preserved or placed in vac. at 40°, it appears to yield ethylidene peroxide. When cautiously distilled under diminished pressure, the synthetic ozonide is transformed into *monoperparacetaldehyde*, $\text{C}_6\text{H}_{12}\text{O}_4$, b.p. 45–46°/12 mm., m.p. about 9°, $d_{20}^{20} 1.0672$. It is hydrolysed by warm, dil. H_2SO_4 to MeCHO (3 mols.) and H_2O_2 (1 mol.) and by alkali with formation of AcOH (1 mol.). H. W.

Oxidation of methylglyoxal by molecular oxygen in presence of hydrocyanic acid. C. V. SMYTHE (Ber., 1932, 65, [B], 1268–1269).—AcOH, CO_2 , and a small quantity of HCO_2H are the main ultimate products formed when methylglyoxal is shaken with O_2 in presence of an excess of HCN. H. W.

Iodometric determination of acetone. K. LESNIGENKO (Chem. Obzor, 1932, 7, 2—4; Chem. Zentr., 1932, i, 2743).—The error is $\pm 0.5\%$, the results usually being too high. A. A. E.

Colorimetric determination of sugars. A. CASTIGLIONI (Annali Chim. Appl., 1932, 22, 570—574).—To 0.3—5.0 c.c. of solution, containing 0.003—0.05 g. of sucrose, glucose, or lactose, 10 drops of 20% alcoholic resorcinol are added, then 2 vols. of HCl (d 1.19), and the mixture is boiled for 1 min. After cooling the ppt. is dissolved in EtOH and the solution is diluted to 20 c.c. with H_2O . The coloration is compared with a standard (1 c.c. of 1% sugar solution) in a Duboscq colorimeter.

O. F. L.

Reactions of carbohydrates and polysaccharides. XL. Magnitude of the angle between the two valency linkings of the oxygen atom in organic compounds and the structure of glucose. J. S. ALLEN and H. HIBBERT (Ber., 1932, 65, [B], 1362—1371).—The hypothesis of a tetrahedral structure of the O atom is not in harmony with experimental data which agree with the assumption that the valency linkings of O form an angle of 90° . The data cannot be regarded as final, but as means for the particular compounds. The systems are to be regarded as kinetic, not static, although the cyclic compounds exhibit a definite, geometrical structure. 2-Hydroxy-2'-dichloromethyl-1:3-dioxalan is described.

H. W.

5-Methylglucose of Ohle and von Vargha. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1932, 97, 751—761).—The 5-methylglucose of Ohle and von Vargha (A., 1929, 1279) (improved prep.) is shown to be 6-methylglucose, m.p. 153—154° (rapid heating, softens 150°) [osazone, m.p. 183° (sinters 180°, decomp. 192°); Ac_4 derivative, m.p. 95—96°; Ba salt of the gluconic acid] (cf. A., 1931, 939).

A. A. L.

Carbohydrates. XIII. Benzylidene and benzoyl derivatives of glucose. P. BRIGL and H. GRÜNER (Ber., 1932, 65, [B], 1428—1434).—4:6-Benzylidene- α -D-glucose, m.p. 172°, $[\alpha]_D^{25} + 39.6^\circ$ to $+4.3^\circ$ in EtOH (cf. Zervas, A., 1931, 1275), is converted by $BzCl$ in C_6H_5N or aq. alkali into 4:6-benzylidene- α -D-glucose 1:2:3-tribenzoate (I), m.p. 193°, $[\alpha]_D^{25} - 10.6^\circ$ in $CHCl_3$, hydrolysed by 2N-HCl in $COMe_2$ at 50° to glucose 1:2:3-tribenzoate ($+ \frac{1}{3}C_6H_6$) (II), m.p. 107—108° after softening at 104°, $[\alpha]_D^{25} + 30.8^\circ$ in $CHCl_3$ or, solvent-free, $[\alpha]_D^{25} + 33.1^\circ$ in $CHCl_3$, which is re-converted into (I) by $PhCHO$ and $ZnCl_2$. (I) is transformed by Ac_2O and $ZnCl_2$ at room temp. or, preferably, by Ac_2O and a little conc. H_2SO_4 into 1:4:6-triacetylglucose 2:3-dibenzoate (III), m.p. 168°, $[\alpha]_D^{25} + 130.7$ in $CHCl_3$ (glucose penta-benzoate is similarly converted by Ac_2O and $ZnCl_2$ into 1-acetylglucose tetrabenzoate, m.p. 160—161°, $[\alpha]_D^{25} + 90.6^\circ$). (I) and $HBr-AcOH$ afford β -methylglucoside 4:6-diacetate 2:3-dibenzoate, m.p. 133°, $[\alpha]_D^{25} + 78.8^\circ$ in $CHCl_3$, also obtained from (III) or from glucose diacetate 1:2:3-tribenzoate (III) by means of $HBr-AcOH$ and Ag_2CO_3-MeOH . Treatment of (II) with $Ac_2O-C_6H_5N$ at room temp. gives (IV), m.p. 14°, $[\alpha]_D^{25} + 36.6^\circ$ in $CHCl_3$; and with $BzCl$ and

C_6H_5N yields glucose 1:2:3:6-tetrabenzoate (V), m.p. 153—154°, $[\alpha]_D^{25} + 27.0^\circ$ in $CHCl_3$. Glucose 4-acetate 1:2:3:6-tetrabenzoate, m.p. 149—150°, $[\alpha]_D^{25} + 55.0^\circ$ in $CHCl_3$, is derived from (V) and $Ac_2O-C_6H_5N$. *iso*Propylideneglucose, $PhCHO$, and $ZnCl_2$ give 1:2-isopropylidene-3:5-benzylideneglucosofuranose, m.p. 149°, $[\alpha]_D^{25} + 23.4^\circ$ in $CHCl_3$, identical with the "1:2-isopropylidene-5:6-benzylideneglucosofuranose" of Levene and Meyer (A., 1923, i, 92). The constitution is established by conversion of the substance into 1:2-isopropylidene-3:5-benzylideneglucose 6-benzoate, m.p. 124°, $[\alpha]_D^{25} + 3.5^\circ$ in $CHCl_3$, and 6-acetate, m.p. 126—127°, $[\alpha]_D^{25} + 11.8^\circ$ in $CHCl_3$, identical with the products derived by the action of $PhCHO$ and $ZnCl_2$ on 1:2-isopropylideneglucose 6-benzoate and 6-acetate. *iso*Propylideneglucose 3-acetate could not be condensed with $PhCHO$ and $ZnCl_2$.

H. W.

Action of titanium tetrachloride on tetracetyl- β -D-glucosidoglycollic ester. (Miss) T. M. REYNOLDS (J. Proc. Roy. Soc. New South Wales, 1932, 66, 167—170; cf. A., 1928, 1118).— $TiCl_4$ and Et tetra-acetyl- β -D-glucosidooxyacetate afford acetochloroglucose and not the α -glucoside.

J. L. D.

Phenomena accompanying the hydrolysis of sucrose. S. BEZZI.—See this vol., 1094.

Characteristic decompositions of sucrose and employment of the decomposition products for the preparation of colloidal solutions of metals. A. H. ERDENBRECHER (Z. ver. Deut. Zucker-Ind., 1932, 82, 718—741).—Decomp. of molasses or sucrose under pressure in presence of alkali gives an acid resembling humic acid. Oxidation of this with HNO_3 gives an acid containing N (Na , K , pyridine, and N_2H_4 salts; anilide, and naphthylamide; Cl , Br , and I derivatives). The NH_4 salt gives up only part of its NH_3 with $NaOH$. Intermediate oxidation products are obtained with varying concn. of HNO_3 . The substances, especially the oxidation products, possess strong protective colloid properties.

A. A. L.

Ketone sugar series. I. Novel form of stereoisomerism in the sugar group. Acetyl and halogenoacetyl derivatives of turanose. E. PACSU (J. Amer. Chem. Soc., 1932, 54, 3649—3661).—Three octa-acetates are obtained by acetylation of cryst. turanose (I) with Ac_2O and $ZnCl_2$ at room temp. instead of the two required by the theory of oxo-cyclo-desmotropy of the reducing sugars. The first octa-acetate (II), m.p. 216—217°, $[\alpha]_D^{25} + 20.5^\circ$ in $CHCl_3$, is a derivative of the semi-orthoacetic anhydride type. All such sugar derivatives contain a new asym. C atom in the mol. and can, therefore, exist in two diastereoisomeric forms. The second octa-acetate (III), m.p. 158°, $[\alpha]_D^{25} + 85.4^\circ$, $[\alpha]_D^{25} + 125.75^\circ$ in $CHCl_3$, is assigned the 2:6-ring structure. The third octa-acetate has m.p. 96°, $[\alpha]_D^{25} + 126.2^\circ$, $[\alpha]_D^{25} + 98.14^\circ$, $[\alpha]_D^{25} + 151.65^\circ$ in $CHCl_3$, and is probably an open-chain derivative. A fourth octa-acetate, m.p. 194—195°, $[\alpha]_D^{25} + 103.16^\circ$ in $CHCl_3$, is obtained together with (II) when the bromide from (II) is treated with $AgOAc$ in Ac_2O ; its properties are identical with those of (II) and it represents the second (above) possible diastereoisomeride. (II) and $TiCl_4$ in $CHCl_3$ give the Cl derivative, m.p. 165° (decomp.).

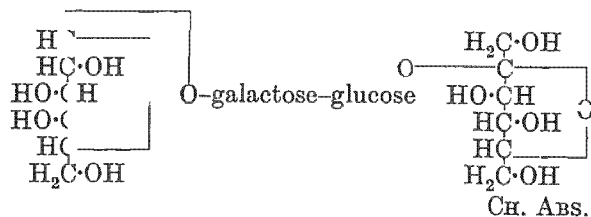
—0.44° in CHCl_3 ; the *Br* derivative, m.p. 133—134° (decomp.), $[\alpha]_D^{20}$ —30.5° in CHCl_3 , is prepared from (II) and *HBr* in AcOH-CHCl_3 or from (I) and *Br* in Ac_2O , whilst the *I* derivative, m.p. 105—106°, $[\alpha]_D^{20}$ —54.2° in CHCl_3 , is obtained from (II) and *HI* in AcOH-CHCl_3 . (III) yields a *Cl* derivative, syrupy, $[\alpha]_D^{20}$ +92.9° in CHCl_3 , and a *Br* derivative, $[\alpha]_D^{20}$ +117.4° in CHCl_3 . The stable halides from (II) are orthoacetyl halide derivatives; thus, the bromide and pyridine give a ketenacetal. The unstable halides from (III) have the regular structure of the α -halogeno-acetyluranes. Since the properties of these substances differ from those of the " α -chloroacetylfructose," it is concluded that the latter cannot be the stereoisomeride of the unstable β -chloroacetylfructose.

C. J. W. (b)

Cellotriose. K. DZIENGEL, C. TROGUS, and K. HESS (Ber., 1932, 65, [B], 1454—1457).—Cellotriose (Zechmeister and others, A., 1929, 544; 1931, 716) gives a Röntgen diagram which differs from those of hydrocellulose and cellobiose and is not altered by dissolution of the substance in H_2O , MeOH , or 95% EtOH and evaporation of the solutions or by fractionation from EtOH . It is therefore regarded as a chemical individual. Conc. of a solution in MeOH at room temp. yields a most sparingly sol. fraction which gives the interferences of hydrocellulose, whereas the other fractions are amorphous. Marked variations in $[\alpha]_D$ or *I* val. among the different fractions are not observed. Gradual addition of Et_2O to the substance dissolved in $\text{C}_5\text{H}_5\text{N}$ yields fractions with interferences of an amorphous substance and marked variation in $[\alpha]_D$ and *I* val. Cellotriose is regarded as a mol. compound of hydrocellulose and an unknown reducing component other than cellobiose.

H. W.

Constitution of stachyose. I. M. ONUKI (J. Agric. Chem. Soc. Japan, 1932, 8, 445—462).—Stachyose, $(\text{C}_{24}\text{H}_{42}\text{O}_{21})_2 \cdot 3\text{H}_2\text{O}$ (anhyd. at 115° in vac.), crystallised on addition of EtOH to the purified $[\text{Pb}(\text{OAc})_2, \text{Hg}(\text{OAc})_2, \text{Ba}(\text{OH})_2, \text{phosphotungstic acid}]$ juice of the bulb of *Stachys tuberosa*, Nd. *Tetradecaacetyl-*, $\text{C}_{24}\text{H}_{28}\text{O}_7(\text{OAc})_{14}$, m.p. 95—96°; *tetradeca-p-nitrobenzoyl-*, m.p. 166°; and *tetradecamethyl-stachyose*, a syrup, $[\alpha]_D^{25}$ +133.3° (C_6H_6), hydrolysed (*HCl*) to 1:3:4:6-tetramethyl-*D*-fructose and 2:3:4:6-tetramethyl-*D*-galactose, were prepared. Stachyose was hydrolysed by 20% AcOH to manninotriose, which was converted by way of *Ca* manninotriurate, and undecamethylmanninotriuronic acid into 2:3:5:6-tetramethyl-*D*-gluconic acid lactone and 2:3:4:6-tetramethylgalactose. Stachyose is assumed to have the structure:



CH. ABS.

Polysaccharides. XII. Acetolysis products of cellulose. W. N. HAWORTH, E. L. HIRST, and

O. ANT-WUORINEN (J.C.S., 1932, 2368—2371).—In agreement with Meyer and Mark (A., 1929, 51) and Freudenberg (*ibid.*, 430) cellobiosan acetate (I) obtained by acetolysis of cellulose under Hess' conditions (A., 1927, 44) is not homogeneous, but is a mixture of cellodextrin acetates of high mol. wt. (>3000 in camphor). Acetolysis of (I) ($\text{AcOH-Ac}_2\text{O-H}_2\text{SO}_4$ at 60°) affords a mixture of cellodextrin acetates (mol. wt. about 1600) and unchanged biosan, whilst under more drastic conditions (105°) there results a mixture of dextrin acetates, separated by crystallisation from EtOH into fractions differing in m.p. and $[\alpha]_D$, and of mol. wt. ranging from 640 to 1300. Methylation of (I) with $\text{Me}_2\text{SO}_4\text{-NaOH}$ in $\text{H}_2\text{O-COMe}_2$ gives methylated cellobiosan, m.p. 213—215°, mol. wt. 1600, increased to 2100 after removal of partly degraded material by fusion with camphor. Acetolysis of cellulose under Bertrand and Benoist's conditions (A., 1923, i, 756) gives procellose free from admixture with cellobiose octa-acetate, the *Ac* derivative, m.p. about 120°, $[\alpha]_D^{20}$ +5° in C_6H_6 , mol. wt. 690, of which with $\text{Me}_2\text{SO}_4\text{-30% NaOH}$ in $\text{H}_2\text{O-COMe}_2$ gives a fully methylated procellose, b.p. about 300°/0.04 mm., $[\alpha]_D^{20}$ +27° in CHCl_3 , hydrolysed by 5% *HCl* to tetramethylglucopyranose and 2:3:6-trimethylglucopyranose. The rate of hydrolysis is similar to that of a methylated trisaccharide (A., 1931, 941). Hence procellose is a trisaccharide and Ost's celloisobiose (A., 1920, i, 423) is probably a mixture of this with cellobiose.

J. W. B.

Polysaccharides. XIII. Chain-length of methylated cellodextrins. W. N. HAWORTH and H. MACHEMER (J.C.S., 1932, 2372—2374).—By repeated fractional pptn. (cf. Bergmann and Machemer, A., 1930, 457) the products of the acetolysis of cellulose (Hess and Friese, A., 1927, 44) are separated into eight fractions ($[\alpha]_D$ in CHCl_3 , decomp. point, and % *OAc* determined) of approx. chain-lengths of 21—12 glucose residues (by *I* val.). Each fraction was converted into the corresponding *Me* derivative (A., 1931, 941; this vol., 1022), again fractionated, and each fraction ($[\alpha]_D$, decomp. point, and % *OMe* determined) hydrolysed and the yield of tetramethylglucose determined. Calc. from the latter, the estimated average no. of glucose residues varies from 26 to 11, a val. in agreement with that of other workers. Cellodextrins are long extended mols. consisting of mutually linked glucopyranose units.

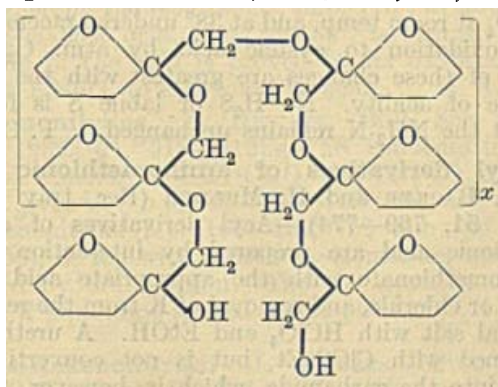
J. W. B.

Polysaccharides. XIV. Molecular structure of amylose and amylopectin. E. L. HIRST, (Miss) M. M. T. PLANT, and (in part) (Miss) M. D. WILKINSON (J.C.S., 1932, 2375—2383).—Separation of potato starch by Ling and Nanji's method (*ibid.*, 1923, 123, 2666) gives amylose (I), $[\alpha]_D^{20}$ +190° in H_2O , and amylopectin (II), $[\alpha]_D^{20}$ +151° in 5% NaOH , which have the same *P* content (0.2%) as the original starch. Acetylation of (I) gives the *Ac*₃ derivative, charring at 173°, $[\alpha]_D^{20}$ +170° in CHCl_3 , which is deacetylated and methylated without mol. degradation. Hydrolysis of the methylated amylose, m.p. 143° (previous softening), $[\alpha]_D^{20}$ +207° in CHCl_3 , affords 5% of tetramethylglucopyranose (+80% of trimethylglucose), corresponding with a chain-length of 22—24 glucose units. According to conditions, acetylation of (II)

gives products varying continuously from the sol. (I) acetate to the insol. (II) acetate, a similar gradation being encountered in the fractions obtained from the deacetylated and methylated product. Hydrolysis of either the viscous or the mobile methylated fractions with fuming HCl at 0° gives 5% of tetramethylglucose, corresponding with the same chain-length of 22–24 glucose units. Both (I) and (II) are probably built up of 24 glucopyranose units linked as in maltose, the presence of α -glucosidic linkings preventing the formation of long straight chains and favouring interlocked, aggregated mols. It is suggested that (II) consists of aggregates of these interlocked macromols. which in H_2O undergo hydration with the formation of a micellar structure. In solutions of (I) there is a less interlocked and more highly hydrated condition. Thus there is a continuous range of products with properties intermediate between those of (I) and (II) and it is found that (I) retrogrades through intermediate stages to the condition of (II).

J. W. B.

Polysaccharides. XV. Molecular structure of inulin. W. N. HAWORTH, E. L. HIRST, and E. G. V. PERCIVAL (J.C.S., 1932, 2384–2388).— Ac_2O and C_5H_5N convert inulin into its Ac derivative, $[\alpha]_D^{20} -33^\circ$ in $CHCl_3$, converted in the usual manner (cf. preceding abstracts) into methylated inulin (I), m.p. 140°, $[\alpha]_D^{20} -54^\circ$ in $CHCl_3$, both products being homogeneous and formed without appreciable degradation of the inulin mol. Hydrolysis of (I) with $MeOH-H_2O-H_2C_2O_4$ affords 3:4:6-tri- (II) and 3.7% of 1:3:4:6-tetra-methylfructofuranose (isolated as the methylfructosides), together with 3% of a hexamethyldifructose anhydride [hydrolysed to (II); cf. following abstract]. Contrary to Irvine (this vol., 502), only a trace of ω -methoxy-5-methylfurfuraldehyde is formed under the mild conditions used. These results support the suggestion that (I), and hence inulin itself, is composed of continuous chains of about 30 fructofuranose residues united through positions 1 and 2 (cf. A., 1928, 510). The



annexed formula has a mol. wt. of 5000 in agreement with the val. previously deduced (*ibid.*, 1360).

J. W. B.

Polysaccharides. XVI. Molecular structure of inulin and of the derived difructofuranose anhydride. E. W. BODYCOTE, W. N. HAWORTH, and C. S. WOOLVIN (J.C.S., 1932, 2389–2391).—The substance $C_{13}H_{18}O_9$, m.p. 123°, obtained by Irvine and Stevenson (A., 1929, 1046) by the action of HNO_3

in $CHCl_3$ on inulin acetate, was impure. It is actually the Ac_6 derivative $C_{24}H_{32}O_{16}$, m.p. 128° (137° on remelting), $[\alpha]_D^{20} +0.65^\circ$ in $CHCl_3$, of difructose-1:2-anhydride (this vol., 724) which is obtained by deacetylation with $NHMe_2$ or $Ba(OH)_2$. It is formed by rupture of the primary valency linkings of the fructofuranose units in inulin (preceding abstract) and their reunion to the more stable difructose anhydride.

J. W. B.

Dependence of the viscosity of cellulose solutions on temperature. K. HESS and B. RABINOWITSCH (Ber., 1932, 65, [B], 1407–1411).—Staudinger's formula, $K_m c M$, based on the behaviour of complex paraffins of known constitution, is valid only when the suspension has the properties of an ideal, dilute solution and η_{sp} is independent of the temp. Since these conditions are not fulfilled by cellite or limit dextrin 2 in $AcOH$ or $COMe_2$, the relationship is inapplicable to cellulose solutions.

H. W.

Cellulose. XLVI. Osmometric investigations with dilute solutions of polymeric carbohydrates. II. Mol. wt. of "hendecamethylcellostriose" and its importance for the constitution of cellulose. K. HESS and M. ULMANN (Annalen, 1932, 498, 77–100).—Mol. wt. determinations [by measurement of osmotic pressures by isothermal distillation (cf. Ulmann, A., 1931, 1367)] of "hendecamethylcellostriose" (I) in aq. solution show that the reversible changes triose \rightleftharpoons biose + monose and biose \rightleftharpoons monose + monose occur. The changes are autocatalytic and depend on concn. and p_H . Calculation of the mol. wt. by van 't Hoff's law is possible only when the concn. is $<0.3\%$ (above this, the increase in osmotic pressure is less than that required by theory). The original must be consulted for details.

(I) should prove useful for the study of the relationship between colloidal properties and chemical constitution, the O linking in the C_6 group, and the properties of cellulose and its derivatives in solution.

H. B.

Behaviour of methylcellulose when melted. K. HESS, E. GARTHE, and C. TROGUS (Cellulosechem., 1932, 13, 156–157).—If methylcellulose is kept at the m.p. a new X-ray diagram is obtained which is ascribed to a double compound, but heating at a higher temp. restores the original lattice.

A. G.

Methylenecellulose. M. SCHENK (Helv. Chim. Acta, 1932, 15, 1088–1102).—Previous results (A., 1931, 717) are confirmed and extended. The max. CH_2O -content of methylenecellulose (I) is 8%, corresponding with the formula $(C_6H_{10}O_5)_2CH_2O$, but most of the immunity to swelling and adsorption of alkali is conferred by the first 1.5–2% of CH_2O introduced. It is considered that the product is of the type $(:C\cdot O)_2CH_2$. The importance of regarding this and other cellulose reactions as taking place on the surface of the micelles is emphasised. (I), prepared by $CH_2(OPr^t)_2$, Ac_2O , and $AcOH$ at 100°, contains also Ac groups (up to 5.73%) which can be removed by $NaOH-EtOH$. The hydrolysed product is also resistant to swelling and alkali. (I) is unaffected by $NaOH-CS_2$ and Schweitzer's reagent, and is harder,

more brittle, less elastic, and tougher than the untreated cellulose. Small amounts (2%) of CH_2O greatly decrease the facility of acetylation of cellulose. (I) is sensitive to acids; its CH_2O -content can be determined by hydrolysis with cold, conc. HCl to glucose and CH_2O , the latter being then determined by combination with phloroglucinol (cf. A., 1931, 1401). R. S. C.

Reinecke's acid applied to some tests on organic bases. A. DANSI, L. MAMOLI, and B. CROCCA (Annali Chim. Appl., 1932, 22, 561—565).—This acid is used in the detection of NMe_3 in presence of NH_2Me , NPhMe_2 in presence of NHPhMe , and in the gravimetric determination of HCO_2NMe_4 . The bases are pptd. as salts of Reinecke's acid. NMe_4 Reineckate may be determined by taking advantage of its relative insolubility (0.0030 g. in 100 c.c. at 15°).

O. F. L.

Reactivity of sodium azide with acid chlorides. J. NELLES (Ber., 1932, 65, [B], 1345—1347).—The passivity of technical NaN_3 towards acid chlorides is due to an unidentified impurity which can be removed by trituration with a trace of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, dissolution in a little H_2O , and pptn. with COMe_3 . Examples of its use are: BzCl to NH_2Ph (yield 69%) and diphenylcarbamide; heptoyl chloride to hexylamine and dihexylcarbamide (total yield, 80%); β -phenylglutaryl chloride to $\alpha\gamma$ -diamino- β -phenylpropane (yield 48%) and the cyclic carbamide

$$\text{CO} \begin{array}{c} \text{NH}\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CH}_2 \end{array} > \text{CHPh}; \text{ cinnamoyl chloride to } \alpha\text{-amino-}\beta\text{-phenylethylene, b.p. } 115\text{--}120^\circ \text{ (yield 77\%).}$$

H. W.

Sugars containing nitrogen. IV. Catalytic reduction of azides. A. BERTHO and J. MAIER (Annalen, 1932, 498, 50—61).—Amines are obtained in good yield by catalytic reduction (usually PtO_2) of azides in MeOH , EtOAc , or H_2O . Benzyl azide gives $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ (93% yield); PhN_3 affords NH_2Ph ; Et azidoacetate furnishes $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$; the Et ester, m.p. 57° , of $\text{dl-}\alpha$ -azidoacetamido- β -phenylpropionic acid, m.p. 104° , yields Et $\text{dl-}\alpha$ -aminoacetamido- β -phenylpropionate (hydrochloride, m.p. 161°), hydrolysed by cold 2N-NaOH to $\text{N-glycyl-dl-phenylalanine}$ and a little of its anhydride; $\alpha\alpha'$ -diazido-adipic acid, m.p. 147° (decomp.) (from Et $\alpha\alpha'$ -dibromo-adipate and NaN_3 in EtOH with subsequent alkaline hydrolysis), gives $\alpha\alpha'$ -diaminoadipic acid, m.p. 280° ; $\text{N-azidoacetylglucosamine}$, m.p. 187° (decomp.), $[\alpha]_D^{25}$ (in H_2O) $+61.8^\circ$ (7 min.) — $+31.8^\circ$ (3 hr.) (from glucosamine and azidoacetyl chloride in dil. NaOH), affords $\text{N-glycylglucosamine}$ (hydrochloride, darkens $180\text{--}190^\circ$); β -azidoacetoglucose yields β -aminoacetoglucose, m.p. 126° (hydrochloride, m.p. about 170°), which with HNO_2 gives glucose tetra-acetate; β -azidoacetogalactose, m.p. 96° , $[\alpha]_D^{25}$ -16.2° in CHCl_3 (from β -acetochlorogalactose and NaN_3 in MeCN), furnishes β -aminoacetogalactose, m.p. 139° , $[\alpha]_D^{25}$ $+26.7^\circ$ in MeOH .

H. B.

Preparation of aliphatic amino-alcohols. H. E. GLYNN and W. H. LENNELL (Pharm. J., 1932, 129, 250—251).— α -Nitro- β -hydroxy- n -hexane (b.p. $120^\circ/20$ mm.), obtained by condensing valeraldehyde with MeNO_2 in presence of KOH , is reduced

by SnCl_2 and HCl to the corresponding NH_2 -alcohol (O-Bz derivative, m.p. 137°). The anæsthetic inactivity of this NH_2 -ester and of $\text{ON-dibenzoyl-}\delta$ -aminopentanol is discussed with reference to cocaine and to several well-known synthetic local anæsthetics.

W. S.

Amino-hydroxy-compounds which show the biuret reaction. VIII. Stereoisomerism of isoserine. M. TOMITA, J. KARASHIMA, Y. NAKAMURA, and M. NAKASHIMA (Z. physiol. Chem., 1932, 211, 38—46; cf. A., 1931, 1428).—Resolution of $\text{dl-benzoylisoserine}$ by means of brucine gives a mixture of two dextrorotatory components, benzoyl- l -isoserine (I), $[\alpha]_D^{25} +11.31^\circ$ (Ba salt, m.p. 276°), and a substance (II), $\text{C}_{20}\text{H}_{24}\text{O}_7\text{N}_2$, m.p. 75° , $[\alpha]_D^{25} +29.46^\circ$, and two levorotatory components, benzoyl- d -isoserine (III), m.p. 110° , $[\alpha]_D^{25} -11.26^\circ$, and a substance (IV), $\text{C}_{20}\text{H}_{24}\text{O}_7\text{N}_2$, m.p. 75° , $[\alpha]_D^{25} -30.03^\circ$. Both (I) and (II) give l -isoserine and BzOH on hydrolysis, (III) and (IV) give d -isoserine. From the benzoylated dl-isoserine a racemic compound of (II) and (IV), m.p. 75° , can be obtained. J. H. B.

μ -Amino- n -tridecoic acid. A. MÜLLER and P. KRAUSS (Ber., 1932, 65, [B], 1354—1358).— $\alpha\mu$ -Dibromo- n -dodecane is transformed by K phthalimide at $155\text{--}160^\circ$ into μ -bromo- α -phthalimido- n -butane, m.p. $63.5\text{--}64^\circ$ (corr.), whence by NaI in boiling EtOH μ -iodo- α -phthalimido- n -butane (I), m.p. $68\text{--}68.5^\circ$ (corr.), is obtained. (I) and KCN in EtOH afford μ -cyanododecamethylenephthalamic acid, converted by HCl (d 1.19) at $170\text{--}180^\circ$ into μ -amino- n -tridecoic acid hydrochloride, m.p. 153° (corr.) [free acid, decomp. about 177° ; chloroplatinate, decomp. about 207° ; benzenesulphonyl, m.p. 102.2° (corr.), and apparently dimorphous, m.p. $110.5\text{--}111^\circ$ (corr.) and about 105° , respectively, and Bz derivatives].

H. W.

Oxidation of cystine in acid solution. J. C. ANDREWS (J. Biol. Chem., 1932, 97, 657—662).—Solutions (0.5—1.0%) of l -cystine (initially partly racemised) in 0.5, 2.5, and 6N- HCl and in 2.5N- H_2SO_4 at room temp. and at 38° undergo racemisation and oxidation to cysteic acid by atm. O_2 . The rates of these changes are greatest with the higher degree of acidity. No H_2S or labile S is formed, whilst the $\text{NH}_2\cdot\text{N}$ remains unchanged. F. O. H.

Acyl derivatives of aminomethiononic acid. H. J. BACKER and H. MULDER (Rec. trav. chim., 1932, 51, 769—774).—Acyl derivatives of aminomethiononic acid are prepared by interaction of K_2 aminomethionate with the appropriate acid anhydride or chloride, and removal of K from the resulting neutral salt with HClO_4 and EtOH . A urethane is obtained with ClCO_2Et , but is not convertible by NH_3 into the carbamide, which is, however, formed by interaction of K H aminomethionate with KCNO . The following are described: acetamido- ($+2\text{H}_2\text{O}$), m.p. 180° (decomp.) [A_2 salt ($+2\text{H}_2\text{O}$) ($+1\text{HNO}_3$, decomposed by H_2O)], propionamido- (as K_2 salt), benzamido- (as K_2 salt), carbamido- ($+2\text{H}_2\text{O}$) (K_2 salt), carboxyethylamino- ($+2\text{H}_2\text{O}$) [K_2 , Ti_2 , and Ba ($+2\text{H}_2\text{O}$) salts], and carboxypropylaminomethiononic acid (as K_2 salt); also strychnine ($+3\text{H}_2\text{O}$), Ba , and Na_2 aminomethionates. H. A. P.

Unsaturated amides. M. VOSSEN (Bull. Soc. chim. Belg., 1932, 41, 331—332).—The following isomeric amides are prepared by slow hydrolysis of the corresponding nitriles (A., 1930, 75) with conc. H_2SO_4 at room temp. (to prevent isomerisation): *cis*-, m.p. 94° (cf. Macq, A., 1927, 652), and *trans*- α -methyl- Δ^2 -pentenamide, m.p. 82° , and α -methylene-*n*-valeramide, m.p. 63° (Macq, *loc. cit.*). Interconversion of these amides does not take place in COMe , in ultra-violet light. H. A. P.

[Butenonitriles and hexenonitriles.] P. BRUYLANTS (Bull. Soc. chim. Belg., 1932, 41, 309—313).—Polemical (cf. this vol., 371). Contrary to Letch and Linstead, the bromometric method of Heim is readily applicable to the hexenonitriles; *n*-valeraldehyde gives a cyanohydrin by Ullée's method, and Pr^CHO and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ condense normally in $\text{C}_5\text{H}_5\text{N}$ to give two stereoisomeric $\alpha\beta$ - and one $\beta\gamma$ -isomeride. Dry-distillation of α -cyano-acids gives a mixture of $\alpha\beta$ - and $\beta\gamma$ -unsaturated nitriles, the latter preponderating. The purity of Letch and Linstead's $\alpha\beta$ -*iso*- (cf. this vol., 258), $\beta\gamma$ -*iso*-, $\alpha\beta$ -*n*-, and $\beta\gamma$ -*n*-hexenonitriles is questioned. H. A. P.

Condensation of cyanoacetic acid with acet-aldehyde. G. HERM (Bull. Soc. chim. Belg., 1932, 41, 320—323).—The products of higher b.p. from the interaction of equimol. amounts of $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, MeCHO , and $\text{C}_5\text{H}_5\text{N}$ (A., 1931, 832) are proved by fractionation and hydrolysis to contain the dimeride of crotononitrile, b.p. 130 — $132^\circ/14$ mm. (cf. A., 1923, i, 1188), and β -methylglutarimide, m.p. 145 — 147° . H. A. P.

Dimeride of pentenonitrile. A. DEWAELE (Bull. Soc. chim. Belg., 1932, 41, 324—326).—The products of higher b.p. from the prep. of *n*-pentenonitrile (this vol., 257) contain about 50% of dimeric pentenonitrile (β -ethyl- α -propenylglutaronitrile), b.p. $150^\circ/10$ mm. (impure), identified by alkaline hydrolysis, distillation of the acid product at 10 mm., and treatment of the resulting syrupy anhydride with aq. NH_3 , whereby the *monoamide*, m.p. 175° , of β -ethyl- α -propenylglutaric acid, m.p. 85 — 86° , is formed. The structure of the acid is proved by its oxidation by alkaline KMnO_4 to ethylsuccinic acid. H. A. P.

Hexenonitriles. A. DEWAELE (Bull. Soc. chim. Belg., 1932, 41, 318—319).—The condensation of equimol. amounts of Pr^CHO , $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{C}_5\text{H}_5\text{N}$ gives *cis*-, b.p. 149 — $150^\circ/756$ mm., and *trans*- Δ^2 -hexenonitrile, b.p. 164 — $165^\circ/752$ mm. (cf. this vol., 258), mixed with a little $\beta\gamma$ -isomeride, which is removed by bromination. The *cis*-isomeride is not formed if piperidine is used in the place of $\text{C}_5\text{H}_5\text{N}$.

$\beta\gamma$ -isoHexenonitrile. J. BAERTS (Bull. Soc. chim. Belg., 1932, 41, 314—317).—The product of interaction of equimol. quantities of Pr^CHO , $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{C}_5\text{H}_5\text{N}$ (cf. A., 1923, i, 661) is separated by fractional distillation at 1 atm. and 20 mm. into *cis*-, b.p. 137 — 138° , and *trans*- β -methyl- Δ^2 -pentenonitrile, b.p. 156 — 157° , and γ -methyl- Δ^2 -pentenonitrile, b.p. 64.6 — $65.6^\circ/20$ mm. It is possible to measure the separation of $\beta\gamma$ - from the $\alpha\beta$ -isomerides by Heim's bromometric method, with an accuracy of approx. 1%. H. A. P.

β -Propylcrotononitrile. G. FESTAET (Bull. Soc. chim. Belg., 1932, 41, 327—330).— β -Methylamyl alcohol, formed in 30% yield, accompanied by δ -dimethyl-*n*-octane, b.p. 160 — $161^\circ/754$ mm., by interaction of $(\text{CH}_2\text{O})_3$ with Mg *sec*-amyl bromide (cf. A., 1909, i, 449), could not be oxidised to the corresponding aldehyde with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 . Condensation of chloroacetone with MgPr^Br , and treatment of the crude product with KCN in EtOH gives β -hydroxy- β -methylhexonitrile, b.p. 112.5 — $113^\circ/10$ mm., converted by distillation with a few drops of conc. H_2SO_4 into *trans*- β -methyl- Δ^2 -hexenonitrile, b.p. 178 — $179^\circ/760$ mm. [*amide*, m.p. 44 — 45° (cold conc. H_2SO_4)], and its $\beta\gamma$ -isomeride (approx. 39% of the total nitrile). H. A. P.

Ethylenic nitriles. Δ^2 -Heptenonitrile. P. BRUYLANTS (Bull. Soc. chim. Belg., 1932, 41, 333—336).—*n*-Hexaldehyde, b.p. 128 — $128.2^\circ/760.6$ mm., is prepared by catalytic oxidation of *n*-hexyl alcohol (cf. A., 1931, 1404). Dehydration of its cyanohydrin, b.p. 126 — $127^\circ/12$ mm., gives a mixture of *cis*-, b.p. 171 — $172^\circ/761$ mm., and *trans*- Δ^2 -heptenonitrile, b.p. 186.6 — $187.4^\circ/759$ mm., and a little $\beta\gamma$ -isomeride (removed by Br in CHCl_3 at -10° to -5°). The corresponding *amides*, prepared by slow hydrolysis with cold conc. H_2SO_4 (6 months), have m.p. 74 — 74.4° , and 124 — 124.6° , respectively. H. A. P.

Catalytic replacement of nitrogen by hydrogen in diazo- and triazo-(azido)compounds. H. WIENHAUS and H. ZIEHL (Ber., 1932, 65, [B], 1461—1467).—The following examples are cited, change being effected in presence of Paal's colloidal Pd : $\text{CH}_2\text{N}_2\cdot\text{CO}_2\text{Et}$ to EtOAc ; NaN_3 to NaNH_2+N_2 and thence to NaOH and NH_3 ; MeN_3 to NH_2Me ; PhN_3 to $\text{NH}_2\text{Ph}+\text{N}_2$; carbamideimidoazide to guanidine; cyanuric triazide to melamine; N_2O to $\text{H}_2\text{O}+\text{N}_2$. H. W.

Physical properties of *tert*-arsines. W. J. JONES, W. J. C. DYKE, G. DAVIES, D. C. GRIFFITHS, and J. H. E. WEBB (J.C.S., 1932, 2284—2293).—By interaction of the appropriate Grignard reagent and substances of the type AsRI_2 or AsR_2I the following arsines are prepared. *Methyl-di-n-propyl*-, b.p. $42^\circ/10$ mm. (*chloromercurate*, m.p. 82° ; *methochloromercurate*, m.p. 95°); *-di-n*-, b.p. $77^\circ/10$ mm. (*chloromercurate*, m.p. 87° ; *methiodide*, m.p. 148° ; *methiodomercurate*, m.p. 68°), and *-diiso*-, b.p. $57^\circ/10$ mm. (*chloromercurate*, m.p. 123° ; *methiodomercurate*, m.p. 93°); *-butyl*-, *-di-n-amyl*-, b.p. $104^\circ/10$ mm. (*chloromercurate*, m.p. 66° ; *methiodide*, m.p. 45 — 47°); *-di-n-hexyl*-, b.p. $134^\circ/10$ mm. (*chloromercurate*, m.p. 56°); *-dicyclohexyl*-, b.p. $127^\circ/4$ mm. (*chloromercurate*, m.p. 162° ; *methiodide*, m.p. 185° ; *methiodomercurate*, m.p. 149°); *-di-p-tolyl*-, b.p. $163^\circ/6$ mm. (*chloromercurate*, indefinite m.p.; *methiodide*, m.p. 177°); *-dibenzyl*-, b.p. $169^\circ/5$ mm., m.p. about 36° (*chloromercurate*, m.p. 158°); and *-di- β -phenylethyl*-, b.p. $190^\circ/4$ mm. (*chloromercurate*, m.p. 165° ; *methiodide*, m.p. 151°), *-arsine: dimethyl-ethyl*-, b.p. $86^\circ/760$ mm. (*chloromercurate*, m.p. 154° ; *methiodomercurate*, m.p. 92°); *-n-propyl*-, b.p. $27^\circ/17$ mm. (*methiodide*, m.p. 211°); (*-n-butyl*-, *-n-amyl*-, and *-dl-amyl*-compounds isolated only as the derivatives *trimethyl-n-butylarsonium iodide*, m.p. 163° , and *iodomercurate*,

m.p. 120°; *dimethyl-n-amylarsine chloromercurate*, m.p. 87°; *trimethyl-n-amylarsonium iodide*, m.p. 172°, and *iodocadmate*, m.p. 186°; *trimethyl-dl-amylarsonium iodide*, m.p. about 145°; -*cyclohexyl*-, b.p. 65°/19 mm. [*methiodide*, m.p. 259° (decomp.); *methiodocadmate*, m.p. 138°; *methiodocadmate*, m.p. 198°], -*p-bromophenyl*-, b.p. 134—136°/9 mm.; -*o*-, b.p. 93°/10 mm. (*dibromide*, m.p. 104°; *hydroxybromide*, m.p. 182°; *methiodide*, m.p. 290°; *methiodocadmate*, m.p. 179°; *methiodomercurate*, m.p. 164°), and -*m*-, b.p. 88°/10 mm. (*dibromide*, m.p. 120°; *methiodide*, m.p. 240°; *methiodocadmate*, m.p. 119°; *methiodomercurate*, m.p. 127°), -*tolyl*-, -*m*-, b.p. 101°/10 mm. (*methiodide*, m.p. 203°; *methiodomercurate*, m.p. 108°), and -*p*-, b.p. 113°/7 mm. (*dibromide*, m.p. 106°; *methiodide*, m.p. 223°; *methiodomercurate*, m.p. 129°), -*xylyl*-, - β -*phenylethyl*-, b.p. 103°/10 mm. (*hydroxybromide*, m.p. 118°; *methiodide*, m.p. 202°; *methiodocadmate*, m.p. 158°; *methiodomercurate*, m.p. 116°; *bis- β -phenylethyltrimethylarsonium iodomercurate*, m.p. 155°); and - β -*naphthyl*-, b.p. 177°/10 mm. (*methiodomercurate*, m.p. 154°), -*arsine*; *tri- β -phenylethylarsine*, b.p. 281°/10 mm. (*methiodide*, m.p. 115°; *methiodomercurate*, m.p. 90°; *dibromide*, m.p. 117°); *ethyl-di-n-butyl*-, b.p. 93°/10 mm. (*oxide*, m.p. 133°; *methiodide*, m.p. 168°); -*di-n-amyl*-, b.p. 119°/10 mm. (*oxide*, m.p. 74°); and -*dicyclohexyl*-, b.p. 161°/10 mm. (*methiodide*, m.p. 135°); *diethyl*-, b.p. 64°/10 mm. (*oxide*, m.p. 103°; *methiodide*, m.p. 128°), and *di-n-propyl*-, b.p. 88°/10 mm. (*oxide*, m.p. 106°; *methiodide*, m.p. 190°; *ethiodide*, m.p. 192°) -*n-butyl*-, *phenyl-di-n-propyl*-, b.p. 125°/10 mm., and -*di-n-amyl*-, b.p. 174°/10 mm.; *diphenyl-n-propyl*-, b.p. 177°/10 mm. (*chloromercurate*, m.p. 152°; *methiodide*, m.p. 153°), -*n*-, b.p. 183°/10 mm. (*methiodide*, m.p. 140°), and -*iso*-, b.p. 185°/10 mm. (*hydroxybromide*, m.p. 116°; *methiodide*, m.p. 152°), -*butyl*-, -*n-amyl*-, b.p. 194°/10 mm., and -*dl-amyl*-, b.p. 195°/10 mm., -*arsine*. The b.p. and vals. of *d*, mol. vol., and [*R_L*] are determined for these arsines and equations given whereby these consts. can be calc. for any particular case. From the [*R_L*] vals. the mean at. refractivity of As is for *F* 12.30, for *D* 11.96, and for *C* 11.83. All m.p. are corr.

J. W. B.

Organogallium compounds. Gallium trimethyl etherate. G. RENWANZ (Ber., 1932, 65, [B], 1308—1309).—The etherate, GaMe₃.Et₂O, b.p. 99°/762 mm. (corr.), is prepared by addition of GaBr₃ in Et₂O to ethereal MgMeBr. It inflames on contact with air and appears to lose 1Me as CH₄ when treated with H₂O.

H. W.

Behaviour of cycloparaffins in the Friedel-Crafts reaction. N. D. ZELINSKI and E. M. TARASOVA (Ber., 1932, 65, [B], 1249—1252).—Quant. isomerisation of cyclohexane to methylcyclopentane does not invariably occur during the Friedel-Crafts reaction; the extent depends on experimental conditions. Mol. quantities of cyclohexane, AlCl₃, and AcCl at 70° do not yield a homogeneous ketone. If excess of AlCl₃ is used, the product contains about 8.7% of unsaturated ketone, whereas in presence of excess of cyclohexane at 35° about 53.7% of unsaturated ketone is formed. If technical, sublimed AlCl₃ (containing 3% of FeCl₃) is used, the proportion

of unsaturated ketone is higher, reaching 85.1% when the complex compound of AlCl₃ and AcCl is employed, and 100% in presence of AlBr₃. Excess of AlCl₃ restricts the dehydrogenation of cyclohexane. In all reactions of cyclohexane with acid chlorides in presence of AlCl₃ there is liberation of H which partly reduces the chloride to aldehyde. There is no fundamental difference between the behaviour of C₆H₆ and of cyclohexane in the Friedel-Crafts reaction, but the yields of ketone are widely different. cycloHexane appears to react in two isomeric forms in the sense of the theory of Sachse and Mohr. The initial change is dehydrogenation leading in the one case to the formation of a *meta* bridge followed by contraction of the ring and in the other case to the production of cyclohexene, whence tetrahydroacetophenone, which is partly reduced to hexahydroacetophenone. H. W.

ψ -Halogens. XXI. Reaction of the silver salts of monobasic acids with iodine in presence of cyclohexene. L. BIRCKENBACH, J. GOUBEAU, and E. BERNINGER (Ber., 1932, 65, [B], 1339—1344; cf. this vol., 933).—The first product of the action of I on the Ag salts of monobasic acids is the iodide of the respective anion; the mixed halogen adds to cyclohexene. I does not react appreciably with cyclohexene in presence of AgI and Et₂O. AgClO₄, I, cyclohexene, and Et₂O afford unstable 2-iodocyclohexyl perchlorate, hydrolysed to 2-iodocyclohexanol, m.p. 41—42°. AgClO₄, Et₂O, and cyclohexene give the compound AgClO₄.2C₆H₁₀. Similarly, 1-chloro-2-iodocyclohexane, b.p. 108°/8 mm., and 2-iodo-1-nitrocyclohexane, b.p. 120—124°/8 mm., are obtained with AgCl and AgNO₂. AgNO₃ scarcely reacts, probably by reason of lack of additive capacity of INO₂. AgIO₃, I, cyclohexene, and Et₂O give a compound C₁₁H₁₈O₂I₂, b.p. 200°/8 mm.; omission of Et₂O or replacement of it by C₆H₆ leads to non-distillable liquids. AgIO₄ affords ill-defined products, whereas AgCN rapidly yields ICN. AgCNS gives 1-iodo-2-thiocyanocyclohexane. 2-Iodocyclohexyl acetate, b.p. 120°/12 mm., is obtained from AgOAc in 80% yield (also obtained by allowing AgOAc and I to react in Et₂O at -80°, filtering, and adding cyclohexene to the filtrate). 2-Iodocyclohexyl benzoate, b.p. 185°/10 mm., is prepared in 60% yield.

H. W.

Hydrogenation and dehydrogenation as coupled reactions. R. VESTERBERG and W. BRAUN (Ber., 1932, 65, [B], 1473—1476).—For the transference of H from one compound to another in presence of a suitable catalyst, it is essential that the maximal useful work (*Am'*) obtained by hydrogenation of the acceptor is greater than the work necessary for dehydrogenation of the donator. The calculation for a no. of org. compounds is based on the Lewis-Gibson equation from Nernst's theorem, $\Delta F = \Delta H - \Delta ST = -Am'$ (ΔF =free energy, ΔH =heat of formation, and ΔS =entropy of the particular compound). S is not a particularly powerful dehydrogenating agent, being greatly inferior to most org. acceptors. The use of Ca is suggested.

H. W.

Decomposition of iodobenzene dichloride. VI. Action of sodium ethylmercaptide. E. V. ZAPPI and P. EGEA (Bull. Soc. chim., 1932, [iv], 51, 748—751).—Interaction of PhICl₂ with EtSN₂ in Et₂O is

substantially in accordance with the equation $\text{PhICl}_2 + 2\text{EtSNa} = 2\text{NaCl} + \text{PhI} + \text{Et}_2\text{S}_2$. PhIO is also formed in small amount, and is regarded as a product of secondary decomp. of an unstable intermediate compound $\text{PhI}(\text{SEt})_2$. H. A. P.

Orienting power of the nitroso-group and the formula of nitrosobenzene. R. J. W. LE FEVRE (Nature, 1932, 130, 400—401).—A discussion.

L. S. T.

Attempts to prepare a compound containing the group $\cdot\text{N}(\text{O})\rightarrow\text{S}$. R. J. W. LE FEVRE (J.C.S., 1932, 2503—2504).—Treatment of PhNO with H_2S_x , Na_2S_x , nascent S from $\text{Na}_2\text{S}_2\text{O}_3$ and acids, HgS , S at 100° , or S in $\text{C}_5\text{H}_5\text{N}$ failed to effect condensation between PhNO and S to give the thio-analogue $\text{PhN}(\text{O})\rightarrow\text{S}$ of PhNO_2 , whilst S is also without action on $\text{RO}\cdot\text{NO}$. Hence PhNO is inadequately represented as a tervalent N compound. $\text{C}_5\text{H}_5\text{N}$ reacts with amyl and cyclohexyl nitrites to give $\text{C}_5\text{H}_5\text{N}\cdot\text{HNO}_3$. J. W. B.

General synthesis of diaryl compounds. F. MAYER and R. SCHIFFNER (Ber., 1932, 65, [B], 1337—1338).—The product of the action of an aromatic Grignard reagent on a hydroaromatic ketone is dehydrated and dehydrogenated. Thus, Mg naphthyl bromide and 2-methylcyclohexanone afford 1-1'-naphthyl-2(or 6)-methyl- Δ^1 -cyclohexene, m.p. $55\text{--}56^\circ$, converted by S into 1-o-tolynaphthalene, m.p. 63° . cycloHexanediene and 2MgPhBr without further dehydrogenation give triphenyl, m.p. 211° , whilst MgPhBr and phenyl-dehydroresorcinol yield an oil, b.p. $240\text{--}280^\circ$, dehydrogenated by S to 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Ph}_3$. H. W.

Fractions of higher b.p. of coal-tar heavy oil. O. KRUBER (Ber., 1932, 65, [B], 1382—1396).—The initial material is the residue, b.p. $273\text{--}295^\circ$, from the acenaphthene fraction. A portion, b.p. $272\text{--}275^\circ$, is subjected to successive treatments with 98% H_2SO_4 at $40\text{--}45^\circ$, whereby a paraffin fraction containing n-nonadecane, b.p. $328^\circ/770\text{ mm.}$, m.p. 33° , remains unattacked. The initial sulphonated mixtures appear highly complex, whereas the later ones afford K 3-methyldiphenyl-4(?) -sulphonate (I) (corresponding amide, m.p. $174\text{--}175^\circ$). (I) is converted by molten KOH into 4(?) -hydroxy-3-methyldiphenyl, m.p. 114° (Me ether, m.p. $75\text{--}76^\circ$; benzeneazo-4(?) -hydroxy-3-methyldiphenyl, m.p. $128\text{--}129^\circ$), and by 70% H_2SO_4 at $160\text{--}170^\circ$ into 3-methyldiphenyl, b.p. $269^\circ/748\text{ mm.}$, which is oxidised by KMnO_4 to diphenyl-3-carboxylic acid, m.p. 165° . The fractions from the final sulphonations yield K 4-methyldiphenyl-2(?) -sulphonate (II) (corresponding Na salt and amide, m.p. $236\text{--}237^\circ$), converted into 2(?) -hydroxy-4-methyldiphenyl, m.p. $155\text{--}156^\circ$ (Me ether, m.p. 109°), oxidised by KMnO_4 to terephthalic acid, which, with PhN_2Cl , gives the dye $\text{C}_{19}\text{H}_{16}\text{ON}_2$, m.p. 117° . (II) and 70% H_2SO_4 at $190\text{--}200^\circ$ afford 4-methyldiphenyl, b.p. $271\text{--}272^\circ/752\text{ mm.}$, m.p. 48° , oxidised to diphenyl-4-carboxylic acid, m.p. 222° .

The neutral fraction, b.p. $296\text{--}299^\circ$, is subjected to successive sulphonations and from the intermediate treatments is isolated K 4 : 5-benzoindanesulphonate (Na salt; amide, m.p. $204\text{--}205^\circ$), transformed by 70% H_2SO_4 at $100\text{--}110^\circ$ into 4 : 5-benzoindane (III),

b.p. $294\text{--}295^\circ/757\text{ mm.}$ (picrate, m.p. 110°). Oxidation of (III) with $\text{K}_3\text{FeC}_6\text{N}_6$ and KOH at 60° yields 1 : 2- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ (anhydride, m.p. $163\text{--}164^\circ$; Me₂ ester, m.p. 85°). (III) is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to 4 : 5-benzoindan-3-one, m.p. 105° (oxime, m.p. $175\text{--}176^\circ$) (cf. Mayer and Sieglitz, A., 1922, i, 740). 6-Hydroxy-4 : 5-benzoindane, m.p. 122° , with PhN_2Cl yields the dye $\text{C}_{19}\text{H}_{16}\text{ON}_2$, m.p. 145° . The later fractions of the sulphonation give a very difficultly separable mixture from which, by fractional treatment with 70% H_2SO_4 , 4 : 4'-dimethyldiphenyl, b.p. $292\text{--}293^\circ$, m.p. $121\text{--}122^\circ$, is isolated. The non-hydrolysed portion yields Na 3 : 4'-dimethyldiphenylsulphonate (corresponding amide, m.p. 204°), converted into 3 : 4'-dimethyldiphenyl, b.p. $288\text{--}289^\circ/752\text{ mm.}$, oxidised by dil. HNO_3 to a monocarboxylic acid, $\text{C}_{14}\text{H}_{12}\text{O}_3$, m.p. $193\text{--}194^\circ$, and thence by KMnO_4 to diphenyl-3 : 4'-dicarboxylic acid, m.p. 332° (Me₂ ester, m.p. $98\text{--}99^\circ$). The bulk of the fraction is not readily adapted to the sulphonation treatment. The action of KOH at $340\text{--}350^\circ/15\text{--}20\text{ atm.}$ on the fraction b.p. $296\text{--}299^\circ$ causes fission of the diphenylene oxides leading to the isolation of 2 : 2'-dihydroxy-3-methyldiphenyl (IV), b.p. $326\text{--}327^\circ/762\text{ mm.}$, m.p. $101\text{--}102^\circ$ (Me₂ ether, m.p. $107\text{--}108^\circ$, oxidised by KMnO_4 to 2 : 2'-dimethoxydiphenyl-3-carboxylic acid, m.p. $122\text{--}123^\circ$, and thence to 2-methoxyisophthalic acid, m.p. 225° after softening at 215°). (IV) and ZnCl_2 at $265\text{--}270^\circ$ give 1-methyldiphenylene oxide, b.p. $298^\circ/760\text{ mm.}$, m.p. 45° (picrate, m.p. 94° , also directly isolable from the tar oil fraction), oxidised to 1-carboxydiphenylene oxide, m.p. $209\text{--}210^\circ$. Evolution of NH_3 during treatment with KOH and isolation of α - and β -naphthoic acids establishes the presence of the corresponding nitriles in this fraction.

The portion, b.p. $310\text{--}316^\circ$, is not adapted to the sulphonation treatment. There is derived from it by treatment with Na at $190\text{--}200^\circ$ a mixture of homologous fluorenes from which, by treatment with Na and CO_2 and subsequent esterification, Me 2-methylfluorene-9-carboxylate, m.p. $104\text{--}105^\circ$, is isolated. From it are derived 2-methylfluorenone, m.p. 92° , and 2-methylfluorene-9-carboxylic acid, m.p. $210\text{--}211^\circ$ [whence, by decarboxylation, 2-methylfluorene, m.p. 104° , oxidised to fluorenone-2-carboxylic acid (V), m.p. 332°]. Oxidation of the homologous mixture (above) establishes in it the presence of 3-methylfluorene. (V) and molten KOH afford diphenyl-2 : 4'-dicarboxylic acid, m.p. 272° after softening at 266° , decarboxylated to Ph_2 and oxidised by KMnO_4 to terephthalic acid. H. W.

Orientation effects in the diphenyl series.

XII. Mono- and di-nitration of 4 : 4'-dimethyldiphenyl. (Miss) E. E. J. MARLER and E. E. TURNER (J.C.S., 1932, 2391—2394).—With HNO_3 (d 1.42) in AcOH, 4 : 4'-dimethyldiphenyl (I) affords only the 2-nitro-derivative (II), b.p. $200\text{--}225^\circ/29\text{ mm.}$, m.p. $69\text{--}70^\circ$, identical with a specimen synthesised from p- $\text{C}_6\text{H}_4\text{MeI}$, 4-bromo-3-nitrotoluene, and Cu-bronze at 220° , but different from the 3- NO_2 -compound (III), b.p. $220\text{--}230^\circ/20\text{ mm.}$, m.p. $80\text{--}81^\circ$, synthesised similarly. Reduction of (II) and (III) with $\text{SnCl}_4\text{--AcOH--HCl}$ affords, respectively, 2-, m.p. $62\text{--}63^\circ$ (Ac derivative, m.p. $118\text{--}119^\circ$), and 3-, m.p.

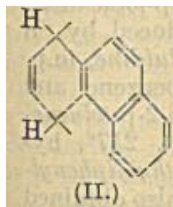
Separation of 1:8- from 1:5-dinitronaphthalene. M. GALLOTTI and P. GALIMBERTI (*Annali Chim. Appl.*, 1932, 22, 600—601).—The mixed isomerides (20 g.) are dissolved in 400 g. of conc. H_2SO_4 ; after stirring for $\frac{1}{2}$ hr. and heating at 45° 5 g. of pure S and 100 g. of oleum (35% SO_3) are added gradually. The temp. is kept at 90 — 95° for 2 hr. The mixture is poured on 2000 c.c. of H_2O and 2000 g. of ice while stirring thoroughly; 1:8- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$, m.p. 170° , is collected whilst 1:5- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ is transformed into naphthazarin, which remains in the filtrate.

O. F. L.

Course of the catalytic hydrogenation of anthracene. K. FRIES and K. SCHILLING [with G. LITTMANN] (*Ber.*, 1932, 65, [B], 1494—1502).—The observation that the hydrogenation of anthracene (I) proceeds continuously to the octahydride raises doubts as to the general validity of the course, (I) \rightarrow 9:10-di- \rightarrow 1:2:3:4-tetra- \rightarrow 1—8-octa-hydroanthracene (cf. Schroeter, A., 1925, i, 127). The 9:10-compound, as true C_6H_6 derivative, is much more slowly hydrogenated than (I) or 1:2:3:4-tetrahydroanthracene. A mixture of (I) and its dihydro-derivative (II) is hydrogenated initially at the same rate as (I); subsequently retardation is observed and the greater part of (II) is recovered unchanged. In the presence of different catalysts (Ni, Pt, or Pd) the absorption of 1H_2 by (I) proceeds very rapidly, but the yield of (II) is only about 12%; more than 50% of the initial material is unchanged and the rest is transformed into more highly hydrogenated compounds. It appears that hydrogenation of (I) proceeds to a minor extent according to Schroeber's scheme, but mainly takes an immediate and direct course to 1:2:3:4-tetrahydro- and thence to 1—8-octahydro-anthracene. Ultimately a perhydride is produced, but evidence of a hexahydride is never obtained. In presence of PtO_2 and AcOH at room temp., (I) gives *perhydroanthracene*, $\text{C}_{14}\text{H}_{24}$, m.p. 61.5° , whereas in absence of solvent at 100° under pressure and with Ni as catalyst an isomeride, m.p. 93° , identical with that described by Ipatiev (A., 1908, i, 330), results.

H. W.

Polynuclear, aromatic hydrocarbons. XV. Constitution of phenanthrene and the polynuclear-ring systems derived therefrom. Separation of aromatic hydrocarbons. E. CLAR and L. LOMBARDI (*Ber.*, 1932, 65, [B], 1411—1420; cf. this vol., 608).—The extinction curve of phenanthrene (I) shows the presence of bands above 300 $\text{m}\mu$ corresponding with the 9:10-diyl condition, of one at 250 $\text{m}\mu$ due to the side nuclei, and of a group between 260 and 300 $\text{m}\mu$ due to a naphthalene complex or the condition (II). The curve of chrysene (freed from a yellow impurity by heating with maleic anhydride in $\text{C}_6\text{H}_4\text{Me}_2$) resembles that of (I), but the 9:10-diyl condition is more marked and the bands at 270—330 $\text{m}\mu$ are more pronounced. The extinction curve of triphenylene indicates that it is 1:2:3:4-dibenzonaphthalene, whereas its dodecahydro-derivative behaves as an alkylbenzene. Comparison of the max. extinction coeffs. of the first R bands of

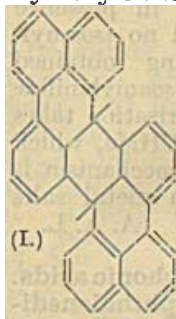


C_{10}H_8 , chrysene, (I), and triphenylene, and the potentials of the corresponding *o*-quinones shows that hydrocarbons not derived from anthracene and produced by angular annelation, which therefore do not contain an *o*-quinonoid linking, are built so that a double linking always exists between two rings. Their inability to react with maleic anhydride is thus explained. 2':3'-Naphtho-9:10-phenanthrene shows bands characteristic of (I) and anthracene; addition of maleic anhydride destroys the anthracene character and the product behaves as an alkylated (I). In 2':3'-naphtho-1:2-phenanthrene the bands due to the anthracene-9:10-diyl overlap those due to phenanthrene-9:10-diyl, whereas the phenanthrene character becomes obvious in the extinction curve after reaction with maleic anhydride. The extinction curve of 2':3'-naphtho-2:3-phenanthrene does not indicate a derivative of (I), the relationships resembling those of 2:3-benzanthracene. If the anthracene character is withdrawn by action with maleic anhydride, the extinction curve of the product is of the pure (I) type.

A method of separation of the individual 2':3'-naphthophenanthrenes from the mixture obtained by pyrolysis of *o*-toluylphenanthrene is based on fractional treatment with maleic anhydride in boiling $\text{C}_6\text{H}_4\text{Me}_2$. The following substances are described: 2':3'-naphtho-2:3-phenanthrene, m.p. 262 — 264° ; 2':3'-naphtho-9:10-phenanthrene, leaflets, m.p. 251 — 253° (decomp.), prisms, m.p. 253 — 255° (decomp.); 2':3'-naphtho-1:2-phenanthrene, m.p. 268 — 269° (decomp.); 2':3'-naphtho-2:3-phenanthrene, m.p. 273° (decomp.), -endo-1':4'- α -succinic anhydride.

H. W.

Polynuclear, aromatic hydrocarbons and their derivatives. XVIII. Synthesis of 1:9-5:10-diperinaphthyleneanthracene. E. CLAR and A. GUZZI (*Ber.*, 1932, 65, [B], 1521—1525).—9:10-Dihydroxy-9:10-di- α -naphthyl-9:10-dihydroanthracene



is converted by AlCl_3 in presence of a trace of $\text{C}_5\text{H}_5\text{N}$ at 90 — 110° into 1:9-5:10-diperinaphthyleneanthracene, m.p. 580° (decomp.; in sealed tube), to which the constitution (I) is assigned, since an analogous hydrocarbon could not be prepared from the corresponding 1:4- Me_2 derivative and with maleic anhydride it gives the colourless 1:9-5:10-diperinaphthyleneanthracene-endo-9:10- α -succinic anhydride, decomp. 310° when rapidly heated. The absorption spectra of (I) and meso-di- α -naphthylanthracene are closely similar. (I) and Br in C_6H_6 immediately afford a pale yellowish-green ppt. from which the hydrocarbon is regenerated when the suspension is heated to boiling or when the ppt. is dried. I does not decolorise the hydrocarbon, whereas Cl_2 appears to yield a more stable product. O_2 does not oxidise (I) in direct light or in the dark, but the possible formation of a very readily dissociable peroxide is not excluded. The free valencies are therefore unusually weak. (I) is considered to form a link between the aromatic hydrocarbons and graphite.

H. W.

Reduction of Schiff bases. II. Polymeric states and structures of methylene-aniline and

-p-toluidine. Condensation of aniline and acet-aldehyde. J. G. MILLER and E. C. WAGNER (J. Amer. Chem. Soc., 1932, 54, 3698—3706; cf. this vol., 378).—Cryst. methylenedianiline (I) and methylene-*p*-toluidine (II) are definitely trimeric at 5–80°, but the average mol. wts. decrease at higher temp. (176°). Reduction of (I) with Zn dust and cold conc. HCl gives 19.2% NH₂Ph, 18.6% NHPHMe, and 8.5% NPhMe₂; at 70°, the respective % are 21.1, 1.8, and 0.4. Reduction (cold) of (II) gives 36.3% *p*-C₆H₄Me·NH₂, 39.5% *p*-C₆H₄Me·NHMe, and 21% *p*-C₆H₄Me·NMe₂. These results indicate that (I) and (II) possess cyclic structures. Amorphous (I) and (II) (the higher polymerides) give similar results on reduction. The primary product of the condensation of NH₂Ph and MeCHO (representing the straight-chain aliphatic aldehydes) is the di-imine; the products hitherto obtained are due to secondary reactions. There is no satisfactory evidence for the intermediate formation of the monomeric azomethine.

C. J. W. (b)

Rearrangement of alkylanilines. V. Trimethylethylene, the intermediate product in the rearrangement of *iso*amylaniline hydrobromide to *p*-amino-*tert*-amylbenzene hydrobromide. W. J. HICKINBOTTOM (J.C.S., 1932, 2396—2400).—*iso*Amylaniline, b.p. 253—254°/751 mm. (*m*-nitrobenzenesulphonyl derivative, m.p. 104—105°), heated with CoCl₂, CoBr₂, or CdCl₂ at 210—280° gives mainly *p*-amino-*iso*amylbenzene, b.p. 262—264°/756 mm. (Bz derivative, m.p. 151—153°; *m*-nitrobenzenesulphonyl derivative, m.p. 99—101°; *diphenyl-p*-*iso*amylthiocarbamide, m.p. 122°), with a little NH₂Ph, a primary amine, b.p. above 290°, unchanged amylamine, and a substance (? a NHPH₂ derivative), b.p. 325—330°. The yield of the last increased with the time of heating and depended on the nature of the promoter. No *p*-amino-*tert*-amylbenzene was detected. NH₂Ph·HBr and CMe₂·CHMe in presence of CoCl₂ or CoBr₂ give only *tert*- and no *iso*amyl-*p*-aminobenzene, similar results being obtained under various conditions with *iso*amylaniline hydrobromide alone. The latter isomerisation takes place through the separation of CMe₂·CHMe, which is always detected, whilst a different mechanism is necessary to explain the action with metal salts alone.

A. A. L.

Arylamine salts of naphthalenesulphonic acids. VII. Salts of 1:5- and 1:6-naphthalenedisulphonic acids. R. B. FORSTER and K. HISHIYAMA (J.S.C.I., 1932, 51, 297—298r).—The arylamine salts of 1:5-C₁₀H₆(SO₃H)₂ are easily prepared, whereas those of the 1:6-acid are much more sol. and are difficult to prepare unless comparatively pure specimens of the base and acid are used. None of the salts prepared is suitable for the separation of the two isomerides, but several of them may be used for characterising the respective acids, e.g., *ψ*-cumidine 1:5-, m.p. 216—217°, 1:6-, m.p. 294°, and *α*-naphthylamine 1:5-, m.p. 231°, and 1:6-, m.p. 272°, -naphthalenedisulphonates. The following were also prepared: *aniline* 1:5-, no m.p., 1:6-, m.p. 298—299°, *o*-toluidine 1:5-, m.p. 338—339°, 1:6-, m.p. 323—324°, *m*-toluidine 1:5-, m.p. 312°, *p*-toluidine

1:5-, m.p. 332°, 1:6-, m.p. 314—315°, *m*-4-*xylylidine* 1:5-, m.p. 338—340°, 1:6-, m.p. 324°, *β*-naphthylamine 1:5-, m.p., 204°, 1:6-, no m.p., *benzidine*, *tolidine*, no m.p., *p*-chloroaniline 1:5-, m.p. 338—339°, 1:6-, m.p. 313—315°, *p*-nitro-*o*-toluidine 1:5-, m.p. 275°, 1:6-, m.p. 282—283°, *p*-anisidine 1:5-, m.p. 322°, and 1:6-, m.p. 299°, -naphthalenedisulphonates. All m.p. are with decomp. except *ψ*-cumidine salts.

Condensation of bromal with nitroanilines.

D. C. KNOWLES, jun., and R. P. JACOBSEN (J. Amer. Chem. Soc., 1932, 54, 3730—3731).—*p*-NO₂·C₆H₄·NH₂ and CBr₃·CHO in C₆H₆ or Et₂O give 48% of *βββ*-tribromoethylidenebis-*p*-nitroaniline, m.p. 127—128°; the *o*-, m.p. 106—107°, and *m*-, m.p. 117—118°, isomerides are similarly prepared.

C. J. W. (b)

Reactivity of sodium azide with acid chlorides.

J. NELLES.—See this vol., 1118.

Nitro-derivatives of diphenylamine.

N. M. CULLINANE and, in part, (MISS) O. E. EMBREY and D. R. DAVIES (J.C.S., 1932, 2363—2364; cf. this vol., 733).—Chloro- or bromo-nitrohydrocarbons with the appropriate amines and NaOAc at 150—160° give (% yields in parentheses) 2:4-dinitro-5-methyl-, m.p. 148° (70), -5:2'-, m.p. 111° (70), and -5:3'-dimethyl-, m.p. 136.5° (80), -5:2':4'-, m.p. 138° (70), and -5:2':5'-trimethyl-, m.p. 114.5°, -2'-methoxy-5-methyl-, m.p. 146° (90), -3'-ethoxy-, m.p. 153° (75), -3'-ethoxy-5-methyl-, m.p. 115° (70), and -4'-ethoxy-5-methyl-diphenylamine, m.p. 148.5° (90), and 2:4-dinitro-5-methylphenylbenzylamine, m.p. 102° (70). The following are obtained similarly at 180°: 2:4-dinitro-2'-methoxy-, m.p. 165.5° (80), and -4'-ethoxy-diphenylamine, m.p. 121—122° (90), and 2:4-dinitrophenylbenzylamine, m.p. 116° (90). 2:4-Dinitro-4'-methoxy-, m.p. 141° (90), and -2':5'-dimethyl-diphenylamine, m.p. 144°, require a temp. of 200°. The following are obtained in EtOH: 2:4-dinitro-2'-ethoxy-, m.p. 172°, 2:4-dinitro-2'-ethoxy-5-methyl-, m.p. 179.5° (75), and 2'-bromo-2:4:6-trinitro-4'-methyl-diphenylamine, m.p. 176° (90) (also obtained in C₆H₆), and 2:4:6-trinitrophenylbenzylamine, m.p. 141.5° (90). 2:4:6-Trinitrophenylmethyl-nitroamine was used to obtain the following in place of picryl chloride: 2:4:6-trinitro-4'-hydroxy-, m.p. 178°, -4'-ethoxy-, m.p. 138.5° (90), and -4'-amino-diphenylamine, m.p. 194° (90). NH₂Bz, picryl chloride, and NaOH in EtOH give *benzo*-2:4:6-trinitroanilide, m.p. 191°.

A. A. L.

Isomeric 2:4-dinitrophenyl derivatives of

3:4-tolylenediamine. K. C. ROBERTS (J.C.S., 1932, 2358—2360).—4-Nitro-*m*-toluidine and *p*-toluenesulphonyl chloride in C₅H₅N give *p*-toluenesulphon-4-nitro-*m*-tolylidide, m.p. 135°, reduced by Sn and HCl to 3-*p*-toluenesulphonamido-*p*-toluidine, m.p. 120°, which with 4-chloro-1:3-dinitrobenzene and NaOAc in PrOH gives 2':4'-dinitro-2-*p*-toluenesulphonamido-4-methyldiphenylamine, m.p. 217°, hydrolysed to 2':4'-dinitro-2-amino-4-methyldiphenylamine, m.p. 162.5° and 173° (two forms), also obtained by fractionation of the condensation product of 3:4-tolylenediamine and 4-chloro-1:3-dinitrobenzene (A., 1891, 299). 2':4'-Dinitro-2-*p*-toluenesulphonamido-, m.p. 184°, and -2-amino-5-methyldiphenylamine, m.p.

195° and 191° (two forms), are similarly obtained. 2':4'-Dinitro-2-aminodiphenylamine has m.p. 147° and 152°.

A. A. L.

Stereochemistry of diphenyl. F. R. SHAW and E. E. TURNER (Nature, 1932, 130, 315).—Optical resolution of the monomethiodide of 2:2'-tetramethyldiaminodiphenyl has been effected. The *d*- and *l*-methiodides have $[\alpha]_D^{20} \pm 48^\circ$ in aq. solution. Activity is retained indefinitely in cold solutions, but at 100° half-racemisation occurs in approx. 2 hr.

L. S. T.

Action of halogens on arylazoacetoacetates and related compounds. II. F. D. CHATTAWAY and R. J. LYE (Proc. Roy. Soc., 1932, A, 137, 489—503; cf. this vol., 377).—Cl₂ or Br reacts with arylazoacetoacetates of the type NHPh·N:Cac·CO₂Et (I), causing both substitution (max. of 2 halogen atoms introduced) in the Ph nucleus and either displacement of the Ac or CO₂Et or halogenation of the Ac group, derivatives of the types R:CX·CO₂Et (II), R:C(CO·CH₂X)·CO₂Et (III), R:C(CO·CHX₂)·CO₂Et (IV) or R:CX·CO·CHX₂ (V) (R=2:4-Br₂C₆H₃·NH·N') being formed according to the experimental conditions. With Cl₂ only stages (II) and (III) are realised, the more vigorous reaction required for stages (IV) and (V) causing disruption of the mol. Thus from (I) are obtained: *Et* α-bromoglyoxylate-*p*-bromo-, m.p. 149—150°, -2:4-dibromo-, m.p. 140°, and -2:4-dichloro-, m.p. 117°, -phenylhydrazone: *Et* α-chloroglyoxylate-*p*-chloro-, m.p. 146—147°, -*p*-bromo-, m.p. 163°; -2:4-dichloro-, m.p. 98°, and -dibromo-, m.p. 108°, -phenylhydrazone [all of type (II)]. By coupling the appropriate diazotised base with *Et* halogenoacetoacetate or halogenation of the arylazoacetate are obtained: *Et* γ-bromo-*p*-bromobenzeneazo-, m.p. 113—114°, *Et* benzeneazo-, m.p. 81°, *Et* 2:4-dichloro-, m.p. 113°, and -dibromo-, m.p. 144—135°, -benzeneazoacetoacetate: *Et* γ-chloro-benzeneazo-, m.p. 92°, -*p*-chloro-, m.p. 102—103°, and -2:4-dichloro-, m.p. 105°, -benzeneazoacetoacetate [all of type (III)]. In the cold Br (3 mols.) in AcOH converts (I) into *Et* γγ-dibromo-*p*-bromobenzeneazoacetoacetate, m.p. 135—138°, but at 60—70° the corresponding acid, m.p. 205° (decomp.), is obtained. *Et* γγ-dibromo-2:4-dibromo-, m.p. 153—154°, and -dichloro-, m.p. 128°, -benzeneazoacetoacetate [type (IV)] are obtained similarly. With excess of Br (I) affords βω-tribromo-α-ketopropaldehyde-2:4-dibromophenylhydrazone, m.p. 140—141°, also obtained from Br in hot AcOH and α-ketopropaldehyde-2:4-dibromophenylhydrazone, m.p. 165° (from C₆H₃Br₂·N·N·Cl and CH₂Ac·CO₂H) [type (V)]. Heated with KOAc in EtOH, derivatives of types (III) and (IV) are cyclised to 4-hydroxypyrazoles with elimination of HX, and thus are obtained: *Et* 4-hydroxy-1-2':4'-dibromophenyl-, m.p. 166° (*Ac*, m.p. 103—104°, and *Bz*, m.p. 137°, derivatives), and its -5-*Br*-derivative, m.p. 189° (*Ac* derivative, m.p. 91—92°); *Et* 4-hydroxy-1-phenyl-, m.p. 85° [in agreement with Wolff (A., 1900, i, 691)]; the substance, m.p. 258—260°, obtained by Favrel (A., 1913, i, 898) cannot be this compound], -1-*p*-bromophenyl-, m.p. 136—137°, and its -5-*Br*-derivative, m.p. 103° (*Ac* derivative, m.p. 134°), -1-*p*-chlorophenyl-, m.p. 137—138°, -1-2':4'-dichlorophenyl-, m.p. 154—

155°, and its -5-*Cl*-, m.p. 161°, and -5-*Br*-, m.p. 176—177°, derivatives, -pyrazole-3-carboxylate.

J. W. B.

Chemical changes involved in the formation of aminoazo-compounds. I. J. C. EARL and N. F. HALL (J. Proc. Roy. Soc. New South Wales, 1932, 66, 157—166).—In MeOH at 0—3°, NH₂Ph·HCl (2 mols.) and NaNO₂ (1 mol.) afford some diazoaminobenzene and unchanged NH₂Ph, but at 14—16° give a good yield of aminoazobenzene. The vol. change shown by dilatometer experiments is probably due to the change of initially formed amine nitrite into a NO- or diazo-compound, this necessitating acidity, which is provided by excess of amine hydrochloride.

J. L. D.

Heteropolarity. XVIII. Colour and structure of diazonium salts. W. DILTHEY, C. BLANKENBURG, W. BRANDT, and W. HUTHWELKER (J. pr. Chem., 1932, [ii], 135, 36—48).—Conversion of [ArNH₃]⁺ into [Ar·N₂]⁺ is accompanied by slight deepening of shade (in the examples quoted from colourless to yellow); this agrees best with the formulation of diazonium salts as carbonium salts, e.g.,

$\left| \text{C}_6\text{H}_5 < \text{N} \right|$ The following NH₂-compounds are

prepared by reduction of the known NO₂-compounds: *p*-aminophenyl *p*-diphenyl ketone, m.p. 203—204° [oxime, m.p. 182—183°; *Ac* derivative, m.p. 204°; hydrochloride, m.p. 218°; diazonium chloride (+1H₂O), m.p. 120° (rapid heating) (+β-naphthol, m.p. 210—212°)]; 4-amino-4'-phenoxybenzophenone, m.p. 125° [*Ac* derivative, m.p. 151—152°; hydrochloride, m.p. 190°; diazonium chloride (+1H₂O), m.p. 114° (decomp.) (+β-naphthol, m.p. 188°)]; 4-amino-4'-phenylthiolbenzophenone, m.p. 155° [oxime, m.p. 164° [diazonium chloride, m.p. 105° (+β-naphthol, m.p. 195—197°)]; *Ac* derivative, m.p. 175°; hydrochloride, m.p. 167—170°; diazonium chloride, m.p. 108—109°].

H. A. P.

Reactions with boron fluoride. III. Condensation of propylene with phenol. F. J. SOWA, H. D. HINTON, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1932, 54, 3694—3698; cf. this vol., 735).—C₃H₆ (0.5 mol.) passed (10 g. per hr.) into a mixture of 1 mol. of PhOH, 5 g. of BF₃, and 100 g. of C₆H₆ at -2° to 2° gives 54% of PhOPr^β and 41% of *o*-C₆H₄Pr^β·OH. When the reaction is carried out at 13—17°, using 2 mols. of C₃H₆, there results PhOPr^β, (mainly) *o*-isopropylphenyl Pr^β ether (I), b.p. 225—227°, and 2:4-diisopropylphenyl Pr^β ether (II), b.p. 248°. (II) results in 39% yield when C₃H₆ is passed into PhOH·BF₃ at 22°; other products are *o*-C₆H₄Pr^β·OH, (I), alkali-sol. products, b.p. 230—240° and 240—256°, and (III) (below). If the reaction is maintained at 30—40° and C₃H₆ passed in until absorption is complete, there results 92% of 2:4:6-triisopropylphenyl Pr^β ether (III), b.p. 263°. The catalyst serves as a condensing and a rearranging agent.

C. J. W. (b)

Catalytic dehydration of phenols; influence of the nature and position of substituents. E. BRINER and A. A. BRON (Helv. Chim. Acta, 1932, 15, 1234—1241).—Dehydration of the following phenols in N₂ by ThO₂, best at the temp. stated,

gives the following percentage yields of others: resorcinol and its Me ether, pyrocatechol, quinol, orcinol, and phloroglucinol, 0; guaiacol (475°), 16; *o*-, *m*-, and *p*-cresol (400°), 2, 7.5, and 28, respectively; 1:3:4-, 1:2:4-, 1:3:5-, 1:2:5-, and 1:2:6-xyleneol (450°), 25, 8, 21, 0, and 0, respectively; creosol (450°), a trace; thymol (450°), 10—15% of an oil; 2-, 3-, and 4-hydroxydiphenyl (550°), 8, 10, and 10—12, respectively. β -Naphthol gives better yields than α -naphthol. The results show the steric effect of *o*-substituents and the hindering effect of OH groups. *Di*-2-, -3-, and -4-diphenyl ethers melt at 75°, 71—72°, and 191°, respectively.

R. S. C.

Optical activity of aluminium pyrocatechoxide. W. D. TREADWELL, G. SZABADOS, and E. HAIMANN (Helv. Chim. Acta, 1932, 15, 1049—1052).—Freshly prepared $\text{Al}(\text{OH})_3$ and pyrocatechol in aq. NH_3 give the complex salt, $(\text{NH}_4)_3[\text{Al}(\text{C}_6\text{H}_4\text{O}_2)_3]$, changed by strychnine sulphate in H_2O into the strychnine salt, which, when washed with successive small portions of H_2O at 10°, gives a residue of the less sol. 1-strychnine-1-aluminium pyrocatechoxide, cryst., $[\alpha]_D -39.2^\circ$ in EtOH. This salt with aq. KI gives insol. strychnine hydriodide and a solution from which COMe_2 ppts. the 1- K_3 salt, cryst., $[\alpha]_D -61.7^\circ$ in H_2O . Al, therefore, has a covalency of 6 in these salts. The racemisation of 1- $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ is a unimol. reaction (time of half change 34.9 min. at 16°). The Al pyrocatechoxide salts racemise at similar rates.

R. S. C.

Preparation of resorcinol monobenzoate. J. BENET (Bull. Soc. chim., 1932, [iv], 963—964).—Partial hydrolysis of resorcinol dibenzoate by $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$ in aq. EtOH gives the monobenzoate, m.p. 133°, in 60% yield. The yield is increased to 90% of theory in presence of CH_2O .

H. A. P.

Hydroxy- and dihydroxy-phenylethylmethylamines and their ethers. J. S. BUCK (J. Amer. Chem. Soc., 1932, 54, 3661—3665; cf. A., 1930, 1575).—Four of the seven previously unknown hydroxy- and dihydroxy-phenylethylmethylamines have been synthesised. The following new intermediates were prepared: β -*o*-methoxyphenylpropionamide, m.p. 110°; β -2:4-dimethoxyphenylpropionamide, m.p. 113°; β -2:5-dimethoxyphenylpropionic acid, m.p. 101° (amide, m.p. 111°); *o*-methoxy-, b.p. 117°/9 mm., *m*-methoxy-, b.p. 118°/6 mm., 2:3-dimethoxy-, b.p. 138°/8 mm., 2:4-dimethoxy-, b.p. 140°/1 mm., and 2:5-dimethoxy-, b.p. 150°/8 mm., β -phenylethylamines. The following substituted β -phenylethylmethylamines are described: *o*-methoxy-, b.p. 115°/9 mm. (hydriodide, m.p. 101°; hydrochloride, m.p. 119°); *m*-methoxy-, b.p. 118°/7 mm. (hydriodide, m.p. 108°; hydrochloride, m.p. 119°); 2:3-dimethoxy-, b.p. 136°/6 mm. (hydriodide, m.p. 90°; hydrochloride, m.p. 117°); 2:4-dimethoxy-, b.p. 136°/4 mm. (hydriodide; hydrochloride, m.p. 145°); 2:5-dimethoxy-, b.p. 155°/8 mm. (hydriodide, m.p. 137°; hydrochloride, m.p. 110°). β -*o*- and -*m*-Hydroxyphenylethylmethylamine hydrochlorides, m.p. 148° and 89°, and β -2:3-, m.p. 149°, and -2:5-, m.p. 128°, dihydroxyphenylethylmethylamine hydrochlorides are prepared.

C. J. W. (b)

Synthesis of pharmacologically important amines. VI. **Synthesis of mescaline.** K. KINDLER and W. PESCHKE (Arch. Pharm., 1932, 270, 410—413; cf. this vol., 843).—Two syntheses of mescaline (I), m.p. 35—36° (lit. an oil), are recorded. The NaHSO_3 compound of 3:4:5-trimethoxybenzaldehyde and aq. KCN give 3:4:5-trimethoxymandelonitrile, yielding with Ac_2O the *Ac* derivative, b.p. 163—165°/0.1 mm., which is hydrogenated (Pd-black) in AcOH to (I). β -Benzoyloxy-*N*-benzoyl- β -3:4:5-trimethoxyphenylethylamine with Pd-black in boiling tetralin affords *N*-benzoylmescaline, slowly hydrolysed by 20% KOH.

R. S. C.

Amino-alcohols derived from methylcyclohexane. J. MATTI (Bull. Soc. chim., 1932, [iv], 51, 974—979).—Interaction of cyclohexene with CH_2O in $\text{AcOH}-\text{H}_2\text{SO}_4$ at 35—40° gives a complex mixture of acetates, of which the fraction of b.p. 120—145°/19 mm. is hydrolysed by KOH in EtOH to a mixture containing 2-hydroxymethylcyclohexanol (I) and its dimeric (?) methylene ether, $(\text{C}_8\text{H}_{14}\text{O}_2)_x$, m.p. 205° (sublimes 120°). This crude mixture of glycols gives with HBr in AcOH the bromohydrin, b.p. 185°/19 mm., and bromoacetin, b.p. 131—135°/21 mm., of (I), mixed with other products. Condensation of the crude bromination mixture with NHMe_2 and subsequent deacetylation gives 2-dimethylamino-methylcyclohexanol (A., 1920, i, 851; 1927, 659); similarly, NHEt_2 gives 2-diethylaminomethylcyclohexanol (II), b.p. 126—128°/17 mm. (benzoate hydrochloride, m.p. 183—183.5°; *p*-nitrobenzoate hydrochloride, m.p. 180°), also obtained by the method of Mannich (*loc. cit.*). The formation of stereoisomerides by this route was not observed. The 1-*Cl*-derivative, b.p. 123°/18 mm., corresponding with (II) is obtained by the action of SOCl_2 in C_6H_6 , and is converted by 8-amino-6-methoxyquinoline at 145° into Δ^2 -diethylaminomethylcyclohexene, b.p. 95—96°/19 mm.

H. A. P.

Pinacolin deamination. II. **Action of nitrous acid on amino-alcohols derived from isovaline.** A. MCKENZIE and W. MITCHELL (Ber., 1932, 65, [B], 1358—1362; of this vol., 382).—*iso*-Valine hydrochloride is transformed into the *Et* ester hydrochloride (I), m.p. 119—120°, converted by MgPhBr into *r*- β -amino- α -diphenyl- β -methylbutanol, m.p. 94° (hydrochloride, m.p. 220.5°), deaminated in AcOH to a liquid, b.p. 171—174°/15 mm., which is free from N and does not react with semicarbazide. (I) and $\text{BrMg}\cdot\text{C}_6\text{H}_4\text{Me}(p)$ yield *r*- β -amino- α -di-*p*-tolyl- β -methylbutanol, m.p. 91.5—92.3° (hydrochloride, m.p. 220—228°), which behaves similarly to the Ph derivative when deaminated. *r*- β -Amino- α -dibenzyl- β -methyl-*n*-butanol, m.p. 81—81.5° (hydrochloride, m.p. 102—105°), from (I) and $\text{ClMg}\cdot\text{CH}_2\text{Ph}$, is converted by HNO_2 into (?) *r*-benzyl α -benzyl- α -methyl-*n*-propyl ketone (II), m.p. 63.5—64°, which does not react with MgPhBr or yield a semicarbazone. (+)-*iso*-Valine, $[\alpha]_D^{25} +13^\circ$ in H_2O , is transformed into the *Et* ester hydrochloride and thence by $\text{ClMg}\cdot\text{CH}_2\text{Ph}$ into (—)- β -amino- α -dibenzyl- β -methyl-*n*-butanol (III), m.p. 91—92°, $[\alpha]_D^{25} -9.1^\circ$ in EtOH, $[\alpha]_D^{25} -20.8^\circ$ in C_6H_6 . (III) and HNO_2 yield (II) and an oil, b.p. 130—145°/1.5 mm., $[\alpha]_D^{25} +14.3^\circ$, which does not yield a semicarbazone or oxime.

H. W.

Manufacture of β -di(arylmethyl)aminoethyl alcohols. I. G. FARBENIND. A.-G.—See B., 1932, 833.

Heteropolarity. XVII. **Constitution and colour.** W. DILTHEY and R. WIZINGER (Ber., 1932, 65, [B], 1329—1333).—In reply to Burawoy (this vol., 792), it is demonstrated that the freely-active NR_2 group in aromatic union generally has a more strongly bathochromic action than a similarly placed OR group. NR, O, or S atoms or groups which close a six-membered ring or are attached directly to the central atom have a hypsochromic or feebly bathochromic effect, but retain their character as auxochromes, since they stabilise the ions in cations. *p*-Dimethylaminotriphenylcarbenium perchlorate, m.p. 198—199°, after softening, is described. H. W.

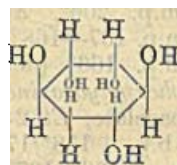
Soluble compounds of cholesterol with various soaps. L. VELLUZ and E. BOUCHARA (Compt. rend. Soc. Biol., 1931, 106, 1131—1132; Chem. Zentr., 1932, i, 1908).—Stable colloidal solutions are obtained when 2% Na oleate or ricinoleate, instead of H_2O , is added to a suspension of cholesterol in COMe_2 . A method employing ricinoleic, linoleic, or linolenic acid is also described. A. A. E.

Water-soluble cholesteryl esters. R. SCHONHEIMER and F. BREUSCH (Z. physiol. Chem., 1932, 211, 19—22).—The alkali salts of the mono-esters of butanetetra-carboxylic acid are very sol. in H_2O . The following esters were obtained as mixtures of the two isomerides: *cholesteryl* H_3 *n*-butane- $\alpha\beta\gamma\delta$ -tetra-carboxylate [separated into less sol. ester, m.p. 240° (decomp.), and more sol. ester, m.p. 186° (decomp.)]; *sitosteryl*, m.p. 168° (decomp.), *ergosteryl* [less sol., m.p. 230° (decomp.), more sol., m.p. 160—168° (decomp.)], *allocholesteryl* (as Na salt), and *vitamin-D*₂ m.p. 100° (decomp.), esters. J. H. B.

Sterol group. XVI. (a) **Molecular formula of ergosterol.** (b) **Oxidation of ergosterol and of α -dihydroergosterol with manganese dioxide and sulphuric acid.** I. M. HEILBRON and J. C. E. SIMPSON (J.C.S., 1932, 2400—2403).—Ergostanone with Br in CHCl_3 gives *bromoergostanone*, m.p. 191° (decomp.). Similarly, β -ergostenone at -15° gives *bromodehydroergostenone*, m.p. 178—179° (decomp.), reduced by Zn and AcOH to *dehydroergostenone*, m.p. 147—148° (*oxime*, m.p. 212—213°), which is also obtained from dehydroergostenol when heated with Cu-bronze. Analyses of the Br-derivatives indicate that the formula of ergosterol is $\text{C}_{28}\text{H}_{44}\text{O}$ (or less probably $\text{C}_{29}\text{H}_{46}\text{O}$) (cf. this vol., 845). Ergosterol with MnO_2 in 57% H_2SO_4 gives benzenepentacarboxylic acid (isolated as the Me ester through the Ag salt), which is similarly obtained in small yield from α -dihydroergosterol. A. A. L.

Inositolphosphoric compounds. **Compounds of ferric inositolphosphate with ammonia and amines.** S. OTOLSKI (Rocz. Chem., 1932, 12, 621—630).—Amines react in aq. solution with $\text{C}_6\text{H}_5\text{O}_3\text{P}_2\text{Fe}_4$ to yield compounds with: NH_3 , NH_2Et , NH_4Et , (6 mols., $8\text{H}_2\text{O}$), NMe_3 , piperidine (6 mols., $12\text{H}_2\text{O}$), $(\text{NH}_2\text{CH}_2)_2$, and piperazine (4 mols., $12\text{H}_2\text{O}$). NH_4Ph , $\text{C}_5\text{H}_5\text{N}$, quinoline, 2-aminopyridine, and hexamethylenetetramine do not yield compounds. R. T.

Configuration of *d*-quercitol. T. POSTERNAK (Helv. Chim. Acta, 1932, 15, 948—955).—*d*-Quercitol (I) and aq. KMnO_4 ($=2.8\text{ O}$) at 0° give a trihydroxyadipic acid, identical with metasaccharic acid (II), m.p. 162° (decomp.) (lit. 155°), an acid [(?) a dihydroxyglutaric acid] (III), $\text{C}_5\text{H}_8\text{O}_6$, m.p. 162—164° (decomp.), and (in one experiment only) an acid, m.p. 158—160°. More (III) is formed when KMnO_4 equiv. to 5 O is used. (I) with HNO_3 gives $\text{H}_2\text{C}_2\text{O}_4$, *l*-trihydroxyglutaric acid, mucic acid, and (in one experiment) a little (II). Kiliani's arguments (A., 1931, 1411) concerning the configuration of (I) are unsound. The 2-deoxypentose obtained from metasaccharin is identical with *d*-2-xylofuranose. The



above and previously known facts and application of Hudson's rule indicate for (I) the annexed configuration. R. S. C.

Structure of glutaconic acids and esters. IV. **Cyclic glutaconic derivatives.** G. A. R. KON and H. R. NANJI. V. α -Benzyl- and α -benzyl- β -methyl-glutaconic acids. G. A. R. KON and E. M. WATSON. VI. **Derivatives of β -phenylglutaconic acid.** B. S. GIDVANI and G. A. R. KON (J.C.S., 1932, 2426—2433, 2434—2443, 2443—2451; cf. this vol., 252, 601).—IV. Et cyclopentanonecarboxylate, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and $\text{C}_5\text{H}_5\text{N}$ (50% yield) or KOEt (59% yield) give Et 2-carbethoxy- Δ^1 -cyclopentenylcyanacetate (I), b.p. 188°/16 mm., giving a K derivative (II) with KOH or KOEt, from which (I) is regenerated with BzOH in Et_2O , or with aq. acid. Ozonolysis of (I) gives Et α -cyano- β -diketosuberate, b.p. 150—190°/30 mm. [diphenylhydrazone, m.p. 256° (decomp.)]. (II) with MeI gives Et α -cyano- α -2-carbethoxy- Δ^1 -cyclopentenylpropionate (III), b.p. 177—178°/17 mm., ozonised to Et α -cyano- β -diketo- α -methylsuberate, b.p. 140—170°/16 mm. (diphenylhydrazone, m.p. 217—218°), and converted by NaOEt into α -2- α -carbethoxy- Δ^1 -cyclopentenylpropionitrile, b.p. 151°/20 mm., which with O_3 gives Et ξ -cyano- β -diketo-octoate [diphenylhydrazone, m.p. 210—211°; semicarbazone, m.p. 242° (decomp.)]. Hydrolysis of (I) with (a) KOH gives a $\text{C}_5\text{H}_5\text{N}$ derivative, $\text{C}_8\text{H}_8\text{O}_2\text{N}$, m.p. 258° (darkens); (b) HCl gives a $\text{C}_5\text{H}_5\text{N}$ derivative (IV), $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$, m.p. 241° (decomp.) (Bz derivative, m.p. 80—100°), and 2-carbethoxy- Δ^1 -cyclopentenylacetic acid (V), m.p. 187° [Et ester (VI), b.p. 155°/20 mm.], which gives an anomalous hydroxyanhydride, $\text{C}_{10}\text{H}_{10}\text{O}_4$, m.p. 150° [anilic acid, m.p. 300° (darkens 240°)], and a little of the normal anhydride, isolated as the semianilide, m.p. 172°; (c) H_2SO_4 gives (IV), and Et 2-carbethoxy- Δ^1 -cyclopentenylmalonamate, m.p. 89°, hydrolysed by HCl to (V). (VI) with O_3 gives Et β -diketosuberate [phenylhydrazine derivative (? phenylhydrazidopyrazolone), m.p. 126°], and is unchanged by NaOEt. The K derivative of (VI) (formed in C_6H_6) with MeI gives Et 2-carbethoxy- Δ^1 -cyclopentenylpropionate, b.p. 149—150°/13 mm. [and unchanged (V)], hydrolysed to the acid, m.p. 151°. Acid or alkaline hydrolysis of (III) gives a $\text{C}_5\text{H}_5\text{N}$ derivative, $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$, m.p. 252°. Et 2-methylcyclopentanonecarboxylate did not react with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$. The following series of

compounds is similarly obtained from Et cyclohexanonecarboxylate: Et 2-carbethoxy- Δ^1 -cyclohexenylcyanoacetate, b.p. 190—191°/19 mm. (yields 18 and 38%), Et α -cyano- β -diketoazolate, b.p. 160—180°/16 mm. (diphenylhydrazone, m.p. 246°), Et α -cyano- α -2-carbethoxy- Δ^1 -cyclohexenylpropionate, b.p. 185°/17 mm., diphenylhydrazone, m.p. 206°, of Et α -cyano- β -diketo- α -methylazolate, α -2-carbethoxy- Δ^1 -cyclohexenylpropionitrile (VII), b.p. 162°/19 mm., isoquinoline derivative, $C_9H_{11}O_2N$, m.p. 206°, Et 2-carboxy- Δ^1 -cyclohexenylmalonamate, m.p. 167—168°, 2-carboxy- Δ^1 -cyclohexenylacetic acid, m.p. 166° (decomp.) (Et ester, b.p. 162°/20 mm.), phenylhydrazine derivative, m.p. 172°, of Et β -diketoazolate, Et 2-carbethoxy- Δ^1 -cyclohexenylpropionate, b.p. 158°/17 mm., and the corresponding acid, m.p. 136—137° (hydroxyanhydride, b.p. 177°/6 mm.; semianilide, m.p. 135—136°), isoquinoline derivative, from (VII), m.p. 172°. The above glutaconic derivatives are all stable in the $\beta\gamma$ -form.

V. The structure of the following esters was determined by ozonolysis. Interaction of the K derivatives of the stereoisomeric Et β -methylglutaconates with CH_2PhCl in C_6H_6 is accelerated by addition of MeI, giving *cis*- (II) and *trans*- $\beta\gamma$ -methylbenzylglutaconic esters (I) (? a little $\alpha\beta$). On hydrolysis (I) gives the *trans*- $\beta\gamma$ -acid (III), stable to ultra-violet light, whilst (II) gives the *cis*- $\alpha\beta$ -acid (IV), m.p. 148° [Et ester, (V), from the Ag salt], converted by ultra-violet light into *trans*- α -benzyl- β -methyl- Δ^a -propene- $\alpha\gamma$ -dicarboxylic acid, m.p. 157—158° (Et ester, b.p. 195—196°/14 mm.). (III) gives (IV) with conc. HCl, whilst the reverse change, studied quantitatively, is effected with KOH. The K derivatives (probably $\alpha\beta$) of (II) and (V) with MeI give a mixture of the $\alpha\beta$ -forms of α -benzyl- β -methyl- and α -benzyl- $\beta\gamma$ -dimethylglutaconic esters, the latter being also obtained in small amount and accompanied by much $\beta\gamma$ -isomeride from the benzylation of Et $\alpha\beta$ -dimethylglutaconate. *trans*- α -Benzyl- Δ^a -propene- $\alpha\gamma$ -dicarboxylic acid (VI) from the corresponding tetracarboxylic acid) with $KMnO_4$ and Na_2CO_3 gives $PhCHO$ and $H_2C_2O_4$. The Et ester, from the Ag salt, or with $EtOH-H_2SO_4$, is mainly $\beta\gamma$ (? a little $\alpha\beta$), whilst that regenerated from the K derivative contains a little Et α -benzylideneglutarate (VII), and gave a little of the corresponding acid on hydrolysis, together with (VI). The hydroxyanhydride (VIII) from (VI) in Et_2O by extraction with $NaHCO_3$ gives *cis*- α -benzyl- Δ^a -propene- $\alpha\gamma$ -dicarboxylic acid (IX), m.p. 149—150° [Et ester, b.p. 189—190°, mainly $\beta\gamma$, with some (VII)], converted by H_2O into a eutectic mixture, m.p. 139° (cf. J.C.S., 1911 99, 2208), and by more prolonged action into the *trans*- $\beta\gamma$ -acid. (IX) with $KMnO_4$ in Na_2CO_3 gives phenylpyruvic acid and no $H_2C_2O_4$. The eutectic mixture gives oxidation products indicating both $\alpha\beta$ - and $\beta\gamma$ -forms (mainly the former), and gives an Et ester similar to that from (IX). (VIII) in $NaHCO_3$ with $KMnO_4$ gives $PhCHO$, $H_2C_2O_4$, and a little $BzOH$. Et α -benzyl- γ -methylglutaconate, b.p. 192°/10 mm. (from Et α -benzylglutaconate), is mainly the $\beta\gamma$ -form, and is hydrolysed to the acid, m.p. 184—185°, which is oxidised to $PhCHO$ (? a little $AcCO_2H$), and gives the above ester in the pure $\beta\gamma$ -form. The more

symmetrical glutaconic derivatives appear to be the more stable.

VI. The products of hydrolysis of Et α -carbethoxy- β -phenyl- α -methylglutaconate are (a) the *trans*- $\beta\gamma$ -acid, m.p. 155° (Et ester, b.p. 165°/5 mm., consisting mainly of the $\beta\gamma$ -form, with a little $\alpha\beta$, and also obtained by the action of MeI in Et_2O on the K derivative of Et β -phenylglutaconate, which may be regenerated from the K derivative), (b) the *cis*- $\alpha\beta$ -acid (I), m.p. 151° (Et ester, b.p. 163°/5 mm., mainly $\alpha\beta$, with a little $\beta\gamma$), (c) *cis*- β -phenyl- α -methyl- Δ^a -propene- $\alpha\gamma$ -dicarboxylic acid, m.p. 130—131° (Et ester, b.p. 159°/4 mm., mainly $\beta\gamma$, with a little $\alpha\beta$), and (d) an acid, $C_8H_{10}O_3$, m.p. 87° (cf. A., 1922, i, 553). Et phenylpropionate and $CN\cdot CHNa\cdot CO_2Et$ give the Na derivative (II) of Et α -cyano- β -phenylglutaconate (III), which with HCl gives a mixture of $\alpha\beta$ - and $\beta\gamma$ -forms, whilst with $BzOH$ in Et_2O it gives the pure $\beta\gamma$ -form, which is similarly obtained from the K derivative (IV). The ester gives phenylhydroxypyridine on hydrolysis. (IV) in Et_2O or C_6H_6 , and (II) only in $EtOH$, with MeI give Et α -cyano- β -phenyl- α -methyl- Δ^a -propene- $\alpha\gamma$ -dicarboxylate. (III) is also obtained in small yield from the action of C_5H_5N on Et benzoylacetate and $CN\cdot CH_2\cdot CO_2Et$. Et γ -sodio- α -carbethoxy- β -phenylglutaconate (this vol., 601) with hot $EtOH$ gives the α -sodio-derivative, converted by $BzOH$ in Et_2O into the parent ester, m.p. 38°. Similar results are obtained with the corresponding α -CN-ester. Et α -carbethoxy- β -phenyl- α -methylglutaconate (J.C.S., 1913, 103, 1569) is unaffected by $NaOEt$. An electronic explanation of this is suggested. The Na derivative with MeI gives a little Et_2CO_3 , and an ester from which (I) was isolated. $CHNa(CO_2Et)_2$ and $CPhCl_3$ with $NaOEt$ give a small yield of Et α -carbethoxy- β -ethoxycinnamate. A. A. L.

Peroxide of hexahydrobenzoic acid. F. FICHTER and W. SIEGRIST (Helv. Chim. Acta, 1932, 15, 1304—1307).—Hexahydrobenzoic acid (I) and its K salt (II) form an acid salt (? or mixture), 3(I):1(II). The anhydride (modified prep.) of (I) and $BaO_2\cdot 8H_2O$ in Et_2O give the Ba salt of (I) and hexahydrobenzoyl peroxide (III), an oil, which decomposes at room temp. to give CO_2 , a little O_2 , cyclohexanol, dicyclohexyl, and the cyclohexyl ester of (I). These products are the same as those obtained by electrolysis of (II). (III) is considered to be formed at the anode and to yield the ultimate products of the reaction by decomp. R. S. C.

Derivatives of 2-iodo-5-nitrobenzoic acid. H. GOLDSTEIN and A. V. GRAMPOLOV (Helv. Chim. Acta, 1932, 15, 1102—1105).—2-Iodo-5-nitrobenzoic acid (I) and HNO_3 (*d* 1.5) at 50° gives 2-iodoso-5-nitrobenzoic acid (II), m.p. 197° (decomp.) (cf. A., 1894, i, 32), reduced to (I) by very dil. KI and H_2SO_4 , and giving with MeOH or EtOH and H_2SO_4 a small amount of the corresponding ester and (?) 2-iodo-5-nitrobenzoic anhydride, m.p. about 200—205° (decomp.). (II) with Ac_2O gives the mixed anhydride, m.p. 187—188° (decomp.), and with NaOCl at room temp. affords 2-iodoxy-5-nitrobenzoic acid, m.p. about 199—202° (defflagration). 2-Chloro-3:5-dinitrobenzoic acid and aq. NH_3 at 100° give the 2- NH_2 -acid, which by

diazotisation etc. affords impure 2-iodo-3:5-dinitrobenzoic acid, m.p. 219° (changed by NaOH to 3:5-dinitrosalicylic acid), and a substance, m.p. 286° (decomp.). R. S. C.

Friedel-Crafts reaction. Unsymmetrical acid anhydrides and their behaviour with benzene and aluminium chloride. J. M. ZEAVIN and A. M. FISHER (J. Amer. Chem. Soc., 1932, 54, 3738—3742).—The following anhydrides are prepared from the appropriate acid and BzCl or AcCl in Et₂O—C₅H₅N at 0°: *mono-o-benzoyloxybenzoic*, m.p. 67—67.8° (from *o*-OH·C₆H₄·CO₂H and BzCl); *mono-o-methoxybenzoic*, m.p. 76.3—77.2°; *mono-p-chlorobenzoic*, m.p. 66.5—70°; *mono-p-bromobenzoic*, m.p. 82—83°; *mono-o-nitrobenzoic*, m.p. 65—65.5°; *benzoic 3:5-dinitrobenzoic*, m.p. 115.5°; *α-naphthoic benzoic*, m.p. 89.5—90.3°; *β-naphthoic benzoic*, m.p. 54—57.5°; *α-naphthoic acetic* (I), a clear brown oil, decomp. readily; *β-naphthoic acetic* (II), m.p. 50.5—51°; *dibenzoic phthalic* (III), m.p. 131—132°. All the anhydrides except the last three give CPh₂ with C₆H₆ and AlCl₃. (I) and (II) give CPhMe; (III) gives BzOH and diphenylphthalide. C. J. W. (b)

General synthesis of α-unsaturated acids from malonic acid. II. M. DALAL and S. DUTT (J. Indian Chem. Soc., 1932, 9, 309—314; cf. A., 1925, i, 882).—The following bases are catalysts for the prep. of cinnamic acid from PhCHO and CH₂(CO₂H)₂ (they are best used in the ratio 1 mol. of base:1 mol. of PhCHO): quinoline, isoquinoline, 2-methylquinoline, α- and β-naphthylquinolines, phenanthroline, acridine, 9-methylacridine; C₅H₅N, 2-methylpyridine, lutidine, collidine, piperidine, NPhMe₂, NPhEt₂, and *N*-benzyl-*N*-methyl- and -ethyl-anilines. The following aldehydes condense with CH₂(CO₂H)₂ in presence of quinoline (1 mol. per 1 mol. of aldehyde) in *o*-, *m*-, and *p*-NO₂·C₆H₄·CHO, *o*-C₆H₄Cl·CHO, *m*- and *p*-OH·C₆H₄·CHO, vanillin, *p*-NMe₂·C₆H₄·CHO, *p*-C₆H₄Me·CHO, *p*-OMe·C₆H₄·CHO, veratraldehyde, piperonal, furfuraldehyde, citronellal, citral, cinnamaldehyde, paracetaldehyde, EtCHO, Pr^oCHO, and Bu^oCHO; the yields of unsaturated acid vary from 10.6 to 82.5%. Cinnamic acid is not produced from PhCHO and CH₂(CO₂H)₂ even at 130°. H. B.

Aromatic fluoro-compounds. XII. Fluorinated amino-acids and their derivatives. II. Fluorophenylalanines. G. SCHIEMANN and W. ROSELIUS (Ber., 1932, 65, [B], 1439—1442).—*o*-Fluorobenzaldehyde, hippuric acid, anhyd. NaOAc, and Ac₂O at 100° afford 4-*o*-fluorobenzylidene-2-phenyloxazol-5-one, m.p. 165.5—166.5° (yield 35%), transformed by NaOH-50% EtOH into α-benzamido-*o*-fluorocinnamic acid, m.p. 209.5—210° (decomp.), reduced and hydrolysed by HI (d 1.96), Ac₂O, and red P to α-amino-β-*o*-fluorophenylpropionic acid, m.p. 258.5—259° (decomp.). From *m*-C₆H₄F·CHO are obtained similarly, 4-*m*-fluorobenzylidene-2-phenyloxazol-5-one, m.p. 156.5—157° (70% yield), α-benzamido-*m*-fluorocinnamic acid, m.p. 203—203.5° (decomp.) (yield 63%), and dl-α-amino-β-*m*-fluorophenylpropionic acid, m.p. 262—263° (decomp.) (Cu salt). *p*-C₆H₄F·CHO yields successively 4-*p*-fluorobenzylidene-2-phenyloxazol-5-one, m.p. 181—181.5°, α-benzamido-*p*-fluorocinnamic acid, m.p.

225° (decomp.), and dl-α-amino-β-*p*-fluorophenylpropionic acid, m.p. 263.5—264° (decomp.) (Cu salt).

H. W.

Action of sodium hydrogen sulphite on derivatives of 1-nitroso-β-naphthol. M. BATTEGAY and E. RIESZ (Bull. Soc. chim., 1932, [iv], 51, 902—916).—Interaction of 1-nitroso-2-hydroxy-3-naphthanilide (I) with NaHSO₃ at 40—45° for a short time gives the NaHSO₃ derivative, converted by HCl into the H₂SO₃ derivative (cf. A., 1924, i, 722; Lantz and Mingasson, A., 1931, 1291), but at 100° 1:2-dihydroxy-3-naphthanilide-4-sulphonic acid (II) is produced (as Na salt; cf. G.P. 70,867). (II) is identified by hydrolysis by conc. aq. HCl at its b.p. to H₂SO₄ and 1:2-dihydroxy-3-naphthanilide, m.p. 167°, also obtained by reduction of 1:2-naphthaquinone-3-carbanilide with Na₂S₂O₄ or SO₂ in AcOH. With oxidising agents in neutral (H₂O₂) or alkaline solution (H₂O₂, air) or with HNO₂ in AcOH (II) gives 2-hydroxy-1:4-naphthaquinone-3-carboxylanilide, m.p. 202°, with liberation of SO₂, and with NH₂Ph (and O₂) the corresponding 4-anil, m.p. 226°, identified by reduction by SO₂ to 1:2-dihydroxy-4-anilino-3-naphthanilide, m.p. 200° (decomp. begins at 160°), is formed.

The stability of the 3-CO·NHPh group, in contrast with the 3-CO₂H group, which is eliminated by NaHSO₃ (cf. Lantz and Mingasson, *loc. cit.*), is in accordance with the behaviour of these compounds as derivatives of β-ketonic acids. Consequently *Me* 1-nitroso-2-hydroxy-3-naphthoate, m.p. 153—154° (from aq. NaNO₂ and *Me* 2-hydroxy-3-naphthoate in AcOH) gives a NaHSO₃ derivative, converted by cold aq. HCl into the H₂SO₃ derivative, and by NaOH at 0° into the original *Me* ester, m.p. 153—154°. H. A. P.

Nitration of benzoic acid and fluorene-carboxylic acid. F. L. ROSE (J.C.S., 1932, 2360—2362).—Benzoic acid and HNO₃, d 1.5, below 0° give (a) 2:2'-dinitrobenzoic acid, m.p. 171—172° (decomp.) (isolated as the NH₂Ph salt), oxidised by CrO₃ in AcOH to 2:2'-dinitrobenzophenone, and reduced to 2:2'-diaminobenzoic acid dihydrochloride, and (b) a mixture of nonacidic isomerides, C₂₀H₁₆O₁₂N₄, oxidised to 2:3'- and 3:3'-dinitrobenzophenone. Fluorene-carboxylic acid in CHCl₃ or CCl₄ with HNO₃, d 1.43, gives 2-nitrofluorene-9-carboxylic acid, m.p. 186—187° (decomp. giving 2-nitrofluorene, oxidised to 2-nitrofluorenone), which with H₂SO₄ gives 2-nitro-7-sulphofluorene-9-carboxylic acid [K salt, decomp. 190° giving nitrofluorenesulphonic acid (A., 1930, 1424); diacid chloride, m.p. 159°]. A similar mixture with HNO₃, d 1.51, gives 2:7-dinitrofluorene-9-carboxylic acid, decomp. 150° giving 2:7-dinitrofluorene, oxidised to the fluorenone. The above nitro-acids with Sn and HCl give 2-amino-, m.p. 207—208° (decomp.) (Ac derivative, m.p. 195°), 2:7-diamino-, m.p. 209—210° (decomp.) (Ac₂ derivative, m.p. 263—264°), and 2-amino-7-sulphofluorene-9-carboxylic acid, darkens at 290°. A. A. L.

Derivatives of di-iodotyrosine and thyroxine. Action of acetic anhydride on di-iodotyrosine. C. S. MYERS (J. Amer. Chem. Soc., 1932, 54, 3718—3725).—*l*-Di-iodotyrosine and Ac₂O in cold 2*N*-NaOH give the ON-Ac₂ derivative (I), m.p. 186—187°, [α]_D²⁰ +21.52° in abs. EtOH; with Ac₂O in boiling

AcOH the *dl*-isomeride (II), m.p. 186°, results. Partial hydrolysis of (I) with NaOH in dil. EtOH gives the *N*-Ac derivative (III), decomp. 198—200°, $[\alpha]_{D}^{30} +34.54^\circ$ in abs. EtOH (*Me* ester, m.p. 152—153.5°, also obtained from the *Me* ester and AcCl or Ac₂O). Hydrolysis of (II) gives the *dl*-*N*-acetyldi-iodotyrosine (IV), decomp. 205—206° (*Me* ester, m.p. 136—137°; *Et* ester, m.p. 140—141°). (III) and Me₂SO₄ in EtOH-5*N*-NaOH give the *l*-*N*-Ac-O-*Me* derivative, m.p. 207—208°, $[\alpha]_{D}^{25.5} +14.5^\circ$ in EtOH, hydrolysed to *l*-*o*-methyl-di-iodotyrosine, m.p. 204—206° (decomp.), $[\alpha]_{D}^{28.5} -3.2^\circ$ in 5% NaOH. The compound obtained by Wheeler and Jamieson (A., 1905, i, 350) is not the simple Ac derivative; it has the empirical formula C₂₄H₁₈O₆N₂I₄ and is probably an anhydride of (III) with the OH groups only partly acetylated. With NaOH it yields (IV), with NaOEt the *Et* ester of (IV), and with aq. NH₃ the *amide*, decomp. 204—206°, of (IV); PhOH gives a mixture of Ph esters of the Ac and Ac₂ derivatives, containing approx. 65% of the latter. Di-iodotyrosine heated gently with Ac₂O until turbidity results gives the *azlactone*, m.p. 135—138°, of (IV); (II) and Ac₂O at 100° yield an *azlactone*, m.p. 87—89°. The *azlactone* is probably an intermediate in the formation of the anhydride. *dl*-*N*-Acetylthroxine and Me₂SO₄ in NaOH-EtOH give the *O*-*Me* derivative, m.p. 214—217°, hydrolysed to *dl*-*O*-methylthroxine, decomp. 210—213°.

C. J. W. (b)

Fluorinated amino-acids and their derivatives.

I. Nuclear fluorinated amino-acids. G. SCHIE-MANN [with W. WINKELMULLER and W. ROSELUS (Ber., 1932, 65, [B], 1435—1438).—The following schemes are outlined: 3-fluoro-*p*-tolyl *Me* ether to 3-fluorotyrosine, decomp. 277°; 3-fluoro-4-methoxybenzaldehyde and hippuric acid to the *azlactone* OMe·C₆H₃F·CH·C<math display="block">\begin{array}{c} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} = \text{CPh} \end{array}, m.p. 206.5°, and thence through α -benzamido-3-fluoro-4-methoxycinnamic acid, m.p. 214°, to 3-fluorotyrosine: *m*-fluorophenylalanine to α -amino- β -3-fluoro-4-nitrophenylpropionic acid, decomp. 209.5°, thence to α -amino- β -3-fluoro-4-amino-phenylpropionic acid and 3-fluorotyrosine: *p*-methoxydiphenyl ether to 3-nitro- and 3-amino-4-methoxydiphenyl ether (to which the BF₃ process could not be satisfactorily applied); *m*-bromofluorobenzene with quinol *Me* ether to 3-4'-methoxyphenoxyfluorobenzene, b.p. 161.5°/14 mm., whence successively 2-fluoro-4:4'-methoxyphenoxybenzaldehyde, the *azlactone*

OMe·C₆H₄·O·C₆H₃F·CH·C<math display="block">\begin{array}{c} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} = \text{CPh} \end{array}, m.p. 155°, and 2-fluorothyronine [α -amino- β -4:4'-hydroxyphenoxy-phenylpropionic acid], decomp. 264.5°; β -3-fluoro-4-hydroxyphenylethylamine (*picrate*, decomp. 194.5°) and β -3-fluorophenylethylamine (*picrate*, decomp. 157°) by decarboxylation of the corresponding acids; *m*-fluorobenzaldehyde successively to *m*-fluorocinnamic acid, m.p. 166.5°, β -3-fluorophenylpropionic acid, m.p. 46°, its *amide*, m.p. 95.5°, and β -3-fluorophenylethylamine, b.p. 87°/15 mm.

H. W.

peri-Condensation of phthalic anhydride. II. Phthalynaphthalene. A. RIECHE, H. SAUTHOFF, and O. MULLER (Ber., 1932, 65, [B], 1371—1381; cf. A., 1931, 1060).—Condensation of phthalic anhydride

with AlCl₃ and the requisite hydroxynaphthalene at 190—210°, 200—220°, and 235—245°, respectively, leads to 1:8-phthalyl-2:6-, m.p. 302°, and -2:7-dihydroxynaphthalene, m.p. 267° (*Ac* derivative, m.p. 233—234°), and 2-hydroxy-1:8-phthalalynaphthalene-3-carboxylic acid, m.p. 276°. Of these, only the last-named is degraded by molten NaOH, whereby β -naphthol-3:8-dicarboxylic acid, m.p. 320°, is produced.

In reply to Fieser (A., 1931, 1292), the 1:8-phthalyl structure of 1:8-phthalyl- β -naphthol (I) is maintained for the following reasons. The "lactone-like" structure cannot be deduced from analysis of the Na or Ba salts. Etherification of the OH group yields *Et* 1:8-phthalyl- β -naphthyl ether, m.p. 163.5°, insol. in boiling alkali. The demonstration of the presence of one CO group by the action of MgPhBr does not exclude the presence of a second CO, masked by the *o*-OH group. Treatment of (I) with PCl₅ and POCl₃ yields 2-chlorophthalalynaphthalene (II), transformed by N₂H₄·H₂O in presence of Pd-CaCO₃ and KOH-MeOH into 1:8-phthalalynaphthalene (III), m.p. 178°, also derived from *o*-1-naphthoylbenzoic acid. (II) and (III) yield only *mono*(dinitrophenyl)-hydrazones, m.p. 265° and 278°, respectively, but (III) is transformed by MgEtBr in hexahydroanisole into a substance, C₂₂H₂₂O₂, both CO groups having reacted. (III) is readily sol. in MeOH-KOH, but titration shows that alkali is not neutralised even after boiling for 2 hr.; since (III) is pptd. by CO₂ or by dilution, it is assumed that the CO can add KOH. Distillation of (I), (II), or (III) with Zn dust in H₂ gives 1:8-oxylidenenaphthalene, m.p. 116.5°, oxidised by a large excess of Na₂Cr₂O₇ in AcOH to (III). In agreement with Fieser (*loc. cit.*), oxidation of (I) with KMnO₄ ultimately yields benzophenone-2:3:2'-tricarboxydilactone, but the intermediate acid is probably C₁₆H₁₂O₆ instead of C₁₆H₁₀O₆. The main product is *Bz*-3-hydroxybenzanthrone. A scheme is suggested.

H. W.

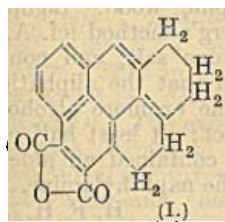
Structure, chemical reactivity, and absorption in the ultra-violet. The acids C₆H₅·[CH₂]_n·CH[CH₂·CO₂H]·CO₂H and their derivatives. (MME.) RAMART-LUCAS and Z. PAPADAKIS (Ann. Chim., 1932, [x], 18, 32—78; cf. this vol., 557).—The ultra-violet absorption curves of the series Ph·[CH₂]_n·CH[CH₂·CO₂H]·CO₂H (*n*=0—4), and, where possible, of their dialkyl and alkyl H esters, anhydrides, and imides, have been examined. The mutual influence of Ph and the succinic acid (etc.) residue (R) is marked where *n*=0, but rapidly diminishes as the series is ascended; the curves of homologues are almost identical when *n*>1, and then approximate to those of an equimol. mixture of PhEt and R.H. Chemical properties, *e.g.*, the formation and rehydration of acid anhydrides, show a closely parallel behaviour. Similarly, the H esters of the higher members, unlike those of phenylsuccinic acid, decompose on distillation into anhydride and neutral ester, whilst the NH₄ salts (the phenylsuccinate alone excepted) give on heating the anhydride as well as the imide. There is a slight difference in absorption between the two isomeric Et H phenylsuccinates, and a corresponding difference in chemical reactivity.

β -Carbethoxy- β -phenylpropionic acid, m.p. 88—89°.

is prepared by partial hydrolysis of Et_2 phenylsuccinate, and Et β -carboxy- β -phenylpropionate, m.p. 95—96°, from phenylsuccinic anhydride and abs. EtOH ; phenylsuccinamide, m.p. 209—210°, is obtained in poor yield from the acid chloride and NH_3 . The acids $\text{Ph} \cdot [\text{CH}_2]_n \cdot \text{CH}[\text{CH}_2 \cdot \text{CO}_2\text{H}] \cdot \text{CO}_2\text{H}$ ($n=1-4$) are prepared by interaction of $\text{CHNa}(\text{CO}_2\text{Et})_2$ with $\text{Br} \cdot [\text{CH}_2]_n \cdot \text{Ph}$, further condensation of the product with $\text{CH}_2\text{Br} \cdot \text{CO}_2\text{Et}$, hydrolysis, and decarboxylation of the resulting tribasic acid (this procedure in some cases yields the anhydride). The products are contaminated with a little unsaturated acid which needs to be removed with H_2 - PtO_2 before the absorption curves are determined. The following are described: Et_3 α -carboxy- α -benzylsuccinate, b.p. 200°/11 mm.; Me_2 benzylsuccinate, b.p. 159°/7 mm.; benzylsuccinimide, m.p. 97—98°, b.p. 200—205°/5 mm.; Et_3 α -carboxy- α -(β -phenylethyl)succinate, b.p. 213°/13 mm. [free acid, m.p. 165° (decomp.)]; β -phenylethylsuccinic acid (Me_2 ester, b.p. 160°/5 mm.; anhydride, m.p. 58°, b.p. 188°/2 mm.; imide, m.p. 78°, b.p. 207—210°/5 mm.); Et_2 γ -phenylpropylmalonate, b.p. 178°/5 mm.; Et_2 α -carboxy- α -(γ -phenylpropyl)succinate, b.p. 217—218°/9 mm. [free acid, m.p. 140° (block, decomp.)]; γ -phenylpropylsuccinic acid [anhydride, m.p. 64°, b.p. 196°/3 mm.; Me_2 , b.p. 168°/4 mm., and Me H esters; imide, m.p. 80° (together with anhydride by heating NH_4 salt)]; Et_2 δ -phenylbutylmalonate, b.p. 180°/5 mm.; Et_2 α -carboxy- α -(δ -phenylbutyl)succinate, b.p. 201—202°/1 mm. [free acid, m.p. 145° (block, decomp.)]; δ -phenylbutylsuccinic acid, m.p. 133° (anhydride, m.p. 76°, b.p. 195—200°/high vac.; Me_2 ester, b.p. 183°/5 mm.; imide, m.p. 86°). Attempts to prepare H esters of definite structure from benzylsuccinic acid failed.

H. A. P.

Polynuclear hydrocarbons. XVII. Preparation of a pyrene derivative from benzantrhrene. E. CLAR (Ber., 1932, 65, [B], 1425—1428).—Benzanthrene is converted by maleic anhydride in boiling



xylene into 2:3-trimethylene-4:5-dihydropyrene-6:7-dicarboxylic anhydride (I), m.p. 227—230° (decomp.). The nature of its extinction curve excludes the possibility that it is an endo-derivative or a phenanthrene compound, but suggests a pyrene compound. Benzantrhrene, phenanthrene, and chrysene do not react with maleic anhydride. The yellow colour of technical pyrene can be removed by prolonged treatment with maleic anhydride in boiling xylene.

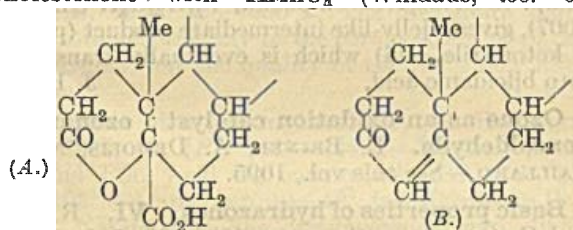
H. W.

Ring-system of sterols and bile acids. O. ROSENHEIM and H. KING (Nature, 1932, 130, 315).—A criticism (cf. this vol., 971).

L. S. T.

Proof of a methylene group in position 1 of the cholesterol ring system. R. TSCHESCHE (Annalen, 1932, 498, 185—193).—The Me ester of the acid $\text{C}_{26}\text{H}_{46}\text{O}_2$ (I) (Diels *et al.*, A., 1928, 169) [prepared by Clemmensen reduction of the acid, $\text{C}_{26}\text{H}_{44}\text{O}_3$ (Windaus, A., 1906, i, 579; 1917, i, 265)] and MgPhBr give a carbinol which, when distilled, passes into the corresponding unsaturated hydrocarbon; oxidation (O_3) of this affords COPh_2 and an acid, $\text{C}_{25}\text{H}_{44}\text{O}_2$ (II), m.p.

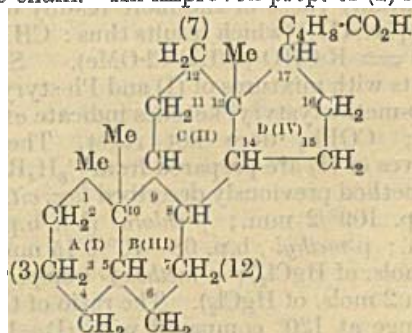
153—154°, $[\alpha]_D^{25} +45.7^\circ$ in CHCl_3 (anilide, m.p. 149—150°), convertible by the same series of reactions into an acid, $\text{C}_{24}\text{H}_{42}\text{O}_2$ (III), m.p. 181—182°, $[\alpha]_D^{25} +15.6^\circ$ in CHCl_3 (anilide, m.p. 105—108°). The CO_2H group of (III) is derived from C_1 of cholesterol [the numbering is that of Wieland and Dane (following abstract)], which must, therefore, exist as CH_2 . The velocity of esterification of (III) with $\text{Bu}^\text{iso}\text{OH}$ at 155° is much smaller than of (I) or (II); (III) eliminates CO_2 extremely readily when treated with conc. H_2SO_4 . These facts indicate that (III) contains the $>\text{CMe} \cdot \text{CO}_2\text{H}$ group, thus supporting Wieland and Dane's structure (*loc. cit.*; cf. Rosenheim and King, this vol., 736). The acid $\text{C}_{27}\text{H}_{44}\text{O}_4$ (Me ester, m.p. 148—149°, $[\alpha]_D^{25} +44^\circ$ in CHCl_3), formed as a by-product in the oxidation of cholestenone with KMnO_4 (Windaus, *loc. cit.*),



probably contains the grouping (A). It is suggested [by E. DANE] that cholestenone [from which (I) is derived] is (B).

H. B.

Constitution of bile acids. XXXIX. 12-Hydroxycholanolic acid. H. WIELAND and E. DANE (Z. physiol. Chem., 1932, 210, 268—281; cf. this vol., 614).—Hydrogenation of 7:12-diketo-cholanolic acid (I) in AcOH in presence of PtO_2 gives 7-keto-12-hydroxycholanolic acid (II), m.p. 176° [semicarbazone (III)]. When heated at 170—175° with NaOEt (III) gives 12-hydroxycholanolic acid (IV), m.p. 96—102° (+ H_2O), oxidised by CrO_3 in AcOH to 12-ketocholanolic acid (V), m.p. 148—150°. Oxidation of (V) with HNO_3 opens ring III and affords the tricarboxylic acid thilobilianic acid, m.p. 260—262° (decomp.) (Me_3 ester, m.p. 109°), forming on vac. distillation the anhydride, m.p. 201°. Thermal decomp. of (IV) yields apocholenic acid. Bromination of (V) gives bromo-12-ketocholanolic acid, m.p. 178° (decomp.). Partial oxidation of 7:12-dihydroxycholanolic acid with CrO_3 affords 12-keto-7-hydroxycholanolic acid (VI), m.p. 178° (+ H_2O). Thermal decomp. of (VI) gave, not the 12-keto-acid, but the lactone, m.p. 217°, by linking of the OH with the CO_2H of the side-chain. An improved prep. of (I) is given.



(The typical C atoms 3, 7, and 12 are shown by parentheses.)

Since ring III of cholanolic acid, although 6-membered, does not yield the 5-membered ketone, the Blanc rule does not hold and it is now unnecessary to suppose ring II is 5-membered. The most probable structure for cholanolic acid now conforms to the chrysene structure (cf. Rosenheim and King, this vol., 736) with the exception of the 5-membered ring IV which is retained.

J. H. B.

Bile acids. XXXVI. M. SCHENCK (Z. physiol. Chem., 1932, 211, 88—96; cf. this vol., 849).—In the inversion of the oximinoamino-acid (cf. A., 1931, 1293, and this vol., 742) a second product, m.p. 226° (decomp.), is obtained. Van Slyke determination indicates that it is a diamino-acid, but it has the same C val. as the original material. With HNO₃ at room temp. the blue NO-compound, C₂₄H₃₃O₈N (A., 1928, 1007), gives a jelly-like intermediate product (possibly a ketonitrile acid) which is eventually transformed into biloidanic acid.

J. H. B.

Ozone as an oxidation catalyst; ozonation of benzaldehyde. E. BRINER, A. DEMOLIS, and H. PAILLARD.—See this vol., 1095.

Basic properties of hydrazones. VI. R. CIUSA and G. OTTOLINO (Gazzetta, 1932, 62, 791—795).—Benzaldehyde- and *m*-nitrobenzaldehyde-phenylmethylhydrazones combine respectively with PhCHO in HCl to give compounds of m.p. 170° (I) (this vol., 51) and 169°, and respectively with *m*-nitrobenzaldehyde to give compounds, m.p. 177° and 181°. By-products of the prep. of (I) are the carbinol, CPh(OH)(C₆H₄·NMe·N:CHPh)₂, m.p. 111° [also obtained by treating (I) with EtOH and NH₃], and the corresponding leuco-base, m.p. 136°; the substance of m.p. 155° (A., 1922, i, 475), also formed, is now regarded as benzylidene-*pp'*-dimethyldihydrazinotriphenylmethane, C₂₈H₂₈N₄.

E. W. W.

Distyryl ketone and triphenylmethane. XV. Thermal decomposition of α -alkoxyalkyl chlorides. F. STRAUS and H.-J. WEBER (Annalen, 1932, 498, 101—128).—Thermal decomp. of α -methoxybenzyl chloride (I) (this vol., 383) into PhCHO and MeCl is best accomplished at 120°; the time of half change is 34 min. (mean val.). α -Methoxycinnamyl chloride (II) and α -chlorodiphenylmethyl Me ether (III) decompose more readily than (I); the ratio of the times of half change at 100° is (III) : (II) : (I) = 1 : 6.8 : 75. Mixtures of (I) and cinnamaldehyde and of (II) and PhCHO show times of half change which are essentially those of the more readily decomposed chloride [i.e., (II)] (which results thus : CHRCl·OMe + R'·CHO \rightleftharpoons R·CHO + CHR'Cl·OMe). Similar experiments with mixtures of (I) and Ph styryl, distyryl, and di-*p*-methoxystyryl ketones indicate exchanges of radicals; CPh₂ does not react. The following derivatives of (I) are prepared from C₆H₄R·CH(OMe)₂ by the method previously described (*loc. cit.*) : *p*-nitro- (IV), b.p. 109°/2 mm.; *p*-chloro- (V), b.p. 80—82°/0.15 mm.; *p*-methyl-, b.p. 68—70°/0.15 mm. (complex with 4 mols. of HgCl₂); *p*-methoxy- (complex, decomp. 90°, with 2 mols. of HgCl₂). The ratio of the times of half change at 120° compared with (I)=1 is (in the order quoted) 10.8 (calc. from $\Delta 10^\circ$) : 2.8 : 0.41 : 0.03 (calc. from $\Delta 10^\circ$); decomp. is facilitated by increase

in the polarity of the C-Cl linking and the positivity of the Me-C atom. These results are compared with the degrees of dissociation of *p*-C₆H₄R·CPh₂Cl (Ziegler and Wollschitt, A., 1930, 545) and the velocities of hydrolysis of *p*-C₆H₄R·CH₂Cl (Olivier). *p*-Chloro-, b.p. 114—115°/19 mm., and *p*-methyl-, b.p. 99—100°/15 mm., benzaldehyde dimethylacetals are new. An equilibrium mixture of (I) and (IV) is obtained from (I) and *p*-NO₂·C₆H₄·CHO or from (IV) and PhCHO.

The rate of decomp. of (I) is accelerated by addition of PhCHO [max. at about 2 mols. per mol. of (I)], C₂H₄Cl₂, PhCN, and PhNO₂, and decreased by PhBr, C₆H₄Me₂, and diisooamyl ether (in this case, 19% of HCl is evolved with MeCl and a Cl-containing residue is obtained); PhOMe also causes acceleration, but the residue contains 10.4% Cl. Similar results are observed with (II), (IV), and (V). The effect of the solvent is proportional to its polarisability. CHPh(OEt)₂ and AcCl give (cf. *loc. cit.*) α -ethoxybenzyl chloride, b.p. 52—54°/0.05 mm., the time of half change of which at 120° is 70 min. α -Methoxybenzyl bromide [from CHPh(OMe)₂ and AcBr at 0°] and its *p*-NO₂-derivative, m.p. 59—60°, decompose much more readily than the corresponding chlorides.

[By N. STANCOVICI.] The dimethylacetal, b.p. 112° (corr.), of PrCHO (VI) with AcCl and a trace of Cu-bronze at 65—70° gives α -methoxy-*n*-butyl chloride, b.p. 29°/12 mm., converted by NaOEt into the methyl-ethylacetal, b.p. 134—135° (corr.), of (VI) and decomp. at 110° to MeCl (20—25%), HCl (30%), and a Cl-containing residue (—about 50% Cl). α -Ethoxy-*n*-butyl chloride, b.p. 47° (corr.)/12 mm., is similarly prepared from the diethylacetal, b.p. 142.5—143.5° (corr.), of (VI). CMe₂(OMe)₂ and PCl₅ below 0° give β -chloro- β -methoxypropane, b.p. 14—15°/88 mm., which decomposes readily at 40° to MeCl (60%) and HCl (40%).

H. B.

Chemistry of pine wood. P. KLASON (Svensk Kem. Tidskr., 1932, 44, 177—188).—A discussion of the chemical constituents of pine wood. Lignin prepared from this by Freudenberg's method (cf. A., 1929, 1046) gives a naphthylamine salt, and consequently the latter's assumption that the aliphatic part of lignin is composed of one or more alcohol groups linked together is incorrect; at least half of Freudenberg's lignin must have contained an aldehyde group, which reacted with the naphthylamine.

H. F. H.

Reactions catalysed by aluminium chloride. IV. Experiments with poisoned catalysts.

C. D. NENITZESCU and I. P. CANTUNIARI (Ber., 1932, 65, [B], 1449—1453; cf. this vol., 744).—The formation of 2-acetyl-1-methyl- Δ^1 -cyclopentene (I), in addition to the saturated ketones, from cyclohexane, AcCl, and AlCl₃ (cf. Unger, this vol., 514) is due to the presence of H₂O in the AlCl₃. Other substances which yield mol. compounds with AlCl₃ (POCl₃, PhNO₂, CPhMe, COMe₂) behave similarly. In presence of COMe₂, nearly homogeneous (I) is obtained. The production of MeCHO during the interaction of cyclohexane, AcCl, and poisoned AlCl₃ is established, whereas only traces of the hydrocarbon C₁₅H₂₂ are produced; H for the reduction of AcCl is derived from the saturated ketone. 2-Acetyl-1-methylcyclopentane is not affected by BzCl and AlCl₃.

suspended in cyclohexane, but behaves as a catalyst poison; the production of PhCHO is accompanied by that of an equiv. amount of $C_{12}H_{22}$. $POCl_3$, $COMe_2$, PhNO, or CPhMe diminishes the activity of $AlCl_3$ so greatly that reaction is scarcely induced between cyclohexane and BzCl. *n*-Hexane reacts with AcCl and $AlCl_3$ similarly to cyclohexane, yielding *Me n-hexyl ketone*, b.p. 154—155° (*semicarbazone*, m.p. 120°), and *Me n-hexenyl ketone*, b.p. 177—178° (*semicarbazone*, m.p. 220°); the production of MeCHO is established. 1-Methyl- Δ^1 -cyclopentene, AcCl, and $AlCl_3$ in CS_2 afford 2-acetyl-1-methyl- Δ^1 -cyclopentene.

H. W.

Stereoisomerism of alicyclic oximes. W. HUCKEL and M. SACHS (Annalen, 1932, 498, 166—184).—The oxime of *trans*-2-ketodecahydronaphthalene (*trans*- β -decalone) exists in inactive stereoisomeric forms, m.p. 99° (I) and 91° (II). These are obtained by hydrolysis of their respective Bz derivatives, m.p. 108—110° (III) and 87°, which are separable by fractional crystallisation of the product (A) obtained by benzylation (pyridine method) of the oxime, m.p. 76°, previously described (A., 1925, i, 258). (I) and (II) are converted into the same mixture, m.p. about 63°, by long heating above their m.p. (III) is a racemate; suitable crystallisation of (A) gives also a Bz derivative, m.p. 135°, $[\alpha]_D^{25} \pm 100^\circ$ in Et_2O , hydrolysed to the oxime, m.p. 87—88°, $[\alpha]_D^{25} + 62.7^\circ$ in Et_2O , which exhibits mutarotation. Fenchone-oxime (from *d*-fenchone) (cf. Wallach, A., 1908, i, 809), in which the C atoms adjacent to the oxime group are not attached to H [hence tautomerism is excluded (cf. Raikowa, A., 1929, 911)], also exists in stereoisomeric forms, m.p. 167°, $[\alpha]_D^{25} + 46.5^\circ$ in 96% EtOH (Bz derivative, m.p. 81°, $[\alpha]_D^{25} + 49^\circ$ in 96% EtOH), and m.p. 123°, $[\alpha]_D^{25} + 148^\circ$ in 96% EtOH (Bz derivative, m.p. 125°, $[\alpha]_D^{25} + 128.5^\circ$ in 96% EtOH); the latter rearranges into the former when heated, but the Bz derivatives are stable. Similarly, *d*-3-methylcyclohexanoneoxime (Wallach, A., 1904, i, 754) exists in stereoisomeric forms, m.p. 60°, $[\alpha]_D^{25} + 3.6^\circ$ in EtOH (Bz derivative, m.p. 99°, $[\alpha]_D^{25} + 22.9^\circ$ in Et_2O), and m.p. 47°, $[\alpha]_D^{25} - 88.5^\circ$ in EtOH (Bz derivative, m.p. 82—83°, $[\alpha]_D^{25} - 86.2^\circ$ in Et_2O). The existence of the above stereoisomeric oximes (structural isomerism is excluded by their reactions) disproves the theory of Raikowa (*loc. cit.*). The vol. and polarisability of substituents affect the stability of oximes; various cases are briefly discussed.

A second isomeride of the following could not be isolated: *cis*- (Bz derivative, m.p. 114°) and *trans*- (Bz derivative, m.p. 138°) α -decaloneoximes; α -tetraloneoxime (Bz derivative, m.p. 125°); α -hydrindone-oxime (Bz derivative, m.p. 133°); 2-cyclopentylcyclopentanoneoxime (Bz derivative, m.p. 70°); cyclohexanoneoxime (Bz derivative, m.p. 63—64°). Contrary to the previous statement (A., 1925, i, 258), *cis*- α -decalone (oxime, m.p. 103°) is not converted into the *trans*-form when treated with NH_4OH , HCl and NaOAc.

H. B.

Action of acetyl chloride on *m*-chlorotoluene. F. MAYER, H. ALBERT, and K. SCHON (Ber., 1932, 65, [B], 1295—1299; cf. Borsche and others, A., 1917,

i, 15).—Condensation of *m*-chlorotoluene with AcCl in presence of $AlCl_3$ and CS_2 gives a mixture of ketones, b.p. 118—127°/14 mm., oxidised to chloroterephthalic and 4-chlorophthalic acid. The mixture yields a *semicarbazone*, m.p. 208—210°, from which 3-chloro-6-acetyltoylene (I) is isolated. Condensation of Et sodioacetoacetate with 3-chloro-*o*-toluoyl chloride and hydrolysis of the product with H_2SO_4 -EtOH gives (I), b.p. 120—122°/14 mm., nitrated to 3-chloro-4-nitro-6-acetyltoylene, m.p. 75—76° (*semicarbazone*, m.p. 221—223°), identical with the product obtained by nitration of the ketone mixture (see above). 3-Chloro-4-acetyltoylene, b.p. 120—126°/14 mm. (*semicarbazone*, m.p. 192°), derived from Et sodioacetoacetate and 3-chloro-*p*-toluoyl chloride, is nitrated to 3-chloro-6-nitro-4-acetyltoylene, m.p. 47—48° (*semicarbazone*, m.p. 228—230°). The Ac group enters *m*-chlorotoluene mainly in the *para* position to Cl, but it is possible that the quality of the $AlCl_3$ may affect the result.

H. W.

Synthesis of 5- ψ -cumylacetone. B. HOLMBERG (Ber., 1932, 65, [B], 1348—1349).—5- ψ -Cumylacetic acid and PCl_5 yield the corresponding chloride, b.p. 100—102°/0.8 mm., m.p. 40—42°, transformed in Et_2O by aq. $NHMe_3$ into the dimethylamide, m.p. 79.5—80.5°, from which 5- ψ -cumylacetone, m.p. 69—70°, is obtained by aid of $MgMeI$. The ketone is identical with that obtained from conifer distillates (cf. A., 1923, i, 226; B., 1929, 158).

H. W.

Mechanism of the pinacol synthesis by the system $Mg + MgI_2$. E. BERGMANN (J. Amer. Chem. Soc., 1932, 54, 3773—3774).—A reply to Bachmann (this vol., 737).

C. J. W. (b)

Reduction of ketones by magnesium+magnesium iodide and by sodium. W. E. BACHMANN (J. Amer. Chem. Soc., 1932, 54, 3774—3775).—A reply to Bergmann (preceding abstract; cf. A., 1931, 1059). The products obtained by addition of Na to aromatic ketones are not radicals existing in the unimol. state but consist for the most part of the bimol. form, viz., Na pinacolate.

C. J. W. (b)

Haloform reaction. VI. α -Halogen derivatives of hindered ketones. C. H. FISHER, H. R. SNYDER, and R. C. FUSON (J. Amer. Chem. Soc., 1932, 54, 3665—3674; cf. this vol., 514).— $\alpha\alpha$ -Dibromopropionylmesitylene is converted by dil. NaOBr into the $\alpha\alpha$ -Br₂-derivative. α -Bromopropionyl chloride, s - $C_6H_4Me_3$, and $AlCl_3$ in CS_2 give 55.5% of α -bromopropionylmesitylene (I), b.p. 174—176°/31 mm. [3 : 5-(NO_2)₂-derivative (II), m.p. 148.5—149°]. Propionylmesitylene and NaOBr give an oil, which on nitration yields $\alpha\alpha$ -dibromo-3 : 5-dinitropropionylmesitylene, m.p. 99—99.5°, also obtained from (I) and NaOBr, followed by nitration, or from (II) and NaOBr. Bromination and subsequent nitration of isobutyrylmesitylene gives the α -bromo-3 : 5-dinitro-derivative, m.p. 124.5—125.5°, also obtained by bromination of 3 : 5-dinitroisobutyrylmesitylene. 3 : 5-Dibromoisobutyrylmesitylene and NaOBr give the α : 3 : 5-Br₃-derivative (III), m.p. 104—106°. Di- β -isoduryloymethane and Br or NaOBr give the bromomethane (IV), m.p. 163.5—164°, converted by NaOBr into the dibromomethane (V), m.p. 136—136.5°; Cl_2 in CCl_4 gives the chloromethane (VI), m.p. 157.5—158°, whilst NaOCl gives

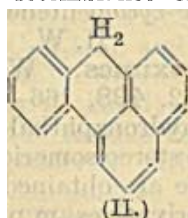
the *dichloromethane* (VII), m.p. 104—104.5°. Cleavage with alkali is effected only in the case of $\alpha\alpha\alpha$ -tribromomesitylene. In some cases the alkali acts as a dehalogenating agent; thus, (V) gives 41% of (IV) and (VII) affords 54% of (VI). These compounds are also dehalogenated by PhOH, *p*-halogenophenols being formed. Thus, $\alpha\alpha\alpha$ -tribromoacetylmesitylene and PhOH at 100° give the $\alpha\alpha$ -Br₂-derivative (60%) and *p*-C₆H₄Br·OH; (V) and PhOH give 47% of (IV). Dehalogenation is also effected by the Grignard reagent; this reaction involves an interchange of radicals. $\alpha\alpha\alpha$ -Tribromoacetylmesitylene and MgEtBr give 68.7% of $\alpha\alpha$ -dibromoacetylmesitylene, m.p. 73—74°, converted by MgEtBr into α -bromoacetylmesitylene, which with MgEtBr gives acetylmesitylene. $\alpha\alpha\alpha$ -Trichloroacetylmesitylene and MgPhBr give 46% of the $\alpha\alpha$ -Cl₂-derivative. α -Chloroacetylmesitylene does not react with MgEtBr. (III) and MgBuBr give the 3:5-Br₂-derivative; BuBr is formed in 57.6% yield. Mg amyl bromide behaves similarly, as do MgPhBr and *p*-C₆H₄Me·MgBr; the corresponding alkyl or aryl bromide is obtained in 60—70% yield.

C. J. W. (b)

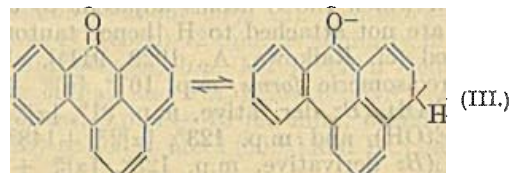
Carbon rings. XIX. 16-Membered *m*- and *p*-benzopolymethylene rings. L. RUZICKA, J. B. BUIJS, and M. STOLL (Helv. Chim. Acta, 1932, 15, 1220—1226; cf. this vol., 253).— ζ' -*m*-Phenylenedihexyl ketone (I), *m*-C₆H₄· $\left[\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \right]_6$ ·CO, is obtained from the appropriate dibasic acid, but $\epsilon\epsilon'$ -*p*-phenylenediamyl ketone could not be prepared by the analogous reaction. The constitution of the ketone (A., 1931, 1290) from ω -*p*-carboxymethylphenylundecic acid is doubtful, (a) because the acid (improved prep.) is not homogeneous, yielding with KMnO₄ terephthalic and (probably) a little phthalic acid, and (b) because it is not proved whether CH₂Ph·CO₂H adds on to the ϵ - or κ -C atom of Δ' -undecenoic acid. Terephthalaldehyde (modified prep.) and malonic acid give *p*-phenylenediacrylic acid, converted by PCl₅ into the acid chloride and thence into the Me₂ ester, m.p. 167—168°, which with Na and EtOH affords $\gamma\gamma'$ -*p*-phenylenedipropyl alcohol, m.p. 55°, b.p. 178—180°/1 mm. This with dry HBr yields the *dibromide*, b.p. 158—162°/1 mm., which by the malonic ester synthesis gives Et₂ 88'-*p*-phenylenedi-*n*-valerate, b.p. about 195°/0.4 mm. This led to $\epsilon\epsilon'$ -*p*-phenylenedi-*n*-amyl alcohol, m.p. 46—47°, b.p. 200—205°/1 mm., which by the cyanide synthesis gives $\epsilon\epsilon'$ -*p*-phenylenedi-*n*-hexoic acid, m.p. 124—125°. *iso*Phthalaldehyde (modified prep.) led by similar reactions to Me₂ $\beta\beta'$ -*m*-phenylenediacrylate, m.p. 133°, $\gamma\gamma'$ -*m*-phenylenedipropyl alcohol, b.p. 165—168°/0.2 mm., the corresponding *dibromide*, b.p. 165—168°/0.2 mm., Et₂ $\epsilon\epsilon'$ -*m*-phenylenedi-*n*-valerate, b.p. 185—187°/0.3 mm., $\epsilon\epsilon'$ -*m*-phenylenedi-*n*-amyl alcohol, b.p. 192—195°/0.3 mm., and Me₂ $\zeta\zeta'$ -*m*-phenylenedi-*n*-heptoate (II), b.p. 207—210°/0.3 mm. The *Ce* salt of the acid from (II) at 400—450° gives an oil, whence (I), b.p. about 205°/0.8 mm. (*semicarbazone*, m.p. 153—155°), was isolated in 2% yield. *m*-Xylylene dibromide and KCN give *m*-xylylene dicyanide, m.p. 27°, b.p. 228—233°/30 mm., which led to Et₂ *m*-phenylenediacetate, b.p. 190—195°/17 mm., and, in very poor yield, $\beta\beta'$ -*m*-phenylenediethyl alcohol.

R. S. C.

Polynuclear hydrocarbons. XVI. Constitution of benzanthrone and its reduction products. E. CLAR and F. FURNARI (Ber., 1932, 65, [B], 1420—1425; cf. Scholl and others, A., 1911, i, 626, 677).—Benzanthrene, m.p. 81—82°, readily prepared by distillation of 9-hydroxy-1:10-trimethylenepheneanthrene with Zn dust, is colourless, insensitive to air in the dark, slowly discoloured by exposure to direct sunlight, and not oxidised to benzanthrone (I) by exposure to air (contrast Scholl, *loc. cit.*). The close resemblance of its extinction curve to that of 1-benzyl-naphthalene suggests the constitution (II).



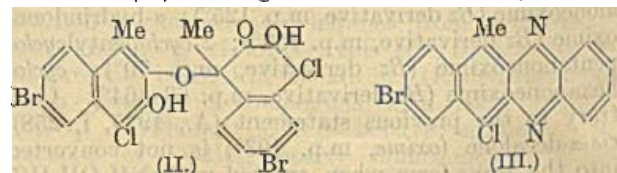
benzylnaphthalene suggests the constitution (II). 1:10-Trimethylenepheneanthrene (Scholl's dihydrobenzanthrone), preparable by treating (I) with P and HI, is colourless when solid or dissolved, insensitive to air, and becomes brownish-yellow when exposed to sunlight without apparent production of (I). Its extinction curve shows marked phenanthrene characteristics. It does not react with maleic anhydride in boiling xylene. Reduction of benzanthrone with Zn dust and NaOH, alkaline Na₂S₂O₄, or Zn, AcOH, and HCl yields 9-hydroxy-1:10-trimethylenepheneanthrene, which slowly darkens when exposed to light, but is not converted in alkaline solution into (I) by air. It appears identical with the 1:9-trimethylenepheneanthran-9-ol of von Braun and Bayer (A., 1926, 172). The ready reduction of (I) and its behaviour towards



Grignard's reagents are explained by the assumption of an equilibrium (III).

H. W.

So-called 2:3-quinone of 1-methylnaphthalene. K. FRIES and K. SCHIMMELSCHMIDT (Ber., 1932, 65, [B], 1502—1507; cf. A., 1909, i, 809).—6-Bromo-3-nitro-1-methyl-1:2-naphthaquinolin in AcOH is reduced by Cu-Zn dust and HCl and the product is transformed by Cl₂ in AcOH into 1:4:4-trichloro-6-bromo-2:3-diketo-1-methyl-1:2:3:4-tetrahydronaphthalene, reduced by Zn dust and AcOH to 4-chloro-6-bromo-2:3-dihydroxy-1-methylnaphthalene (I), m.p. 184°. Treatment of the Pb salt of (I) with I in CHCl₃ yields "4-chloro-6-bromo-1-methyl-2:3-naphthaquinone" (*loc. cit.*), to which the structure (II) is assigned for the following reasons.



The low vals. for the mol. wt. in EtOAc are due to decomp., whereas accurate vals. are observed in C₆H₆. Whereas conc. KOH causes decomp., (II) is sol. in cold dil. NaOH with formation of an unstable $\Delta\alpha$ salt. With Ac₂O and H₂SO₄ it gives an Ac₂ derivative,

m.p. 237°. It affords the naphthophenazine (III). (II) is smoothly reduced by Zn dust in boiling AcOH to the initial material. With $\text{NHPh}\cdot\text{NH}_2$ (II) suffers fission with production of the *monohydrazone* $\text{C}_{11}\text{H}_7\text{OClBr}\cdot\text{N}_2\text{Ph}$, from one portion of the mol.

Repeated failure to obtain naphtha-2:3-quinone or its derivatives leads to the conclusion that only Erlenmeyer's formulation of C_{10}H_8 is satisfactory.

H. W.

Anthracene derivatives. VIII. E. DE B. BARNETT (Ber., 1932, 65, [B], 1301—1304).—Condensation of 3:6-dichlorophthalic acid with *p*-xylene in presence of AlCl_3 and tetrachloroethane leads through the corresponding phthaloyl acid to 5:8-dichloro-1:4-dimethylantraquinone (I), not molten below 310°, which scarcely becomes coloured when treated with NaOH , NH_3 , and Zn or $\text{Na}_2\text{S}_2\text{O}_4$, but is reduced by Al and conc. H_2SO_4 to 5:8-dichloro-1:4-dimethylanthrone (II), m.p. 221° after softening, from which 5:8-dichloro-1:4-dimethylanthranyl acetate, m.p. 220°, is obtained by means of Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at 100°. (II) is reduced by Zn dust and KOH to 5:8-dichloro-1:4-dimethylanthrane, m.p. 230°, which yields 5:8-dichloro-9:10-dibromo-1:4-dimethyl-9:10-dihydroanthracene, decomp. 170°, with Br in CS_2 . (II) and Br in CS_2 slowly afford 5:8-dichloro-10-bromo-1:4-dimethylanthrone, decomp. 210—220°, whence the corresponding -10-anilino-, m.p. 195°, -10-piperidino-, m.p. 225°, -10-methoxy-, m.p. 181°, -10-phenyl-, m.p. 224°, and -10-benzyl-, m.p. 179° after softening, compounds. 1:4-Dichloro-10-methoxyanthrone, m.p. 114°, is obtained from 1:4-dichloro-10-bromoanthrone, MeOH, and CaCO_3 .

H. W.

Specific oxidising agents in the preparation of aminoanthraquinones. K. LAUER (J. pr. Chem., 1932, [ii], 135, 7—14).—A study of the effect of addition of various oxidising agents on the yield and purity (using technical methods of isolation) of aminoanthraquinones prepared by the reaction: $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{SO}_3\text{H} + \text{NH}_2\text{R} = \text{C}_{14}\text{H}_7\text{O}_2\cdot\text{NHR} + \text{H}_2\text{SO}_3$. The purity of the product is evaluated in terms of the yield and purity (shade) of a derived dye. The three oxidising agents in order of val. which give the best results in individual cases are as follow: 1- NH_2 [*m*-nitrobenzenesulphonic acid (I), MnO_2 , KBrO_3]; 2- NH_2 [$\text{K}_2\text{Cr}_2\text{O}_7 + \text{NH}_4\text{Cl}$ (II), Na_2HAsO_4 , MnO_2 , (I)]; 1:5-(NH_2)₂ [MnO_2 , (I), Na_2HAsO_4]; 2:6-(NH_2)₂ [Na_2HAsO_4 , MnO_2 , (II)]; 1-NHMe [KBrO_3 , (I), MnO_2]; 1:5-(NHMe)₂ [(I), KBrO_3 , MnO_2]. $\text{K}_2\text{Cr}_2\text{O}_7$ alone, KClO_3 , and KNO_3 are not beneficial, and are often harmful.

H. A. P.

1:4-Dihydroxy-compounds of 2-acetylanthraquinone from 4-acetylphthalic acid. F. MAYER, O. STARK, and K. SCHÖN (Ber., 1932, 65, [B], 1333—1337).—PhCl is transformed by AcCl in presence of AlCl_3 and CS_2 into *p*-chloroacetophenone, b.p. 108—111°/13 mm., converted by HNO_3 - H_2SO_4 at -12° into 4-chloro-3-nitroacetophenone (I), m.p. 104° (*semicarbazone*, m.p. 256—257°) and a little 4-chloro-3-nitrobenzoic acid, m.p. 181°. (I) is converted by NH_3 in presence of C_6H_6 and H_2O at 150° into 3-nitro-4-aminoacetophenone, m.p. 153—154° (*Ac* derivative, m.p. 140—141°), transformed by diazotisation and

treatment with CuSO_4 and NaCN into 3-nitro-4-cyanoacetophenone (II), m.p. 115°, which with dil. AcOH and Fe filings yields 2-amino-4-acetylbenzamide, m.p. 203—204°, hydrolysed by KOH- H_2O to 2-amino-4-acetylbenzoic acid, m.p. 236°. The *Me* ester, m.p. 121°, is obtained in unusually poor yield by means of MeOH-HCl. 2-Hydroxy-4-acetylbenzoic acid, m.p. 197° (*Ac* derivative, m.p. 118°), is described. (II) is hydrolysed by boiling 55% H_2SO_4 to 2-nitro-4-acetylbenzoic acid, m.p. 178—179°, the *Me* ester, b.p. 211—214°/22 mm., m.p. 58°, of which is reduced to *Me* 2-amino-4-acetylbenzoate (III). Diazotisation of (III) followed by treatment with NH_3 , CuSO_4 , and NaCN leads to *Me* 2-cyano-4-acetylbenzoate, m.p. 109—110°, hydrolysed by boiling conc. HCl to 4-acetylphthalic acid (II), m.p. 210—211° (*anhydride*, m.p. 107—110°; *imide*, m.p. 220—223°); the yield is 13% (calc. on PhCl). Quinol, (IV), NaCl, and AlCl_3 at 160—190° afford 5:8-dihydroxy-2-acetylanthraquinone, m.p. 202—203° (*Ac* derivative, m.p. 180—181°). Similarly, 5:8-dihydroxy-2-acetyl-6(or 7)-methylantraquinone, m.p. 188—200° (*Ac*₂ derivative), and 5:8-dihydroxy-2-acetyl-6:7-benzanthraquinone, m.p. 230—250°, are derived from toluquinol and naphthaquinol, respectively.

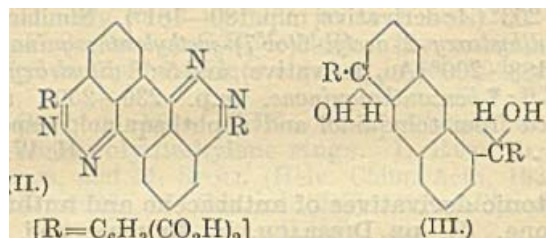
H. W.

Ketonic derivatives of anthracene and anthraquinone. H. DE DIESBACH, H. LEMPEN, and H. BENZ (Helv. Chim. Acta, 1932, 15, 1241—1250).—The preps. of anthraquinone-2-carboxylic acid (I), 1- and 3-chloroanthraquinone-2-carboxylic acid (II) and (III) are modified. The acid chloride of (I), anthracene, and AlCl_3 in $\text{C}_6\text{H}_3\text{Cl}_3$ at 100° give 9-anthracyl 2-anthraquinonyl ketone (IV), m.p. 242—244° (decomp.), 2-anthracyl 2-anthraquinonyl ketone (V), m.p. 297°, and substances (VI) and (VII), $\text{C}_{29}\text{H}_{16}\text{O}_4$, m.p. about 323° (decomp.) (giving in H_2SO_4 violet and pale green colours, respectively). The constitution of (IV) is proved by oxidation by CrO_3 to anthraquinone and (I), and that of (V) by synthesis. (VI) slowly changes into (VII) when kept, and more of (VI) and (VII) is formed at the expense of (IV) if the Friedel-Crafts reaction be prolonged. (VII) is probably ?-hydroxy-9-anthracyl 2-anthraquinonyl ketone, since when oxidised it yields (I) only. (VI) possibly contains a OH group in the anthraquinone nucleus, since in one experiment oxidation afforded a hydroxyanthraquinonecarboxylic acid. (II) gives similarly 9-anthracyl 1-chloro-2-anthraquinonyl ketone, m.p. 263—264° [oxidised to anthraquinone and (II)], 2-anthracyl 1-chloro-2-anthraquinonyl ketone, m.p. 277°, and a substance (possibly containing a OH group), which is oxidised to (II) only. (III) yields similarly 9-anthracyl 3-chloro-2-anthraquinonyl ketone, m.p. 232°, 2-anthracyl 3-chloro-2-anthraquinonyl ketone, m.p. 263°, and another substance. 3:3'-Diamino-4:4'-dimethylbenzophenone (modified prep.) affords (Sandmeyer) 3:3'-dicyano-4:4'-dimethylbenzophenone, m.p. 172°, hydrolysed to the corresponding dicarboxylic acid, m.p. 308°, the chloride of which with AlCl_3 and C_6H_6 at 100° gives 3:3'-dibenzoyl-4:4'-dimethylbenzophenone, m.p. 127—128°. This with Cl_2 in $\text{C}_6\text{H}_3\text{Cl}_3$ at 180° gives di-9:9-dichloro-2-anthranyl ketone, m.p. 212—215°, rapidly changed to (V) by H_2SO_4 at 100°.

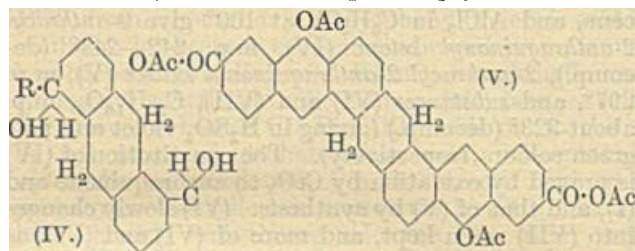
R. S. C.

2:2'-Dianthraquinonyl ketone. F. MAYER and O. HOFFMANN (Ber., 1932, 65, [B], 1338).—3:3'-Dinitro-4:4'-diaminobenzophenone is transformed into benzophenone-3:3':4:4'-tetracarboxylic anhydride (I), which is condensed with $2C_6H_6$; the product is transformed by H_2SO_4 into 2:2'-dianthraquinonyl ketone, m.p. 300—301°. (I) and quinol in presence of $AlCl_3$ -NaCl afford 5:8:5':8'-tetrahydroxy-2:2'-dianthraquinonyl ketone, m.p. 350°.

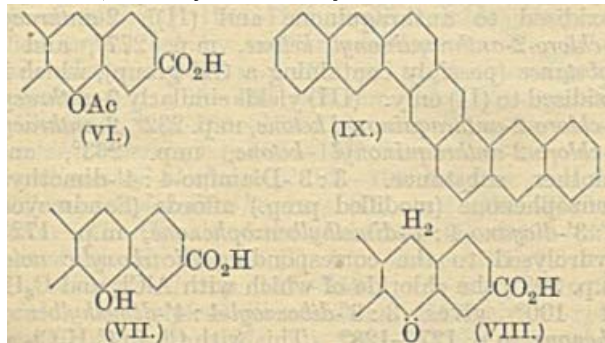
Syntheses in the field of trans-bisang-diphthalylanthraquinone. R. SCHOLL and K. MEYER [with H. VON HOESSLE and F. RENNER] (Ber., 1932, 65, [B], 1396—1406; cf. A., 1929, 190).—1:5-Di-m-xyloylanthraquinone is oxidised by dil. HNO_3 at 180—190° to 1:5-dibenzoylanthraquinone-2':4':2'':4''-tetracarboxylic acid (I) (corresponding quinol derivative), converted by $N_2H_4 \cdot H_2O$ into the di-o-diazine-tetracarboxylic acid (II). (I) is reduced by Zn, NaOH,



and $CuSO_4 \cdot NH_3$ at 120° or by Zn and NaOH at 200° to a mixture of the carbinoltetracarboxylic acids (III) and (IV). (III) and boiling $POCl_3$ yield the cor-



responding dilactone. (IV) is converted by boiling Ac_2O containing HI through 1:5-dibenzyl-9:10-dihydroanthracene-2':4':2'':4''-tetracarboxylic acid into the mixed anhydride (V), transformed by moist C_5H_5N or boiling conc. HCl into the diacetyldicarboxylic acid (VI), by hot dil. NaOH into the anthranolcarboxylic acid (VII), and by moderately conc. HCl at 220° into



the anthronecarboxylic acid (VIII), not attacked by P and HI at 240—250°. Oxidation of (V), (VI), (VII), or (VIII) with CrO_3 in boiling AcOH followed

by CrO_3 in dil. H_2SO_4 or HNO_3 at 210° leads to 1:2:5:6-diphthalylanthraquinone-4:4'-dicarboxylic acid (corresponding bis-o-diazine, $C_{32}H_{12}O_6N_4$, and its sulphate). 2':3':2'':3''-Dinaphtho-1:2:5:6-anthracene (IX) is prepared by reduction of trans-bisang-diphthalylanthraquinone with P and HI at 220° and dehydrogenation of the hexahydro-compound thus obtained by sublimation with Cu powder in CO_2 at 460°/vac. or by reduction and decarboxylation of (VIII) by distillation with Zn dust in CO_2 at 500°/20 mm.

Anthracene-1:5-dicarboxylic acid is converted by successive treatments with PCl_5 and $FeCl_3$ in m-xylene into di-m-xyloylanthracene, m.p. 214°, oxidised by CrO_3 in AcOH to di-m-xyloylanthraquinone and passing when distilled into 6':6''-dimethyl-2':3':2'':3''-dinaphtho-1:2:5:6-anthracene, readily oxidised to the corresponding quinone.

The following compounds are incidentally described: 2:6-di-m-xyloylanthraquinone, m.p. 256°, from the 2:6-dicarboxylic acid, m-xylene, and $AlCl_3$; 1:5-dichloro-2:6-dimethylantraquinone, m.p. 295°, from 2:6-dimethylantraquinone, I, and SO_2Cl_2 in $PhNO_2$; oxidised by HNO_3 (d 1.1) at 200—220° to 1:5-dichloroanthraquinone-2:6-dicarboxylic acid, m.p. 320—330° (decomp.); 2:6-dimethylantraquinone-1-carboxylic acid, m.p. 234°, from dimethylbenzanthrone.

H. W.

Rearrangements in the condensation of methylated derivatives of o-α-naphthoylbenzoic acid. L. F. FIESER and M. A. PETERS (J. Amer. Chem. Soc., 1932, 54, 3742—3751).—o-2-Methyl-α-naphthoylbenzoic acid (I) heated with NaCl- $AlCl_3$ gives mixture of 2'- and 3'-methyl-1:2-benzanthraquinones, necessitating the migration of the phthalic acid residue to a β-position of the originally unsubstituted ring. The following alkyl derivatives of o-α-naphthoylbenzoic acid are prepared: 2':6'- Me_2 , m.p. 238° (Me ester, m.p. 162°); 2':7'- Me_2 , m.p. 210° (Me ester, m.p. 131°); 2':3'- Me_2 , m.p. 205° (Me ester, m.p. 170°; Et ester, m.p. 165°). Oxidation of (I) gives diphthalic acid, m.p. 277°, whilst reduction affords o-2-methyl-α-naphthylmethylbenzoic acid, m.p. 187°. The above o-dimethyl-α-naphthoylbenzoic acids are converted into 2':4-, 3':4-, and 2':3'-dimethyl-1:2-benzanthraquinones, m.p. 190°, 195°, and 236°, respectively. 1:2':3'-Trimethyl-2:3-benzanthraquinone has m.p. 275°. 1-Benzoyl-2:3-dimethylnaphthalene, m.p. 126°; 4-methyl-1:2-benz-9-anthrone, m.p. 150°; 4-methyl-1:2-benzanthracene, m.p. 107° (picrate, m.p. 119—120°), and 4-methyl-1:2-benzanthraquinone, m.p. 167° (quinol diacetate, m.p. 220°), are also described.

C. J. W. (b)

Dibenzanthraquinones. H. WALDMANN (J. pr. Chem., 1932, [ii], 135, 1—6).—Condensation of naphthalene-1:2-dicarboxylic anhydride with $C_{10}H_8$ under the influence of $AlCl_3$, and cyclisation of the product with P_2O_5 in $PhNO_2$ gives 1:2:5:6- (cf. A., 1918, i, 494) and 1:2:7:8-dibenzanthraquinone (I), m.p. 226°. The identity of (I) is proved as follows: bis-o-nitrobenzylidene-m-phenylenediacetic acid, m.p. 240° (from K m-phenylenediacetate and o- $NO_2 \cdot C_6H_4 \cdot CHO$ in Ac_2O), is reduced to the $(NH_2)_2$ -compound, decomp. 140—150°, which is diazotised and treated with Cu; the dicarboxylic acid thus

formed gives on decarboxylation 1:2:7:8-dibenzanthracene, m.p. 195—196°, which is oxidised to (I) by CrO_3 -AcOH. Reduction of 5:8-dihydroxy-1:2:6:7-dibenzanthraquinone with HI at 160°, and oxidation of the resulting crude hydrocarbon with CrO_3 -AcOH, gives, not the expected 1:2:6:7-dibenzanthraquinone, but 2:3-phthaloylphenanthraquinone, m.p. 318°.

H. A. P.

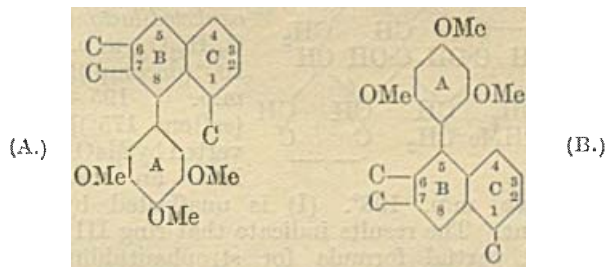
Manufacture of ketones [and vat dyes] of the anthraquinone series [from 5- and 8-nitroanthraquinone-2-carboxylic halides]. A. CARPMAEL. From I. G. FARBENIND. A.-G.—See B., 1932, 879.

Yellow dyes of ergot. I. Ergoflavin. II. Ergochrysin. W. BERGMANN (Ber., 1932, 65, [B], 1486—1488, 1489—1494).—I. The yellow dyes present in ergot vary in nature with different samples of material. Extraction of the residues from the technical prep. of the alkaloids with C_6H_6 causes dissolution of the greater part, but addition of light petroleum to the extract ppts. only amorphous, yellow material similar to that obtained by acidifying alkaline solutions of ergochrysin (cf. II). The undissolved portion when treated with Et_2O gives ergoflavin, $\text{C}_{15}\text{H}_{14}\text{O}_7$, m.p. 344° (cf. Freeborn, Proc. C.S., 1912, 71). It is converted by Ac_2O and $\text{C}_5\text{H}_5\text{N}$ or boiling Ac_2O into the Ac_5 derivative, m.p. 244°. Contrary to Freeborn, it is converted by short boiling with dil. aq. KOH or KOH-EtOH into *ergoflavic acid*, $\text{C}_{15}\text{H}_{16}\text{O}_8$, m.p. above 340° after becoming yellow at 200°, which passes into ergoflavin when its aq. solution is boiled. The dye therefore contains 5 OH and one lactone group.

II. A second sample of technical residues (see above) was extracted with Et_2O , which dissolved ergosterol, and the residue was treated with CHCl_3 yielding ergochrysin (I), $\text{C}_{28}\text{H}_{28}\text{O}_{12}$, m.p. 266°, identical with Jacobi's product and sclero-crystallin of Dragendorff and Podwyssotzki. The secalonic acid of Kraft (A., 1906, i, 979) appears to be $\text{C}_{28}\text{H}_{28}\text{O}_{12} \cdot 0.5\text{H}_2\text{O}$ and is derived from ergochrysin by dissolution in warm $\text{C}_5\text{H}_5\text{N}$ and addition of EtOH. (I) and boiling Ac_2O containing a little $\text{C}_5\text{H}_5\text{N}$ yield the Ac_{10} derivative, m.p. 240°, in very small yield. Methylation of (I) does not give cryst. material. Distillation of (I) with Zn dust or, preferably, sand affords a *phenol*, $\text{C}_9\text{H}_{10}\text{O}_3$, m.p. 92° (Ac_1 derivative, m.p. 65°), in very poor yield. Aq. or alcoholic alkali converts (I) into amorphous, yellow, ill-defined substances, whereas molten KOH at 250—260° gives AcOH , $\text{H}_2\text{C}_2\text{O}_4$, 5-hydroxy-*m*-toluic acid, m.p. 208°, resorcinol, and 2:4:2':4'-tetrahydroxydiphenyl (II), m.p. 224° (Ac derivative, m.p. 118°). It is improbable that (II) is formed from resorcinol during the fusion. Treatment of (I) with conc. HNO_3 at room temp. yields the compound $\text{C}_{16}\text{H}_{15}\text{O}_9\text{N}$, m.p. 260°.

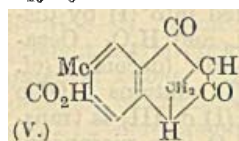
Constitution of podophyllotoxin and picro-podophyllin. E. SPATH, F. WESSELY, and L. KORNFIELD (Ber., 1932, 65, [B], 1536—1549).—The residue obtained from the CHCl_3 extract of *Podophyllum indicum* is dissolved in EtOH and pptd. with C_6H_6 . After crystallisation from dil. EtOH, podophyllotoxin (I), m.p. 117° (decomp.), is obtained, identical with the products of Dunstan and Henry (J.C.S., 1898, 73, 209) and Borsche (this vol., 618)

and containing C_6H_6 , H_2O , and, apparently, small and varying amounts of EtOH. When dried at 110°/high vac. and crystallised from aq. EtOH or CHCl_3 -light petroleum it gives a *modification* (II), m.p. 158°, containing only H_2O and converted into (I) by dissolving in EtOH and adding C_6H_6 and H_2O . Occasionally, a third form, m.p. 106—107° (decomp.) (cf. Borsche, *loc. cit.*), is obtained. (I) contains 3 OMe groups and 1 OH (Zerevitinov). (I) or (II) is transformed by NH_3 in hot EtOH- H_2O into picro-podophyllin (III), which when air-dried contains only H_2O (cf. Borsche) and after desiccation has m.p. 228°, $[\alpha]_D^{25} +9.38^\circ$ in CHCl_3 , $[\alpha]_D^{25} +9.58^\circ$ in COMe_2 ; in agreement with Borsche, it is $\text{C}_{22}\text{H}_{22}\text{O}_8$, and contains a lactone and 3 OMe groups, but only 1 OH. (I) and boiling Ac_2O or $\text{C}_5\text{H}_5\text{N}$ and Ac_2O gives *monoacetyl-podophyllotoxin*, m.p. 204° after softening at 200° (not identical with Borsche's product), whereas boiling Ac_2O and NaOAc afford monoacetyl-picro-podophyllin, m.p. 214°, also obtained from (III) and Ac_2O with $\text{C}_5\text{H}_5\text{N}$ or NaOAc. Boiling Ac_2O transforms (III) into a substance (IV), $\text{C}_{22}\text{H}_{20}\text{O}_7$, m.p. 216°, $[\alpha]_D^{25} +75.72^\circ$ in COMe_2 , apparently identical with Borsche's *apropicro-podophyllin*. (I) and (III) appear to give identical salts as judged from the $[\alpha]_D^{25}$ of alkaline solutions. Oxidation of (I) and (III) with KMnO_4 affords 3:4:5-trimethoxybenzoic acid, whilst distillation with Zn dust yields 1:6-dimethylnaphthalene (V) in small amount. Since derivatives of *o*-phthalic acid are never obtained by oxidation, it follows that the C_6H_6 nuclei obtained in (V) are so substituted as to be readily oxidised. If the mol. is opened to attack by demethylating (I) or (III) with fuming HCl at 110° and the crude product is treated with KMnO_4 , 1:2:4:5- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ (identified as the Me_4 ester) is obtained. Dehydrogenation of (I) or (III) with spongy Pd gives an optically inactive substance, $\text{C}_{20}\text{H}_{18}\text{O}_7$ (VI), m.p. 266° after softening at 264°, which contains 3 OMe and one lactone group but no OH; it is also obtained from (IV). Oxidation of (IV) or (VI) by successive treatment with HNO_3 and alkaline KMnO_4 yields $\text{C}_6\text{H}(\text{CO}_2\text{H})_5$. The presence of the skeletons A or B is therefore established.

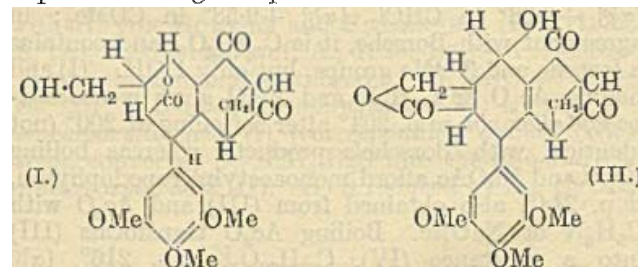


The action of the HI and AcOH on (I) or (III) gives podophyllomeric acid, $\text{C}_{13}\text{H}_{10}\text{O}_4$ (VII), m.p. 240°, best purified through the *Me* ester, m.p. 130.5°, on account of the simultaneous formation of a *by-product*, m.p. 284°, in very small amount. (VII) is readily acetylated by Ac_2O and $\text{C}_5\text{H}_5\text{N}$, but the ready hydrolysis of the *Ac* derivative indicates that it is probably an enolic *Ac* compound; the *Me* ester does not contain an OH group (Zerevitinov). Energetic oxidation of (VII) leads to pyromellitic acid, whereas milder treatment gives Borsche's acid,

$C_7H_5(CO_2H)_3$, oxidised further to (III) and thus characterised as *toluene-2:4:5-tricarboxylic acid*. Distillation of (VII) with Zn dust yields 1:6- $C_{10}H_6Me$, whilst it is stable towards alkali, resistant

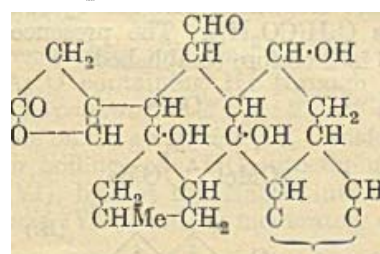


to catalytic hydrogenation under mild conditions, but apparently attacked by Na-Hg and HI. The annexed constitution is tentatively suggested. For (I) and (III) the subjoined formulæ are advanced, in which the details of nucleus C of the naphthalene ring are speculative.



H. W.

Strophanthin. XXVII. Ring III of strophanthidin and related aglucones. W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1932, **97**, 727—737; cf. this vol., 948).—Monoanhydrodihydrostrophanthidin with $KMnO_4$ gives in $COMe_2$ or C_5H_5N (less good) *anhydrodihydrostrophanthidinic acid*, m.p. 185—186° (decomp.), and in NaOH a *tetrahydroxy-lactone acid*, $C_{23}H_{34}O_8$, m.p. 215—218° (decomp., softens 160°). The *Me* ester, m.p. 207—208° (*di-p-bromobenzoate*, m.p. 297—298°), of the latter with Kiliani's CrO_3 solution gives a *Me H diketohydroxy-lactonedicarboxylate*, $C_{24}H_{32}O_9$, m.p. 220—221° (decomp.) [*Me*₂ ester, m.p. 180° (softens 116—118°)], reduced with Adams and Shriner's catalyst to a *dihydroxydilactone ester*, $C_{24}H_{34}O_8$, (I), m.p. 280—281° [*Ac* derivative, m.p. 216—217°; *sulphite*, m.p. 229° (decomp.)], and a little *isomeride*, decomp. 243—244°, and then m.p. 281—282°.



(I) with CrO_3 in AcOH gives a *hydroxyketodilactone ester*, m.p. 159—160° (decomp.) [*oxime*, m.p. 195—200° (softens 175°)], converted by $MeOH-HCl$ into an *anhydro-* derivative, m.p. 198°. (I) is unaffected by this treatment. The results indicate that ring III in the annexed partial formula for strophanthidin is a methylcyclopentane ring attached to ring I by C atoms (5) and (6).

A. A. L.

Constituents of the leaves of *Ginkgo biloba*, L. I, II. S. FURUKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **19**, 27—38, 39—42).—I. The EtOH-extract of the air-dried leaves contains sitosterol and its *d*-glucoside, a *substance A* (I), $C_{11}H_{14}O_5 \cdot H_2O$, m.p. 325° (decomp.), $[\alpha]_D^{25} -54.8^\circ$ in EtOH (*diacetate*, m.p. 290—292°, $[\alpha]_D^{25} -103^\circ$ in EtOH; amorphous *Me ether*, m.p. about 215°), a *substance B* (II), $C_{16}H_{12}O_5 \cdot H_2O$, m.p. 238—240°

(*diacetate*, m.p. 226—228°; *Me*₂ derivative, m.p. 225—227°; *demethyl* derivative, $C_{15}H_{10}O_5$, not melted at 300°), and *ginnol* (III), $C_{29}H_{50}O$ (cf. Kawamura, Jap. J. Chem., 1928, **3**, 2, 89), m.p. 82.5—83° (*acetate*, m.p. 43.5—44°). (I) is converted by 33% KOH into a OH-acid (*Ag salt*), whilst KOH fusion of (II) gives *p-OH-C₆H₄-CO₂H*. Oxidation of (III) with CrO_3 in AcOH affords *ginnone*, $C_{29}H_{58}O$, m.p. 74—74.5° (*oxime*, m.p. 50—51°).

II. Beckmann rearrangement (H_2SO_4 -AcOH) of ginnoneoxime gives *eicos-n-nonylamide*, m.p. 83.5—84°, hydrolysed by EtOH-KOH to eicosoic acid and *n-nonylamine*, indicating that ginnone is nonacosan- κ -one. This is proved by synthesis of the latter from eicosoic and decoic acids and P_2O_5 at 200—250°. (III) is, therefore, nonacosan- κ -ol. H. B.

Betulin. III. R. VESTERBERG (Ber., 1932, **65**, [B], 1305—1307).—Gentle oxidation of betulin monoacetate gives acetoxybetulin ketone, $C_{30}H_{47}(CO) \cdot OAc$, m.p. 182—183°, $[\alpha]_D^{25} +30.26^\circ$, apparently identical with a product obtained by Trautenberg (A., 1912, i, 261, 972) by the oxidation of betulin by CrO_3 in AcOH. The hydroxy-ketone, m.p. 207°, $[\alpha]_D^{25} +19.97^\circ$, derived therefrom appears identical with *hydroxybutelone* of Dischendorfer and the *hydroxybetulin* of Postovski and Trautenberg. *alloBetulone* is also obtained by this oxidation. Gentle oxidation of dihydrobetulin with CrO_3 gives a *ketone*, $C_{30}H_{50}O_2$, m.p. 180—182°, $[\alpha]_D^{25} +10.43^\circ$, whereas more drastic treatment yields the ketone $C_{30}H_{48}O_3$, m.p. 252—253°, $[\alpha]_D^{25} +12.79^\circ$, apparently identical with Ruzicka's dihydrobetulonic acid (this vol., 750). Oxidation of dihydrobetulin with HNO_3 in AcOH at -5° affords *dihydrobetulindicarboxylic acid*, $C_{30}H_{48}O_8$, m.p. 140 (anhydride; *Me*₂ ester), which absorbs $4H_2$ when hydrogenated, and *dihydrobetulonedicarboxylic acid*, $C_{30}H_{46}O_6$, m.p. 285°, $[\alpha]_D^{25} -22.80^\circ$ (*Me*₂ ester), which contains the CO group and yields a ketone when heated in CO_2 or in a high vac. The last-named acid is also obtained by oxidising dihydrobetulonic acid with HNO_3 in AcOH. Betulin monoacetate is transformed by PCl_5 into *apobetulin acetate*, $C_{30}H_{47}O(OAc)$, m.p. 203—204°, $[\alpha]_D^{25} -44.38^\circ$, hydrolysed to the monohydric alcohol, $C_{30}H_{48}O$, m.p. 186—187°, $[\alpha]_D^{25} -28.69^\circ$, identical with Ruzicka's β -*apoallobetulin* (*loc. cit.*). When heated with fuller's earth, dihydrobetulin affords the liquid hydrocarbon $C_{30}H_{48}$, obtained by Ruzicka (*loc. cit.*) by the action of $2-C_{10}H_7 \cdot SO_3H$. Dihydrobetulin has $[\alpha]_D^{25} -22.0^\circ$, whereas betulin has $[\alpha]_D^{25} +19.96^\circ$ in C_6H_5N . It is not possible to prepare a monoacetate by partial hydrolysis of dihydrobetulin diacetate. H. W.

Reversible hydrogenation and dehydrogenation of polyenes. R. KUHN and P. J. DRUMM (Ber., 1932, **65**, [B], 1458—1460).—Dehydrogenation of methyl dihydrobixin to β -methylbixin (yield 70—80%) and of dihydrocroetin *Me*₂ ester to croetin *Me*₂ ester occurs when the substances in C_5H_5N are shaken with air. The quality of the base is very important. More than 1 O is rapidly absorbed, so that the double linkings are partly attacked. Reaction is not measurably impeded by HCN. Similar change is observed in α -pipecoline, NH_4Et_2 , tropine, and piperazine, but not in coniine, nicotine, C_5H_5N , α -

picoline, 2-methylquinoline, or NH_2Ph . Me_2 dihydro-muconate and $\alpha\beta$ -diphenyl- $\Delta^{8,9}$ -octatriene in piperidine are not affected by O. H. W.

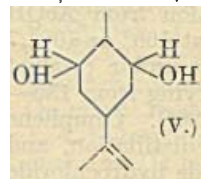
Caoutchouc and thioglycolic acid. B. HOLMBERG (Ber., 1932, 65, [B], 1349—1354).—Crepe rubber is converted by very prolonged contact with thioglycolic acid at room temp. into a substance of the approx. composition $(\text{C}_5\text{H}_9\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_n$, from which cryst. salts could not be prepared. Successive treatments with the acid brings caoutchouc almost completely into solution. AcOH is unsuitable as diluent, but C_6H_6 can be used if only incomplete action is desired. Rise in temp. expedites the change, which becomes irregular. The behaviour of balata closely resembles that of caoutchouc, whereas guttapercha scarcely reacts with thioglycolic acid. H. W.

Production of synthetic *l*-menthol and *d*-menthol. J. READ and W. J. GRUBB (J.S.C.I., 1932, 51, 329—332r).—Details are given for the resolution of *dl*-menthol by crystallisation of the *l*-menthoxyacetate from MeOH . The m.p. of the stereoisomeric menthyl menthoxyacetates and their binary mixtures are discussed, as is also the m.p. of *dl*-menthol.

Solvent influence. V. Dipole moments of solvents and rotatory power of dissolved menthyl dialkylmalonates. H. G. RULE and J. T. R. RITCHIE.—See this vol., 1083.

Autoxidation of $\alpha\beta$ -unsaturated ketones. V. Course of the change and products of the autoxidation of carvone. W. TREIBS (Ber., 1932, 65, [B], 1314—1324; cf. A., 1931, 1299, 1421; this vol., 398).—Carvone oxide [cf. (I)], b.p. 120—122°/15 mm., d^{20}_D 1.033, α_D -86.4° , is prepared by the action of 30% H_2O_2 on a well-cooled solution of carvone in

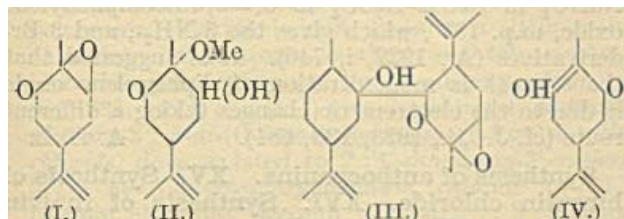
therefore assigned to $\text{C}_{11}\text{H}_{18}\text{O}_3$ (contrast A., 1931, 1299). Hydroxycarvone [cf. (IV)] is hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to the keto-acid, $\text{C}_{10}\text{H}_{16}\text{O}_3$, b.p. 189—190°/20 mm. (semicarbazone, m.p. 158°). Reduction



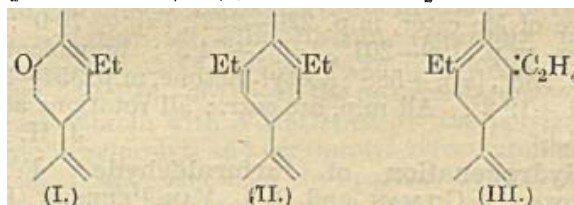
with Na and Pr^nOH yields the menthenediol, $\text{C}_{10}\text{H}_{18}\text{O}_3$ [cf. (V)], m.p. 105—106°, whereas H in presence of Pd-MeOH transforms acetoxycarvone into its dihydro-compound, $\text{C}_{12}\text{H}_{18}\text{O}_3$, b.p. 150—154°/15 mm., from which hydroxydihydrocarvone, m.p. 180°, is derived. The *tert.* nature of the OH in $\text{C}_{20}\text{H}_{28}\text{O}_3$ is established by the ready evolution of H_2O at 250°. Prolonged treatment of $\text{C}_{20}\text{H}_{28}\text{O}_3$ with KOH-anhyd. MeOH affords the isomeric compounds $\text{C}_{20}\text{H}_{28}\text{O}_3$, m.p. 136° and 176°, respectively, which behave as monobasic acids and develop the characteristic odour of dihydroresorcinols when exposed to air. Prolonged action of KOH leads to non-cryst. acids. The compound $\text{C}_{20}\text{H}_{16}\text{O}_3$, m.p. 132°, most readily prepared by the rapid oxidation of carvone with H_2O_2 , behaves as a monobasic acid. With $\text{MeOH-H}_2\text{SO}_4$ it gives a *Me* derivative, b.p. 150—155°/15 mm., slowly hydrolysed by $\text{KOH-H}_2\text{O}$ to the initial material.

The residue obtained by the prolonged action of KOH-MeOH on carvone at room temp. in absence of air is a polycarvone, $(\text{C}_{10}\text{H}_{14}\text{O})_n$ (n = about 3). In AcOH it adds 1 HBr per $\text{C}_{10}\text{H}_{14}\text{O}$ unit. It is depolymerised by heat to the monomeric carvone with the initial $[\alpha]_D$. The action therefore consists of an aldol condensation between several carvone mols. which is reversed by heat. Cryst. dimeric carvone is obtained by the action of KOH-MeOH . H. W.

Action of Grignard's reagent on hydroxycarvone and transformation of the products of the reaction into aromatic compounds. W. TREIBS (Ber., 1932, 65, [B], 1324—1329).—Hydroxycarvone (cf. preceding abstract) is converted by a large excess of MgEtBr into an unstable adduct which readily loses H_2O when decomposed, giving ethylcarvone (I), b.p. 142°/15 mm. (semicarbazone, m.p. 160—161°). (I) with CMeEt_2OH is more



MeOH in presence of a little KOH . It is transformed by boiling KOH-anhyd. MeOH mainly into the compound $\text{C}_{11}\text{H}_{18}\text{O}_3$ [cf. (II)] with a little hydroxycarvone; the relative proportions of the compounds are reversed if H_2O is present in the alkaline solution. Carvone and its oxide in hot KOH-MeOH afford the compound $\text{C}_{20}\text{H}_{28}\text{O}_3$ [cf. (III)]. Autoxidation of carvone in presence of KOH-MeOH without (A) or with addition of H_2O (B) gives $\text{C}_{20}\text{H}_{28}\text{O}_3$ (yield A, 10—15%, B, 3—5%), hydroxycarvone (yield A, very small; B, 6—8%), $\text{C}_{10}\text{H}_{16}\text{O}_3$, m.p. 132° (yield 1—2%), and much brown resin. The compound $\text{C}_{11}\text{H}_{18}\text{O}_3$ gives an acetate, $\text{C}_{13}\text{H}_{20}\text{O}_4$, b.p. 152—155°/15 mm., α_D -34° , and a benzoate. It absorbs 2H, yielding $\text{C}_{11}\text{H}_{18}\text{O}_3$, b.p. 150—156°/18 mm., α_D -46° ($l=1$). When hydrolysed by KOH-MeOH it affords the *OH-acid* $\text{C}_{11}\text{H}_{16}\text{O}_4$, readily transformed into the lactone $\text{C}_{11}\text{H}_{18}\text{O}_3$, b.p. 162—166°/15 mm., α_D $+7.6^\circ$ ($l=1$), reduced to the dehydrolactone, $\text{C}_{11}\text{H}_{20}\text{O}_3$, b.p. 159—162°/15 mm. The constitution (II) is



readily prepared from acetoxycarvone and MgEtBr , (I) absorbs 2Br without loss of HBr in CHCl_3 and 2H when hydrogenated (Skita). With KOH-MeOH and 30% H_2O_2 it affords the keto-oxido-compound, $\text{C}_{12}\text{H}_{18}\text{O}_2$, b.p. 137—139°/13 mm. (I) is transformed by MgEtBr into a *tert.*-alcohol which immediately loses H_2O to form the hydrocarbon $\text{C}_{14}\text{H}_{22}$ [(II) or (III)], b.p. 124—125°/15 mm., unstable to air and readily absorbing 4Br in CHCl_3 . (I) at its b.p. is transformed by a trace of I into ethylcarvacrol, b.p. 265° (phenylurethane, m.p. 157°; benzoate, m.p. 53—54°); under similar conditions, the hydrocarbon $\text{C}_{14}\text{H}_{22}$ (see above) yields diethylcymene, b.p. 243—245°. H. W.

Attempts at fractionation of solid pinene hydrochloride. R. BOUSSER (Bull. Soc. chim., 1932, [iv], 51, 947—952).—The fractionation of *d*-, *l*-, and *dl*-pinene hydrochlorides has been carried out by distillation at 150 mm. (*d*-), crystallisation from AcOH and CHCl_3 (*l*-), and by sublimation at 160° or $100^\circ/7$ mm. (*d*-, *l*-, *dl*-). In every case a similar product was obtained, the recorded m.p. varying from 136 — 138° to 139 — 140° (initial m.p. about 126°). Camphene was isolated from the products of distillation, and could also be removed from the crude hydrochloride by partial acetylation with AcOH and PbSO_4H .

H. A. P.

Optically active diazo-compounds. VI. Diazocamphor. W. A. NOYES and E. MEITZNER (J. Amer. Chem. Soc., 1932, 54, 3768—3773; cf. A., 1931, 358).—Amino-*d*-camphor is resolved by $\text{H}_2\text{C}_2\text{O}_4$ into two amines, $[\alpha]_D^{25} +17.5^\circ$ in EtOH, and $+55.5^\circ$ in EtOH (corresponding oxalates, m.p. 212° and 203° , $[\alpha]_D^{25} +8.49^\circ$ and $+43.3^\circ$ in H_2O , respectively), both of which give the same diazocamphor. The theoretical aspect is discussed. C. J. W. (b)

Saponin group. XI. Hydroxytriterpene acid glucosides of the *Araliaceae*. A. WINTERSTEIN and G. STEIN (Z. physiol. Chem., 1932, 211, 5—18; cf. this vol., 856).—The aglucone of the saponin of *Aralia japonica* is a mixture of oleanolic acid (I) and hederagenin. The saponin araligenin, taraligenin, taragenin, and panaxsaponin are either identical with (I) or are mixtures of it with saponins containing more oxygen. The formula for hederagenin now accepted is $\text{C}_{30}\text{H}_{48}\text{O}_4$, i.e., a dihydroxytriterpene acid, thus emphasising the relationship to (I). Glucosides of (I) of different origin differ in their hæmolytic action. The physical properties of hederagenin and derivatives of (I) differ somewhat from those previously given; hederagenin: Ac_2 derivative, m.p. 160 — 180° , $[\alpha]_D^{25} +77.2^\circ$; Me ester, m.p. 236 — 238° , $[\alpha]_D^{25} +71.7^\circ$; Ac_2 derivative of Me ester, m.p. 190° , $[\alpha]_D^{25} +75.3^\circ$; lactone, m.p. 354° , $[\alpha]_D^{25} +16.2^\circ$; diacetyl-lactone, m.p. 244° , $[\alpha]_D^{25} +33.8^\circ$; bromolactone, $[\alpha]_D^{25} +72.5^\circ$; (I), m.p. 305 — 308° , $[\alpha]_D^{25} +75.2^\circ$; Ac derivative, m.p. 263 — 266° , $[\alpha]_D^{25} +70.9^\circ$; Ac derivative of Me ester, m.p. 220 — 222° , $[\alpha]_D^{25} +70.0^\circ$; Me ester, m.p. 199 — 201° , $[\alpha]_D^{25} +74.3^\circ$; bromolactone, m.p. 238° , $[\alpha]_D^{25} +58.8^\circ$; acetyl-lactone, m.p. 354 — 355° , $[\alpha]_D^{25} +19.2^\circ$. All m.p. are corr.; all rotations are in CHCl_3 . J. H. B.

Hydrogenation of furfuraldehyde. F. E. BROWN, H. GILMAN, and R. L. VAN PEURSEM (Iowa State Coll. J. Sci., 1932, 6, 133—136).—Hydrogenation at 175 — 275° at atm. pressure, with Cu-asbestos as catalyst, afforded only furfuryl alcohol (max., 4.0—4.3% of theoretical at 215 — 225° ; with Ni at 200° , 5%). Furfuryl *H* phthalate has m.p. 85° (decomp. 135°). CH. ABS.

Condensations of furan derivatives. I. Mutual relationships of furfurylideneacetone with other [aldehyde]acetone condensation products. V. V. TSCHELINCEV and E. K. NIKITIN (Bull. Soc. chim., 1932, [iv], 51, 875—883).—Interaction of furfuraldehyde in slight excess with benzylidene-, vanillylidene-, or piperonylidene-acetone in aq. H_2SO_4 results in displacement of the aldehyde concerned and

formation of furfurylideneacetone. Furfuraldehyde is displaced from furfurylideneacetone by CH_2O , MeCHO , citral, heptaldehyde, and cinnamaldehyde.

H. A. P.

Condensation of α -formylphenylacetone nitriles with phenols. II. I. C. BADHWAR and K. VENKATARAMAN (J.C.S., 1932, 2420—2423; cf. A., 1931, 963).—Hydroxyquinol triacetate (I) and α -formylphenylacetone nitrile by the Hoesch reaction give 6:7-dihydroxy-3-phenylcoumarin, m.p. 242° (Ac , derivative, m.p. 190 — 191°), also obtained by condensing (I) with Et hydroxymethylenephylacetate in 80% H_2SO_4 . Benzoyloxymethylenephylacetone nitrile (II) did not react by the Hoesch method with (I), the latter giving 2:4:5-trihydroxyacetophenone. Condensation of (II) with β -naphthol gives 2-phenyl-3:4- β -naphthapyrone (III) and a substance, m.p. 242° , converted into (III) by the action of NaOEt. β -Naphthoxyacetophenone, m.p. 108° (from Na β -naphthoxide and CH_3BzBr) in Et_2O with KCN and 30% H_2SO_4 gives α -2-naphthoxymethylmandelonitrile, m.p. 115 — 116° , converted by HCl and ZnCl_2 in Et_2O into (III) and 2-hydroxy-2-phenyl-1:4- β -naphthapyranone, m.p. 124° (Ac derivative, m.p. 125 — 126°), which with conc. H_2SO_4 gives 2-phenyl-1:4- β -naphthapyrone, m.p. 129 — 130° . A. A. L.

Diphenylene oxide series. III. N. M. CULLINANE (J.C.S., 1932, 2365—2367).—Nitration of diphenylene oxide gives 2:6-dinitrodiphenylene oxide (I), m.p. 245° (A., 1923, i, 534), reduced with Sn or Fe in HCl to the 2:6-diamine, m.p. 152° (yield 80%) (Ac_2 derivative, decomp. 290°), not identical with 2:7-diaminodiphenylene oxide (Ac_2 derivative, m.p. 322°). (I) with NH_4HS in EtOH gives 6-nitro-2-aminodiphenylene oxide, m.p. 268° , converted by NaNO_2 in EtOH — H_2SO_4 to 6(=3)-nitrodiphenylene oxide, m.p. 151° , which gives the 3- NH_2 , and 3-Br-derivatives (A., 1922, i, 746). It is suggested that the anomalous mononitration of diphenylene oxide is due to the electromeric changes taking a different route (cf. J.C.S., 1923, 123, 684). A. A. L.

Synthesis of anthocyanins. XV. Synthesis of hirsutin chloride. XVI. Synthesis of malvin chloride. XVII. Syntheses of pelargonin, peonin, and cyanin chlorides. R. ROBINSON and A. R. TODD (J.C.S., 1932, 2293—2299, 2299—2305, 2488—2496).—XV. 2-O-Tetra-acetyl- β -glucosidyl-4-O-methylphloroglucinaldehyde, 4-acetoxy-3:5-dimethoxy- ω -O-tetra-acetyl- β -glucosidoxyacetophenone (I), and dry HCl in EtOAc give hydrated (?) 4'-hydroxy-7:3':5'-trimethoxy-3:5-di-(O-tetra-acetyl- β -glucosidoxy)flavylium chloride (?), decomp. 125 — 128° (sinters at 75°), which when treated with cold 10% NaOH in H_2 and then with warm 2% HCl affords 4'-hydroxy-7:3':5'-trimethoxy-3:5-di- β -glucosidoxyflavylium chloride ($+4\text{H}_2\text{O}$) (II). This is identical with natural hirsutin chloride (Karrer and Widmer, A., 1927, 1197); both chlorides show identical colour reactions (in buffered and other solutions), distribution ratios (BuOH), and absorption spectra. The effects of co-pigments on solutions of (II) are discussed. 3- β -Glucosidylhirsutidin chloride ($+1.5\text{H}_2\text{O}$) (an *æmin* chloride Me ether), prepared (as above) from (I) and 2-O-benzoyl-4-O-methylphloroglucinaldehyde with

subsequent hydrolysis, resembles conin chloride in many of its properties.

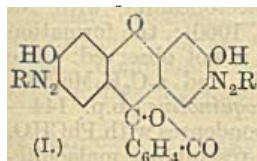
XVI. Phloroglucinaldehyde, tetra-acetylglucosidyl bromide, and 10% KOH in cold MeCN give 2-O-tetra-acetyl- β -glucosidylphloroglucinaldehyde (+0.5H₂O) (III), m.p. 77–80°, [α]_D²⁰ –47.84° in CHCl₃, 2:4-di-(O-tetra-acetyl- β -glucosidyl)phloroglucinaldehyde, m.p. 194–195°, [α]_D¹⁹ –52.5° in CHCl₃, and a little of a substance, m.p. 109–110° (see below). ω :4-Dihydroxyacetophenone, (III), and dry HCl in CHCl₃-EtOAc afford 3:7:4'-trihydroxy-5-O-tetra-acetyl- β -glucosidoxyflavylium chloride (+H₂O), hydrolysed (dil. NaOH followed by dil. HCl) to pelargonin chloride (A., 1931, 1423). (I) and (III) similarly give 7:4'-dihydroxy-3':5'-dimethoxy-3:5-di- β -glucosidoxyflavylium chloride (+2H₂O), decomp. 165°, identical with natural malvin chloride.

2:4-Dicarbethoxyphloroglucinaldehyde, m.p. 76°, from the aldehyde, ClCO₂Et, and 5% NaOH in COMe₂, condenses with ω -hydroxyacetophenones to give flavylium salts.

XVII. A somewhat better yield of (III) is obtained when MeCN is replaced by COMe₂ in the above method; the substance, m.p. 109–110°, is probably 2-O-monoacetyl- β -glucosidylphloroglucinaldehyde (IV), [α]_D²¹ –49.32° in CHCl₃. ω :4-Dihydroxyacetophenone and (IV) condense to give pelargonin chloride, whilst 4-acetoxy- ω -O-tetra-acetyl- β -glucosidoxyacetophenone and (IV) condense (HCl-EtOAc) to 7-hydroxy-4'-acetoxy-5-O-monoacetyl- β -glucosidoxy-3-O-tetra-acetyl- β -glucosidoxyflavylium chloride (+2H₂O), deacetylated to 7:4'-dihydroxy-3:5-di- β -glucosidoxyflavylium chloride (+4H₂O) [pelargonin chloride], m.p. about 187° (sinters at 178°). The absorption spectra curves of pelargonin (synthetic), monardin, and salvinin chlorides agree very closely, but differ slightly from that of natural pelargonin chloride (which contains a little malvin chloride). 4-Acetoxy-3-methoxy- ω -O-tetra-acetyl- β -glucosidoxyacetophenone (improved prep. given; cf. A., 1931, 1423) and (III) give 7-hydroxy-4'-acetoxy-3'-methoxy-3:5-di-(O-tetra-acetyl- β -glucosidoxy)flavylium chloride, de-acetylated to 7:4'-dihydroxy-3'-methoxy-3:5-di- β -glucosidoxyflavylium chloride (+5H₂O) [peonin chloride], decomp. 165–167°. 3:4-Diacetoxy- ω -O-tetra-acetyl- β -glucosidoxyacetophenone and (III) give 7-hydroxy-3':4'-diacetoxy-3:5-di-(O-tetra-acetyl- β -glucosidoxy)flavylium chloride (+2H₂O), de-acetylated to 7:3':4'-trihydroxy-3:5-di- β -glucosidoxyflavylium chloride (+3H₂O) [cyanin chloride], m.p. 205° (decomp.). Various tests are given showing the identity of the synthetic and natural products.

H. B.

Some lactonic fluorescein compounds. F. INGRAFFIA (Gazzetta, 1932, 62, 781–790).—Fluorescein yields a bisbenzeneazo-compound (I), m.p. 187°, which gives an Ac₂ derivative, m.p. 170°, and must therefore be lactonic (I). The following are also described. Benzeneazo-, m.p. 170°, bis-p-nitrobenzeneazo-, m.p. 190°, p-nitrobenzeneazo-, bis-o-tolueneazo-, m.p. 190°, and o-tolueneazo-, m.p. 210°, -fluorescein; these all form Ac₂ derivatives,



m.p. 142°, 230°, 241°, 160°, and 190°, respectively. (I) is reduced by NHPH-NH₂ to diaminofluorescein (dihydrochloride), identical with that prepared from dinitrofluorescein (cf. A., 1905, i, 897). E. W. W.

Derivatives of dioxan. R. K. SUMMERBELL and R. CHRIST (J. Amer. Chem. Soc., 1932, 54, 3777–3778).—The results of Butler and Cretcher (this vol., 949) are confirmed. Dichlorodioxan (I) reacts with Grignard reagents to give disubstituted dioxans; 1:2-diphenyldioxan, m.p. 49°, is prepared. Pyrocatechol and (I) give a compound similar to 1:4:5:8-naphthodioxan. C. J. W. (b)

Electrolytic reduction of pyrrolones and Δ^2 -pyrrolines. R. LUKES (Coll. Czech. Chem. Comm., 1932, 4, 351–363).—Electrolytic reduction of 1-methyl-5-ethyl-2-pyrrolone in 50% H₂SO₄ gives 1-methyl-5-ethylpyrrolidine (I), b.p. 123°, and 1-methyl-5-ethyl-2-pyrrolidone, b.p. 229–230° (corr.) (hydrolysed by HCl at 180° to γ -methylaminohexanoic acid). 1-Methyl-2-ethyl- Δ^2 -pyrroline gives (I). 5-Hydroxy-5-phenyl-1-methyl-2-pyrrolone gives 2-phenyl-1-methylpyrrolidine, b.p. 96°/11 mm. (chloroplatinate, +H₂O, m.p. 118–120°; picrate, m.p. 145°; chloraurate, m.p. 114–115°) (also formed from 2-phenyl-1-methyl- Δ^2 -pyrroline), and 5-phenyl-1-methyl-2-pyrrolidone, b.p. 175°/10 mm. 5-Benzyl-1-methyl-2-pyrrolone gives 2-benzyl-1-methylpyrrolidine, b.p. 113.0° (corr.)/12 mm. (chloroplatinate, m.p. 183–184°; picrate, m.p. 144°) [also obtained from 2-benzyl-1-methyl- Δ^2 -pyrroline, b.p. 155°/10 mm. (perchlorate, m.p. 109–110°), prepared from 1-methyl-2-pyrrolidone and CH₂Ph·MgBr], and 5-benzyl-1-methyl-2-pyrrolidone, b.p. 191°/11 mm. The duration of the reduction of the pyrrolones does not affect the relative yields of pyrrolidine and pyrrolidone derivatives, and the latter cannot be further reduced electrolytically; it is, therefore, presumed that the pyrrolone, or the hydroxypyrrolidone which is (sometimes) in equilibrium with it, is reduced in either of two independent ways, and that reduction does not proceed by way of the pyrrolidone or the open-chain NH₂-acid.

R. S. C.

Isolation of glycylserylprolyltyrosylproline and serylprolyltyrosylproline in the progressive degradation of silk fibroin (*Bombyx mori*). E. ABDERHALDEN and A. BAHN (Z. physiol. Chem., 1932, 210, 246–267).—In the progressive degradation of silk fibroin with N-NaOH at 37° the polypeptides glycylserylprolyl- and serylprolyltyrosylproline were isolated and identified by partial hydrolysis. In determining structure use was made of the observation that the N-Bz group of serine, in contrast to those of aliphatic NH₂-acids having no OH group, is very easily hydrolysed by dil. acid. Dibenzoyl-glycylserine, when warmed with 25 vol.-% H₂SO₄, yields BzOH, hippuric acid, and glycine. J. H. B.

Oxidation of pyrrole [by hydrogen peroxide; catalysis by iron]. A. QUILICO (Gazzetta, 1932, 62, 478–487).—Oxidation of pyrrole to hydroxypyrrole-black is strongly catalysed by salts of Fe, and to a smaller degree by those of Cu (which gives a brown product) and V; Mn, Ni, Co, and U are inactive. Variations in the yield according to the amount of Fe or H₂O₂ used are studied. E. W. W.

Action of ozone on heterocyclic compounds.

I. **Pyrrole.** M. FRERI (Gazzetta, 1932, 62, 600—605).—Passage of O_2+O_3 through pyrrole, alone or suspended in H_2O , or dissolved in $AcOH$ or dil. H_2SO_4 , gives oxidation products of high mol. wt., similar to pyrrole-blacks. The product in Et_2O is unstable, and may be an ozonide. E. W. W.

Indoles. II. Preparation of some derivatives of 5:6-dimethoxyindole. F. LIONS and (MISS) M. J. SPRUSON (J. Proc. Roy. Soc. New South Wales, 1932, 66, 171—180).—Interaction of 3:4-dimethoxybenzenediazonium chloride with esters of the type $CHRAc\cdot CO_2Et$ in $NaOH-EtOH$ gives hydrazones (oils, except the monoveratrylhydrazone of $\beta\gamma$ -diketo- α -phenylbutane, m.p. 173°) which with HCl in $EtOH$ yield indoles. The following are described: 3-methyl-, m.p. 208° (decomp.) (*Et* ester, m.p. 182°), and 5:6-dimethoxy-3-phenylindole-2-carboxylic acid, m.p. 203° (decomp.) (*Et* ester, m.p. 167°); *Et* (5:6-dimethoxy-2-carbethoxy-3-indolyl)butyrate, m.p. 163°; 5:6-dimethoxy-2-acetyl-3-phenylindole, m.p. 181°. J. L. D.

5-Ethoxyindolinones. K. BRUNNER and H. MOSER (Monatsh., 1932, 61, 15—28).—*n*-Valer-p-ethoxyphenylhydrazide, m.p. 125.5°, heated with CaO gives 21.6% of 5-ethoxy-3-propyl-2-indolinone, m.p. 119°; *o*-ethoxy-3-isopropyl-, m.p. 132°, and 5-ethoxy-3-methyl-3-ethyl-, m.p. 158°, -2-indolinones are similarly prepared from isovaler-, m.p. about 120°, and α -methylbutyr-, m.p. 146°, -p-ethoxyphenylhydrazides, respectively. isovaler-, m.p. 80.5°, and α -methylbutyr-, m.p. 78°, -as-p-ethoxyphenylmethylhydrazides are similarly converted into 5-ethoxy-1-methyl-3-isopropyl-2-indolinone, m.p. 40°, and 5-ethoxy-1:3-dimethyl-3-ethyl-2-indolinone (I), m.p. 41° (cf. Stedman and Barger, A., 1925, i, 292) [*Br*-, m.p. 115—116°, and (NO_2)₂-, m.p. 195°, derivatives], respectively. (I) is reduced by Na and $EtOH$ to the corresponding indolinol (indolinium picrate, m.p. 146—147° with darkening). The indolinone from valer-as-p-ethoxyphenylmethylhydrazide, m.p. 63°, could not be obtained cryst. as-p-Ethoxyphenylmethylhydrazine, b.p. 137—140°/10 mm., is prepared by reduction (Zn dust, aq. $AcOH$) of the NO -derivative, m.p. 49°, of $p-OEt\cdot C_6H_4\cdot NHMe$ (hydrochloride; picrate, m.p. 168°). H. B.

Toad poisons. V. Basic components of toad secretion. H. JENSEN and K. K. CHEN (Ber., 1932, 65, [B], 1310—1314).—The secretion, after being dried at room temp., is extracted with 95% $EtOH$. The extract is evaporated nearly to dryness in vac. and the residue extracted with H_2O . The aq. solution is shaken repeatedly with amyl alcohol and then with $CHCl_3$. The bufotenins are isolated as the flavianates. The same bufotenin flavianate.

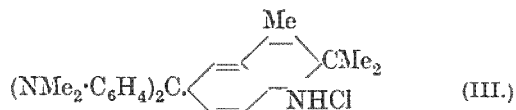
$C_{12}H_{20}O_2N_2\cdot C_{10}H_6O_8N_2S$, m.p. 200.5°, 199°, and 198—199°, respectively, is isolated from *Ch'an Su*, *Bufo bufo gargarizans*, and *B. Fowleri*. The flavianates $C_{12}H_{18}O_2N_2\cdot C_{10}H_6O_8N_2S$, m.p. 186—187°, 180—181°, and 170°, respectively, from *B. formosus*, *B. bufo bufo*, and *B. viridis viridis* form a closely related group nearly resembling the first group. The bufotenin from *B. valliceps* (flavianate, m.p. 261—262°) appears identical with tryptophan; those from *B. marinus* (flavianate, m.p. 270—271°) and *B. alvarius* (flavianate,

m.p. 224—225°) are probably methyltryptophan and methyltetrahydrotryptophan, respectively. The bufotenins from *B. arenarum* and *B. viridis viridis* (flavianate, $C_{12}H_{20}O_2N_2\cdot C_{10}H_6O_8N_2S$, m.p. 130—131°) appear identical. The probable relationship of the bufotenins to β -3-indolyethylamine is indicated. Cinobufotenin flavianate evolves NMe_3 when heated with 10% KOH . H. W.

Preparation of iodinated derivatives of phenolisatin. W. C. SUMPTER (J. Amer. Chem. Soc., 1932, 54, 3766—3768).—Conc. H_2SO_4 and 5-iodoisatin in molten $PhOH$ give 70% of 5-iodophenolisatin (5-iodo-3:3-di-p-hydroxyphenyloxindole), m.p. 220°, resolidifying with m.p. 264—265° (Ac_3 derivative, m.p. 169—170°); 5:7-di-iodo-3:3-di-p-hydroxyphenyloxindole, m.p. 239—240° (Ac_2 derivative, m.p. 256—257°), is prepared similarly. Phenolisatin and *N*-I (in KI) in conc. aq. NH_3 give about 80% of impure 3:3-bis-(3':5'-di-iodo-4'-hydroxyphenyloxindole, not melted at 265° (Ac_3 derivative, m.p. 267—268°); 5-iodo- (Ac_3 derivative, m.p. 272—273°) and 5:7-di-iodo- (Ac_2 derivative, m.p. 255—256°) -3:3-bis-(3':5'-di-iodo-4'-hydroxyphenyloxindoles are prepared similarly. C. J. W. (b)

Supposed acetoneanil. G. REDDELIEN and A. THURN (Ber., 1932, 65, [B], 1511—1521).—Re-examination of the acetoneanil of Knoevenagel (A., 1921, i, 785) shows it to be 2:2:4-trimethyl-1:2-dihydroquinoline (I), b.p. 134°/13—14 mm., m.p. 25—26°. It is obtained in 32% yield by the action of I on a boiling mixture of $COMe_2$ and NH_2Ph (*loc. cit.*), whereby much NH_2Ph remains unchanged and the true acetoneanil is produced in very small amount; evidence of the formation of mesityl oxide anil, $CMe_3\cdot CH\cdot CMe\cdot NPh$, b.p. 125°/16 mm. (obtained from mesityl oxide and NH_2Ph without catalyst), is not afforded. Greatly improved yields are secured by the gradual addition of an excess of $COMe_2$ to NH_2Ph and I at 155—160°. (I) is unchanged by boiling dil. HCl , but with conc. HCl affords the hydrochloride, m.p. 209°; the sulphate and perchlorate, m.p. 146—147°, are described. (I) combines readily with MeI to the methiodide, m.p. 148°, transformed by KOH into 1:2:2:4-tetramethyldihydroquinoline, b.p. 142°/13 mm. ("methylacetoneanil," *loc. cit.*). (I) is indifferent towards HCN and $NaHSO_3$. The presence of the NH group in (I) is established by the isolation of 1-acetyl-, m.p. 53°, readily hydrolysed by boiling dil. HCl , and 1-benzoyl-, m.p. 83°, -2:2:4-trimethyldihydroquinoline. 2:2:4-Trimethyldihydroquinolinophenylcarbamide, m.p. 125°, and the corresponding compound, m.p. 135°, from "acetone-p-tolil" are described. (I) with H at 100°/10 atm. in presence of $Ni\cdot SiO_2$ yields 2:2:4-trimethyltetrahydroquinoline (II), b.p. 119—122°/10 mm., m.p. 41°, identical with 2:2:3:3-tetramethylindoline obtained by reduction of "acetoneanil" with Na and boiling $EtOH$ (A., 1922, i, 1060); the formation of NH_2Ph during the process is not observed. The product of the action of $COMe_2$ and $p-C_6H_4Me\cdot NH_2$ is 2:2:4:6-tetramethyldihydroquinoline, b.p. 144—145°/15 mm., m.p. 40.5°. (I) condenses with $PhCHO$, yielding when oxidised a dye resembling malachite-green, whilst with Michler's ketone it yields the dye

(III), bluer than crystal-violet and exhibiting a much more marked affinity for mordanted cotton. With



diazotised sulphanilic acid (I) couples with marked evolution of gas, giving a dye of the helianthin class, whereas (II) couples normally.

isoPropylaniline, b.p. 203—204° from NH_2Ph and Pr^iCl at 120°, gives an *Ac* derivative, m.p. 38°.

H. W.

Iodo-derivatives of quinoline. L. MUSAJO (Gazzetta, 1932, 62, 566—570).—2-Phenylquinoline-4-carboxylic acid with ICl in $AcOH$ forms a compound, $C_{16}H_{12}O_2NCl_2 \cdot 5EtOH$, m.p. 155—156° (decomp. from 200°). 5-Iodoisatin (cf. A., 1924, i, 1342; prep. modified) condenses with *p*-iodoacetophenone to 6 : 4'-di-iodo-2-phenylquinoline-4-carboxylic acid, m.p. 285—286°, from which the base, m.p. 228°, is obtained on heating.

E. W. W.

Manufacture of therapeutically valuable compounds. A. CARPMAEL. From I. G. FARBENIND. A.-G.—See B., 1932, 912.

Alkylated diketopyrazolidines and tetraketopyrazoles from alkylmalonic esters and hydrazine. A. W. DOX (J. Amer. Chem. Soc., 1932, 54, 3674—3678).—The N_2H_4 condensation with homologous alkylmalonic esters (cf. Conrad and Zart, A., 1906, i, 608) invariably gives pyrazolones of type (I) with the dialkylated esters, whereas monosubstituted esters afford the double condensation product of type (II). In neither case could the type be interchanged by varying the proportions of the reacting substances. The following are



prepared from the appropriate malonic esters and $N_2H_4 \cdot HCl$ or $NHPh \cdot NH$, in $EtOH-NaOEt$: 4 : 4-diethyl-, m.p. 267°, 4 : 4-dipropyl-, m.p. 254°, 4 : 4-dibutyl-, m.p. 220°, 4 : 4-diisopropyl-, m.p. 289—290°, 4-ethyl-4-isopropyl-, m.p. 228°, 4-ethyl-4-hexyl-, m.p. 182°, 4-sec-butyl-4-allyl-, m.p. 186—187°, 4-phenyl-4-ethyl-, m.p. 196—197°, 1-phenyl-4-ethyl-, m.p. 108°, 1-phenyl-4-sec-butyl-, m.p. 94°, and 1-phenyl-4 : 4-diethyl-, m.p. 114°, -3 : 5-diketopyrazolidines; 2 : 6-diethyl-, m.p. 246—247°, 2 : 6-dipropyl-, m.p. 278°, and 2 : 6-di-sec-butyl-, m.p. 207°, -1 : 3 : 5 : 7-tetraketopyrazo-(1 : 2- α)-pyrazoles. The last three compounds with Br in $AcOH$ give the 2 : 6- Br_2 -derivatives, m.p. 171—173°, 138°, and 111°, respectively. Diketodiethylpyrazolidine does not condense with $CH_3Et(CO_2Et)_2$. A tentative explanation of the difference in behaviour between the mono- and di-alkylmalonic esters is a possible enolisation of the intermediate diketomonoalkylpyrazolidine which renders it capable of further reaction to form the pyrazole. Compounds of type (I) show some antipyretic properties but no hypnotic action.

C. J. W. (b)

Decomposition of alkylpyrazolinecarboxylates. K. VON AUWERS and F. KÖNIG (Annalen, 1932, 496, 252—282).—Thermal decomp. of the simpler alkyl

pyrazolinecarboxylates usually gives alkyl alkene-carboxylates (I) as the main product, whilst the more complex esters generally afford a preponderance of alkyl cyclopropanecarboxylates (II). Mixtures of (I) and (II) are often formed; the amount of (I) is determined by Br titration (when possible). Carbalkoxy-groups have a marked influence on the decomp.; (I) generally predominates with pyrazoline-monocarboxylates, whilst (II) is usually the main product with pyrazolinedicarboxylates. Δ^2 -Pyrazolines give a preponderance of (I), whilst Δ^1 -pyrazolines afford mainly (II); in the last case, no H is eliminated during the decomp. *cis*- and *trans*-Pyrazolinedicarboxylates give almost entirely *cis*- and *trans*-cyclopropanedicarboxylates, respectively. Resinous material is formed in all cases. *Me* pyrazoline-3-carboxylate gives *Me* Δ^2 -butenoate; *Me* 5-methylpyrazoline-3-carboxylate affords (mainly) *Me* Δ^2 -pentenoate (impure dibromide, b.p. 104—106°/13 mm.); *Me* 4-methylpyrazoline-3-carboxylate (*N-Ac*, b.p. 140—142°/10 mm., 208—210°, m.p. 60—61°, and *N-Me*, b.p. 120—126°/1 mm., derivatives) yields *Me* β -methyl- Δ^2 -butenoate (dibromide, b.p. 90—94°/12 mm.) and a trace of *Me* 4-methylpyrazole-3(5)-carboxylate; *Me* 4 : 5-dimethylpyrazoline-3-carboxylate furnishes *Me* β -methyl- Δ^2 -pentenoate {free acid, b.p. 200—204° (lit. 199°) [chloride, b.p. 48—50°/12 mm.; amide, m.p. 126—127° (lit. 124°)]}; *Et* 4-methylpyrazoline-3 : 5-dicarboxylate, m.p. 69° (from *Et* crotonate and $CHN_2 \cdot CO_2Et$), gives *Et* β -methylglutaconate (probably admixed with some *Et* methylcyclopropanedicarboxylate); *Et* 5-methyl- Δ^1 -pyrazoline-5-carboxylate affords *Et* 1-methylcyclopropane-1-carboxylate and *Et* tiglate in the ratio 37 : 63; *Me* 4 : 5-dimethyl- Δ^1 -pyrazoline-5-carboxylate yields *Me* $\alpha\beta$ -dimethyl- Δ^2 -butenoate (dibromide, b.p. 104—105°/13 mm.) and *Me* 1 : 2-dimethylcyclopropane-1-carboxylate in the ratio 77 : 23; *Me* 3 : 4 : 5-trimethyl- Δ^1 -pyrazoline-5-carboxylate furnishes *Me* 1 : 2 : 3-trimethylcyclopropane-1-carboxylate, b.p. 68—70°/39 mm. (free acid, b.p. 210—211°), and *Me* $\alpha\beta$ -dimethyl- Δ^2 -pentenoate in the ratio 86 : 14; *Et* 4-methyl- Δ^1 -pyrazoline-5 : 5-dicarboxylate gives *Et* isopropylidenemalonate, b.p. 112°/12 mm.; *Me* pyrazoline-3 : 4-dicarboxylate affords (cf. von Pechmann, A., 1894, i, 438) *Me* mesaconate and *Me* *cis*- and *trans*-cyclopropane-1 : 2-dicarboxylates in the ratio 65 : 2 : 23; *Me* *cis*-5-methyl- Δ^1 -pyrazoline-4 : 5-dicarboxylate yields mainly *Me* *cis*-1-methylcyclopropane-1 : 2-dicarboxylate, a little of the *trans*-ester, and some *Me* dimethylmaleate; *Me* 4-methylpyrazoline-3 : 4-dicarboxylate furnishes *Me* *trans*-1-methylcyclopropane-1 : 2-dicarboxylate; *Me* *trans*-5-methyl- Δ^1 -pyrazoline-4 : 5-dicarboxylate gives mainly *Me* *trans*-1-methylcyclopropane-1 : 2-dicarboxylate and a trace of *Me* α -methylitaconate; *Me* *cis*-4 : 5-dimethyl- Δ^1 -pyrazoline-4 : 5-dicarboxylate gives *Me* *cis*-1 : 2-dimethylcyclopropane-1 : 2-dicarboxylate, b.p. 215—216° (free acid, m.p. 115—117°), and the *trans*-isomeride in the ratio 95 : 5; *Me* *trans*-4 : 5-dimethyl- Δ^1 -pyrazoline-4 : 5-dicarboxylate affords *Me* *trans*-1 : 2-dimethylcyclopropane-1 : 2-dicarboxylate, b.p. 210° (free acid, m.p. 230—231°), and a trace of the *cis*-isomeride; *Me* Δ^1 -pyrazoline-4 : 5-dicarboxylate-5-acetate (from *Me* aconitate and

diazomethane) yields *Me* cyclopropane-1:2-dicarboxylate-2-acetate, b.p. 146—148°/14 mm., and *Me* pyrazole-3:4(4:5)-dicarboxylate in the ratio of about 2:1. Et 3:5-dimethylpyrazoline-5-carboxylate decomposes readily, giving some Et 3:4(or 5)-dimethylpyrazole-5(or 4)-carboxylate [*hydrobromide*, m.p. 150—152° (decomp.)], the formation of which involves migration of *Me* or CO_2Et . Numerous spectrochemical data are recorded. H. B.

Chromoisomerism of nitrosoantipyrine. G. ROSSI and A. BENZI (Gazzetta, 1932, 62, 411—414).—Green nitrosoantipyrine is depolymerised by prolonged boiling with EtOH into a more sol. yellow *isomeride*, decomp. 175°. E. W. W.

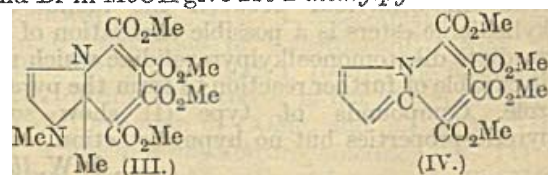
Formation of 4(5)-aminoglyoxalines. II. Non-reactivity of the halogen atom in 4(5)-bromoglyoxaline-5(4)-carboxylic acid. I. E. BALABAN (J.C.S., 1932, 2423—2425).—Et 2:5-dibromoglyoxaline-4-carboxylate is converted (partly) by boiling with aq. Na_2SO_3 into the Et ester of 4(5)-bromoglyoxaline-5(4)-carboxylic acid (I) (King and Murch, J.C.S., 1923, 123, 621) [NH_4 salt, m.p. 259°, formed from (I) and conc. aq. NH_3 or EtOH- NH_3 at 150°]. (I) is recovered (partly) or completely destroyed when treated with KCN, Na_2SO_3 , Na_3AsO_3 , or $\text{CH}_2(\text{CO}_2\text{Et})_2$ in EtOH; with Cu-bronze, no satisfactory product is obtained. Et glyoxaline-4(5)-carboxylate and aq. NH_3 (d 0.88) at 150° give *glyoxaline-4(5)-carboxylamide* (+ H_2O), m.p. 215° (*picrate*, m.p. 228°), which could not be converted (Hofmann reaction) into 4(5)-aminoglyoxaline, is reduced (Na-Hg, dil. H_2SO_4) to a little 4(5)-hydroxymethylglyoxaline, and with Br (1 mol.) in CHCl_3 gives (mainly) 2:5-dibromoglyoxaline-4-carboxylamide, m.p. 256°. An NH_2 group could not be introduced into glyoxaline or 5-chloro-1-methylglyoxaline by NaNH_2 in xylene. H. B.

Amino-acids. III. Piperonylalanine. V. DEULOFEU and J. MENDIVE (Z. physiol. Chem., 1932, 211, 1—4; cf. this vol., 949).—*Piperonylalanine* (I), m.p. 262—264° (*phenylcarbimido*-derivative, m.p. 192—193°), was obtained from piperonal (II) in good yield by various methods. (1) Erlenmeyer synthesis: (II) + hippuric acid \rightarrow azlactone \rightarrow piperonyl-*N*-benzamidoacrylic acid \rightarrow *N*-benzoylpiperonylalanine (III), m.p. 181—182°. Hydrolysis of (III) with aq. $\text{Ba}(\text{OH})_2$ yields (I). (2) Condensation with hydantoin: (II) + hydantoin \rightarrow piperonylidenehydantoin \rightarrow piperonylhydantoin, m.p. 182—183° \rightarrow [with aq. $\text{Ba}(\text{OH})_2$] (I). Similarly, thiohydantoin \rightarrow piperonylidene-2-thiohydantoin, m.p. 288—290° (decomp.) \rightarrow piperonylidenehydantoin. (3) (II) condenses with diketopiperazine, giving *bis*(piperonylidene)diketopiperazine, m.p. not below 300°, which on reduction with Zn forms *bis*(piperonyl)diketopiperazine, m.p. 251—252°. Hydrolysis of the last with aq. $\text{Ba}(\text{OH})_2$ at 115° affords (I). J. H. B.

Pyrimidines. CXXX. Synthesis of 2-keto-1:2:3:4-tetrahydropyrimidines. K. FOLKERS, H. J. HARWOOD, and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 3751—3768).—Condensation of $\text{CO}(\text{NH}_2)_2$, a β -ketonic ester, and an aldehyde (cf. Biginelli, A., 1893, i, 645) is accelerated by HCl and occurs in abs. EtOH or glacial AcOH. PhCHO ,

$\text{CO}(\text{NH}_2)_2$, and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ in EtOH containing a little conc. HCl give 78.5% of Et 2-keto-4-phenyl-6-methyl-1:2:3:4-pyrimidine-5-carboxylate, m.p. 202—204°. The following 4-substituted Et 2-keto-6-methyl-1:2:3:4-tetrahydropyrimidine-5-carboxylates are prepared: *p*-hydroxyphenyl, m.p. 227—229°; *anisyl*, m.p. 201—202°; *p*-nitrophenyl, m.p. 207—208.5°; *m*-nitrophenyl, m.p. 226—227.5°; *styryl*, m.p. 238—239.5°; β -phenylethyl, m.p. 179.2—180.2°; *hexyl*, m.p. 151—152°; *methyl*, m.p. 180—190°; *p*-aminophenyl, m.p. 220—221°, and *m*-aminophenyl, m.p. 208.2—209.5°, prepared by catalytic reduction of the NO_2 -derivatives; 4'-hydroxy-3'-methoxyphenyl, m.p. 232—233°; 3':4'-dimethoxyphenyl, m.p. 178—178.5°; 3':5'-di-iodo-4'-hydroxyphenyl, m.p. 216°; 2':4':6'-trimethoxyphenyl, m.p. 185—185.5°; *o*-hydroxyphenyl, m.p. 201—202°; 2':4'-dihydroxyphenyl, m.p. 225.5—226.5°; *furyl*, m.p. 204.5—205°; 3':4'-methylenedioxyphenyl, m.p. 187—188°; β -dimethyl- Δ^{α} -heptadienyl, m.p. 150.5—151.5° (accompanied by a substance, m.p. 110—111.5°). Et 2-keto-6-methyl-1:2:3:4-tetrahydropyrimidine-5-carboxylate has m.p. 253.8—256°. C. J. W. (b)

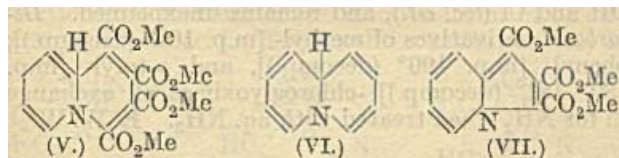
Synthesis in the hydroaromatic series. O. DIELS and K. ALDER. XVI, XVII. "Diene syntheses of heterocyclic nitrogen compounds. 4. Syntheses with pyrroles, glyoxalines, and pyrazoles. [With H. WINCKLER and E. PETERSEN.] 5. Syntheses with pyridine, quinoline, 2-methylquinoline, and isoquinoline. [With T. KASHIMOTO, FRIEDRICHSEN, W. ECKARDT, and H. KLARE] (Annalen, 1932, 498, 1—15, 16—49).—XVI. 2-Methylpyrrole and *Me* acetylenedicarboxylate (I) give an *adduct*, m.p. 52°, in addition to that (m.p. 111°) previously described (A., 1931, 849); both are reduced (H_2 , colloidal Pd, MeOH) to *Me* α -2-methyl-5-pyrrolsuccinate (*ibid.*, 1428), indicating that they are *cis-trans*-isomerides. 2:3-Dimethylpyrrole and aq. maleic anhydride give α -2:3-dimethyl-5-pyrrolsuccinic acid, m.p. 113° (decomp.) [*Me* ester (II), m.p. 82°]; with (I), isomeric (maleate and fumarate) *adducts*, m.p. 98° and 132° [both reduced (Pd) to (II)], are produced. 2:3:4-Trimethylpyrrole and maleic anhydride in C_6H_6 afford an *adduct*, $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$, m.p. 148° (decomp.); with (I), an *adduct*, $\text{C}_{13}\text{H}_{17}\text{O}_4\text{N}$, m.p. 137—138° (H_2 derivative, m.p. 95°), results. Prolonged interaction of 1-methylindole and (I) gives *Me* α -di-(1-methyl-2-indolyl)succinate, m.p. 157—158°. 4(5)-Methylglyoxaline and (I) in Et_2O afford *Me* α -4-methyl-2(or 5)-glyoxalinylmaleate, m.p. 103—104°, whilst 1:2-dimethylglyoxaline similarly gives *Me* 1:8-dimethyl-1:8-dihydropyriminazole-4:5:6:7-tetracarboxylate (III), m.p. 163° (decomp.), formed by addition of 2 mols. of (I) to the $\text{N}:\text{CMe}$ group. (III) and Br in MeOH give *Me* 2-methylpyridine-3:4:5:6-



tetracarboxylate, m.p. 73° (the free acid is converted by distillation with CaO into 2-methylpyridine). Treatment of (III) with AcOH affords NH_2Me and

the *indolizine ester* (IV), m.p. 138—139°. Pyrazole and (I) in Et₂O give an *adduct*, C₁₂H₁₄O₄N₄, m.p. 158° (in one case an *isomeride*, m.p. 139°, was obtained), whilst 3 : 5-dimethylpyrazole similarly affords *adducts*, C₁₁H₁₄O₄N₂, m.p. 58°, and C₁₆H₂₂O₄N₄, m.p. 188°.

XVII. Addition of (I) to C-H₅N and related compounds occurs in a manner analogous to that with 1 : 2-dimethylglyoxaline. C₅H₅N and (I) in AcOH give [by polymerisation of (I)] *Me mellitate*; in Et₂O, *Me quinolizine-1 : 2 : 3 : 4-tetracarboxylate* (V), yellow, m.p. 187—188° (becoming red) [*chloroplatinate*, m.p. 197—198° (decomp.); *dinitrate*, decomp. 103—105°], and an *isomeride*, red, m.p. 124—125° (slight decomp.) [converted into (V) by crystallisation from hot MeOH, MeCN, or 50% AcOH], are produced. Reduction (H₂, PtO₂, AcOH) of (V) gives a *H₄ derivative*, m.p. 144°, whilst oxidation with H₂O₂ in AcOH affords an *acid*, C₉H₇O₅N, m.p. 161° (decomp.), which when heated to about 180° passes into pyridine-*N*-oxide and on reduction (H₂, PtO₂, AcOH) gives piperidine-2-carboxylic acid. (V) is converted by boiling dil. HCl into an *acid hydrochloride*, C₁₀H₁₀O₂NCl (*octahydro-derivative*, m.p. 249—250°), and by boiling anhyd. HCO₂H into *Me₃*, m.p. 75°, and *Me₂ H*, m.p. 200°, *quinolizinetetracarboxylates* [the *Me H₂* ester (+H₂O), m.p. 245° (decomp.)], is obtained by hydrolysis of the *Me₂* and *Me₃* esters with dil. HCl or moist HCO₂H]. Hydrolysis of (V) with aq. KOH gives first a *salt*, C₁₅H₁₁O₈NK₂·H₂O, and then the K salt of *quinolizinedicarboxylic acid*, m.p. 229° (decomp.). Distillation of this acid with CaO affords *quinolizine* (VI), b.p. 210—220° (*picrate*, m.p. 96°), reduced (H₂, PtO₂,



AcOH) to *octahydroquinolizine*, b.p. 166—167° (*picrate*, m.p. 203°), which is converted by CNBr into 2-*n*-butylpiperidine (*hydrochloride*, m.p. 191°). Oxidation of (V) with dil. HNO₃ or Na₂Cr₂O₇-AcOH gives *Me indolizinetetracarboxylate* (VII), m.p. 151—152°, hydrolysed by aq. KOH to a *salt*, C₁₁H₆O₆NK, which when heated with dil. HCl affords (by loss of CO₂) *indolizine-monocarboxylic acid*, m.p. 240—242° (darkens from about 220°). Distillation of this with CaO gives *indolizine*, m.p. 75° (*picrate*, m.p. 101°), the *H₈* derivative (*picrate*, m.p. 225°) of which is converted by CNBr into *dl*-coniine. A small amount of a *Me₄* ester (VIII), C₁₆H₁₃O₈N, m.p. 186—187°, is formed in addition to (V) and its *isomeride* from C₅H₅N and (I); (VIII) is also obtained [as *nitrate*, m.p. 92—93° (decomp.)] from (V) and cold fuming HNO₃. (VIII) is reduced (H₂, PtO₂, AcOH) to a *H₆* derivative, m.p. 153—154°, is oxidised by H₂O₂ in AcOH to the acid, C₉H₇O₅N (above), and is hydrolysed by dil. HCl to a *Me H₂* ester, m.p. 190—191° (decomp.) [converted by diazomethane into (VIII)].

The *adduct*, C₂₁H₁₉O₈N, m.p. 165—167° (becoming red), from *isoquinoline* and (I) is oxidised by dil. HNO₃ to a *compound*, C₁₈H₁₅O₆N, m.p. 154—155°. Quinoline and (I) in Et₂O give an *adduct*, C₂₁H₁₉O₈N, m.p. 181—182° (becoming red), whilst 2-methylquinol-

ine affords two isomeric *adducts*, C₂₂H₂₁O₈N, yellow, m.p. 174—175° (becoming red), and red, m.p. 204°.

H. B.

Products of condensation of *o*-homophthalimide with aromatic aldehydes. A. MEYER (Bull. Soc. chim., 1932, [iv], 51, 953—963; cf. A., 1928, 773).—The m.p. of *o*-vanillylidenehomophthalimide is now given as 311°. Interaction of *o*-aminobenzaldehyde with homophthalimide under the standard conditions gives 7-keto-7 : 8-dihydro-2 : 3 : 5 : 6-dibenzo-1 : 8-naphthyridine, m.p. 246° (cf. A., 1927, 1089).

H. A. P.

Attempted synthesis of pentazole. Action of diazomethane on azoimide. E. OLIVERI-MANDALÀ (Gazzetta, 1932, 62, 716—720).—This reaction, in Et₂O, gives only methylazoimide.

E. W. W.

Acetylene and its isooxazolic derivatives. IX. Some *isooxazole derivatives*. A. QUILICO and M. FRERI (Gazzetta, 1932, 62, 436—444).—P₂O₅ converts *isooxazole-5-carboxylamide* (A., 1930, 622) into 5-*cyanoisooxazole* (I), b.p. 168°, easily hydrolysed by dil. H₂SO₄, and very easily degraded by alkalis to cyanoacetic acid and HCN. Attempts to reduce (I) to the amine did not succeed; with MeMgI in Et₂O, (I) gives 5-*acetylisooxazole* (II), m.p. between 20° and 35° [*NaHSO₃* compound; *phenylhydrazone*; *p*-nitro-*phenylhydrazone*, m.p. 220—221°; *semicarbazone*, m.p. 207° (decomp.)]. (II) is converted by warm HNO₃ (*d* 1.41) into 5 : 5'-*diisooxazoloylfuroxan* [*phenylhydrazone*, m.p. 145° (decomp.)], obtainable from C₂H₂ (cf. A., 1931, 968) and *isooxazole-5-carboxylic acid*. NaOEt opens the ring of (II), giving CN·CH₂·CHO.

E. W. W.

Curtius degradation applied to isooxazole-5-carboxylic acid and 5-methylisooxazole-3-carboxylic acid. M. FRERI (Gazzetta, 1932, 62, 457—463).—*isooxazole-5-carboxylamide* (A., 1930, 622) yields *isooxazole-5-carboxylhydrazide*, m.p. 141—142° (decomp.), oxidised by NaNO₃ and HCl at 0° to the 5-*carboxylazide*, m.p. 37° (decomp.), explosive, from which the 5-*urethane*, m.p. 74—75°, is obtained (EtOH), but in insufficient amount for the prep. of the amine (cf. A., 1931, 1170). *Me 5-methylisooxazole-3-carboxylate* yields successively the 3-*carboxylhydrazide*, m.p. 131—132°, the 3-*carboxylazide*, m.p. 112° (decomp.), explosive, and the 5-*urethane*, m.p. 82°. The last, decomp. on heating with conc. HCl in a sealed tube, gives with dil. HCl a product (I) which forms a *Bz* derivative (II), m.p. 160—161°, not of an amine, but of a OH-compound. Since (I) gives no colour with FeCl₃, (II) is considered to be 2-benzoyl-5-methylisooxazol-3-one, an isomerisation having taken place after the hydrolysis.

E. W. W.

New ketomorpholine derivatives. G. SANNA (Gazzetta, 1932, 62, 555—557; cf. A., 1931, 747).—*o*-α-Bromoisovaleramidophenol, m.p. 114°, obtained from α-bromoisovaleroyl chloride, in presence of KOH condenses to 2-isopropylphenmorpholone,

C₆H₄ < $\begin{matrix} \text{NH} \\ \text{CO} \end{matrix}$ O-CHPr³, m.p. 125°. *o*-α-Bromoisohexamidophenol, m.p. 115°, similarly yields 2-isobutylphenmorpholone, m.p. 128°.

E. W. W.

Acetylene and its isooxazolic derivatives. XI. Structure of reaction products of nitric acid and

acetylene. A. QUILICO (Gazzetta, 1932, 62, 503—518).—The explosive compound $C_4H_5O_7N_6$ (I), the hydrochloride $C_4H_5O_3N_5Cl$ (II), the yellow compound $C_4H_5O_3N_5$ (III), and the compound $C_4H_5O_3N_4$ (IV) (A., 1931, 194) were re-investigated. With conc. HCl, (III) [*Ag*, *Cu* salts; *Ac* derivative, m.p. 195° (decomp.); *Bz* derivative, m.p. 218°] forms in the cold a hydrochloride, m.p. 100—105° (decomp.), but in the hot it is decomposed to CO_2 , NH_2OH , HCl, and NH_4Cl . By the action of $SnCl_2$ and HCl (III) takes up the elements of H_2O to form (II), which is reconverted into (III) by KOH. With KBr, (III) yields α -isooxazolediazoimide (this vol., 171); it is therefore identified as α -isooxazoleazoforamidoxime,

$\begin{array}{c} CH \cdot CH \\ N - O \end{array} \gg N : N \cdot C(N \cdot OH) \cdot NH_2$. From this, (II) would

probably be $\begin{array}{c} CH \cdot CH \\ N - O \end{array} \gg NH \cdot NH \cdot C(N \cdot OH) \cdot NH \cdot OH, HCl$.

That (I) is α -isooxazoleazotrinotromethane,

$\begin{array}{c} CH \cdot CH \\ N - O \end{array} \gg N : N \cdot C(NO_2)_3$, is proved by synthesis. Benz-

eneazotrinotromethane is prepared from PhN_2Cl and the NH_3 salt of $CH(NO_2)_3$; it explodes violently on percussion or at 70—75°, but when heated slowly in AcOH it forms a compound, $C_7H_5O_2N_3$, m.p. 83°, very similar to (IV). *p*-Nitrobenzeneazotrinotromethane is also prepared, and when heated forms a compound, m.p. 160°. The product from α -isooxazolyamine and the NH_4 salt of nitroform is identical with (I).

E. W. W.

Dioximes. LXXXVII, LXXXVIII. G. PONZIO. LXXXIX. G. CARBONE. XC. M. MILONE. XCI. G. PONZIO. XCII. G. LONGO (Gazzetta, 1932, 62, 415—423, 424—427, 428—431, 432—435, 633—639, 640—644).—LXXXVII. The substance considered by Boeseken (A., 1912, i, 723) to be *p*-hydroxy-3-benzoyl-1 : 2 : 4-oxadiazole (A., 1926, 1159) is 5-phenyl-1 : 2 : 4-oxadiazole-3-carboxylic acid (*Ag* salt), since on boiling with H_2O it loses CO_2 and isomerises to benzoylcyanamide, and since its *K* salt reacts with $POCl_3$ followed by aq. NH_3 to form 5-phenyl-1 : 2 : 4-oxadiazole-3-carboxylamide (A., 1930, 1410), which is hydrolysed again to the acid, and is the first product from KOEt and 4-amino-3-benzoyl-1 : 2 : 5-oxadiazole. 4-Amino-3-*p*-toluoyl-1 : 2 : 5-oxadiazole (A., 1928, 414) with KOEt gives 5-*p*-tolyl-1 : 2 : 4-oxadiazole-3-carboxylic acid (*Ag* salt), which (+0.5 H_2O) loses CO_2 at 130°, or in boiling H_2O , forming *p*-tolylcyanamide, m.p. 155—156° [*Ag* salt, m.p. 260° (decomp.)], also prepared from cyanamide.

LXXXVIII. α -Chloro- β -methyl- and α -chloro- β -phenyl-glyoximes with $AgNO_2$ in Et_2O form, not the NO_2 -derivatives, but $\beta\gamma\delta$ -tetraoximinohexane diperoxide (A., 1925, i, 79) and $\alpha\beta\gamma\delta$ -tetraoximino- $\alpha\delta$ -diphenylbutane diperoxide, m.p. 162° (decomp.), respectively. The mechanism of the reaction is discussed.

LXXXIX. α -Chloro- β -methylglyoxime with NaI in $COMe_2$ yields α -iodo- β -methylglyoxime, m.p. 173° (decomp.) [*Ni* salt; *Ac*, derivative, m.p. 122° (decomp.)]; *Bz*, derivative, m.p. 190° (after decomp.)], which with Na_2CO_3 gives diacetylglyoxime dioxime peroxide, with KCN the α -CN-compound, and with $AgNO_2$ in Et_2O gives $\beta\gamma\delta$ -tetraoximinohexane diperoxide. α -Chloro- β -phenylglyoxime similarly yields α -iodo- β -phenylgly-

oxime, m.p. 179° (after decomp.) (*Bz*, derivative, m.p. 187°), which has similar properties, and with NaOAc and AcOH gives hydroxyphenylglyoxime. α -Iodo- β -*p*-tolylglyoxime has m.p. 170° (decomp.).

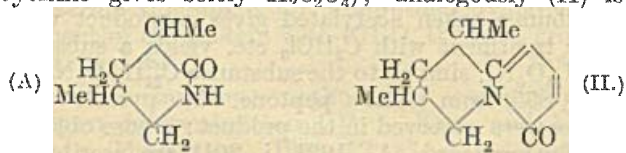
XC. The absorption spectra (cf. this vol., 558) of phenyl-, *p*-bromophenyl-, *p*-methoxyphenyl-, 3 : 4-methylenedioxyphenyl-, and 3 : 4-dimethoxyphenyl-methylglyoxime peroxide confirm the structures which have been assigned to them (A., 1928—1931). *p*-Bromophenylmethyloxadiazole, m.p. 64°, is prepared by reducing *p*-bromophenylmethylfuroxan (A., 1928, 888) with $SnCl_2$.

XCI. The isomeric form of dibenzoylglyoxime peroxide (cf. A., 1888, 275), new m.p. 188°, new prep. from oximinophenacyl chloride in an acetate buffer of p_H 4.6, is regarded as 4 : 5-dibenzoyl-1 : 2 : 3 : 6-dioxadiazine, ($CBz \begin{array}{c} N \\ N \cdot O \cdot O \end{array}$). It is converted by 5% NaOH into cyanoformhydroxamic acid, $CN \cdot C(OH) : NOH$ (+0.5 H_2O), m.p. 114—115° (decomp.), which is hydrolysed by 20% H_2SO_4 to CO_2 , HCN, and NH_2OH .

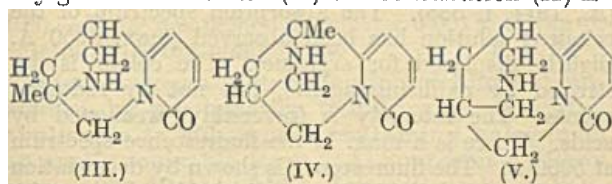
XCII. α -Chloroglyoxime (I) (A., 1930, 1409) forms with $PhNCO$ a dicarbanil derivative (cf. this vol., 513), m.p. 156—157° (decomp.), converted by aq. NH_3 into (I), and by aq. HCl into β -chloroglyoxime (*loc. cit.*), of which the dicarbanil derivative, m.p. 163—164° (decomp.), is converted by aq. NH_3 into aminoglyoxime. Since substitution in the oximino-groups of (I) and (II) thus does not affect the reactivity of the Cl atoms, the isomerism of (I) and (II) is not thought to be due to *syn-anti* configurations of OH and Cl (*loc. cit.*), and remains unexplained. Dicarbanil derivatives of methyl- [m.p. 166° (decomp.)], phenyl- [m.p. 190° (decomp.)], and *p*-tolyl- [m.p. 180—181° (decomp.)] -chloroglyoximes all exchange Cl for NH_2 when treated with aq. NH_3 . E. W. W.

Constitution of cytosine. E. SPATH and F. GALINOVSKY (Ber., 1932, 65, [B], 1526—1535).—The Hofmann degradation of cytosine gives bimol. products in its first stage when performed according to Partheil (A., 1893, i, 119; 1894, ii, 558; 1895, ii, 119, 254) or Ing (A., 1931, 1171). Elimination of H_2O from the quaternary base from methylcytosine methiodide occurs readily at 90°/vac. and the product is readily hydrogenated to *de*-N-dimethyldihydrocytosine (I), b.p. 150—160° (bath)/0.001 mm. (*picrate*, m.p. 174—175°, $[\alpha]_D^{25}$ —46.94° in MeOH); at a higher temp., bimol. products result which are not readily hydrogenated. (I) and MeI in MeOH afford the methiodide, converted by successive treatment with Ag_2O and heating at 100—120°/10 mm. into NMe_3 and dihydrohemicytisylenes, $C_{11}H_{13}ON$, b.p. 140° (bath)/0.01 mm., $[\alpha]_D^{25}$ —1.1° in C_6H_6 (chloroplatinate), hydrogenated in aq. MeOH in presence of Pd-C to tetrahydrohemicytisylenes (II), b.p. 130—140° (bath)/0.001 mm., $[\alpha]_D^{25}$ —0.26° (chloroplatinate), which does not contain a NMe group. Since attempts to show the presence of a 1-methyl-2-quinolone complex in (II) were unsuccessful and the presence of a 2-pyridone ring is established (Spath, A., 1919, i, 451, 453), it follows that the N atom of (II) belongs to two rings and that the quinoline ring of the degradation products of Freund (A., 1904, i, 263) and of Spath (*loc. cit.*) is not initially present in

cytisine. Further evidence is deduced from the degradation of tetrahydrodeoxycytisine, transformed through the methiodide and the corresponding hydroxide and subsequent hydrogenation (Pd-C in AcOH) into *dihydrode-N-dimethyltetrahydrodeoxycytisine* (III), b.p. 132°/11 mm. (chloroplatinate). (III) affords two (?) stereoisomeric dimethiodides, $C_{15}H_{32}N_2I_2$, cryst., decomp. 325—327° (vac.), and amorphous. The base from the cryst. compound at 90—100°/vac. affords NMe_3 and a base which contains 1 NMe group and absorbs $2H_2$ (Pd-C in AcOH) with production of the compound $C_{13}H_{25}N$ (IV), b.p. 90—110° (bath)/10 mm. The final stage of the degradation leads through the non-cryst. methiodide to a base containing 2 Me groups attached to N and hydrogenated to the compound $C_{13}H_{29}N$. Further evidence of the existence of the pyridone complex is obtained by hydrogenating cytisine to *tetrahydrocytisine*, m.p. 113—114° (vac.), oxidised by 1% $KMnO_4$ at room temp. to $H_2C_2O_4$ and glutaric acid (similar treatment of cytisine gives solely $H_2C_2O_4$); analogously (II) is



converted into *octahydrohemicytisylen*, b.p. 120—130° (bath)/0.05 mm., oxidised to glutaric acid identified as the dianilide, m.p. 225°. Ozonolysis of (II) affords the *lactam* (A), m.p. 70—75° after softening at 65°, transformed by conc. HCl at 100° into an NH_2 -acid, oxidised by $KMnO_4$ in hot, feebly alkaline solution to a mixture of the inactive forms of $\alpha\alpha'$ -dimethylglutaric acid. To (II) the constitution (II) is



assigned. For cytisine the structure (III), (IV), or (V) is suggested. H. W.

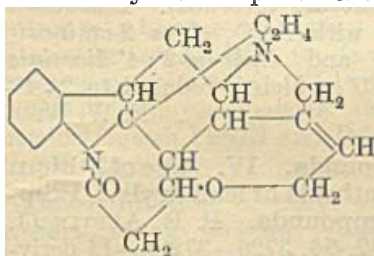
Ergot alkaloids. I. Oxidation of ergotinine. W. A. JACOBS (J. Biol. Chem., 1932, 97, 739—743).—Oxidation of ergotinine with HNO_3 gives, besides $BzOH$ and $p-NO_2 \cdot C_6H_4 \cdot CO_2H$, a tribasic acid, $C_{14}H_9O_8N$, m.p. $>350^\circ$ (darkens 265° , sinters 290°) [*Me* ester, m.p. $>350^\circ$ (darkens 260° , sinters 285°)]. A. A. L.

Detection of solanine. B. ALBERTY (Z. Unters. Lebensm., 1932, 64, 260—262).—Solanine or solanidine give a yellow colour with conc. H_2SO_4 , and reddish-purple, intensifying on keeping, when conc. H_2SO_4 and 1 drop of either 1% CH_2O or 0.5% H_2O_2 are added in succession to a solution of the alkaloid residue in conc. AcOH. The sensitiveness of the latter reaction is 0.0025 mg. (Autenrieth's H_2SeO_4 reagent, 0.025 mg.) and it is inert towards saponins and most alkaloids; morphine reacts with CH_2O , but not with H_2O_2 . J. G.

Strychnine and brucine. XX. Derivatives of ψ -strychnine. Comments on a recent memoir

of H. Leuchs, "Über Strychnos-alkaloide." LXVIII. B. K. BLOUNT and R. ROBINSON (J.C.S., 1932, 2305—2310).— ψ -Strychnine (Warnat, A., 1931, 1312) [*perchlorate*, not melted at 300° (blackens above 240°); *ferrichloride*, m.p. 234—235° (decomp.) after darkening] is reduced (Zn dust, $2N-HCl$) to strychnine and is relatively stable to alkaline $K_3Fe(CN)_6$. The *methiodide*, m.p. 213° (decomp.) (depends on rate of heating), of *O*-methyl- ψ -strychnine (*loc. cit.*) is converted by aq. KOH in MeOH into *de-N*:*O*-dimethyl- ψ -strychnininium hydroxide, m.p. 174—175° (decomp.), which with $PhCHO$ and a little KOH in MeOH gives substances, m.p. 153° and 189—193° (sinters at 180°), and is hydrolysed by dil. HCl at 100° to *-methylchano- ψ -strychnine*, m.p. 270—271° (decomp.) [*perchlorate*, blackens at 250° and explodes at 295° ; *dibenzylidene* derivative, m.p. 284—285° (decomp.) (previous darkening)]. ψ -Strychnine is most probably hydroxystrychnine, which contains the group $:N(b) \cdot C(OH) \cdot$ and probably the group $:N(b) \cdot C(OH) \cdot CH_3 \cdot$.

Contrary to the opinion of Leuchs (this vol., 953),

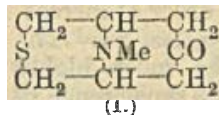


strychnine does not behave like a dihydroindole (or even hexahydrocarbazole); hence, one (α or β) of the C atoms of the indole group must be attached by a C chain to N (b). The β -C atom is probably at-

tached to H, since dioxonucidine is readily monobrominated (Leuchs, *loc. cit.*). The annexed constitution best expresses the known chemical behaviour of strychnine (and its derivatives). H. B.

Hydroferro- and hydroferri-cyanides of the alkaloids. W. M. CUMMING and J. A. STEWART (J.S.C.I., 1932, 51, 273—276T).—An extension (cf. J.S.C.I., 1925, 44, 110T; 1928, 47, 84T). The *hydroferro-* and *hydroferri-cyanides* of the following have been prepared in acid, neutral, and EtOH solutions: papaverine, benzamine, quinidine, quinaldine, berberine, thebaine, atropine, hyoscyamine (*l*-atropine), arecoline, cotarnine, perein, stovaine, tropacocaine, triacetoneamine, diamorphine. Their constitutions have been determined, and photomicrographs of some of the most characteristic cryst. formations are given. No salts were obtainable from benzocaine, orthocaine, borocaine, ephedrine, and diacetoneamine. The only stable hydroferri-cyanides in neutral solution so far isolated are those of berberine and cotarnine, both bases of the NH_4OH type.

Analogues of ψ -pelletierine, namely, thiotropinone, selenotropinone, and *N*-methylaztropinone. B. K. BLOUNT and R. ROBINSON (J.C.S., 1932, 2485—2487).—Thiobisacetaldehyde, Ca acetonedicarboxylate, and aq. NH_2Me condensed essentially by the method previously described (A., 1917, i, 581; 1924, i, 1335) give *thiotropinone* (I), m.p. 126—127° (*dipiperonylidene* derivative, m.p. 241°; *picrate*, darkens at 230° and explodes at 255°). Chloroacetal,



Na_2Se , and KI in aq. EtOH in absence of air give

impure *selenobisdiethylacetal*, b.p. 145—155°/0.1 mm., hydrolysed by warm 0.5% HCl to *selenobisacetaldehyde* [*di-p-nitrophenylhydrazone*, m.p. 205—210° (decomp.)], convertible (as above) into *selenotropinone* (I, S=Se), m.p. 142° (*dipiperonylidene* derivative, m.p. 240°). *N*-Methylaztropinone (I, S=NMe) [*dipicrate*, m.p. 198° (decomp.)]; *dipiperonylidene* derivative, m.p. 214—216°] is prepared similarly from methyliminobisacetaldehyde (by hydrolysis of its dimethylacetal). H. B.

Arsenical derivatives of diphenyl: molecular size of some arseno-derivatives. C. FINZI and E. BARTELLI (*Gazzetta*, 1932, 62, 545—555).—3 : 3'-Dimethyldiphenyl-4 : 4'-diarsinic acid (A., 1924, i, 1247) with HNO₃ (*d* 1.52) forms a (NO₂)₂-derivative, C₁₄H₁₄O₁₀N₂As₂, reduced (Na₂Hg₂) to the (NH₂)₂-derivative, stable to 290°. 3 : 3'-Dicarboxydiphenyl-4 : 4'-diarsinic acid (*loc. cit.*) [(NO₂)₂- and (NH₂)₂-derivatives] is reduced by H₃PO₃ to 4 : 4'-*arsenodiphenyl-3 : 3'-dicarboxylic acid* (?) (mol. wt. determinations with the Na salt are recorded). Diazotised 2 : 4'-diaminodiphenyl with As₂O₃ gives 2-aminodiphenyl-4'-arsinic acid, and diphenyl-2 : 4'-diarsinic acid, no m.p. below 320°, which is reduced to 2 : 4'-*arsenodiphenyl* (?). E. W. W.

Organic lead compounds. IV. Use of lithium derivatives in the synthesis of lead aryls. Preparation of amino-compounds. P. R. AUSTIN (*J. Amer. Chem. Soc.*, 1932, 54, 3726—3729).—Li derivatives are generally applicable to the prep. of org. compounds of Hg, Sn, and Pb. Li *p*-tolyl and HgCl₂ give 89% of Hg di-*p*-tolyl; *p*-NMe₂·C₆H₄·Li affords 12% of Hg(C₆H₄·NMe₂-*p*)₂; LiPh and PbCl₂ give 48% of PbPh₃ (the initial product, PbPh₂, is transformed into PbPh₃ by heat; if the heating is interrupted, a mixture of PbPh₃ and PbPh₄ is formed). PbPh₃Cl and Li *p*-tolyl give 41% of Pb triphenyl *p*-tolyl, m.p. 124—125°; PbPh₂Cl₂ similarly gives 38% of Pb diphenyl ditolyl, m.p. 121—122°. PbCl₂ heated with *p*-NMe₂·C₆H₄·Li gives 17% of Pb tetra-*p*-dimethylaminophenyl, m.p. 197—198°; PbPh₃Cl similarly affords 77% of Pb triphenyl *p*-dimethylaminophenyl (I), m.p. 124—125°, whilst PbPh₂Cl₂ gives 16% of Pb diphenyl di-(*p*-dimethylaminophenyl), m.p. 134—135°. SnCl₄ and Li *p*-tolyl give 91% of Sn tetra-*p*-tolyl; Sn tetra-(*p*-dimethylaminophenyl), m.p. 198—199°, is prepared in 58% yield. (I) and AcOH give some Ph₃PbOAc, m.p. 206—207°. PbEt₄ and Li *p*-tolyl in C₆H₆-Et₂O give some di-*p*-tolyl. C. J. W. (b)

Transference of a phenyl radical from an organometallic derivative to another metal. A. E. SHUROV and G. A. RAZUVAIEV (*Ber.*, 1932, 65, [B], 1507—1511).—The appropriate metallic phenyl is heated with the requisite metal, prepared by pptn. from the metallic salt by Zn, at 150—300°, or, less advantageously, in presence of C₆H₅Me₂, whereby the following sequence is observed in order of increasing affinity to Pb : Hg, Bi, [Pb], Sb, As, Sn. The product consisted invariably of the most highly phenylated derivative of the metal. Transference of Ph occurs at temp. markedly lower than those of decomp. of the Ph derivative even when, as in the

case of Pb, the second metal does not participate in the change. H. W.

[Metallic derivatives of thiophen.] G. RENWANZ (*Ber.*, 1932, 65, [B], 1556; cf. this vol., 762).—A reply to Steinkopf (*ibid.*, 950). H. W.

Relation of structure to rate of hydrolysis of peptides. VII. Hydrolysis of dipeptides by alkali. P. A. LEVENE, R. E. STEIGER, and A. ROTHEN (*J. Biol. Chem.*, 1932, 97, 717—726).—The following dipeptides were prepared and their rates of hydrolysis by 0.5*N*-NaOH at 25° determined: *dl*-valylglycine, *dl*-leucylglycine, glycyl-*dl*-valine, glycyl-*dl*-leucine, *d*-alanyl-*d*-alanine, *d*-leucyl-*d*-leucine. Comparison with the corresponding ketopiperazines indicated that any two radicals (attached to the same C) have the same relative effect on the stability of the peptide linking as on that of the ring structure. F. O. H.

Structure of proteins. II. A. BERNARDI and M. A. SCHWARZ (*Gazzetta*, 1932, 62, 464—468).—Ovalbumin when acetylated gives a product which after treatment with C₂HCl₃ etc. yields a substance C₁₈H₂₄O₅N₂, similar to the substance C₂₄H₃₀O₅N₂ (A., 1931, 855) from Witte's peptone. No pyrrole derivatives were observed in the product; those obtained by Troensegaard (A., 1921, i, 201) are ascribed to secondary reactions. E. W. W.

Colour reaction and fluorescence of proteins and their derivatives in presence of diacetyl. (MME.) A. ROCHE (*Bull. Soc. Chim. biol.*, 1932, 14, 1026—1031).—The colour reaction and fluorescence are independent, being sp. for different groupings. The former depends on the grouping NH₂C(NH₂)·NH·R (A., 1911, i, 588). The absorption spectrum of the coloured solution has been observed (max. 5250 Å. slightly displaced for arginine). The colour is destroyed by oxidising agents, but not by reducing agents. The intensity is (reversibly) weakened by acids. There is a max. in the fluorescence spectrum at 5950 Å. The fluorescence is shown by degradation products of proteins down to dipeptides, but not by NH₂-acids, and the intensity increases during proteolysis. It is more slowly destroyed by oxidising agents than the coloration, and is unaffected by acids. A. A. L.

Constitution of the keratin molecule. C. RIMINGTON (*Nature*, 1932, 130, 401).—A reply (cf. this vol., 867). L. S. T.

Constitution of the keratin molecule. J. B. SPEAKMAN (*Nature*, 1932, 130, 401; cf. preceding abstract). L. S. T.

Basic amino-acids of crystalline ovalbumin. H. B. VICKERY and A. SHORE (*Biochem. J.*, 1932, 26, 1101—1106).—Cryst. ovalbumin yields after acid hydrolysis histidine 1.42%, arginine 5.39%, and lysine 4.97%. S. S. Z.

Preparation of methionine from caseinogen. N. W. PIRIE (*Biochem. J.*, 1932, 26, 1270—1274). The acid hydrolysate, previously cleared by Pb(OAc)₂, is extracted with BuOH from which methionine is removed by extraction with NaOH. The yield is 1.4%. S. S. Z.

Determination of methionine in proteins. H. D. BAERNSTEIN (J. Biol. Chem., 1932, 97, 663—668).—Zeisel (OMe) procedure gave vals. from 0.54 (arachin) to 5.29% (albumin). The negative results given by the method on 11 NH_2 -acids show that true methionine vals. are obtained. F. O. H.

Sulphur distribution in proteins. H. D. BAERNSTEIN (J. Biol. Chem., 1932, 97, 669—674).—Determinations of the (thiol+disulphide)-S and of the methionine-S of 32 proteins give vals. accounting for $101.5 \pm 6\%$ of the total S, of which the first fraction forms 17.7—84.3% and the second 26.0—90.0%. F. O. H.

Point of attachment of heavy metals to proteins. F. LIEBEN and L. LOWE (Biochem. Z., 1932, 252, 64—69; cf. Ettisch, this vol., 465).—At reactions near to neutral the K in K-caseinogen compound is almost quantitatively replaced by Cu or Ag on addition of CuSO_4 or AgNO_3 . Since the amount of the compound produced by addition of KOH to caseinogen or to serum-albumin is not diminished by previous treatment of the protein with CH_2O , the NH_2 groups do not bind K. W. McC.

Micro-combustion method for carbon and hydrogen determination. P. L. KIRK and A. G. McCALLA (Mikrochem., 1932, 12, 87—97).—Apparatus and procedure are described for combustion of 2—2.5 mg. of substance in O_2 using Mn_2O_3 (prepared by reducing NH_4MnO_4 with MeOH) as catalyst. E. S. H.

Micro-analytical methods in the industrial laboratory. IV. Application of micro-Dumas [method] to substances with small nitrogen content. F. VETTER (Mikrochem., 1932, 12, 102—108).—Using a capillary nitrometer 0.001% N can be determined in org. compounds. E. S. H.

Micro-halogen determination without combustion by precipitation from organic solvents, applicable to substances containing halogen in an easily ionisable form. A. SCHLOEMER (Mikrochem., 1932, 12, 114—116).—Interaction with AgNO_3 — HNO_3 , is effected in EtOAc , AcOH , COMe_2 , EtOH , or MeOH . E. S. H.

Determination of chlorine and bromine in organic substances by combustion in the calorimetric bomb. F. GARELLI and B. SALADINI (Atti R. Accad. Sci. Torino, 1931, 66, 406—409; Chem. Zentr., 1932, i, 2870—2871).—In a modification of Valeur's method, the substance (0.1—0.3 g.) is treated with decalin (0.5—0.8 c.c.) and burned in a calorimetric bomb containing 10 c.c. of aq. NH_3 (d 0.93), the halogen being titrated by Volhard's method. A. A. E.

Determination of sulphur in organic compounds. R. J. ROSSER and F. N. WOODWARD (J.C.S., 1932, 2357—2358).—A modification of Asboth's method (A., 1896, ii, 448), in which a Ni test-tube replaces the crucible, gives trustworthy results with all org. S compounds. J. W. B.

Microanalytical determination of sulphur in organic substances by a volumetric method. A. FRIEDRICH and O. WATZLAWECK (Z. anal. Chem., 1932, 89, 401—411).—The low vals. for S sometimes

given by the method previously described (A., 1929, 1328) are due to incomplete oxidation of SO_2 to H_2SO_4 , even after passing through aq. H_2O_2 . By neutralising before evaporation loss of SO_2 is avoided, and, on subsequent evaporation, the Na_2SO_3 is oxidised to Na_2SO_4 . When adding H_2SO_4 and evaporating, as a preliminary to the NaHSO_4 back-titration, care must be taken that salts of volatile acids do not separate around the edge while unused H_2SO_4 remains at the bottom of the dish. The method is applicable in the presence of Cl and Br, but not in the presence of I. M. S. B.

Determination of propyl alcohol in mixtures of ethyl alcohol and water. O. NOETZEL (Z. Unters. Lebensm., 1932, 64, 288—293).—The sample is adjusted to contain 40 vol.-% of total alcohols and distilled with CrO_3 and H_2SO_4 , the distillate being collected at 0° , and 0.6 c.c. heated for 6 min. at 65° with 3 drops of a 2% solution of vanillin in EtOH and 4 c.c. of fuming HCl . The cool solution is orange if 3% of Pr°OH is present (the limit of the test), reddish-brown for 10%, and deep purple for 20%, and the colour may be matched against a standard mixture or a solution of colloidal Cu ferrocyanide. A similar reaction is given by $\text{CH}_3\text{Pr}^\circ\text{OH}$, which, however, differs in its physical consts. Measurements of n will not distinguish Pr°OH and Pr^βOH in the presence of EtOH and H_2O . J. G.

Determination of ethyl ether in presence of water, ethyl alcohol, and acetaldehyde. A. LALANDE (Bull. Soc. chim., 1932, [iv], 51, 916—921).—An apparatus is described in which the Et_2O is entrained by a current of air or O_2 , freed from EtOH and MeCHO by conc., strongly alkaline K_2MnO_4 (or KMnO_4 ?), and absorbed in acidified aq. $\text{K}_2\text{Cr}_2\text{O}_7$ (the excess of which is determined iodometrically), or, alternatively, determined by combustion with CuO . H. A. P.

Action of ultra-violet light on pyridine. I. New test for some primary amines and pyridine. H. FREYTAG and W. NEUDERT (J. pr. Chem., 1932, [ii], 135, 15—35; cf. A., 1911, ii, 242).—Irradiation of $\text{C}_5\text{H}_5\text{N}$ with light of $\lambda < 300 \mu$ gives rise to *photopyridine*, a yellowish-brown microcryst. solid, which may be isolated by irradiation in EtOH and removal of excess of $\text{C}_5\text{H}_5\text{N}$ with ZnCl_2 . The reaction is accelerated by acids or by solvents that give rise to them on irradiation (COMe_2 , EtOH), and by many inorg. salts, and is retarded or completely inhibited by strong bases, alkali-metal salts, HgCl_2 , CoCO_3 , and NiCl_2 . Photopyridine is decomposed by heat and by cold H_2O into $\text{C}_5\text{H}_5\text{N}$ and unidentified cryst. products. It reacts with primary arylamines to form highly coloured substances, which are in general sensitive to acids and alkalis; this reaction is a sensitive test for $\text{C}_5\text{H}_5\text{N}$ or the amine in question. The red product obtained with $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ is isolated in a cryst. state; it melts with decomp. and formation of a white cryst. sublimate. H. A. P.

Determination of aniline by means of picryl chloride. I. Determination of aromatic amines by means of picryl chloride. II. B. LINKE, H. PREISSECKER, and J. STADLER (Ber., 1932, 65, [B], 1280—1282, 1282—1284).—An approx. 0.1M solu-

tion of NH_2Ph in EtOAc is treated with an equally conc. solution of picryl chloride in the ratio 1 : 1.5 and about 0.1 g. of NaHCO_3 for 15 min. at room temp. After addition of H_2O , the mixture is heated for 15 min. on the water-bath, kept for 3 hr., and filtered. Cl' is determined in the filtrate gravimetrically or volumetrically (Mohr). The reaction is $\text{NH}_2\text{Ph} + \text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_3 + \text{NaHCO}_3 = \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} + \text{NHPH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$.

II. In EtOAc aromatic amines with negative substituents react incompletely or not at all with picryl chloride. *o*- and *p*-Toluidine react quantitatively, whereas *m*-toluidine gives irregular results. *p*-Aminophenol gives low vals., but its Me ether can be determined. *o*- and *p*-Anisidine react quantitatively. *sec*-Amines are almost without action. Both NH_2 groups of benzidine undergo nearly quant. change, but the base is not readily determined by this method owing to the difficultly filterable ppt. $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$ condenses uniformly to the extent of about 97%, whereas the β -compound behaves irregularly.

H. W.

Analysis of hydrazines. Y. G. VENDELSHTEIN (Anilinokras. Prom., 1932, 2, No. 1, 37—39).—Richter's method for determining arylhydrazinesulphonic acids by oxidation with 2 mols. of CuSO_4 gives 68—89% of the total N; quant. vals. are obtained by the use of a 10-fold excess of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in HCl .

CH. ABS.

Detection and determination of phenylalanine. R. KAPPELLER-ADLER (Biochem. Z., 1932, 252, 185—200).—The violet colour of the NH_4 salt of the *diacdinetrocyclohexadienecarboxylic* acid (cf. Meisenheimer, A., 1919, i, 389) produced when phenylalanine (or *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, which is an intermediate product; BzOH is not produced) is nitrated with $\text{KNO}_3 + \text{H}_2\text{SO}_4$ and the product reduced with NH_2OH in aq. NH_3 is used as a basis for the detection and colorimetric micro-determination of these two substances (0.1 mg. of the former in 15 c.c. of H_2O can be determined). The method can be applied to protein hydrolysates, provided that histidine is removed with phosphotungstic acid and tyrosine by oxidation with acid KMnO_4 .

W. McC.

Micro- and histo-chemical identification of putrescine, cadaverine, phenylethylamine, tyramine, and histamine. G. KLEIN and S. D. BOSER (Arch. Pharm., 1932, 270, 374—385).—The following new m.p. for, first, the hydrochlorides, and, secondly, the Bz derivatives, are recorded: putrescine (I), decomp. 315° , m.p. $175\text{—}177^\circ$; cadaverine (II), m.p. 275° , $130\text{—}135^\circ$; histamine (III), m.p. $233\text{—}240^\circ$ (decomp.), $188\text{—}190^\circ$; β -phenylethylamine (IV), m.p.

$205\text{—}206^\circ$, $108\text{—}112^\circ$; and tyramine (V), m.p. $260\text{—}270^\circ$, $169\text{—}171^\circ$. These derivatives cannot be separated by micro-sublimation. The dihydrochloride of (II) can be separated from mixtures by its solubility in Et_2O . The following reagents give characteristic ppts. with the bases stated, even when all five are present in the mixture: AuBr_3 (V); AuI_3 , none; PtI_4 (III); picric acid (III), (IV), and (V); picrolonic acid (I), (II), and (V); trinitroresorcinol (II) and (III) [mixtures of (I) and (II) give mixed crystals]; trinitrobenzoic acid (II); phosphotungstic acid (V). Alcoholic extracts of ergot give with these reagents only the picrate and trinitroresorcinol test for (III). Ergot, freed from fat by CHCl_3 , and then extracted with EtOH etc., gives positive tests for (I), (II), (III), and (V). When treated for 3 hr. with 5% H_2SO_4 at 1.3 atm., ergot gives positive tests for all five bases.

R. S. C.

Adenylic acid and adenine nucleotide. R. KLIMEK and J. K. PARNAS (Biochem. Z., 1932, 252, 392—396).—The pentose residue of adenylic acid is, and of adenine nucleotide of yeast nucleic acid is not, able to form a complex Cu compound such as is obtained with polyhydric alcohols. When the H_3PO_4 of adenine nucleotide is removed, the resulting adenosine (m.p. 229°) readily forms such a complex. The bearing of this reaction on the structure of these substances is discussed.

P. W. C.

Extremely sensitive reaction of caffeine and its application to the local detection of this purine derivative in vegetable tissue. A. MARTINI (Mikrochem., 1932, 12, 109—110).—A characteristic ppt., probably $\text{C}_8\text{H}_{11}\text{O}_2\text{N}_4 \cdot \text{AuBr}_4 \cdot 2\text{H}_2\text{O}$, is formed when 0.1% aq. caffeine hydrochloride is added to 10% HAuCl_4 , followed by saturated aq. NaBr . The test can be made in the vegetable tissue.

E. S. H.

Sensitive micro-chemical reaction of cocaine. A. MARTINI (Mikrochem., 1932, 12, 111).—Characteristic micro-crystals are formed by adding aq. KPbI_3 to aq. cocaine hydrochloride, preferably in presence of COMe_3 . The reaction with KPbBr_3 is less sensitive.

E. S. H.

Reduction indicator. L. MICHAELIS.—See this vol., 1102.

Iodometric determination of purines and their derivatives. M. Z. GRYNBERG (Biochem. Z., 1932, 253, 143—145).—Xanthine, guanine, and uric acid, whether free or after liberation from combination by hydrolysis (but not hypoxanthine, adenine, caffeine, theophylline, or theobromine), can be determined by titration with I.

W. McC.

Biochemistry.

Importance of the time element in determining respiratory metabolism of fishes. N. A. WELLS (Proc. Nat. Acad. Sci., 1932, 18, 580—585).

Respirometry. I. Combined gas burette-interferometer respirometer. W. R. THOMPSON. II. Influence of infra-red radiation on carbon

dioxide respiration of *Drosophila* imagos in dry air. III. Application of refractovolumetric respirometry to the observation of continuous respiratory changes in wet or dry systems. W. R. THOMPSON and R. TENNANT (J. Gen. Physiol., 1932, 16, 5—22, 23—26, 27—31).—I. A respirometer is described by means of which the concn. of O_2 and

CO₂ in a vol. of gas may be determined by interferometric measurements of refractive indices.

II. The R.Q. of *Drosophila* imago is increased when they are exposed to light from an electric lamp. The effects of visible and of infra-red irradiation have been examined.

III. The O₂ uptake and CO₂ output of *Drosophila* imago have been followed in dry and moist conditions. The mean R.Q. is approx. the same in both states. W. O. K.

Sulphur content of human hæmoglobin. Z. ASZÓDI (Biochem. Z., 1932, 252, 387—391).—A table summarises the S contents of the hæmoglobins of 32 hospital cases. The vals. vary from 0.60 to 0.69%, mean val. 0.65%. P. W. C.

Hæmoglobin-building properties of soya-bean products. W. H. ADOLPH and H. C. KAO (Chinese J. Physiol., 1932, 6, 257—263).—Soya-bean products had a curative action on rats rendered anæmic by an exclusive diet of cows' milk. Analyses of these products indicated an appreciable Fe and Cu content. The rate of recovery appeared to be approx. proportional to the Fe and Cu content of the ingested food, but it could not be said that the soya-bean products owed their curative activity to the presence of these metals. R. N. C.

Effect of chlorophyll on formation of hæmoglobin. S. AOKI (Sei-i-kwai Med. J., 1931, 50, No. 5, 1—11).—Injection of chlorophyll into the normal rabbit does not affect the blood-hæmoglobin, but in experimental (particularly NHPh·NH₂) anæmia rapid recovery of hæmoglobin occurs. CH. ABS.

Influence of pyrrole nucleus in the formation of hæmoglobin. L. VILLA (Annali Chim. Appl., 1932, 22, 515—517).—2-Acetopyrrole was dissolved in a solution of known Fe content. Once a day 2-c.c. doses (corresponding with 0.05 g. of ferro-pyrrole compound) were injected intramuscularly into 25 patients suffering from different forms of anæmia. Except in 4 cases, after 20—30 days' treatment the hæmoglobin content of the blood increased 30—100%. O. F. L.

Factors influencing the blood-benzidine reaction as applied to the micro-determination of hæmoglobin. W. D. MCFARLANE and R. C. M. HAMILTON (Biochem. J., 1935, 26, 1050—1060).—Conditions under which hæmoglobin can be determined in small amounts of blood are described. S. S. Z.

Improved benzidine test for blood in urine and other clinical material. J. INGHAM (Biochem. J., 1932, 26, 1124—1126).—"Hyperol," a dry stable powder containing 35% H₂O₂, can be used for blood tests in clinical laboratory practice. S. S. Z.

Oxygen affinity of chlorocruorin. H. M. FOX (Proc. Roy. Soc., 1932, B, 111, 356—363).—The O₂ dissociation curves of chlorocruorin in the diluted blood of the worm *Spirographis spallanzanii* determined spectrophotometrically over a p_{H} range from 7.35 to 8.2 and at 10—26° are sigmoid in type and similar to those of hæmoglobin. At p_{H} 7.35 and 26° half saturation is obtained at an O₂ pressure of 29 mm. in presence of 40 mm. CO₂. In equilibrium

4 H

with air at atm. pressure approx. 96% saturation is reached. W. O. K.

Mol. wts. of the blood-pigments of *Arenicola* and of *Lumbricus*. T. SVEDBERG and I. B. ERIKSSON (Nature, 1932, 130, 434—435).—The mol. wt. of the blood-pigment of *Arenicola*, determined by the sedimentation velocity method, is of the order $n \times 10^6$. The sedimentation const. is of the same order as that of *Octopus* and *Helix* hæmocyans, but is different from that of vertebrate hæmoglobin. There is a small difference between the consts. of the blood-pigments of *Arenicola* and *Lumbricus*. Hæmoglobin with its relatively low mol. wt. may be strictly confined to the blood of vertebrates, and the respiratory pigments of high mol. wt. to that of invertebrates. L. S. T.

Physico-chemical properties of hæmocyanins. II. J. ROCHE (Bull. Soc. Chim. biol., 1932, 14, 1032—1043).—The hæmocyanin from *Helix pomatia* has an isoelectric point at p_{H} 5.2, acts as a monacid base of p_{K} 3.2, and as a tribasic acid of p_{K} 10.5, 8.6, and 7.6, the last changing to 7.0 in oxyhæmocyanin. The hæmocyanins from different sources are different, but respiratory chromoproteins all appear to have an acid function at about p_{K} 7 which varies with the state of oxidation. A. A. L.

Influence of hydrochloric acid on the combination of oxygen with the hæmocyanin of *Limulus polyphemus*. A. C. REDFIELD, E. D. MASON, and E. N. INGALLS (J. Cell. Comp. Physiol., 1932, 1, 93—112).—The hæmocyanin reacts with HCl to produce a colourless compound which does not combine with dissociable O₂. Its formation is not the result of the removal of Cu from the hæmocyanin mol. Equilibrium between HCl and hæmocyanin depends on the formation of a salt in which only a proportion of the total basic groups (possibly those of the radical associated with O₂ transport) is involved. A. G. P.

Spectrochemical analysis of serum-pigments. P. MÜLLER (Klin. Woch., 1932, 11, 189—192; Chem. Zentr., 1932, i, 2198).—All normal sera show the violet hæmoglobin bands. Spectra of hæmoglobin, lipochrome, and bilirubin are distinguished, and results are given for sera of static icterus, hæmolytic icterus, pernicious anæmia, and Biermer's anæmia. The yellow colour of blood-serum is due to hæmoglobin. A. A. E.

Composition of membrane of red blood-corpuscles. T. P. CHOU (Chinese J. Physiol., 1932, 6, 277—280).—Analysis of the membrane, free from sol. material, showed a composition of 50% protein and 46% lipins. Phosphatide calc. as lecithin amounted to 27%, and total cholesterol to 14%. R. N. C.

Catalase content of white blood-corpuscles. K. IGLAUER (Magyar Orvosi Arch., 1932, 33, 135—145; Chem. Zentr., 1932, i, 2961).—The greatest catalase activity (3—4 times that of erythrocytes) is shown by polynuclear neutrophile leucocytes; myelocytes show less, and lymphocytes and myeloblasts only slight activity. A. A. E.

Chemical changes in blood during preservation. I. S. BALACHOVSKI, F. GINSBURG, R. FARBEROVA, T. PALITZINA, and S. RZHUINA (Biochem. Z., 1932, 252, 370—377).—During preservation of blood the sugar content, the osmotic resistance of the erythrocytes, and the power to unite with O_2 tend to decrease, the inorg. P content to increase, whilst the catalase and residual N contents are unaffected. Blood may, however, be kept without change for a long time by addition of citrate or physiological saline. P. W. C.

Constitution of the fractions of human serum-protein. K. LANG and A. BRAUN (Arch. exp. Path. Pharm., 1932, 167, 708—716).—The proteins of normal and pathological sera were fractionated and the contents of arginine (I), tyrosine (II), tryptophan (III), and cystine (IV) determined. With (II), (III), and (IV), but not with (I), the proportions are related to the distribution of the protein fractions. The abs. content of any one acid varies in different persons with the same disease by as much as 50%; hence the accuracy of the refractometric determination of serum-proteins appears doubtful. Pathological sera show characteristic abnormalities in composition. F. O. H.

Colorimetric determination of glutathione in blood and tissues. B. BRAIER and A. D. MARENZI (Compt. rend. Soc. Biol., 1932, 109, 319—321; Chem. Zentr., 1932, i, 2872).—Deproteinised ($CCl_3 \cdot CO_2H$) blood, plasma, or tissue-extract filtrate (2 c.c.) (glutathione 0.7—2.8 mg.) is shaken with 20% Na_2SO_3 (0.2 c.c.) and then treated with 20% Li_2SO_4 (0.2 c.c.), 20% Na_2CO_3 (2 c.c.), and Folin-Marenzi phosphotungstic acid reagent (2 c.c.). After 4 min. the solution is diluted to 25 c.c. with 2% Na_2SO_3 and compared within 10 min. with a similarly treated solution of cystine (0.4 mg. in 2 c.c.). A. A. E.

Determination of residual nitrogen in blood by means of the step photometer. C. URBACH (Biochem. Z., 1932, 252, 406—413).—The N content of deproteinised blood is determined by direct Nesslerisation using the step photometer. P. W. C.

Total nitrogen of the blood-plasma of normal albino rats at different ages. P. P. SWANSON and A. H. SMITH (J. Biol. Chem., 1932, 97, 745—750).—The total plasma-N increases from 0.81 (21—28 days) to 1.22 g. per 100 c.c. (360 days), the greatest increase being during the first 50 days. A slight but definite temporary decrease occurs at an age of approx. 100 days, and is probably correlated with the onset of sexual maturity. F. O. H.

Colorimetric micro-determination of labile blood-iron. G. BARKAN (Klin. Woch., 1932, 11, 598—599; Chem. Zentr., 1932, i, 2871—2872).— Fe^{++} and Fe^{+++} are determined with the aid of Et_2O free from, or containing, peroxide. A. A. E.

Volumetric determination of sodium in blood-serum. S. RUSZNYAK and E. HATZ (Biochem. Z., 1932, 252, 414—419).—The serum is deproteinised by $CCl_3 \cdot CO_2H$ or by heating with H_2SO_4 — HNO_3 , the PO_4^{---} removed by treatment with alcoholic $Zn(OAc)_2$, and the Na pptd. as $(UO_2)_3ZnNa(OAc)_9 \cdot 6H_2O$. This is finally determined by boiling with 0.05M- Na_2HPO_4

and titrating the excess with uranyl acetate using cochineal as indicator. P. W. C.

Obtaining representative samples of blood for inorganic phosphorus in dairy heifers. H. O. HENDERSON and A. H. VAN LANDINGHAM (J. Dairy Sci., 1932, 15, 313—319).—Considerable daily variation in the inorg. P content of the blood of heifers is recorded. Representative samples are obtained by alternate-day sampling over a period of 12 days. No appreciable changes in the inorg. P content occurred during the storage of blood at 2° for 2 weeks. A. G. P.

Calcium and phosphorus contents of the blood of pigs. E. H. HUGHES and H. HART (Proc. Amer. Soc. Animal Produc., 1932, 24, 274—277).—The normal pig's serum-Ca is slightly >12 mg. per 100 c.c. of blood; the inorg. P is 8—9 mg. The serum-Ca of brood sows was materially reduced by feeding with a ration low in Ca and vitamin-A and relatively high in P. CH. ABS.

(a) Calcium content of the blood of dogs during twenty-four hours. (b) Calcium content of the blood of dogs kept in cages. (c) Variation in the calcium content of dogs in a state of inanition. (d) Calcium content of the arterial blood of dogs according to age, sex, and weight. J. CHEYMOL and A. QUINQUAUD (Bull. Soc. Chim. biol., 1932, 14, 1044—1045, 1046—1047, 1048—1050, 1051—1066).—(a) The variation is small.

(b) The variations were slightly greater than the daily variations, and were independent of changes in wt., which first decreased and then increased.

(c) The Ca content falls considerably with time, after passing through a min.

(d) The content falls with age, is usually slightly higher in females, and is the higher the heavier is the animal. A. A. L.

Effect of intravenous injection of glycine on the serum-calcium. N. MORRIS, J. B. RENNIE, and S. MORRIS (Brit. J. Exp. Path., 1932, 13, 132—134).—With rabbits and goats the serum-Ca is diminished. Comparatively little of the $NH_2 \cdot N$ remains in the blood. Return to normal serum-Ca vals. is probably due to deamination of the glycine and release of Ca from the tissues. Excessive NH_2 -acid production after parathyroidectomy may play a part in lowering serum-Ca. CH. ABS.

Determination of lactic acid and ketonic substances in the same small amount of blood. R. STURM (Arch. exp. Path. Pharm., 1932, 167, 654—659).—The blood (2—4 c.c.) is deproteinised and the lactic acid determined by a modified method of Brehme and Brahdy (A., 1926, 1282). Following the iodometric titration for $MeCHO$, the distillate is oxidised by Na_2O_2 and the unchanged $COMe_3$ distilled over into aq. $NaHSO_3$, which is finally titrated iodometrically. F. O. H.

Distribution of glucose in human blood. E. M. MACKAY (J. Biol. Chem., 1932, 97, 685—689).—Glucose occurs in the same concn. in the H_2O contained in the plasma and erythrocytes of freshly-drawn blood. Addition of glucose after withdrawal

is followed by a simple diffusion leading again to equality of concn. F. O. H.

Lipins and immunity. F. M. MIRANDA (Los prog. clin., 1930, 38, No. 8).—Organs have a sp. serological val. Antibodies produced by pancreas extract are related to the lipins of the organ; similar results were obtained with the thyroid, liver and brain (ox), and kidney (man). The testicle is not sp.; proteins of the ovary are only slightly sp. and the lipins not at all. The adrenal cortex is sp. with regard to the lipins applied in the rat, but of insignificant proteinic sp. action in the rabbit. Brain, liver, and thyroid show related lipins. CH. ABS.

Immunological properties of alkali-treated proteins. L. R. JOHNSON and A. WORMALL (Biochem. J., 1932, 26, 1202—1213).—Alkalis have a more marked destructive effect than acids on the power of horse-serum proteins to react with antibodies to the untreated serum-proteins. Up to about p_H 11 there is, however, very little loss of antigenic properties in 24 hr. at 19°. Iodination is not as effective in regenerating antigenic properties in alkali-treated proteins as is nitration. S. S. Z.

Animal tissue-proteases. X. Appearance of defence enzymes in blood-serum of rabbits. H. KLEINMANN and G. SCHARR (Biochem. Z., 1932, 252, 343—361).—The cathepsin and trypsin contents of normal rabbits' serum is very const., varying by not more than $\pm 5\%$ for cathepsin and $\pm 7\%$ for trypsin. The vals. are the same when taken either immediately after or 14 hr. after food, and are uninfluenced by intravenous or subcutaneous injection of solutions at blood- p_H of foreign proteins, e.g., caseinogen, edestin, and horse serum. P. W. C.

Fraction- and species-specificity of serum-proteins. I. GYORFFY (Magyar Orvosi Arch., 1932, 33, 147—158; Chem. Zentr., 1932, i, 2969).—Relative species-specificity of horse serum-protein fractions is indicated. A. A. E.

Analysis of mixtures of antigens by adsorption. H. RUDY (Biochem. Z., 1932, 253, 204—214).—The components of two-component mixtures of antigens can be completely or almost completely separated by treatment with an appropriate adsorbent [$Al(OH)_3$, $CaCO_3$, kaolin, etc.] which removes one component. The latter can then be separated from the adsorbent by elution (elution of *S. pallida* antigen has not yet succeeded). The method has been applied with one natural and four artificial mixtures (brain, Wassermann, Forssmann heterogenetic, and *S. pallida* antigens used). W. McC.

Specific substance of [blood-]group. A. K. FREUDENBERG, H. EICHERL, and W. DIRSCHERL (Naturwiss., 1932, 20, 657—658).—From the urine of blood-group A a highly conc. prep. of the sp. substance has been obtained, 0.02×10^{-6} g. of which can be detected serologically; it retains 80% of the original activity of the urine, is laevorotatory, contains 4—5% N, reduces Fehling's solution after boiling with acid, and is probably a polysaccharide. A. C.

Serological differentiation between the anterior and posterior pituitary lobes. E. WITTEB-

SKY and H. O. BEHRENS (Z. Immunität., 1932, 73, 415—428; Chem. Zentr., 1932, i, 2058).—In rabbits suspensions of the anterior pituitary lobe produce only species-sp. antibodies. The posterior lobe produces antisera which react only with their homologous antigen, with brain extract (slightly), and with spinal cord extract (very slightly). A. A. E.

Osmotic relationships in the hen's egg, as determined by colligative properties of yolk and white. E. HOWARD (J. Gen. Physiol., 1932, 16, 107—123).—The osmotic pressures of the white and yolk of a hen's egg determined by the direct f.-p. method, by dialysis, or by v.-p. measurements are equal. The yolk and white are in osmotic equilibrium, and no vital activity in the membrane to maintain the osmotic pressure need be postulated. Certain experimental difficulties may account for the abnormally high vals. for the osmotic pressure of the yolk previously recorded. W. O. K.

Alkaline hydrolysis of lecitho-vitellin with particular reference to the separation of an organic fraction containing iron and copper. W. D. McFARLANE (Biochem. J., 1932, 26, 1061—1071).—During hydrolysis there is a gradual evolution of NH_3 and a steady increase in the amount of non-protein-N, but no increase in free NH_3 groups. CCl_3CO_2H , or neutralisation with $AcOH$, ppt. a protein which contains about 50% of the lecitho-vitellin-N, but does not contain Fe or P. Part of the non-protein-N is contained in a fraction pptd. from acid solution by $Pb(OAc)_2$. Two different samples of lecitho-vitellin contained practically the same amount of Cu (0.0033%) and Fe (0.046%). S. S. Z.

Intra-uterine development in cattle. W. W. YAPP (Proc. Amer. Soc. Animal Produc., 1932, 24, 133—136).—The liver and spleen of bovine foeti contained 0.0065—0.201% Fe and 0.00171—0.00315% Cu; very little Ca was deposited before the sixtieth day, the oldest foeti containing most (1.43%). The P content was about half the Ca content. CH. ABS.

Presence of potassium, sulphur, magnesium, manganese, arsenic, and phosphorus in the foetal liver of vertebrates. G. ROUSSEL and DUFOUR-DEFLANDRE (Compt. rend. Soc. Biol., 1931, 106, 1118—1119; Chem. Zentr., 1932, i, 1917).—In oxen and sheep the above elements (little Mn, much P) were found. A. A. E.

Combined creatine in frog muscle. S. OCHOA, F. GRANDE, and M. PERAITA (Biochem. Z., 1932, 253, 112—118).—In oxygenated frog muscle (especially during rest) the amount of combined creatine is sometimes greater than that corresponding with the phosphagen-phosphate content. On the average 140 mols. of the total creatine of the muscle are found for each 100 mols. of directly determinable phosphate. W. McC.

Denaturation of proteins in muscle juice by freezing. D. B. FINN (Proc. Roy. Soc., 1932, B, 111, 396—411).—Denaturation of protein occurs when fresh ox-muscle juice, expressed after the onset of rigor, is stored at temp. below its f.p., the max. attained after a period of 25—40 days at -2° to -3° reaching about 20% of the total coagulable N.

When the muscle juice is adjusted to various p_H vals., the denaturation which occurs on freezing is low at p_H 6.0—7.0 and increases rapidly on the acid side of p_H 6.0. On the acid side of p_H 6.0 there exists a certain salt concn. at which max. denaturation occurs, which at p_H 5.2 is 0.8*M*. At -2° to -3° the salt concn. in muscle-juice is 0.8*M* and the $[H^+]$ is on the acid side of p_H 6.0, whilst at temp. below -3° the p_H tends to exceed 6.0 and the salt concn. is $>0.8M$. The protein fraction denatured by freezing is probably part of the myogen fraction of von Furth (Ergebn. Physiol., 1919, 17, 382). W. O. K.

Glycogen distribution in Urodela and seasonal variation. I. CHUNG (J. Chosen Med. Assoc., 1931, 21, 569—603).—The glycogen contents of all the organs of *Diemictylus pyrrhogaster* are generally low and scarcely change during different seasons, although the central nervous system, testicles, and ovaries show slight increases in the winter. CH. ABS.

Reducing substances in brain. I. Distinguishing the reducing power of the sugar from that of the creatinine. Determination of true blood-sugar. II. Carbohydrate metabolism in brain. Sugar content of the blood of rabbits treated in various ways. H. MARUYAMA (Biochem. Z., 1932, 253, 161—171, 172—184).—I. Since glucose (also galactose, fructose, arabinose), creatine, and creatinine exhibit different degrees of stability towards boiling dil. solutions of alkali hydroxides and carbonates, it is possible by methods described to determine sugar and creatinine in brain, spinal cord, blood, and other biological material. Human blood contains 64.7 mg. of true sugar per 100 c.c.

II. Rabbit brain immediately after death contains free sugar, which rapidly disappears, and glycogen. The post-mortal increase in the amount of lactic acid in the brain results from the disappearance of the sugar and the reduction in the glycogen content. The lactic acid, creatine, and creatinine contents of EtOH extracts of the brain, its content of glycogen, the sugar content of rabbits' blood, and the effect on these vals. of fasting, of administration to the rabbits of luminal, strychnine, or insulin, and of anaesthesia with Et₂O have been determined. W. McC.

Mechanism of oxidation in sympathetic [nervous] tissue. S. HUSZAK (Biochem. Z., 1932, 252, 397—400).—Sympathetic ganglia and the suprarenal medulla (different from all the other tissues investigated, e.g., muscle, liver, kidney, suprarenal cortex, sensory ganglia, grey matter of brain) do not contain any cytochrome-respiration enzyme (indophenol-oxidase system). P. W. C.

Existence of paracrystals and their distribution in cerebrosides and phosphatides as plasmatic components. F. RINNE (Kolloid-Z., 1930, 60, 288—296).—A description of the forms of growth of kersin, nervon, lecithin, and sphingomyelin. E. S. H.

Determination of thymonucleic acid by means of fuchsin-sulphurous acid. T. CASPERSSON (Biochem. Z., 1932, 253, 97—111).—The acid, after hydrolysis, is determined by a modification of the method of Widstrom (A., 1928, 1393). Two con-

current reactions take place between the reagent and the hydrolysate. W. McC.

Occurrence of melanogen, particularly o-dihydroxybenzene-substances, in the organism. II. H. SCHMALFUSS and H. BARTHEMEYER [with W. HINSCH] (Z. indukt. Abstamm. Vererbungslehre, 1931, 58, 332—371; Chem. Zentr., 1932, i, 2191).—There is no direct relationship between the colour of the case of beetles and the content of o-C₆H₄(OH)₂-substances (I), although in Tenebrionids the white portions are free from such substances. In all insects the more is present, the harder is the case. The substance is formed together with chitin, but their origins are unconnected. Non-insects cannot form excess of (I), but form excess of melanogen as do insects. A. A. E.

Detection of small amounts of formic acid in blood and tissues, especially in skin. H. DROLLER (Z. physiol. Chem., 1932, 211, 57—64).—A method is described for the colorimetric determination of HCO₂H in biological material. It detects 0.04 mg. in 5—10 c.c. aq. solution. It depends on reduction of the protein- and sugar-free tissue filtrates with Mg ribbon and 25% HCl in presence of fuchsin-SO₂, with which the CH₂O formed gives a bluish-violet colour. J. H. B.

Isolation of chemically unstable substances from animal tissues. M. G. EGGLETON and P. EGGLETON (Nature, 1932, 130, 275).—A method using Na₂SO₄ is described for obtaining a protein-free solution of the H₂O-sol. constituents of muscle in a conc. form. Anserine has been obtained from the muscles of sheep, goats, and rabbits, and carnosine from ox and frog. L. S. T.

Mallory's connective tissue stain following hæmatoxylin. S. WEISS (Stain Tech., 1932, 7, 131—133).—The combination of these stains is useful in bringing out nuclei, as well as in differentiating tissue. H. W. D.

Determination of milk-proteins by formaldehyde titration. G. H. PYNE (Biochem. J., 1932, 26, 1006—1014).—The vals. obtained by the method as hitherto used are composite, determined mainly by the protein of the milk, but affected in various directions by both colloidal and sol. phosphates, to an extent which depends on the type of alkali used in the titration. The disturbing effects of both classes of phosphate can be avoided by treating milk with an oxalate prior to titration. S. S. Z.

Absorption of milk precursors by the mammary gland. V. Physico-chemical aspects of milk secretion. J. H. BLACKWOOD and J. D. STIRLING (Biochem. J., 1932, 26, 1127—1137).—Analytical data for the composition and yield of milk from six cows do not support the view that milk consists of a conc. and transformed blood-plasma minus colloids; they are more in consonance with the hypothesis of selective absorption of milk precursors at the membranes separating the secreting cells from the blood supply. According to this theory, milk secretion does not require the expenditure of any energy by the gland cells other than that necessary for the synthesis of milk constituents. S. S. Z.

Effect of maize oil on milk and butter-fat production and on the composition of butter-fat in the dairy cow. T. S. SUTTON, J. B. BROWN, and E. W. JOHNSON (*J. Dairy Sci.*, 1932, 15, 209—211).—Ingestion of 1 lb. of maize oil per day did not affect the milk yield or the % of fat in milk, but markedly changed the composition of the butter-fat. The fatty acids were more unsaturated and of higher mean mol. wt. The sol. volatile acids decreased.

A. G. P.

Effect of cod-liver oil in the ration on the quantity and quality of cows' milk. W. E. PETERSON (*J. Dairy Sci.*, 1932, 15, 283—286).—Addition of cod-liver oil (5 oz. daily) to the ration reduced the fat content of the milk without affecting the quantity of milk produced.

A. G. P.

Effect of thyroidectomy alone and in conjunction with treatment with extract of the anterior lobe of the pituitary gland or with placenta extract and corpus luteum on milk secretion in goats. T. VON FELLEBERG and F. GRÜTER (*Biochem. Z.*, 1932, 253, 42—63).—In the milk of normal cows and goats the ratio $P_2O_5 : CaO$ varies but slightly and is independent of the abs. content of the substances concerned. The ratio, which depends on the function of the thyroid gland, is reduced by administration of cod-liver oil, but increased by that of white cabbage. Extirpation of the thyroid gland results in moderate decrease in P content of the milk, very great increase in the Ca, and increase in the Cl contents. It also results in reduction in the alkalinity of the ash of the milk and alters the fat content. Administration of extracts of the anterior lobe of the pituitary gland after extirpation of the thyroid results in increase in the mineral content of the milk, but does not alter the $P_2O_5 : CaO$ ratio, whilst it increases the Cl content and reduces the alkalinity of the ash. Administration of foetal placenta extract or of this extract together with corpus luteum before the extirpation does not alter the effects of the latter.

W. McC.

Milk of cows in heat. A. MEYER (*Z. Unters. Lebensm.*, 1932, 64, 235—250).—Analytical data of samples taken twice daily for several consecutive days before and after the beginning of heat are tabulated for 14 cows. A fall and rise in quantity followed by a fall to normal was observed in 9 cases, and in the course of 3 days the fat content decreased and then returned to normal. Acidity, caseinogen/ (albumin+globulin), and coagulation capacity in the fermentation test decreased, conductivity, f.p., and catalase val. increased (cf. B., 1931, 315), n ($CaCl_2$ -serum) showed slight fluctuations, and solids, lactose, ash, and total protein did not change. Except for the fluctuations (0.4—1.2%) in fat content, these variations are masked on admixture with 80% of normal milk.

J. G.

Isolation from bile of a pigment having a direct Van den Bergh reaction. W. J. GRIFFITHS (*Biochem. J.*, 1932, 26, 1155—1163).—The pigment, cholebilirubin, $C_{32}H_{50}O_{11}N_2$, was prepared by pptg. from alkaline solution of the Et_2O - and $CHCl_3$ -extracted dried bile with $COMe_2$, extracting the ppt.

with 80% $COMe_2$, and pptg. the $COMe_2$ product by acid from its aq. solution.

S. S. Z.

Gall-bladder function. VIII. Fate of bile pigment in hepatic bile subjected to gall-bladder activity. C. RIEGEL, C. G. JOHNSTON, and I. S. RAVIDIN (*J. Exp. Med.*, 1932, 56, 1—11).—In dogs bile pigment is not absorbed from the gall-bladder bile. Cholesterol is probably not normally secreted in the gall-bladder.

CH. ABS.

Anavenoms. VII. Paravenoms. M. ARTHUS (*J. physiol. path. gén.*, 1932, 30, 75—86).—Cobra venom (1%) in $CaCl_2$ (1%) immunises rabbits against the venom. Venoms treated with $CaCl_2$ are "paravenoms" in the class of anavenoms.

CH. ABS.

Secretion of urine in man. C. BRUNNER (*Biochem. Z.*, 1932, 253, 119—136; cf. Descombes, this vol., 535).—In human urine the excretion of creatinine is parallel with that of sulphate. Confirmation is thus provided for the theory of Brandt-Rehberg. When the sulphate content of the blood is calc. from that of the urine in accordance with the theory, vals. in agreement with those in the literature are obtained.

W. McC.

Luminescence analysis of urine. Y. YONEYAMA (*Z. ges. exp. Med.*, 1931, 76, 680—688; *Chem. Zentr.*, 1932, i, 2872).—Urea, uric acid, NH_3 , $NaCl$, and phosphate exhibit no luminescence in ultra-violet light, whether alone or in admixture. Urobilin in $EtOH$ (acid) gives a deep reddish-brown, or (ammoniacal) yellowish-green; in NH_3 - $EtOH$ - $ZnCl_2$ it is light green. Uroerythrin in $EtOH$ (acid) is yellowish-red, or (alkaline) green; after oxidation with $KMnO_4$ it is greyish-white. Haematoporphyrin in $EtOH$ (acid) is dark pinkish-red; urochrome in H_2O (acid or alkaline) is yellowish-white, bilirubin in $EtOH$ (neutral) is deep yellow, biliverdin in $AcOH$ is greenish-black, indirubin in Et_2O is bluish-white. Indigotin suspension is dark olive-green; after reduction with $Na_2S_2O_4$ it is opaque greenish-blue.

A. A. E.

Determination of total nitrogen in urine by the step photometer. C. URBACH (*Biochem. Z.*, 1932, 252, 292—304).—The method uses 1 c.c. of urine, distillation and titration are avoided, and the accuracy is of the same order as with the macro-Kjeldahl process.

P. W. C.

Direct colorimetric determination of urea in urine. J. F. BARRETT and E. B. JONES (*Biochem. J.*, 1932, 26, 1246—1250).—Interfering substances are removed from the urine by $FeCl_3$ and $NaHCO_3$ and the urea is pptd. from the filtrate by xanthhydrol. The ppt. is centrifuged in presence of $BaSO_4$ and its N content determined colorimetrically after micro-Kjeldahl digestion.

S. S. Z.

Distribution of organic acids in human urine. M. LAFARGUE (*Bull. Soc. Chim. biol.*, 1932, 14, 1017—1025).—Fatty acids up to C_5 are determined after acidifying with tartaric acid by distillation in vac. at 40—45°, and titration of the distillate. CO_2 is first removed from urine of $p_H > 5.8$ by application of a vac. at room temp. after acidifying. Hippuric and lactic acids are determined in the remainder of the org. acids extracted as previously described (A., 1931,

1082). The composition of the acids in normal urine is discussed. A. A. L.

Determination of small quantities of oxalic acid [in urine]. E. C. DODDS and E. J. GALLIMORE (Biochem. J., 1932, 26, 1242—1245).—By preliminary esterification and distillation the $\text{H}_2\text{C}_2\text{O}_4$ in urine is freed from interfering substances. It can then be pptd. as CaC_2O_4 . S. S. Z.

Equol, a new inactive phenol isolated from the ketohydroxyœstrin fraction of mare's urine. G. F. MARRIAN and G. A. D. HASLEWOOD (Biochem. J., 1932, 26, 1227—1232).—*Equol*, $\text{C}_{15}\text{H}_{12}\text{O}(\text{OH})_2$, m.p. 189—190.5°, $[\alpha]_{5461} -21.5^\circ$ [*Me*₂ ether, m.p. 89°; *diacetate*, m.p. 122.5°; *dibenzoate*, m.p. 187—189° and 223.5—225° (liquid crystal formation)], was prepared by distillation of the ketohydroxyœstrin fraction at 160—180°/0.01—0.03 mm. subsequent to distilling at 100—110°. S. S. Z.

Determination of uric acid in poultry excrement. K. SUZUKI and A. NISHIZAKI (J. Agric. Chem. Soc. Japan, 1931, 7, 507—514).—The dry material (1 g.) is boiled with H_2O (20 c.c.) for 1 min.; conc. HCl (5 c.c.) is added, boiling and stirring being continued for a few sec. After 12 hr. (cold) the mixture is filtered; the residue is washed with cold H_2O , 90% EtOH , and Et_2O , and then boiled for several min. with H_2O (20 c.c.). Aq. NH_3 (5 c.c.) is added, and after 1 hr. at room temp. the solution is evaporated and the residue heated at 100° for several hr. Boiling with 5% HCl (20 c.c.) for 1 min. again liberates uric acid, which is collected from the cold liquid and washed with cold H_2O . The filtrate and washings are evaporated to about 10 c.c. and then diluted with abs. EtOH to 100 c.c., 50 c.c. being treated with a slight excess of dil. alcoholic KOH and the NH_3 distilled with steam into standard H_2SO_4 . The quantity of uric acid is calc. from that of NH_3 . The error is 0.5%. CH. ABS.

Content of reduced glutathione in tissues of rabbits in acidosis and alkalosis. S. TATSUZAWA (Sci-i-kwai Med. J., 1931, 56, No. 11, 70—86).—When neutral phosphate is given orally, only the heart (slight increase) shows a change in glutathione content. In alkalosis produced by NaHCO_3 , Na_2HPO_4 orally, or subcutaneous injection of O_2 or N_2 the adrenal-glutathione is markedly increased; acidosis produced by NaH_2PO_4 (orally) is accompanied by a similar increase. Vals. for alkali reserve, urinary pH , $\text{NH}_3\text{-N}$, and total N are recorded. CH. ABS.

Catalase and glutathione content of red blood-corpuscles in experimental anaemia. E. BACH and B. KORPASSY (Klin. Woch., 1931, 10, 2312; Chem. Zentr., 1932, i, 1677).—In rabbits with experimental anaemia the red blood-corpuscles contained a relatively increased amount of catalase and glutathione, possibly connected with increased respiration. A. A. E.

Tissue factor (glutathione) which affects the oxygen tension of venous blood in normal and (veneselected) anaemic rabbits. G. LITARCZEK, H. AUBERT, I. COSMULESCO, and B. NESTORESCO (Compt. rend. Soc. Biol., 1931, 106, 110—112; Chem. Zentr., 1932, i, 2341).—It is assumed that in

the erythrocytes there is between the glutathione and haemoglobin an equilibrium such that the O_2 affinity of the latter or its dissociation curve represents a resultant of the activities of the oxido-reduction system haemoglobin-glutathione. A. A. E.

Extrinsic (deficiency) factor in pernicious and related anaemias. M. B. STRAUSS and W. B. CASTLE (Lancet, 1932, 223, 111—115).—The extrinsic factor essential for the sp. reaction with the intrinsic factor of normal human gastric juice in the production of haemopoiesis in pernicious anaemia is a substance closely related to, if not identical with, vitamin-B₁₂. L. S. T.

Autolysed liver therapy in pernicious anaemia. W. F. HERRON and W. S. McELROY (Science, 1932, 76, 127). L. S. T.

Is there a relation between ergosterol and calcification of the aorta in human atherosclerosis? R. SCHONHEIMER (Z. physiol. Chem., 1932, 211, 65—68).—In the fat from atherosclerotic aortae vitamin-D could not be detected. A substance with absorption band at 238 μ was present. J. H. B.

Glycaemia in cachexia of nurslings. E. JASO (Amer. J. Dis. Children, 1932, 43, 1051—1061).—The blood-sugar of under-nourished infants is up to 43% lower than the normal val. CH. ABS.

Production of cancer by pure hydrocarbons. I. J. W. COOK, I. HIEGER, E. L. KENNAWAY, and W. V. MAYNEORD. II. J. W. COOK (Proc. Roy. Soc., 1932, B, 111, 455—484, 485—496).—I. Of all the polycyclic hydrocarbons, composed only of C_6 rings, tested, only 1:2:5:6-dibenzanthracene and some closely related compounds have produced cancers. In a very pure state (method of purification given) this substance shows undiminished carcinogenic power. Other impure hydrocarbons have produced tumours, but the active substances have not been isolated.

II. 6-*iso*Propyl-1:2-benzanthracene, m.p. 131—132°, is carcinogenic together with other compounds containing the 1:2:5:6-dibenzanthracene ring. Mol. structure consisting of new rings attached to the 1:2- and 5:6-anthracene positions is particularly efficacious in promoting carcinogenic activity. H. G. R.

Inhibition of enzymes by carcinogenic compounds. E. BOYLAND (Nature, 1932, 130, 274—275).—The oxidation of lactate by lactic dihydrogenase of yeast or muscle is inhibited by dil. C_6H_6 or PhMe solutions of certain hydrocarbons exposed to air and light. Carcinogenic hydrocarbons, e.g., 1:2:5:6-dibenzanthracene and 5:6-cyclopenteno-1:2-benzanthracene, have a greater effect than anthracene, 1:2-benzanthracene, or chrysene. The inhibiting factor may be an *o*-(OH)₂-derivative. L. S. T.

Growth(-promoting) substance of malignant tumours. E. MASCHMANN (Naturwiss., 1932, 20, 721—722).—Mouse and fowl sarcoma and mouse carcinoma contain a substance which promotes growth in *Avena coleoptiles*, and the amount is greater in rapidly growing than in necrotic tumour tissue. It is a thermostable weak acid with aliphatic ethylenic

linkings, sol. in H_2O , $MeOH$, $EtOH$, $COMe_3$, and Et_2O , insol. in light petroleum and C_6H_6 . It also occurs in the livers of cancerous and healthy mice, fowls, and fowl embryos, and is closely related to, if not identical with, rhizopin (A., 1931, 1091) and auxin (this vol., 661). A. C.

Comparison of the reducing power of some typical transplantable tumours and of tumours produced by filterable viruses. E. S. G. BARRON (J. Exp. Med., 1932, 55, 829—835).—The tissues of Rous chicken sarcoma and of infectious myxoma of the rabbit do not contain succinodehydrogenase. Filterable-virus diseases produce in the affected tissues a partial inhibition of succinodehydrogenase.

CH. ABS.

Cataphoresis experiments on the filterable agent of Rous chicken sarcoma. H. NAKAJIMA and W. NAKAHARA (Gann, 1932, 26, 181—189).—The causative agent has a negative charge and is constantly associated with the tissue proteins.

CH. ABS.

Properties of the causative agent of a chicken tumour. III. Attempts at isolation of the active principle. J. B. MURPHY, E. STURM, A. CLAUDE, and O. M. HELMER. IV. Association of an inhibitor with the active principle. J. B. MURPHY and E. STURM. V. Antigenic properties of the chicken tumour. I. J. B. MURPHY, E. STURM, G. FAVILLI, D. C. HOFFMAN, and A. CLAUDE (J. Exp. Med., 1932, 56, 91—106, 107—116, 117—129).—III. There can be separated a protein fraction carrying all the tumour-producing agent, which can be largely separated from the protein by absorption of the latter with $Al(OH)_3$.

IV. Desiccated tumour is more active after washing with H_2O , and a tumour extract is more potent after removal of some factor by adsorption on $Al(OH)_3$. When the tumour-producing factor in an extract of a slow-growing tumour has been destroyed by heating at 55° , it has the property of neutralising a highly active tumour extract. The inhibiting property is destroyed by heating above 65° .

V. Tumour extract largely free from protein induces in rabbits the formation of neutralising antibodies, but not of precipitins. Highly purified tumour agent did not induce precipitins, and only 2 out of 15 sera gave evidence of neutralising bodies. CH. ABS.

Chemical and morphological phases of the blood of normal and cholera-infected swine. I. E. A. HEWITT (Iowa State Coll. J. Sci., 1932, 6, 143—226).—Non-protein-N, creatinine, and creatine are high, whilst urea-N, sugar, P, and Ca are low with cholera-infected swine. CH. ABS.

Blood-glutathione in dermatoses. Y. MATSUMOTO (Japan J. Dermat. Urol., 1931, 31, 1136—1152).—Conditions associated with high, low, and normal vals. are recorded. CH. ABS.

Relative proportion of fermentable and non-fermentable reducing substances of hyperglycaemic bloods of diabetics without glycosuria. I. M. RABINOWITCH (Biochem. J., 1932, 26, 963—969).—Hyperglycaemia in diabetes is due chiefly to

fermentable sugar and not to other reducing substances which are ordinarily present in blood.

S. S. Z.

Afternoon glycosuria. V. J. HARDING, D. L. SELBY, and A. R. ARMSTRONG (Biochem. J., 1932, 26, 957—962).—"Afternoon glycosuria" (I) has been found in 14 out of 28 subjects who showed "sugar" (Benedict test) on routine examination. Renal glycosurias can show (I). More than 60% of the total subjects show a blood-sugar peak after 50 g. of glucose higher at 4 p.m. than at 9 a.m. One subject showing almost identical a.m. and p.m. glucose tolerance curves gave marked (I).

S. S. Z.

Influence of diet or treatment with insulin on the sugar dose test. R. BOLLER and K. UEBERRACK (Klin. Woch., 1932, 11, 511; Chem. Zentr., 1932, i, 2481).—Administration of glucose to normal persons who have been kept on a diabetic diet causes an abnormally high rise in blood-sugar. A similar result follows pre-treatment with insulin. A. A. E.

Galactose, a substitute carbohydrate. H. KOSTERLITZ and H. W. WEDLER (Klin. Woch., 1932, 11, 553; Chem. Zentr., 1932, i, 2862).—Addition of galactose to the diet in diabetes causes the appearance of much less urinary glucose than administration of an equal amount of glucose. A. A. E.

Urinary excretion of the anterior pituitary hormone in endocrine disease. H. U. HIRSCH-HOFFMANN (Klin. Woch., 1932, 11, 94—97; Chem. Zentr., 1932, i, 1546).—A clinical report. A. A. E.

Water and mineral balances in epileptic children. I. J. McQUARRIE, R. C. MANCHESTER, and C. HUSTED (Amer. J. Dis. Children, 1932, 43, 1519—1543).—The urinary K : Na ratio is markedly increased during positive H_2O balance. CH. ABS.

Basal oxygen consumption of goitrous and non-goitrous rats. A. W. SPENCE (Brit. J. Exp. Path., 1932, 13, 149—157).—The basal O_2 consumption was not definitely disturbed in goitrous rats, although some animals showed subnormal vals. after 9 months. CH. ABS.

Pathogenesis of exophthalmic goitre. Diminished excretion or decomposition of thyroxine? P. VOGT-MOLLER (Acta med. Scand., 1931, 76, 437—452; Chem. Zentr., 1932, i, 1679—1680).—Tyrosine and tyramine do not give the Reid Hunt reaction (resistance of mice towards nitriles after administration of thyroid); sera of persons with "hyperthyroid const.," exophthalmic goitre, or progressive nephritis, or of normal persons immediately after intravenous administration of thyroxine, give a positive reaction. The reaction was negative after administration of KI. It is supposed that in certain disabilities over-production of thyroxine takes place, excretion and metabolic decomp. also being diminished. A. A. E.

Influence of insulin on sulphur metabolism in exophthalmic goitre. S. TASAKA and S. NISIKORI (Folia endocrinol. Japon., 1931, 7, 1).—Increased N and S metabolism (particularly $RHSO_4$ and neutral S) is arrested. CH. ABS.

Fluorides in the treatment of exophthalmic goitre and hyperthyroidism. L. GOLDENBERG

(Semana med., 1932, I, 1659—1665).—The action of NaF is explained by its paralysing effect on the lipases and oxidases of the thyroid; it ppts. thyroxine. CH. ABS.

Supposed presence of fluorine in the blood in hæmophilia. W. BRANDES (Z. klin. Med., 1932, 119, 504—507; Chem. Zentr., 1932, i, 1680).—Both normal and hæmophilic blood contain similar min. traces of F. A. A. E.

Plasma-proteins in hookworm disease. G. G. VILLELA and J. C. TRINTEIRA (Mem. Inst. Oswaldo Cruz, 1930, 23, 50—58).—As in lipin nephrosis, fibrinogen was generally increased, serum-albumin greatly decreased, globulins normal or slightly increased, and non-protein-N normal. CH. ABS.

Skin pigmentation and urinary bile pigments in icterus. I. Determination of bilirubin and more highly oxidised bile pigments in urine. K. FRANKE (Z. ges. exp. Med., 1931, 79, 107—124; Chem. Zentr., 1932, i, 2873).—Solutions of bilirubin (Homburg) and icteric urine (or its amyl-alcoholic extract) exhibit very similar extinction curves. On slow oxidation (0.1% KMnO₄) they show a similar increase in reddish-yellow adsorption (max. 610—590 mμ). On oxidation beyond the biliverdin-cholecyanin stage the red absorption decreases. By means of the spectrocoulometer biliverdin can be determined by comparison with standard bilicyanin solutions. Determination of biliverdin before and after oxidation gives the bilirubin content. A. A. E.

Blood-serum-calcium in leprosy. G. G. VILLELA (Ciencia Med., 1928, 6, No. 3, 19 pp.).—Vals. were low: nervous 8.06, mixed 8.42, nodular 9.26, tubercular 9.34 (average of all types 8.82) mg. per 100 c.c. CH. ABS.

Liver function. IV. Glycuronic acid. V. Urobilin. S. BOKU and T. KIN (J. Chosen Med. Assoc., 1931, 24, 67—78, 190—200).—IV. The urine of non-hepatic patients contained (average) 0.013% of glycuronic acid, or 0.057% after oral administration of camphor (0.5 g.); that of hepatic cases contains practically no glycuronic acid in either event. Rabbits poisoned with P or CCl₄ show a marked decrease in the production of camphorglycuronic acid.

V. Urine of non-hepatic patients contained (average) 0.63 mg. of urobilin per 100 c.c. (10.46 mg. per day); in hepatic cases vals. were 10.09 and 122.11 mg., and in cancer of the liver 3.73 and 32.07. In severe salvarsan jaundice the urine often contained no urobilin; in rabbits poisoned with P or CCl₄ urinary urobilin was increased. CH. ABS.

Cause of existence of two types of the van den Bergh bilirubin reaction. N. SOFUE (Japan. J. Med. Sci., IV, Pharmacol., 1929, 3, 137—172).—The velocity of the reaction depends on the amount of urobilin and the inhibiting effect of the cell stromata; if the former is larger the reaction occurs quickly. If the inhibition is accompanied by the oxidising action of the stromata, the urobilin is partly changed and gives a permanent yellow colour, i.e., a retarded reaction. CH. ABS.

Respiratory quotient in obese subjects. D. M. LYON, D. M. DUNLOP, and C. P. STEWART (Biochem. J.,

1932, 26, 1107—1117).—In a series of 34 observations on subjects on a diet of 2000 g.-cal. or more there was a loss of wt., the average R.Q. being 0.755. Of these, 3 were below 0.70. When the diet was reduced to 1000—1200 g.-cal., the average R.Q. in 117 observations was 0.721, with 51 below 0.70. When the carbohydrate content of the latter diets was reduced without altering the calorific val., the average R.Q. fell to 0.678, 12 out of 15 being below 0.70. Administration of thyroid to the subjects on this diet produced a slight increase in the R.Q., the average of 70 determinations being 0.727, with only 14 below 0.70. Ketonuria was usually absent and when present only slight. S. S. Z.

Experimental oedema produced by plasma-protein depletion. M. J. LEPORE (Arch. Int. Med., 1932, 50, 488—505).—In dogs, the plasma-protein content of which had been lowered by removing daily a quantity of blood and returning the erythrocytes suspended in Ca-free Locke's solution, general oedema developed. This development is hastened by the administration of large quantities of 0.9% NaCl solution by mouth. Storage of NaCl runs parallel to the storage of H₂O, but the percentage of Cl' to H₂O stored in different organs is not const., being higher in the muscles than in the skin. During recovery increase of plasma-protein occurs, H₂O is removed by diuresis, excess of NaCl is also excreted, whilst there is decreased absorption of H₂O from the intestine. W. O. K.

Action of tartaric acid in chronic opisthorchiasis. A. ERIHARDT and W. KEIL (Arch. exp. Path. Pharm., 1932, 167, 334—337).—Of the four optical isomerides of tartaric acid only the *d*-acid is efficient in the treatment of opisthorchiasis in cats as indicated by the excretion of eggs. This is probably due to its partial conversion into dihydroxymaleic acid, which is more effective than *d*-tartaric acid. Dihydroxytartaric acid is ineffective. F. O. H.

Metabolic studies in a case of osteitis deformans. I. M. RABINOWITZ (J. Nutrition, 1932, 5, 346).—Metabolic balances of inorg. materials are recorded and discussed. A definite loss of S is associated with the diseased condition. A. G. P.

Iron-deficiency hypothesis in pellagra. G. A. WHEELER (Science, 1932, 76, 101).—A criticism (cf. this vol., 419). L. S. T.

Diets in pregnancy in relation to low blood-serum-calcium at lactation. H. T. FRENCH and C. E. BOLSER (New Engl. J. Med., 1932, 206, 14—16).—The serum-Ca decreases at the beginning of lactation and is normal after 3—4 days. The serum-Ca of women who normally have low vals. increases at the beginning of lactation and tends to remain high. CH. ABS.

Blood-inorganic sulphate in eclampsia. D. F. ANDERSON and S. L. THOMPSETT (Brit. J. Exp. Path., 1932, 13, 130—132).—High vals. not found so markedly in normal gestation or in toxæmias of pregnancy other than eclampsia, were observed. Inorg. SO₄ may be less readily excreted than N. CH. ABS.

Serum-calcium content in eclampsia. D. F. ANDERSON (Brit. J. Exp. Path., 1932, 13, 182—188).—In eclampsia (36 of 44 cases) the vals. were subnormal (± 9 mg. per 100 c.c.); in nephritic and pre-eclamptic toxæmia (10 of 17 cases), and in normal pregnancy (6 of 17 cases) the vals. were also subnormal.

CH. ABS.

[Clinical] action of potassium. I. On pruritus. II. Experimental. J. SAUER (Dout. Arch. klin. Med., 1931, 172, 219—222, 223—227; Chem. Zentr., 1932, i, 1263).—II. Large oral doses of KOAc lead to a rise in blood-serum- and cerebrospinal fluid-K and (serum-)Ca; the -Na falls. There is no parallelism between the effect of K in pruritus and the serum-K.

A. A. E.

Urea clearance test as an index of renal function. I. Studies of normal subjects. II. Effect of ingestion of glucose. M. BRUGER and H. O. MOSENTHAL (Arch. Int. Med., 1932, 50, 351—357, 358—361).—I. Determinations of urea clearance (standard and max.; cf. McIntosh and Van Slyke, J. Clin. Invest., 1928, 6, 427) on 8 normal subjects showed marked variations in the vals. obtained with a tendency towards vals. above the average during moderate exercise. Clinical importance is to be attached to low vals. only when these are given by a subject consistently.

II. Ingestion of 100 g. of glucose by 6 subjects who were normal except that some showed glycosuria did not significantly affect urea clearance.

W. O. K.

Uric acid content of duodenal bile of patients subjected to mud treatment. A. BICH (Minerva Med., 1932, I, 600—605).—Vals. for rheumatic patients were 0.5—3.3 mg. per 100 c.c. The ratio blood-: duodenal bile-uric acid was 2.05—3.08. No direct relation was observed between the increase in blood- and bile-uric acid.

CH. ABS.

Experimental rickets. III. Influence of ammonium chloride on mineral metabolism of the rachitic rat. F. ROGOZINSKI (Bull. Acad. Polonaise, 1931, B, 555—566).—Addition of 4% of NH_4Cl to Steenbock and Black's rachitic diet causes a large increase in the inorg. P of the urine of rats receiving it, but fails to affect the general P balance or to alleviate the rachitic condition.

P. G. M.

Effect of rachitogenic diets on the thyroid gland of the albino rat. J. THOMPSON (J. Nutrition, 1932, 5, 359—377).—Development of hyperplasia in rats is associated with I deficiency and excess of CaCO_3 in the diet.

A. G. P.

Effect of ammonium chloride administration on metabolism in infantile tetany and rickets. N. MORRIS and O. MACCRAE (Arch. Dis. Childhood, 1932, 7, 47—58).—Increased retention of Ca, P, and excess Cl, and increased excretion of titratable acid (but not acidosis), are caused.

CH. ABS.

Metabolism in tetany. I. GREENWALD (Biochem. J., 1932, 26, 954—956).—Criticism of Morris, Watson, and Morris (A., 1931, 979).

S. S. Z.

New error of tyrosine metabolism: tyrosinosis. Intermediary metabolism of tyrosine

and phenylalanine. G. MEDES (Biochem. J., 1932, 26, 917—940).—The condition which was studied in one patient consists in a slowing of the first steps in the intermediary metabolism of tyrosine and a complete stop at the stage of *p*-hydroxyphenylpyruvic acid (I), which in the case of exogenous tyrosine metabolism is at first excreted with tyrosine and then with *l*-*p*-hydroxyphenyl-lactic acid (II), and when the tyrosine metabolism is raised also with *l*-3:4-dihydroxyphenylalanine. 1.6 g. of (I) is excreted daily as a result of endogenous tyrosine metabolism. Phenylalanine when fed causes elimination of tyrosine, increased elimination of (I), and excretion of traces of (II) which is not metabolised when consumed directly. In the case of hydroxyphenylalanine it is excreted partly unchanged, and causes elimination of tyrosine and increased elimination of (I). (I) when ingested reappears unchanged, and also causes elimination of (II), but does not give rise to tyrosinuria. Homogentisic acid is oxidised without influencing the above compounds. Melanin was not detected in the urine. In the case of a normal patient, N-free melanin prepared from (I) was recovered quantitatively from the urine.

S. S. Z.

Application of the chain reaction theory to biochemical processes. D. RICHTER (Diss., Oxford, 1932, 8 pp.).—Evidence is discussed concerning the view that biochemical processes are propagated by chain reactions, the energy transfer from an activated mol. being sp. and occurring most readily to another similar mol.

J. W. S.

Relation of ultra-violet light to nutrition. H. CHICK (Lancet, 1932, 223, 325—329, 377—383).—Two lectures.

L. S. T.

Metabolic rate and habitat. H. M. FOX and B. G. SIMMONDS (Nature, 1932, 130, 277—278).—The metabolic rate of the fresh-water species *Gammarus pulex* is $1\frac{1}{2}$ times that of the marine *G. locusta* and *G. marinus*; that of the fresh-water *Asellus aquaticus* is 3 times that of the marine *Idotea neglecta*. The metabolic rates of fresh-water animals living in rapid streams are greater than those of animals inhabiting still water.

L. S. T.

Effect of atmospheric humidity on the metabolism of the fasting mealworm (*Tenebrio molitor*). K. MELLANBY (Proc. Roy. Soc., 1932, B, 111, 376—390).—Analyses of fasting mealworms show that they live chiefly on fat, and to some extent on carbohydrate (chiefly glycogen) and protein. The loss of H_2O is approx. proportional to the saturation deficiency of the air at 8°, 23°, 30°, and 37° and at most humidities, but in hot dry air the worms conserve their H_2O , whilst in moist air of 90% R.H. they take up H_2O from the atm. at 8°, 23°, or 30°. At 23° metabolism is so regulated that the % of H_2O to dry matter in the worms remains const., and therefore necessarily is a function of the humidity. At higher temp. the metabolism and rate of formation of H_2O are greater, and in moist warm air accumulation of H_2O results.

W. O. K.

Combination of water in muscle. E. ERNST [with K. CZIMMER] (Pflüger's Archiv, 1931, 228,

683—689; Chem. Zentr., 1932, i, 2604).—Dried muscle takes up H_2O partly by swelling. The crystalloids present in fresh muscle cannot be freely diffusible. The lowering of v.p. of fatigued muscle is due to increased swelling caused by lactic acid.

A. A. E.

Rôle of potassium, phosphate, and lactic acid in muscle contraction. E. ERNST and I. TAKÁCS (Pflüger's Archiv, 1931, 228, 690—699; Chem. Zentr., 1932, i, 2604).—Indiffusible K and PO_4 compounds are present in muscle; stimulation leads to renewed ionisation. The phenomenon is not observed under physiological conditions.

A. A. E.

Specific function and metabolism of muscle. E. ERNST [with I. FRICKER] (Pflüger's Archiv, 1931, 228, 700—709; Chem. Zentr., 1932, i, 2604—2605).—Extended muscle contains more lactic acid than non-extended. The production of lactic acid is a truly metabolic phenomenon. The osmotic theory of muscular contraction is discussed.

A. A. E.

Metabolism of carbohydrate after starvation. M. W. GOLDBLATT and R. W. B. ELLIS (Biochem. J., 1932, 26, 991—1005).—Intolerance for carbohydrate manifested after starvation for about 40 hr. is not due to either ketosis or acidosis. Insulin does not completely re-establish normal carbohydrate oxidation in human subjects after 40 hr. starvation.

S. S. Z.

Non-fermentable residue in the blood in galactose metabolism. N. FIESSINGER and A. SCHRUMPF (Compt. rend. Soc. Biol., 1932, 109, 289—290; Chem. Zentr., 1932, i, 2059).—Galactose is practically non-fermentable by yeast, but when glucose is added the reducing val. diminishes rapidly and becomes const. at the val. attained in the fermentation of glucose alone. *In vivo* the non-fermentable residue of the reducing val. of the blood rises after administration of galactose, and falls rapidly if glucose is simultaneously administered.

A. A. E.

Influence of succinic, fumaric, malic, and acetic acids on the deposition of liver-glycogen. A. P. PONSFORD and I. S. MACLEAN (Biochem. J., 1932, 26, 1340—1344).—In the normal rat addition of succinic, malic, or fumaric acid to a diet poor in carbohydrate leads to an increase of liver-glycogen. AcOH does not produce this effect.

H. W. D.

Metabolism of normal and tumour tissue. VI. Conversion of fructose and glucose into lactic acid by embryonic tissue. F. DICKENS and G. D. GREVILLE (Biochem. J., 1932, 26, 1251—1269).—In the anaerobic conversion of the sugars by foetal membranes at p_H 7.5, the whole embryo and its tissues have been studied. Whilst glucose is readily converted into lactic acid by most embryonic tissues, the conversion of fructose depends on both the tissue and the species, varying from zero to a val. equal to that observed with the same tissue in glucose. For a given tissue the degree of conversion of fructose or glucose may show a considerable variation.

S. S. Z.

Effect of sulphur on carbohydrate metabolism. I, II. T. KOYASAKO (Folia endocrinol. Japon., 1931, 7, 9).—Daily application of S (15%) ointment to the skin of rabbits for 1 month had no effect on blood-

sugar, but raised the sugar tolerance. It increased hypoglycaemia after insulin and changed hyperglycaemia after adrenaline.

CH. ABS.

Metabolism of pectin. K. IMHAUSER (Arch. exp. Path. Pharm., 1932, 167, 702—707).—Oral administration of pectin to dogs is followed by neither an appreciable increase in the blood-sugar nor, in phloridized dogs, a prevention of fat deposition in the liver. In the latter case, however, there is a marked decrease in the excretion of ketonic substances, indicating a definite utilisation of at least part of the pectin carbohydrate.

F. O. H.

Value of vegetarian diet for maintenance. S. WAN and H. WU (Chinese J. Physiol., 1932, 6, 251—256).—The body-wts. of rats on a vegetarian diet increased at a lower rate than those of rats on a normal diet. There was also some suggestion that the mortality rate was higher on the vegetarian diets.

R. N. C.

Role of the spleen in carbohydrate and fat metabolism. M. RUBINSTEIN (Biochem. Z., 1932, 253, 193—201).—In rabbits and dogs to which adrenaline and insulin are administered splenectomy has inconst. effects on the sugar and cholesterol contents of the blood.

W. McC.

Fat metabolism in the lactating goat. R. C. BENDER and L. A. MAYNARD (J. Dairy Sci., 1932, 15, 242—253; cf. A., 1930, 636).—A low-fat ration equicaloric with a normal ration caused considerably reduced yields of milk and total butter-fat. Marked changes in blood-lipins follow variations in fat intake. Curves for total lipins, phospholipins, and cholesterol show a general parallelism. A low-fat diet and also a coconut-oil diet produced fat of higher saturation and lower mean mol. wt. than a linseed-oil diet. Variations in I and sap. vals. of milk-fat resulting from diet changes showed an inverse relationship throughout.

A. G. P.

Influence of the lungs on the blood-volatile fatty acids. L. BINET, E. AUBEL, and M. MARQUIS (Compt. rend. Soc. Biol., 1932, 109, 2—4; Chem. Zentr., 1932, i, 2197).—On perfusion of the isolated lung with citrated blood the quantity of added HCO_3H , AcOH, $EtCO_3H$, or $PrCO_3H$ diminishes.

A. A. E.

[Non-]relation between blood-cholesterol and basal metabolic rate. G. P. GRABFIELD and A. G. CAMPBELL (New England J. Med., 1931, 205, 1148—1149).

CH. ABS.

Cholesterol metabolism of various tissues. IV. Effect of extirpation of thyroid and adrenal. O. YOSHIMURA (J. Chosen Med. Assoc., 1931, 21, 1079—1092).—The course of hypercholesterolaemia following removal of one adrenal gland or the thyroid gland from the rabbit or dog is described.

CH. ABS.

Fate of intravenously injected phosphatides. L. PASTERNAK and I. H. PAGE (Biochem. Z., 1932, 252, 254—277).—When moderate or small doses of cephalin emulsions are intravenously injected into rabbits, the plasma-lipin content is considerably increased, but returns to normal val. in 30 min. With large doses. 30 min. after injection, the liver-phosphatide content is greatly increased, but the fat

content remains normal. The latter then begins to increase, and remains high for several days after the phosphatide val. has returned to normal (12 hr.). The phosphatide val. of brain does not increase. Increased urinary excretion of PO_4''' is often, and changes in the cholesterol content of the organs, especially in brain, may be occasionally, observed. The effect also of injection of oleic, ricinoleic, and linolenic acids, mixed liver-oil fatty acids and their esters, lanolin, human fat, and mixed cerebrosides and phosphatides is also examined. P. W. C.

Relations of intermediary protein metabolism to carbohydrate economy. Intermediary amino-acid metabolism. K. PASCHKIS (Z. ges. exp. Med., 1932, 81, 156—168; Chem. Zentr., 1932, i, 2603).—After oral administration of NH_2 -acid, human blood- NH_2 -N increases; sugar causes a decrease. In fasting or after insulin the blood- NH_2 -N slowly falls. After simultaneous administration of sugar and NH_2 -acid the blood- NH_2 -N usually rises less than after ingestion of NH_2 -acid alone. A. A. E.

Influence of insulin and glucose on purine metabolism. T. OGAWA (Folia endocrinol. Japon., 1931, 7, 7—9).—Injection of insulin or administration of glucose lowers the total excretion of N, particularly of allantoin-N. Intravenous injection of hypertonic glucose solution decreases the total N and increases the urinary purine substances. CH. ABS.

Influence of adrenaline on purine metabolism. T. OGAWA (Folia endocrinol. Japon., 1931, 7, 6—7).—Subcutaneous injection of adrenaline (0.35 c.c. of 0.1% solution per kg.) into dogs increases the urinary N; the allantoin- and uric acid-purine base-N was increased both absolutely and relatively. CH. ABS.

Effect of the amount of feed consumed by cattle on the utilisation of its energy content. H. H. MITCHELL and T. S. HAMILTON (J. Agric. Res., 1932, 45, 163—191).—With a steer receiving the same feed in varying amounts the most complete digestibility of all nutrients occurred with the lowest level of feeding. With increasing amounts fed, there was a steady decline in the digestibility of the N-free extract, Et_2O extract, and total dry matter. The metabolisable energy per kg. of dry matter and the % metabolisability of the gross energy increased from the highest to the lowest levels of feeding. The net energy of a ration may be defined, not by a const., but by a linear equation relating it to the intake of dry matter. A. G. P.

Nutritive value of muscle in growth and reproduction. A. SCHEUNERT and C. VENUS (Biochem. Z., 1932, 252, 231—253).—In feeding experiments with young growing rats on a synthetic diet, the best growth was obtained when 10% muscle-protein of ox or sheep was used as the source of protein. Differences in nutritive val. were not obtained when the muscle was given raw, boiled, or roasted, and there was no difference between fresh and frozen flesh. For the best results as to reproduction 2% muscle-protein should be used, although a partial replacement with caseinogen does not seriously interfere with its val. Again no difference was observed between fresh and frozen flesh. P. W. C.

Addition of raw beef or meat scraps to a whole-milk diet. W. C. RUSSELL (J. Nutrition, 1932, 5, 347—357).—In feeding experiments with rats the addition of meat to a wheat and milk diet improved reproduction and increased the growth rate and vigour of the young. The effect cannot be attributed to the increased Ca or P. Use of dried yeast with the wheat and milk ration slightly improved reproduction, but was without effect on the young. A. G. P.

Growth and reproduction of rats on an improved stock diet. H. WU, S. WAN, and T. T. CHEN (Chinese J. Physiol., 1932, 6, 295—306).—A new diet on which growth and reproduction are better than on the best diets now in use is described. R. N. C.

Comparison between ground soya beans and linseed-oil meal as protein supplements for growing dairy calves. J. H. HILTON, J. W. WILBUR, and S. M. HAGUE (J. Dairy Sci., 1932, 15, 277—281).—For heifer calves on a lucerne diet ground raw soya beans and linseed meal were equally effective protein supplements. A. G. P.

Rabbits maintained on barley or lucerne. F. BISCHOFF, W. D. SANBURN, M. L. LONG, and R. D. EVANS (J. Nutrition, 1932, 5, 403—411).—No significant differences occurred in the CO_2 content of the blood or the p_{H} of the plasma of rabbits fed for nearly 2 years on a barley diet (p_{H} of urine 5.2—6.2) or of those on lucerne (p_{H} of urine 8.2—9.5). A. G. P.

Cottonseed meal [as food]. C. H. HUNT (Ohio Agric. Exp. Sta. Bimonth. Bull., 1932, No. 158, 178—182).—When fed to rats, cottonseed meal proved deficient in certain NH_2 -acid constituents of the protein and in minerals, but may be satisfactorily supplemented by caseinogen and yeast. The meal retains some of the toxic principle (gossypol), the effects of which may be minimised by suitably arranged rations, but not by additions of Fe_2O_3 . A. G. P.

Mineral requirements of pregnant sows. R. E. EVANS (J. Min. Agric., 1932, 39, 544—548).—For pregnant sows (not having good grazing) a daily ration of 1 oz. of a mixture of ground chalk and common salt (4:1) is satisfactory. During lactation the quantity is increased to 2½ oz. A. G. P.

Mineral metabolism of the lactating cow. E. B. HART, G. C. HUMPHREY, and J. A. KEENAN (Proc. Amer. Soc. Animal Produc., 1932, 24, 120—126).—The ration need not be supplemented by Ca and P unless the daily intake is much lower than 25—28 g. of Ca. CH. ABS.

Calcium and phosphorus metabolism in dairy cows. V. Relative assimilation of calcium from grades 1 and 3 of timothy hay. W. A. TURNER, E. A. KANE, and W. S. HALE (J. Dairy Sci., 1932, 15, 267—276; cf. A., 1931, 869).—Ingestion of Na citrate had little effect on the Ca and P metabolism. For heavily milking cows good quality timothy hay was more favourable to Ca assimilation than were inferior grades. A. G. P.

Utilisation of calcium in soya-bean diets. W. H. ADOLPH and S. CHEN (J. Nutrition, 1932, 5, 379—385).—Cows' milk and soya bean were equally

effective sources of Ca for Chinese adults. The attainment of a Ca equilibrium was facilitated by increasing the protein intake.

A. G. P.

Microscopically detected metabolism of iron. G. WALLBACH (Klin. Woch., 1932, 11, 353—356; Chem. Zentr., 1932, i, 1683).—Deposition of Fe in the cells does not indicate the degree of blood decomp., but only that the cell has reached a particular functional condition associated with deposition of Fe pigment. Endogenous Fe metabolism can be followed microscopically.

A. A. E.

Excretion of sulphur and nitrogen by fasting dogs during short periods. B. M. JACOBSON (Arch. exp. Path. Pharm., 1932, 167, 358—364).—The distribution of N and S in the urine of dogs at various stages of starvation indicates that the renal excretion during 24 hr. or shorter periods is not const. Hence control experiments with the same animals are essential in the investigation of hormonal or nervous influence on renal excretion of these elements.

F. O. H.

Value of iodine for livestock in central Pennsylvania. E. B. FORBES, G. M. KARNS, S. I. BECHDEL, P. S. WILLIAMS, T. B. KEITH, E. W. CALLENBACH, and R. R. MURPHY (J. Agric. Res., 1932, 45, 111—128).—Administration of I to cows infected with *B. abortus* did not affect the course of the disease. Heavy I feeding during the last 6 months of pregnancy was not harmful to cows, but milk and cream produced had an objectionable odour and contained much I. Calves, sheep, pigs, or chickens were not appreciably affected by I feeding.

A. G. P.

Control of luminescence in the male lampyrid firefly (*Photurus pennsylvanica*) with special reference to the effect of oxygen tension on flashing. P. A. SNELL (J. Cell. Comp. Physiol., 1932, 1, 37—51).—Reduced O₂ tension (to 20 mm. Hg) decreased the intensity of the flash, but not its duration. With O₂ tension of 20—4 mm. the duration of the flash lengthened and at <4 mm. no flash occurred.

A. G. P.

Quantitative measurement of cell permeability. M. H. JACOBS and D. R. STEWART (J. Cell. Comp. Physiol., 1932, 1, 71—83).—Permeability consts. for ethylene glycol, NH₄Ac, propion- and butyr-amide, and glycerol are recorded. Vals. for the three amides increase with their mol. wt.

A. G. P.

Effect of fertilisation on the permeability of eggs of *Arbacia* and *Asterias* to ethylene glycol. D. R. STEWART and M. H. JACOBS (J. Cell. Comp. Physiol., 1932, 1, 83—92).—Fertilisation and, to a smaller extent, exposure to distilled H₂O increase the permeability of the eggs to ethylene glycol.

A. G. P.

Osmotic passage of water and gases through the human skin. A. R. G. WHITEHOUSE, W. HANCOCK, and J. S. HALDANE (Proc. Roy. Soc., 1932, B, 111, 412—429).—Moisture passes through the skin under normal conditions mainly by osmosis, increasing very rapidly as the skin-temp. rises, until completely interrupted by the presence of a covering of liquid sweat. In the intermediate stage this has a

considerable influence on the regulation of body-temp. Passage of gas through the skin runs a parallel course.

H. G. R.

Influence of amputation on blood-sugar, -calcium, -inorganic phosphorus, and -non-protein-nitrogen. S. HONGO (Sci-i-kwai Med. J., 1931, 50, No. 8, 39—44).—Amputation of the femur of male rabbits causes a fall in blood-Ca and a rise in -inorg. P and -sugar. Blood-non-protein-N is unaffected. Rabbits similarly treated, but without injury to the bone, showed a similar rise in -inorg. P.

CH. ABS.

Biological action of parenterally injected ethyl alcohol. W. MILBRADT (Z. ges. exp. Med., 1932, 80, 782—802; Chem. Zentr., 1932, i, 2485).—Intravenous or intramuscular injection of 0.05—0.5 c.c. EtOH in 1 c.c. H₂O leads in man to accelerated clotting, retarded deposition of corpuscles, and diminution of surface tension and plasma-stability of the blood, apparently owing to alteration of the plasma-colloids. Blood-NH₂-acid increases and -sugar diminishes.

A. A. E.

Passage of ethyl alcohol into human parotid saliva. P. LINDE (Arch. exp. Path. Pharm., 1932, 167, 285—291).—The EtOH content of the parotid saliva of normal fasting humans increases after ingestion of aq. EtOH, whilst the content in plasma or whole blood follows a parallel course, although the concn. is higher in the saliva than in the blood. The passage of EtOH into the saliva is due to a simple diffusion process.

F. O. H.

Influence of cortical and subcortical narcotics on blood-catalase. N. HIKARU (J. Chosen Med. Assoc., 1931, 21, 129—141).—CHCl₃, Et₂O, EtCl, and morphine cause in rabbits a decrease in blood-catalase in the first 10—15 min. (min. val. 30 min. after sleep); luminal, veronal, and urethane decrease the catalase 10—15 min. after injection (min. 60—100 min. after injection). The narcotic power is parallel with the power of decreasing blood-catalase.

CH. ABS.

Detoxication of various doses of avertin. L. LENDLE (Arch. exp. Path. Pharm., 1932, 167, 590—598).—Continuous intravenous injection of avertin into rabbits is followed by a rate of detoxication which bears a linear relationship to the dosage.

F. O. H.

Pharmacological influence on the detoxication of avertin. A. BECK and L. LENDLE (Arch. exp. Path. Pharm., 1932, 167, 599—608).—The action of various analeptics, thyroxine, and insulin on the detoxication of avertin in rabbits was investigated.

F. O. H.

Effect of drugs on purine economy. H. SEEL and G. CREUZBERG (Z. ges. exp. Med., 1932, 80, 806—818; Chem. Zentr., 1932, i, 2607).—Normally, and in gout, administration of atophan, santonin, or uricedin diminishes the blood- and increases the urinary uric acid. Excretion of allantoin is increased by atophan, arrested by uricedin, and unaffected by santonin. In rabbits atophan causes a diminution of the allantoin excretion without affecting the uric acid excretion. Santonin causes a small increase in uric acid, allantoin, and quantity of urine. Uricedin increases the excretion of uric acid and diminishes

that of allantoin. In all three cases the blood-uric acid is slightly and transiently increased. A. A. E.

Physiological properties of some furan derivatives. H. GILMAN, A. P. HEWLETT, and J. B. DICKEY (Iowa State Coll. J. Sci., 1932, 6, 137—141).—Skin reactions are described. CH. ABS.

Effect on blood-sugar of some organic compounds with labile sulphur. A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1932, 20, 78—86).—Piperidine and Na *N*-piperidylthiocarbamates cause intense hyperglycaemia of long duration in rabbits. Intravenous injection of 2 mg. per kg. produces a marked effect. Oral administration has no action. R. K. C.

Influence of Chosen ginseng on excretion of glycuronic acid in urine. Y. OSHIMA (J. Chosen Med. Assoc., 1931, 21, 562—565).—Urinary glycuronic acid increased proportionally to the dose. CH. ABS.

Influence of Chosen ginseng on glutathione contents of animal tissue. Y. OSHIMA (J. Chosen Med. Assoc., 1931, 21, 566—570).—In rats the tissue-glutathione was decreased. CH. ABS.

Detoxification of certain poisons by Congo-red. I. P. PETROV (Arch. sci. biol., Russia, 1931, 31, 59—66).—Congo-red forms ppts. with strychnine, curare, and cobra-venom; this explains the (non-uniform) diminution of the toxic effect of these substances on frogs and mice. The toxicity of cobra-venom was not reduced by pptn. with Congo-red, but previous injection renders animals more resistant to the venom. CH. ABS.

Pharmacological action of papaverine derivatives. H. LANGECKER and E. STARKENSTEIN (Klin. Woch., 1931, 10, 2257—2261; Chem. Zentr., 1932, i, 1926).—A comparison of the behaviour of papaverine with that of 6:7-diethoxy-1:3:4-dimethoxy-, 6:7-dimethoxy-1:3:4-diethoxy-, and 6:7-diethoxy-1:3:4-diethoxy-benzylisoquinoline. A. A. E.

Effect of taxin on blood-sugar. H. TORATANI (Sei-i-kwai Med. J., 1931, 50, No. 7, 1—19).—Neither subcutaneous nor intravenous injection of small amounts of taxin HCl (< 1 mg. per kg.) affects the blood-sugar of normal rabbits; larger amounts produce slight decreases. In hyperglycaemia subcutaneous (1—5 mg. per kg.) or intravenous (0.5—2 mg.) injection produced normal vals. CH. ABS.

Pharmacology of thebaine and its derivatives. III. Influence on blood-cells and hæmoglobin. IV. Effects on blood-calcium, -chlorine, and -magnesium. V. Influence on fatty acids and lipins contained in the blood and central nervous system. Y. TAKEUCHI (Sei-i-kwai Med. J., 1931, 50, No. 5, 58—76; No. 6, 56—64; No. 8, 45—61).—III. Subcutaneous injection into rabbits of 1 c.c. of 1% thebaine hydrochloride per kg. decreases the blood-hæmoglobin by 18%; larger, but non-convulsive, doses increase the hæmoglobin.

IV. On injection of thebaine, dihydrothebaine, hydroxycodone, or dihydrohydroxycodone hydrochloride into rabbits the blood-Mg is unchanged, but the -Cl and -Ca decrease.

V. Subcutaneous injection of the alkaloids respectively caused the following decreases in blood-lipin-P: (a) 0.008 g. per kg., 33.2% within 1 hr.; (b) 0.012, 39% within 2 hr.; (c) 0.012, 35.3% within 2 hr.; (d) 0.016, 18% within 7 hr. All caused a decrease in blood-cholesterol of 34.3—36.7% and in -fatty acids of 34.9—36.7% within 2—3 hr. With mice, lethal doses of the first 3 drugs caused a decrease in the fatty acid, lipin-P, and cholesterol content of the spinal cord, whilst only the fourth caused a decrease of these lipins in the cerebellum. CH. ABS.

Effect of ephedrine on the blood-lactic acid. I. I. NITZESCU and N. MUNTEANU (Compt. rend. Soc. Biol., 1931, 106, 1173—1175; Chem. Zentr., 1932, i, 2197).—Injection of ephedrine into the dog (or, less markedly, the rabbit) increases the blood-lactic acid and -sugar. The increase in lactic acid arises from increased formation in the muscle. Ephedrine has a similar, but less regular and less intense, effect. A. A. E.

Quinine and spleen blood. L. BINET and R. FABRE (Compt. rend. Soc. Biol., 1931, 106, 1116—1118; Chem. Zentr., 1932, i, 2197).—The blood of the spleen of dogs, after treatment with quinine HCl, contains twice the amount of quinine as is present in arterial blood, corresponding with the quantity of red corpuscles. The plasma was free from quinine. A. A. E.

Pharmacological action of "mussel poison." M. PRINZMETAL, H. SOMMER, and C. D. LEAKE (J. Pharm. Exp. Ther., 1932, 46, 63—73).—The poisonous principle separated from *Mytilus californianus*, sol. in H₂O and EtOH, insol. in Et₂O and CHCl₃, paralysed respiration and had a definite but complex effect on blood-pressure and heart-rate and was without action on smooth muscle in perfusion experiments. It is slowly absorbed from the gastro-intestinal tract and rapidly excreted by the kidneys. W. O. K.

Pharmacology of salamander alkaloids. O. GESSNER and P. MOLLENHOFF (Arch. exp. Path. Pharm., 1932, 167, 638—653).—The principal alkaloid (cf. A., 1930, 1204) is samandarine, m.p. 190° [hydrochloride (I), m.p. 325°]. The min. lethal dose of (I) for *Rana esculenta* is 0.019 mg. per g. body-wt. Conens. as low as 1:10⁶ have a paralysing action on salamander larvæ. It induces convulsions in the snake, rabbit, and mouse, has no hæmolytic action, and does not stimulate isolated skeletal muscle. For the rabbit's cornea a concn. of 1:500 causes an anæsthesia lasting about 1 hr. A second alkaloid has properties identical with, but less pronounced than, those of (I). F. O. H.

Diuretic effects and changes in blood- and urinary metabolites after digitalis in normal and in cedematous persons. A. B. STOCKTON (Arch. Int. Med., 1932, 50, 480—487).—The diuresis which sometimes follows administration of digitalis is accompanied by a decrease in the blood-Cl and -uric acid, and thus differs from the diuresis produced by metallic compounds and purine derivatives, where a rise in blood-Cl is found. W. O. K.

Diuretic action of *Digitalis* glucosides on the isolated frog's kidney. B. C. COSTOPANAGIOTIS

(Arch. exp. Path. Pharm., 1932, 167, 660—680).—All the glucosides investigated, except gitoxin, produced irreversible vaso-constriction, especially in the arterial system. The diuresis persisted despite subsequent perfusion with normal fluids. The diuresis was accompanied by an increased urine-NaCl which persisted after the cessation of diuresis. The mechanism of the action of the glucosides on the glomeruli is discussed. F. O. H.

Assay of commercial and pharmaceutical *Digitalis* preparations. B. BEHRENS, GROS, and HILDEBRANDT (Arch. exp. Path. Pharm., 1932, 167, 365—380).—A statistical application of the frog method failed to yield an exact evaluation of the preps. Various preps. kept at room temp. for a year exhibited no loss of activity greater than the limits of error of the method of assay. F. O. H.

Action of saponins. M. BING (Z. ges. exp. Med., 1932, 80, 511—522; Chem. Zentr., 1932, i, 2734).—The surface tension of saponin solutions falls with increasing concn. to a min., and then rises. With quillaia saponin the min. is 34.03 dynes per cm. at 0.01—0.025%; with guaiacum saponin it is 47.18 at 0.01%. C suspensions and a C-H₂O-xylene system are stabilised by saponin. Saponin solutions of concn. considerably below the contraction threshold sensitise the frog's heart for digitalis. A. A. E.

Saline and alkaline drinking waters. V. G. HELLER (J. Nutrition, 1932, 5, 421—429).—Deleterious effects of drinking H₂O containing high proportions of dissolved salts are related more nearly to osmotic effects than to the action of any sp. ion. The safe max. of sol. salts is 1.5—1.7%. Animals are less susceptible to sol. salts than are plants. Cl⁻ is less injurious than SO₄²⁻, org. salts less than inorg. salts, and alkalis are more harmful than salts. A. G. P.

Sulphur content of the liver after administration of a sulphate- or alkali-water. W. ARNOLDI, G. LISS, and L. ROSAM (Z. ges. exp. Med., 1932, 80, 633—636; Chem. Zentr., 1932, i, 2484).—Both natural waters increased the total and neutral S in rats; only the former increased the SO₄-S. A. A. E.

Absorption of lead and its distribution in the organism in experimental poisoning. II. F. WEYRAUCH (Z. Hyg., 1931, 112, 559—568; Chem. Zentr., 1932, i, 2351).—Ingestion and inspiration of "white Pb" are compared. A. A. E.

Modifications in methods of chemico-toxicological tests for mercury. D. GANASSINI (Arch. Ist. Biochim. Ital., 1932, 4, 239—244).—The success of the test for Hg by the formation of "whiskers" on Al foil depends on the purity of the Al. If the "whiskers" are treated with starch-iodide solution and CuSO₄ solution containing a trace of FeSO₄, a blue colour is formed, dependent on the simultaneous presence of Hg and H₂O₂.

After subliming Hg from a deposit on Cu it may be converted into iodide by subliming a fragment of I in the same tube. A very sensitive test is the red colour given by Cu₂I paper in Hg vapour (e.g., from heated Cu on which Hg is deposited). R. K. C.

Thallium. II. **Thallium acetate and hæmatoporphyrin.** P. TESTONI (Arch. Int. Pharmacodyn. Ther., 1931, 40, 45—53; Chem. Zentr., 1932, i, 2733).—Tl acetate did not cause hæmatoporphyrinuria in rabbits or dogs. A. A. E.

Feeding potassium iodide to pregnant ewes. J. A. SCHULZ, C. C. CULBERTSON, B. H. THOMAS, and J. M. EVVARD (Proc. Amer. Soc. Animal Produc., 1932, 24, 215—219).—Daily ingestion of KI (0.05 grain) increased the thyroid-I of the lambs, but not the I content of the thyroid-free carcasses; the latter was increased by 0.8—3.5 grains. CH. ABS.

Influence of potassium cyanide poisoning on the glycogen content of the liver and muscles, especially the relation of potassium cyanide poisoning to insulin action. T. KOYASAKO (Folia endocrinol. Japon., 1931, 6, 117—118).—Injection of KCN (1%) into rabbits decreases the liver- and slightly decreases the muscle-glycogen; the decrease is checked by simultaneous injection of insulin. CH. ABS.

Fate of reduced glutathione content in tissues of rabbits in which the temperature is raised by puncture of the corpus striatum and by peptone injection. S. HONGO (Sei-i-kwai Med. J., 1931, 50, No. 8, 20—31).—Average glutathione contents for rabbits are: heart 0.0341, lung 0.0739, liver 0.2166, adrenal 0.0357, kidney 0.0714, testicles 0.0730, muscle 0.0230%. After heat puncture the heart, spleen, testicles, muscle, adrenals (markedly), and lung (later) gave increased vals. With rabbits injected with peptone increases also occur, but only after 24 hr. CH. ABS.

Influence of the temperature of *Rana nigromaculata* on the reduced glutathione content in tissues. T. YAZAWA (Sei-i-kwai Med. J., 1931, 50, No. 8, 32—38).—The glandular tissue of frogs is richest in glutathione; the effect of a low temp. (4—7°) is to decrease the glutathione content of all the tissues except testicle, kidney, and adrenals. CH. ABS.

Blood-calcium of the dog during ultra-violet irradiation and after parathyroidectomy. J. CHEYMOL and A. QUINQUAUD (J. Pharm. Chim., 1932, [viii], 16, 233—235).—The serum-Ca of two dogs exposed to ultra-violet light decreased 4.6 and 8.2%, respectively, and after parathyroidectomy further decreases occurred, death of the animals taking place after 4 and 2½ days, respectively, when Ca had decreased by 54% in both cases. A. L.

Mechanism of the action of X-rays on living tissues. V. E. KINSEY (Nature, 1932, 130, 436).—Living tissues, normal or pathological, evolve H₂ when irradiated with X-rays. L. S. T.

Second oxygen-carrying enzyme and its absorption spectrum. O. WARBURG and W. CHRISTIAN (Naturwiss., 1932, 20, 688).—The prep. of the enzyme from bottom yeast is described. Its concn. appears to be greater in anaerobic cells. It is orange in colour, with an absorption band extending over the range 410—560 mμ. The colour is lost on reduction. It is destroyed by warming the solution containing it at 60° for 10 min., is reduced by shaking with active

hexosemonophosphoric acid, but is again oxygenated by shaking with O_2 . A method of determining the concn. and O-carrying power of the enzyme is described. A. J. M.

Formation of pigment in the skin, with special reference to the optical specificity of dopa-oxidase. B. BLOCH and F. SCHAAF (Klin. Woch., 1932, 11, 10—14; Chem. Zentr., 1932, i, 1913).—Dopa-oxidase is not identical with tyrosinase; it reacts only with *l*- and not with *d*-3:4-dihydroxyphenylalanine. A. A. E.

Optical specificity of dopa-oxidase. S. M. PECK, H. SOBOTKA, and J. KAHN (Klin. Woch., 1932, 11, 14; Chem. Zentr., 1932, i, 1912—1913).—Dopa-oxidase reacts with *l*- and *r*-, but not with *d*-3:4-dihydroxyphenylalanine. The formation of melanin probably depends on the dopa-reaction. A. A. E.

Oxidations catalysed by horse-radish- and milk-peroxidases. K. A. C. ELLIOTT (Biochem. J., 1932, 26, 1281—1290).—Horseradish-peroxidase (I), which is not identical with milk-peroxidase (II), does not oxidise, in the presence of H_2O_2 , nitrile, tryptophan, formate, acetate, lactate, oleate, glucose, fructose, glycerol, EtOH, MeCHO, glycine, glutamic acid, phenylalanine, histidine, or brucine. Phenolic substances, with the exception of resorcinol which is oxidised by (I) but not by (II), are oxidised by both enzymes in the presence of H_2O_2 . Resorcinol, pyrrole, and C_5H_5N have an inhibitory influence on both enzymes. S. S. Z.

Product of the oxidation of glucose by glucose-dehydrogenase. D. C. HARRISON (Biochem. J., 1932, 26, 1295—1299).—More than 60% of the theoretical amount of *d*-gluconic acid has been isolated (A., 1931, 1189). It is probably the sole product of the oxidation. S. S. Z.

Co-enzyme of lactic acid oxidation. I. BANGA, A. SZENT-GYORGYI, and L. VARGHA (Z. physiol. Chem., 1932, 210, 228—235).—The prep. of the co-enzyme is described. *d*-Lactic acid is oxidised with great rapidity by washed heart-muscle in presence of the co-enzyme. The *l*-acid, although not oxidised, does not hinder the oxidation of the *d*-form. The $OH\cdot CHMe\cdot CO_2H$ utilises 3 mols. of O_2 , indicating complete oxidation to CO_2 and H_2O . $PO_4^{''''}$ produces practically no increase in the rate of oxidation. J. H. B.

Quinones as enzyme models. VI. Catalysis of the oxidative deamination of glycyl-*l*-tyrosine. B. KISCH (Biochem. Z., 1932, 252, 380—386).—With most of the catalysts used, glycyl-*l*-tyrosine (I) is oxidatively deaminised to the same extent and at the same optimal p_H as glycylglycine (II) and glycyl-leucine (III). Hydroxyquinol, however, occupies a special position in that the yield of NH_3 from (I) is twice as high as from (II) or (III) and four times as high as from glycine. (I) is not first split into tyrosine and glycine. Tyrosine itself is not perceptibly deaminised over the p_H range 7—12. P. W. C.

Determination of the action of amylase. E. A. SYM (Biochem. Z., 1932, 253, 1—10; cf. this vol., 1063).—A method and apparatus are described. W. McC.

Ultra-violet inactivation of invertase in its dependence on hydrogen-ion concentration and ozone. G. GORBACH and H. PICK (Monatsh., 1932, 61, 29—38).—Yeast autolysates are inactivated by ultra-violet irradiation much less readily than purified preps. (by dialysis, adsorption, elution); inactivation of the latter proceeds initially at a uniform rate and then diminishes gradually. Somewhat more inactivation occurs at p_H 3.2 and 8.2—9.2 than at p_H 7; the differences are, however, relatively small. Inactivation is accomplished very readily with O_3 alone. More inactivation occurs when irradiation is carried out in N_2 than in O_2 , showing that O_3 is not the inactivator in the latter case; in presence of O_2 an activation of the invertase occurs after 10 min. probably owing to the decomp. (by activated O_2) of some substance which retards enzyme action. H. B.

Re-inactivation of irradiated invertase solutions and influence of added tryptophan and yeast-gum. G. GORBACH and D. KIMOVEC (Monatsh., 1932, 61, 39—46).—Invertase solutions irradiated for 10 min. or longer lose their residual activity when kept; the loss is accelerated by addition of tryptophan or (more readily) yeast-gum both at p_H 7 and 9.6. Solutions irradiated for < 10 min. remain stable. H. B.

Action of emulsin. I. Hydrolysis of 3-methylpentanol- β -*d*-glucoside by means of emulsin. S. VEIBEL and E. BACH (Biochem. Z., 1932, 252, 401—405).—The prep. of 3-methylpentanol- β -*d*-glucoside, $[\alpha]_D^{25} -34.7^\circ$, and its hydrolysis by emulsin are described. The rotation of the alcohol isolated after 62% of the material had been hydrolysed was $+0.20^\circ$ and after complete hydrolysis -0.57° . It appears that partial separation of the optically active forms of the hexyl alcohol occurs during hydrolysis. P. W. C.

Enzymic hydrolysis of malto- and lactobionic acids. C. NEUBERG and E. HOFMANN (Biochem. Z., 1932, 252, 434—439).—Enzyme solutions prepared from fresh or dried bottom yeast hydrolyse maltobionic acid (50% of the substrate being hydrolysed). Lactobionic acid is hydrolysed by emulsin at p_H 4.3 (17% hydrolysed) and much more readily by enzyme solutions prepared from three species of lactose-fermenting yeasts (*Saccharomyces fragilis*, Jørgensen, *S. Kefir*, and a third species—69% hydrolysed). P. W. C.

Optimum p_H for the hydrolysis of vegetable oils by castor-seed lipase. R. GUILLEMET (Compt. rend. Soc. Biol., 1931, 108, 781; Chem. Zentr., 1932, i, 2857).—No definite optimum can be determined, since vals. depend on the method of prep. and on the buffer solution used. A. A. E.

Yeast lipase. G. GORBACH and H. GÜNTHER (Monatsh., 1932, 61, 47—60).—Yeast lipase, best obtained by extraction of yeast with a phosphate buffer during 1 hr., shows optimum activity at p_H 6.6—6.8 and at 30° ; the velocity coeff. decreases more rapidly on the acid side of the optimum, and is increased (not proportionally) by the use of larger amounts of yeast. Compressed yeast contains more lipase than brewer's yeast. The lipase content of

cultured yeast is higher than that of commercial; in both cases it is increased by artificial fattening (max. after 6–7 days). The activity of lipase is decreased (to varying extents) by CHCl_3 , Et_2O , PhMe , and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$; removal of these substances after autolysis increases the lipase vals. Active lipase preps. are obtained by addition of glycerol to yeast autolysates. H. B.

Relationships between the activation of pancreatic lipase and the surface effects of the compounds involved. Mechanism of inhibition and activation. D. GLICK and C. G. KING (J. Biol. Chem., 1932, 97, 675–684).—The isoelectric points of the proteins related to pancreatic lipase and esterase are markedly different. The action of the lipase on tributyrin is accelerated by the following compounds in decreasing order of activity: hexylresorcinol, octyl alcohol, amyl iodide, hexyl alcohol, amyl alcohol, PhOH , hexoic acid, *cyclohexanol*, resorcinol. Bile salts show a slight inhibition. The ability to lower the surface tension of H_2O is approx. in the same order. The activation is therefore due to a concn. of the activator on the substrate resulting in a decrease of interfacial tension between enzyme and substrate. F. O. H.

Characteristic properties of enzymes in the fission of optically-active substances. M. WERNER (Klin. Woch., 1931, 10, 2314–2317; Chem. Zentr., 1932, i, 1675).—The esterases show stereochemical specificity in the fission and synthesis of optically-active substances. The total specificity of an enzyme is a combination of the affinity- and degradative specificity, and depends on the concn. of substrate, the optically-active substance added, and the mode of prep. of the enzyme. A. A. E.

Relationship between chemical constitution and physiological action. IV. Inhibitory action of certain synthetic urethanes on the activity of esterases. E. STEDMAN and (MRS.) E. STEDMAN (Biochem. J., 1932, 26, 1214–1222).—Urethanes, which behave as parasympathetic stimulants (A., 1931, 1190), inhibit the activity of liver-esterases in general. This inhibitory property also extends to the esterase of the blood-serum of the guinea-pig and of certain other species. Miotine is without action on kidney-phosphatase. S. S. Z.

Histaminase. I. Histamine-histaminase reaction. II. Purification. III. Species distribution. E. W. McHENRY and G. GAVIN (Biochem. J., 1932, 26, 1365–1376).—Previous to the actual inactivation of histamine by histaminase there is a lag period which varies with the enzyme concn. The rate of inactivation proceeds as a unimol. reaction. The inactivation is accelerated by O_2 and is inhibited in an atm. deficient in O_2 . KCN inhibits, $\text{Na}_4\text{P}_2\text{O}_7$ has no effect on, and $\text{PO}_4^{'''}$ augments the reaction. At p_{H} 7.2 and 8.8 the enzyme liberates one atom of N as NH_3 . At p_{H} 5.9 less NH_3 is liberated. Histaminase is absent from the kidney of the rat, guinea-pig, and chicken and is present in that of a no. of mammals. Pig kidney is the best source. A stable active powder can be prepared from pig kidney by extraction of the fats with COMe_2 , removal of COMe_2 with Et_2O ,

and subsequent drying. The enzyme can be removed from the powder by extraction at 38° with phosphate buffer of p_{H} 7.0–7.2. S. S. Z.

Influence of narcotics on the autolytic degradation of histamine. Å. BERGWALL and F. TECHNER (Arch. exp. Path. Pharm., 1932, 167, 609–620).—The inhibitory effect of CHCl_3 , EtOH , or Et_2O on the disappearance of depressor substances and of added histamine from autolysing ox lung is greater than that on the proteolysis. Hypnotics (avertin and somnifen) have no action, whilst 0.0025M-KCN strongly inhibits the degradation. The presence of a histaminase is therefore indicated. F. O. H.

Crystalline pepsin. IV. Hydrolysis and inactivation by acid. J. H. NORTHROP (J. Gen. Physiol., 1932, 16, 33–40).—When cryst. pepsin is hydrolysed by various concns. of HCl , the peptic activity of the hydrolysate is proportional to the amount of protein which remains. When various protein substrates are used, the relative rates of action of the partly hydrolysed pepsin remain const. None of the fission products of the protein mol. therefore appears to possess activity comparable with that of the original protein. W. O. K.

Pepsin activity units and method for determining peptic activity. J. H. NORTHROP (J. Gen. Physiol., 1932, 16, 41–58).—Methods are described for determining the activity of pepsin by measuring the rate of change of viscosity of solutions of gelatin, caseinogen, edestin, and milk-powder, the rate of formation of non-protein-N from caseinogen and edestin solutions, and the increase of the formal titration of solutions of the protein. Units of pepsin activity are defined. W. O. K.

Determination of pepsin with hæmoglobin. M. L. ANSON and A. E. MIRSKEY (J. Gen. Physiol., 1932, 16, 59–63).—Pepsin is added to a solution of dialysed ox CO-hæmoglobin, acidified with HCl , and after 5 min. at a const. temp. $\text{CCl}_3\cdot\text{CO}_2\text{H}$ is added to ppt. the pigment and undigested hæmoglobin. The digested hæmoglobin in the filtrate is determined by means of the blue colour developed when it is treated with a phenol reagent. W. O. K.

Spectral analysis of the mitogenetic radiation in peptic digestion and in the fission of glycylglycine by erepsin. E. BILLIG, N. KANNEGIESSER, and L. SOLOVIEV (Z. physiol. Chem., 1932, 210, 220–227).—The mitogenetic spectra of the two processes show a general agreement and must be due to the fission of the $\text{CO}\cdot\text{NH}$ group, since glycylglycine contains no other hydrolysable group. The action of pepsin is apparently limited to the fission of peptide linkings. J. H. B.

Antitrypsin. III. Nature. IV. Hormonal and pharmacological effect on the albumin:globulin quotient and the antitryptic titre in human serum. V. Antitryptic titre in human serum. VI. Is the antitrypsin reaction a cachexia reaction? F. CHROMETZKA (Z. ges. exp. Med., 1932, 80, 395–407, 408–419, 420–438, 439–443; Chem. Zentr., 1932, i, 2193–2194).—III. The anti-enzyme theory is rejected and the physico-chemical theory is supported; a certain physico-

chemical condition of protein confers on the blood and tissues protection against tryptic action. In widely different pathological conditions an increase in the serum-globulin (possibly also the appearance of sp. globulins) increases the antitryptic titre. Formation of albuminate by chemical or thermal treatment diminishes the antitryptic titre.

IV. Parenteral administration of thyroxine, "praphyson," pituitrin, insulin, adrenaline, atropine, or pilocarpine affects the antitryptic titre, which is thus subject to neuro-hormonal regulation, apparently by way of the albumin-globulin equilibrium.

V. Of 216 malign tumours 85.6% gave an increased, 9.2% a normal, and 5.2% a decreased titre; 7 benign tumours gave normal vals.

VI. A discussion.

A. A. E.

Morphine and enzymes. I. E. KEESER (Arch. exp. Path. Pharm., 1932, 167, 267—284).—The *in vitro* actions of pepsin, trypsin, cathepsin, phenolase, and pig's liver-esterase are affected by the presence of morphine only to a slight extent, but those of reductase, urease, lecithase, phosphatase, lipase, and tyrosinase are either inhibited or accelerated, according to the concn. of the alkaloid. With the latter group the formation of an intermediate oxidation product which influences the degree of toxicity of morphine does not occur. Simultaneous injection of urea or of glutathione increases the toxicity of morphine.

F. O. H.

Nuclein metabolism. XXX. Enzymic fission of yeast-nucleic acid with nucleotidase from intestinal mucosa. F. BIELSCHOVSKY and F. KLEMPERER (Z. physiol. Chem., 1932, 211, 69—74; cf. this vol., 776).—Guanosine, inosine, uridine, cytidine, and guanylic acid were isolated from the products of enzymic fission of yeast-nucleic acid. At the p_H employed (8.8), guanylic acid is produced even in absence of the enzyme, but there is no liberation of H_3PO_4 .

J. H. B.

Tumour-arginase. I. Activatability of liver-arginase by cysteine and glutathione. G. KLEIN and W. ZIESE (Z. physiol. Chem., 1932, 211, 23—37).—Passage of O_2 and particularly of CO_2 through suspensions of calf- and ox-liver inhibited arginase action. Cysteine and glutathione showed strong inhibition both in the acid and in the alkaline region at concns. of 0.045—0.45 mg. per c.c. There was no evidence of activation in EtOH-extracted liver or rat sarcoma extract. HCN inhibited, but H_2S was inactive.

J. H. B.

Preparation and enzymic hydrolysis of amyl phosphates. F. F. VON FALKENHAUSEN (Biochem. Z., 1932, 253, 152—160; cf. this vol., 142).—*dl*-Mono- and -tri-amyl phosphates are obtained by Limpricht's method (Annalen, 1865, 134, 347). Takaphosphatase hydrolyses the mono-compound (the *l*-component being slightly more rapidly attacked than the *d*), but not the tri-compound.

W. McC.

Preparation and enzymic hydrolysis of *l*- and *dl*-fenchyl pyrophosphates. E. OCHIAI (Biochem. Z., 1932, 253, 185—192).—*l*- and *dl*-*Difenchyl pyrophosphates*, $(C_{10}H_{17})_2H_2P_2O_7$, m.p. 176° (decomp.) (*l*-compound, $[\alpha]^{22}_D -13.92^\circ$), prepared by the action

4 R

of $POCl_3$ on the corresponding alcohols, are hydrolysed (in the form of their Na_2 salts) by takaphosphatase. The hydrolyses are about 57% complete after 268 hr. and, in the case of the *dl*-compound, the process is asymmetric, about 50% of the alcohol liberated being laevorotatory. The H phthalate of the *dl*-alcohol was prepared from the hydrolysate. The NH_4 and Ag salts of $C_{10}H_{17}H_2PO_4$ and a substance, m.p. $181-182^\circ$ (decomp.), $[\alpha]_D -14.17^\circ$, are obtained as by-products. The substance contains $C_{10}H_{17}H_2PO_4$.

W. McC.

Chemistry of alcoholic fermentation. K. MYRBÄCK (Svensk Kem. Tidskr., 1932, 44, 207—222).—A discussion.

H. F. H.

Indene and indones in alcoholic fermentation. F. PIRRONE (Annali Chim. Appl., 1932, 22, 501—508).—Indene, β -phenyl- α -methyl- and -ethyl-indone produce max. acceleration in the fermentation of glucose by yeast when the concn. is, respectively, 5.71, 0.98, 0.95, and 0.96 mg. per 100 c.c. of solution. The accelerative power in indones containing an aromatic group is less than in those containing an aliphatic group. In the latter the accelerative power increases with the no. of C atoms.

O. F. L.

Inhibition of fermentation by halogen compounds. E. SIMON (Biochem. Z., 1932, 253, 218—221).— $CH_2I \cdot COMe$ (concn. 1 : 5000), $CH_2I \cdot CHO$, and $CH_2Br \cdot CHBr \cdot CHO$ (concn. 1 : 1000) inhibit alcoholic fermentation, but $CBr_3 \cdot CH_2 \cdot OH$, $CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot OH$, $CH_2I \cdot CH(OEt)_2$, $CH_2Br \cdot CHBr \cdot CH_2 \cdot OH$, $CH_2I \cdot CH_2 \cdot OH$, and $CH_2I \cdot CH(OH) \cdot CH_2 \cdot OH$ in concn. of 1 : 1000—1 : 5000 do not.

W. McC.

Trehalose content of, and the power to form trehalose of, bottom yeast. S. VEIBEL (Biochem. Z., 1932, 252, 305—308).—Quant. evidence is brought in support of the view of Robison and Morgan (A., 1928, 1285) that trehalosephosphate is actually synthesised during fermentation and not merely the result of phosphorylation of trehalose preformed in the yeast, as suggested by Kluyver (this vol., 428).

P. W. C.

Classification of cultivated yeasts by means of the cytochrome spectrum. H. FINK (Z. physiol. Chem., 1932, 210, 197—219).—The cytochrome spectra of a no. of strains of cultivated yeast may be divided into two types: (a) the four-banded spectra typical of reduced cytochrome, belonging to the baker's yeast or respiration type of organism, (b) the two-banded spectra characteristic of brewer's, distiller's, and, in general, fermentation yeasts. The wild yeasts belong to type (a). The cytochrome factor in type (a) is about double that of (b). A change of one type into the other does not occur spontaneously, but may be induced by suitable cultivation. It is particularly easy to convert baker's yeast into the fermentation type. The method may be used for detecting adulteration of baker's yeast with the cheaper brewer's variety.

J. H. B.

Respiration of moulds. I. Respiratory quotient and the influence of oxidation-reduction processes on the gaseous metabolism of the cell. II. Energetics of growth. H. TAMURA (Acta Phytochim., 1932, 6, 227—263, 265—304).—I. The

gaseous exchanges of *Aspergillus oryzae* and of other moulds during rest and in presence of various C-providing substrates were investigated. The R.Q. is proportionately $>$ or $<$ the combustion quotient (C.Q.) of the substrate, according to whether the val. for the C.Q. is $>$ or $<$ approx. 0.875, a val. equal to the C.Q. of the mould constituents taken as a whole. Thus the differences recorded depend on the increased or decreased provision of CO_2 and O_2 together with the effect due to growth and variations in metabolism.

II. Various theoretical concepts of the energy exchange are applied to moulds utilising different substrates as a supply of C. The energy resulting from respiration during vital synthesis appears to be mainly utilised for (a) the maintenance of enzymic and structural energy, (b) replacement of heat loss during certain stages of synthesis, and (c) the activation of the substrate necessary for acceleration of the velocity of the reactions during synthesis.

F. O. H.

Alcoholic fermentation by *Aspergillus oryzae*. K. SAKAGUCHI and M. NAKANO (J. Agric. Chem. Soc. Japan, 1932, 8, 115—122).—Conditions for fermentation lead to classification of varieties of *A. oryzae*.

CH. ABS.

Production of acids by *Aspergillus niger*. VI. Production of glycollic and glyoxylic acids from acetates. K. BERNHAUER and Z. SCHEUER. VII. Conversion of alcohol into citric acid. VIII. Conversion of aconitic into citric acid. Degradation of acetic acid. K. BERNHAUER and N. BOCKL. IX. Fixing of acetaldehyde in mould cultures. K. BERNHAUER and H. THELEN (Biochem. Z., 1932, 253, 11—15, 16—24, 25—29, 30—36; cf. A., 1929, 218; 1931, 1333).—VI. The $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I), which is produced by many strains of *A. niger* from $\text{Ca}(\text{OAc})_2$ and NaOAc , rapidly disappears from the cultures and is replaced by $\text{CHO}\cdot\text{CO}_2\text{H}$, which is also produced concurrently. Since NaOAc yields more $\text{H}_2\text{C}_2\text{O}_4$ than does $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ and sometimes more than does Na succinate , it is concluded that AcOH is converted into $\text{H}_2\text{C}_2\text{O}_4$ by way of succinic acid rather than by way of (I). The last two acids may be converted not only into $\text{H}_2\text{C}_2\text{O}_4$, but also into citric acid.

VII. Certain strains of *A. niger* convert EtOH (2% solution) in presence of KHCO_3 into citric acid (best yield 36%). $\text{H}_2\text{C}_2\text{O}_4$, malic acid (especially), tartaric acid, and reducing substances (probably sugars) are also produced. The yield of citric acid from EtOH is greater than that from acetates, but the yield of $\text{H}_2\text{C}_2\text{O}_4$ from the latter is greater than that from EtOH .

VIII. Although most strains of *A. niger* produce only small amounts or traces of citric acid from K aconitate, a yield of $> 20\%$ was obtained with one strain, which also converted citric into aconitic acid. Usually $\text{H}_2\text{C}_2\text{O}_4$ and sometimes also reducing substances were simultaneously produced.

IX. Under suitable conditions and in presence of Na_2SO_3 , MeCHO is sometimes obtained in 60% yield from sucrose by the action of *A. niger*. If Na_2SO_3 is absent, considerable amounts of $\text{H}_2\text{C}_2\text{O}_4$ and citric acid are produced, but when MeCHO is produced these acids are not.

W. McC.

Production of acids from sugar by *Aspergillus niger*. V. Production of malic acid along with citric acid. K. BERNHAUER, N. BÖCKL, and H. SIEBENÄUGER (Biochem. Z., 1932, 253, 37—41).—Together with almost theoretical yields of citric acid small amounts (2 g. from 975 g. of sucrose) of malic acid are obtained by the action of *A. niger* on sucrose.

W. McC.

Acid formation and mycelium production by *Aspergillus niger*. A. FREY and H. POSCHENRIEDER (Arch. Mikrobiol., 1932, 3, 409—421).—The effect of K on the wt. of mycelium, and especially on the amount of acid produced by *A. niger*, varies with the age of the culture. In the determination of the available K content of soil by means of *A. niger*, dissolution of soil-K by org. acids produced by the organism is negligible.

A. G. P.

Biological synthesis of *m*-digallic acid. M. NIERENSTEIN (Biochem. J., 1932, 26, 1093—1094).—The acid was isolated as Me pentamethyl-*m*-digallate from solutions of gallic acid which had been acted on by *Aspergillus niger* or tannase.

S. S. Z.

Inhibiting influence of colloidal starch, inulin, and agar on the stimulation of *Aspergillus niger* by zinc sulphate. K. B. STEHLE (Bull. Torrey Bot. Club, 1932, 59, 191—217).—Stimulation by ZnSO_4 did not occur when the concn. of sugar was below a certain level, when starch or inulin was used instead of sugar, or when agar-agar was added to the sugar. The presence of a colloid also protects the fungus from the effects of otherwise lethal concns. of ZnSO_4 . Adsorption of Zn is partly responsible.

CH. ABS.

Effect of organic stimulants on the production of kojic acid by *Aspergillus flavus*. O. E. MAY, G. E. WARD, and H. T. HERRIC (Zentr. Bakt. Par., 1932, 86, II, 129—134).—Among numerous org. compounds examined ethylene chlorohydrin alone (100 mg. per litre) stimulated kojic acid production. Thiourea, thioglycollic acid, NaCNS , chloroacetone, and *o*- and *p*-chlorophenol were inhibitory.

A. G. P.

Effect of olive oil on the metabolism of certain fungi. I. R. S. KATZNELSON (Arch. sci. biol., Russia, 1931, 31, 385—398).—*Aspergillus flavus* (I), *Penicillium sylvaticum* (II), and a white fungus (III) utilised (15—70%) olive oil as a source of C. The mycelium-N and H_2O were diminished. Addition of olive oil to a medium containing glucose diminishes the consumption of glucose by (I) and (III). Addition of glucose to a medium containing olive oil increases the consumption of the oil by (I) and diminishes it by (II) and (III). On the basis of dry wt. the addition of glucose diminishes oil utilisation by all forms. Glycerol gives similar results when used with olive oil in the media. The acidity of the residual oil does not depend on the composition of the medium. Sap. and I vals. were relatively unchanged. The Reichert-Meissl val. was raised by (I) and (II) and lowered by (III).

CH. ABS.

Iron, zinc, and *Aspergillus*. R. A. STEINBERG (Zentr. Bakt. Par., 1932, II, 86, 139—142).—A reply to Bortels (Angew. Bot., 1929, 11, 285). The rôle of

Zn as an essential nutrient rather than a stimulant is emphasised. A. G. P.

Action of certain moulds on solutions of aldoses. IV. Formation of oxalic acid from *d*-gluconic acid. A. ANGELETTI (Annali Chim. Appl., 1932, 22, 404—407; cf. A., 1930, 1620; this vol., 145).—Cultures of *Penicillium luteum purpurogenum* (strain 2A) convert a 3% solution of Ca *d*-gluconate, at 22—25°, almost quantitatively in 3 months into CaC₂O₄; no traces of other acids are found. E. W. W.

Effect of fat-soluble vitamin on the growth of some parasitic fungi. Y. TOCHINAI and M. TERUI (J. Fac. Agric. Hokkaido, 1932, 32, 71—107).—Retardation of the growth of pathogenic fungi from rice is reported. CH. ABS.

Growth requirement of *Staphylococci*. T. P. HUGHES (J. Bact., 1932, 23, 437—447).—The constituent of meat extract capable of stimulating the growth of *Staphylococci* belongs to the class of "natural bases." Its chemical properties are recorded and its possible relationship to vitamin-B is discussed. A. G. P.

Application of the autocatalytic growth curve to microbial metabolism. H. C. PULLEY and J. D. GREAVES (J. Bact., 1932, 24, 145—168).—The rates of nitrate accumulation by mixed cultures of soil organisms and of CO₂ by *Saccharomyces cerevisiae* may be represented by equations derived from that expressing the rate of a unimol. autocatalysed reaction. A. G. P.

Isolated occurrence of carboxylase. Enzymic actions of the acetic bacterium *Bordeaux*. C. NEUBERG and E. SIMON (Biochem. Z., 1932, 253, 225—230; cf. Simon, A., 1930, 1477; Quere, A., 1931, 1334).—Under the conditions formerly chosen *B. Bordeaux* does not attack sugar. It contains carboxylase and mutase, but no zymase, and it produces methylglyoxal from hexosediphosphate, converts methylglyoxal into lactic acid, and attacks pyruvic acid. It is doubtful whether it is similar to *B. acetigenum*, Henneberg. W. McC.

Fermentation citric acid. J. H. FRYDLENDER (Mon. Prod. chim., 1932, 14, No. 155, 3—13; Chem. Zentr., 1932, i, 1961).—A discussion. A. A. E.

Nitrogen requirements of the lactic acid bacteria. B. A. EAGLES and W. SADLER (Nature, 1932, 130, 278).—In the fermentation of carbohydrates by lactic acid streptococci, both the source (proteose, peptone, and sub-peptone) and the amount of N employed are crit. L. S. T.

***Lactobacillus* genus with special reference to xylose fermentation by *L. pentoaceticus*.** L. WEINSTEIN and L. F. RETTGER (J. Bact., 1932, 24, 1—28).—Fermentation of xylose by *L. pentoaceticus* yields AcOH and *r*-lactic acid in the approx. ratio 42:58. Excess of base, e.g., CaCO₃, must be present to ensure complete reaction. The total acid yield corresponds with 88.90% of the xylose destroyed and is not influenced by the O₂ tension. A. G. P.

Transformation of acetylene by *Mycobacterium lacticola*. L. BIRCH-HIRSCHFELD (Zentr. Bakt. Par., 1932, II, 86, 113—129).—C₂H₂ is oxidised

by *M. lacticola* with the production of CO₂. MeCHO is an intermediate product. The activity of the organism is favoured by the presence of soil extracts. Growth is retarded in an atm. containing > 40% O₂ or > 80% C₂H₂. A. G. P.

Lipins of tubercle bacilli. XXVII. Composition of the phosphatide fraction of *Bacillus leprae*. R. J. ANDERSON and N. UYER (J. Biol. Chem., 1932, 97, 617—637).—The phosphatides from the EtOH-Et₂O extract of *B. leprae* (this vol., 307) are more stable than those from other acid-fast bacteria. Hydrolysis by EtOH-KOH liberates fatty acids and glycerophosphoric acid, whilst a polysaccharide complex is left intact. The latter, on hydrolysis with dil. acids, yields mannose, inositol, and a reducing hexose (invert-sugar or fructose). The fatty acids include palmitic acid, a saturated acid of high mol. wt., two unsaturated acids which yield palmitic and stearic acid, respectively, on reduction, and a saturated, optically active, liquid acid. The Et₂O extract contains an unsaturated, optically active, wax-like substance of high mol. wt. F. O. H.

Nitrogen changes produced in certain nitrogenous compounds by *Azotobacter* and the nitrogen fixed in presence of these compounds. L. G. THOMPSON, jun. (J. Agric. Res., 1932, 45, 149—161).—Four species of *Azotobacter* decomposed NaNO₃, KNO₃, KNO₂, urea, and asparagine (amide-N only) with the production of NH₃, which was then utilised by the organisms. All compounds inhibited the fixation of free N, and in some cases there was a loss of NH₃. NH₂-acids were utilised to only a small extent. In general, the simpler compounds were utilised more easily, and had a greater depressive action on the fixation of free N₂, than the more complex materials. With all species except *A. vinelandii*, high N fixation in N-free media and high NO₃⁻ consumption in NO₃⁻ media were coincident. A. G. P.

Influence of molybdenum and of soil extract constituents on nitrogen fixation by *Azotobacter chroococcum*. L. BIRCH-HIRSCHFELD (Arch. Mikrobiol., 1932, 3, 341—361).—The ratio of N fixed to sugar consumed by *A. chroococcum* is markedly increased by addition to media of soil extract or Na₂MoO₄. The rate of growth of the organism is accelerated by soil extracts, but not by Na₂MoO₄, the effect of the former being apparent during the assimilation of either free N₂ or of NO₃-N. The NO₃-N assimilated per unit sugar consumption is not influenced by either stimulant. Soil extracts contain both org. and inorg. activators, the former being associated with accelerated growth rates. The ash of soil extracts increases the N₂ fixed per unit of sugar consumed to approx. the same extent as does Na₂MoO₄, but does not affect growth rates. A. G. P.

Identification of *Brucella*, isolated in France, by means of the bacteriostatic action of dyes and the production of hydrogen sulphide. R. M. TAYLOR, M. LISBONNE, and G. ROMAN (Ann. Inst. Pasteur, 1932, 49, 284—302).—Strains of *Brucella* may be classified into the types *Br. melitensis*, *Br. abortus bovis*, and *Br. abortus suis* by means of (1) the bacteriostatic action of dyes (thionine and basic

fuchsin), (2) production of H_2S , and (3) the necessity of a CO_2 atm. for the growing culture. W. O. K.

Biological oxidations. I. Oxidations produced by gonococci. E. S. G. BARRON and C. P. MILLER, jun. (J. Biol. Chem., 1932, 97, 691—715).—Glucose, but not fructose, galactose, mannose, arabinose, or xylose, is fermented by the organism to $AcOH$ and CO_2 . Intermediate products are $AcCO_2H$ and lactic acid, which are formed by the action of two distinct enzymes. α -OH- and -keto-acids are oxidised by gonococci. The stability and p_H optima of the enzymes concerned are investigated. F. O. H.

Biochemistry of bacteriospores. A. I. VIRTANEN and L. PULKKI (Suomen Kem., 1932, 5, B, 46).—In *B. mycoides* the spores and corresponding vegetative cells are similar in composition with regard to H_2O , ash, N, and fat. The thermostability of the spores is therefore not due to their characteristic composition. The vegetative cells contain catalase, and four times as much polypeptidase as the spores, and ferment 80% of glucose to lactic acid. The spores contain no catalase, and do not ferment glucose. A. C.

Directive influences in biological systems. II. Lipase actions of types I and II pneumococci. K. G. FALK and G. MCGUIRE (J. Biol. Chem., 1932, 97, 651—655).—The hydrolysing properties of various batches of broth media in which the pneumococci had been grown show marked differences when tested on four different esters. Hence the resulting enzyme action of such a culture medium is partly determined by the broth itself. F. O. H.

Antipneumococcic immunity reactions of individuals of different ages. W. D. SUTLIFF and M. FINLAND (J. Exp. Med., 1932, 55, 837—852).

CH. ABS.

Specific antibody response of human subjects to intracutaneous injection of pneumococcus products. M. FINLAND and W. D. SUTLIFF (J. Exp. Med., 1932, 55, 853—865).—Simultaneous injection of the sp. polysaccharides of all three types of pneumococcus and of proteins and autolysates derived from types I and II produced or increased pneumococcal power in the whole defibrinated blood and generally caused the appearance of mouse-protective antibodies and agglutinins for one or more types. Injection of the protein-free type-sp. polysaccharide of I, II, or III usually produced antibodies against the homologous, but not against the heterologous, type. Injection of the protein did not appreciably produce sp. antibodies. Autolysates from virulent strains of I, II, or III caused a rise in the pneumococcal power with (in 33% of cases) the appearance of homologous type agglutinins and protective antibodies. CH. ABS.

Adsorption of diphtheria antitoxin with aluminium hydroxide. A. HANSEN (Compt. rend. Soc. Biol., 1931, 108, 570—572; Chem. Zentr., 1932, i, 2727).—The active constituent is not specifically adsorbed by $Al(OH)_3$, but from dil. serum protein is adsorbed together with the antibody. A. A. E.

Diphtheria toxoid precipitated with alum. D. M. WELLS, A. H. GRAHAM, and L. C. HAVENS (Amer. J. Pub. Health, 1932, 22, 648—650).—Com-

plete pptn. of toxoid with alum effects concn.; >50% of the original protein remains in the filtrate.

CH. ABS.

Effect of aliphatic amines and amides on diphtheria toxin. S. SCHMIDT (Compt. rend. Soc. Biol., 1931, 108, 536—537; Chem. Zentr., 1932, i, 2727).—At p_H 7.5, hexamethylenetetramine, valine, and glutamic acid have a slight detoxicating action; NH_2OH , choline, neurine, putrescine, and cadaverine are inactive. Urea has a very slight detoxicating effect. A. A. E.

Effect of benzene derivatives on diphtheria toxin. S. SCHMIDT (Compt. rend. Soc. Biol., 1931, 108, 537—539; Chem. Zentr., 1932, i, 2727).— $PhOH$, resorcinol, and cresols (particularly *m*- and *p*-) are strong detoxicants; of the aminobenzoic acids the *p*-compound is least active. Vanillin, eugenol, anisaldehyde, cinnamaldehyde, $PhCHO$, $BzOH$, $COPhMe$, and $NMe_2 \cdot C_6H_4 \cdot CHO$ are active; camphor, nicotine, and salicin are inactive. A. A. E.

Properties of cryptotoxins. H. VINCENT (Compt. rend. Soc. Biol., 1932, 109, 15—17; Chem. Zentr., 1932, i, 2338).—Chemically detoxicated bacterial toxins are not decomposed by the detoxication. The complex toxin-detoxicant can regenerate the toxin, e.g., at p_H 7, or in the animal body by overdosage. A. A. E.

Agglutinogens of the vibron septique. Comparative value of anti-O and antitoxic serum. M. WEINBERG, J. DAVESNE, and P. HABER (Ann. Inst. Pasteur, 1932, 49, 303—318).—The existence of the two agglutinogens, O and H, of Felix and Robertson, (Brit. J. Exp. Path., 1930, 19, 14) in the vibron is confirmed. Anti-O serum has no advantage over the usual antitoxic serum prepared by immunisation with the living bacterium. W. O. K.

Comparison of results [of bacteriological examination of water] with standard-lactose, brilliant-green bile, and Dominick-Lauterbroths. N. J. HOWARD (J. Amer. Water Works Assoc., 1932, 24, 1305—1310).—In raw H_2O samples brilliant-green bile produced 1.4% and Dominick-Lauterbroth 0.7% more confirmed results than lactose broth. In filtered H_2O lactose broth gave 2.4% more than either of the others, but in chlorinated H_2O out of 29 fermented lactose tubes only one or 3.4% was confirmed, whereas the other broths had each two fermented tubes of which one was confirmed. It is suggested that extended use might be made of brilliant-green bile broth as a confirmatory medium. C. J.

Intake of soluble matter by bacteria. II. Theory of Gram staining. H. HABS (Z. Hyg., 1932, 114, 1—10).—Gram-positive bacteria fix more I from I solutions than do negative organisms. Pretreatment with gentian-violet does not affect this action. Differences in I-fixation are probably related with variations in the lipin content. A. G. P.

Action at a distance of metals on *Bacillus coli*. E. LAGRANGE (Compt. rend. Soc. Biol., 1932, 109, 4—5; Chem. Zentr., 1932, i, 2339).—A thin Pb foil placed over an endo-fuchsin-agar plate inoculated with *B. coli* causes the reddening of the nutrient to

disappear. Ag, Fe, and Zn behave similarly; Ni has a less marked action, whilst brass, Cu, and mica are inactive. The foil becomes oxidised. The phenomenon is probably allied to the oligodynamic effect.

A. A. E.

Relationship between hydrogen-ion concentration and bactericidal action of various dyes. M. TAGAMI (Tohoku J. Exp. Med., 1932, 18, 482—511).—Fuchsin is most bactericidal in alkaline solution, Mc-green at p_H 6.97—6.58, and auramine at approx. neutrality. The germicidal action of crystal-violet, methylene-blue, and trypanflavine on streptococci and *B. coli* increases with alkalinity; safranin is most active at neutral or alkaline reaction, pyocyanine in neutral or slightly acid solution, and gentian-violet (0.01%) in alkaline solution. Cyanine and gentian-violet (0.2%) are independent of p_H . Brilliant-green and malachite-green are most active in acid, and rivanol in alkaline, solution. CH. ABS.

Relationship between hormones and the effect of non-specific cell activity on the blood-cholesterol. T. MIWA (J. Chosen Med. Assoc., 1931, 21, 21—36).—Cholesterolæmia was produced in rabbits by intravenous injection of caseinogen, but not if parathyroid, thyroid, thymus, or testicles were previously removed. CH. ABS.

Action of certain secretions on the intestinal dehydrogenation of fat. N. BEREND (Biochem. Z., 1932, 252, 366—369).—Ovarian and thyroid extracts increase the formation *in vitro* of triarachidonate from tristearin, whilst insulin and synthalin are inactive.

P. W. C.

Effect of internally secreting organs and nutrition on the calcium content of serum. A. BEZNAK (Magyar Orvosi Arch., 1931, 32, 438—450; Chem. Zentr., 1932, i, 1546).—Extirpation of spleen and pancreas is followed by a temporary fall in serum-Ca. A diet of potato or pickled cabbage raises it. No substance which increased serum-Ca could be obtained from these organs or foods. Insulin has no effect. L. S. T.

Influence of liver extract on liver metabolism. W. MILBRADT (Z. ges. exp. Med., 1932, 81, 256—267; Chem. Zentr., 1932, i, 2603—2604).—"Hepatrat" (I) produces increased ability to maintain high blood-sugar after insulin. Excretion of NH_2 -acid is less than under treatment with gelatin alone. In the mouse the glutathione content of the liver increases after injection of (I).

A. A. E.

Spleen as hormonal organ. E. SCHLIEPHAKE (Deut. Arch. klin. Med., 1932, 172, 523—538; Chem. Zentr., 1932, i, 2859—2860).—Injection of prosplen (I) into rabbits normalises the acid val. in hyper- and sub-acid conditions. The serum-protein falls, then rises above normal, and again falls. (I) is considered hormonal in nature.

A. A. E.

Spleen hormone. P. TREMONTI (La Riforma Med., 1930, 46, No. 35).—The hormone is probably acetylcholine. CH. ABS.

Action of adrenaline and its destruction in bodies of normal, starved, and phosphorus-poisoned rabbits with special regard to adrenaline poisoning by disturbance of liver function.

E. MARUI and H. MACHI (Fol. Pharmacol. Japon., 1932, 13, No. 3, 338—355).—Starved or P-poisoned animals are more sensitive, and there is less destruction of adrenaline with these animals. CH. ABS.

Effect of lactic acid on adrenaline glycogenolysis in the liver. S. KITAHARA (J. Chosen Med. Assoc., 1931, 21, 1031—1039).—Addition of lactic acid to Ringer solution used to perfuse the liver of bull-frogs *in situ* caused greater glycogenolysis than Ringer solution alone. The increased glycogenolysis persisted after removal of the reagents. CH. ABS.

Effects of thymocrescin and of extracts of lymph glands on growth. P. ROTHLSBERGER (Biochem. Z., 1932, 253, 137—142).—Extracts from lymph glands, prepared in the same way as those containing thymocrescin, have no growth-promoting effect on rats. W. McC.

Physiology of glands. CXXVIII. Thymocrescin. L. ASHER and A. ZENKLUSEN (Biochem. Z., 1932, 252, 309—324).—Further attempts to purify the active principle of thymocrescin solutions have been made (cf. A., 1930, 1615; 1931, 878). Thymocrescin is peptide-like, does not cause changes of blood-Ca and -P, but accelerates growth, especially of the sexual organs. P. W. C.

Thymus and glycaemic curve. P. NUZZI (Morgagni, 1931, 78, No. 8).—Thymus extract causes very slight hyperglycaemia. CH. ABS.

Glycogen test for thyroxine in the blood of the hyperthyroidised dog. A. WITTGENSTEIN (Pflüger's Archiv, 1932, 229, 299—310; Chem. Zentr., 1932, i, 2599).—The liver extract of male mice contains no glycogen when the mouse has been injected with thyroxine or with the blood of pregnant, exophthalmic goitrous, or hyperthyroidised dogs.

A. A. E.

Relationship between the effect of coccus toxin and hormone. Y. MURO (J. Chosen Med. Assoc., 1931, 21, 173—189).—Experiments on guinea-pigs indicate that thyroid hormone is specially necessary for resisting *Staphylococcus* toxin.

CH. ABS.

Secretin. J. MELLANBY (Proc. Roy. Soc., 1932, B, 111, 429—436; cf. A., 1928, 1403).—The prep. from duodenal mucosa and properties are described. Analysis and physical properties suggest a polypeptide structure. It is rapidly destroyed by proteolytic enzymes and will not dialyse through collodion membranes. Physiological actions are discussed.

H. G. R.

Chemical nature of secretin. R. N. CUNNINGHAM (Biochem. J., 1932, 26, 1081—1092).—A secretin concentrate is prepared as follows: extraction of dog's intestine with H_2O acidified with HCl, pptn. by saturation with NaCl, removal of protein by boiling on acid side of neutrality, pptn. with CCl_3CO_2H , extraction with 85% EtOH, pptn. with $COMe_2$ and Et_2O , pptn. as picrate, and pptn. with $COMe_2$ from an aq. EtOH-HCl solution of the picrate. The concentrate is free from depressor substance, insol. protein, NaCl, and picric acid. The threshold dose is about 0.5 mg. for a cat of 2.5 kg. body-wt. Secretin is a secondary protease. It is adsorbed by pptd.

protein from acid and neutral solution and by BzOH . The adsorbing power of the proteins is destroyed by denaturation with org. solvents. It passes through cellophane, but is retained by collodion membranes permeable to peptones. S. S. Z.

Hypoglycæmic action of callicrein. H. HERBIG (Arch. exp. Path. Pharm., 1932, 167, 555—572).—Injection of callicrein does not affect the blood-sugar level of starving or fed rabbits and dogs, whilst a marked decrease of the hypernormal level occurs with depancreatised dogs. The hyperglycæmia due to adrenaline is reduced to a variable extent by callicrein, the relationship of which to insulin is discussed. F. O. H.

Fundamental nature of parathormone action. J. P. MCGOWAN (Biochem. J., 1932, 26, 1138—1143).—The injection of large doses of parathormone intramuscularly into laying hens produces a deposition of $\text{Ca}_3(\text{PO}_4)_2$ inside the blood-vessels. S. S. Z.

Articular changes produced by various neurochemical agents. Denervation, administration of parathormone and vitamin-D. E. PRETO (Arch. Ist. Biochem. Ital., 1932, 4, 245—258).—Denervation of the limb causes but slight histological changes in the knee-joints of rats. Marked decalcification and other changes are observed after high doses of parathormone or of vitamin-D, aggravated in the first case by denervation. R. K. C.

Insulin and hyperglycæmia. WICHELS and LAUBER (Deut. Arch. klin. Med., 1932, 172, 613—621; Chem. Zentr., 1932, i, 2860).—Cryst. insulin gives no initial hyperglycæmia. The anti-insulin present in ordinary preps. is inactivated at definite [Novo insulin and Wellcome insulin, 5.8 (immediately), 6.6, 7 (gradually)]. A. A. E.

Effect on insulin of red and ultra-violet radiation. H. KÜSTNER and W. EISSNER (Klin. Woch., 1932, 11, 499—501; Chem. Zentr., 1932, i, 2481).—Red irradiation does not affect the activity of insulin, but ultra-violet light causes a marked transient loss. A. A. E.

Insulin and pituitocin. K. FREUDENBERG, E. WEISS, and H. EYER (Naturwiss., 1932, 20, 658).—Quant. study of the inactivation of insulin by BzO_2H indicates a mol. wt. of 10,000—30,000 for insulin, affording further evidence that the active grouping is linked in a protein chain. The pituitary hormone is not affected by pepsin or erepsin, but is inactivated by trypsin or papain. It is of high mol. wt. or is associated with a substance of protein nature. A. C.

Pituitary and metabolism. B. A. HOUSSAY (Rev. Circulo méd. Arg. y centro estud. méd., 1931, 356).—Pituitary gland activity stimulates protein metabolism. Deficiency of the gland has no influence on blood-sugar in normal conditions, but intensifies hypoglycæmic conditions. CH. ABS.

Composition of the tissues of albino rats treated with alkaline anterior pituitary extracts. E. BIERRING and E. NIELSEN (Biochem. J., 1932, 26, 1015—1021).—Only a small part of the increase in the wt. of rats induced by bovine anterior pituitary extracts is due to retention of H_2O . S. S. Z.

Effect of castration on the occurrence in guinea-pigs of the anterior pituitary hormone having an excito-secretory action on the thyroid gland. M. ARON and J. BENOIT (Compt. rend. Soc. Biol., 1931, 108, 784—786; Chem. Zentr., 1932, i, 1546—1547).—A few days after castration young guinea-pigs show marked thyroid activity; the serum and urine of these animals have the same effect on the thyroid of normal animals as the implantation of 0.001 g. of the anterior lobe of the ox. A. A. E.

Effect of castration on the occurrence in the fowl and the duck of the anterior pituitary hormone having an excito-secretory action on the thyroid gland. J. BENOIT and M. ARON (Compt. rend. Soc. Biol., 1931, 108, 786—788; Chem. Zentr., 1932, i, 1547).—The serum of the castrated fowl is most active towards the thyroid of guinea-pigs in spring; that of the normal fowl is of const. low activity. A. A. E.

Anterior pituitary gland, thyroid gland, and carbohydrate metabolism of the liver. H. EITEL and A. LOESER (Arch. exp. Path. Pharm., 1932, 167, 381—403).—Intraperitoneal injection of a thyrotropic extract of the anterior pituitary lobe into guinea-pigs is followed in 2 hr. by functional and morphological changes in the thyroid gland together with a decrease in the liver-glycogen, which returns to normal levels within 24 hr. Further stimulation of the thyroid gland results in a decrease in liver-glycogen only after a latent period of approx. 4 days. Continued effective stimulation renders the liver nearly glycogen-free. The increased activity of the thyroid gland and the decrease in liver-glycogen are both reversible. No marked change occurs in the muscle-glycogen. Thyroidectomy inhibits this decrease in liver-glycogen. F. O. H.

Anterior pituitary gland and thyroid gland. (a) Effect of anterior pituitary on the activity of the thyroid gland. (b) Iodine contents of blood and thyroid gland following administration of anterior pituitary extracts. W. GRAB (Arch. exp. Path. Pharm., 1932, 167, 313—333, 413—441).—(a) The thyrotropic influence of the anterior pituitary lobe was investigated in dogs by means of the MeCN toxicity method. Intraperitoneal injection of anterior lobe suspensions resulted in an increased secretion of the thyroid hormone into the blood-stream followed by a compensatory increase in the activity of the thyroid gland.

(b) Intraperitoneal injection of COMe_2 -dried anterior pituitary lobe is followed in normal but not in thyroidectomised dogs by a marked and prolonged decrease of the I and colloid matter of the thyroid gland, together with a more transient increase in the blood-I, especially in the EtOH -insol., protein-bound fraction. Between the injection and the excretion of I in the urine intervenes a latent period of approx. 3 days, the total urinary I forming only a fraction of that liberated into the blood. Hypophysectomy results in a decrease in blood-I. F. O. H.

Hormonal-nervous regulation of the function of the anterior pituitary lobe. W. HOHLWEG and K. JUNKMANN (Klin. Woch., 1932, 11, 321—323; Chem. Zentr., 1932, i, 1548). A. A. E.

Prolongation of pregnancy. A. M. HAIN (Nature, 1932, 130, 402).—Experiments on rats indicate the existence of a substance, possibly in the anterior pituitary, and probably neither gonadotropic nor growth hormone, which exerts an inhibiting effect on uterine motility. L. S. T.

Hormonal action of the placenta. E. PHILIPP (Deut. med. Woch., 1932, 58, 217—219; Chem. Zentr., 1932, i, 1546).—In pregnancy the placenta is the source of the anterior pituitary sexual hormone. L. S. T.

Gonadotropic hormones (ρ -factors). III. **Purification and properties.** P. G. MARSHALL (Biochem. J., 1932, 26, 1358—1364).—The hormones can be purified by ultrafiltration. The purified product contains a polypeptide containing tyrosine. The presence of a sugar complex or of tryptophan is doubtful. 0.1 mg. of the product will induce rupture of the follicles with probable ovulation in the rabbit within 24 hr. S. S. Z.

Surface films of oestrin derivatives. N. K. ADAM, J. F. DANIELLI, G. A. D. HASLEWOOD, and G. F. MARRIAN (Biochem. J., 1932, 26, 1233—1241).—Surface pressure and surface potential measurements of diacetyltrihydroxyoestrin Me ether and triacetyltrihydroxyoestrin indicate that the mols. probably have an anthracene or phenanthrene skeleton or a system of four condensed rings with two alcoholic OH groups near one end of the mol., and one phenolic group near the other end. The alcoholic groups are probably in the *cis*-position relative to each other on adjacent C atoms and are inclined at a steep angle to the plane of the ring in which they are situated. *cyclo*Hexanols with long chains in the *para*-position to the OH group give condensed films of area about 30 sq. Å. per mol., slightly smaller than the cross-section of the oestrin mols. S. S. Z.

Rat and mouse units of folliculin. A. LIPSCHUTZ (Compt. rend. Soc. Biol., 1931, 108, 754—756; Chem. Zentr., 1932, i, 1546).—Six injections during 60 hr. show that the rat unit is three times as strong as the mouse unit. L. S. T.

New isomeric follicular hormone from mare's urine. E. SCHWENK and F. HILDEBRANDT (Naturwiss., 1932, 20, 658—659).—In addition to the isomeric hormones of Butenandt and Stormer (this vol., 781), a further *isomeride*, termed "*o*-hormone," $C_{18}H_{22}O_2$, m.p. 209°, $[\alpha]_D +46.33^\circ$ in $CHCl_3$ (benzoate, m.p. 177°, $[\alpha]_D +36.48^\circ$), has been isolated, with much higher activity. It also differs from other isomerides in the deeper colour of conc. H_2SO_4 solution. A. C.

Concomitance of male and female sexual hormones. B. FRATTINI and M. MAINO (Biochem. Z., 1932, 253, 202—203).—The male sexual hormone occurs in the glands and fluids of the male only, the female sexual hormone in those of the female only, but both hormones have a common action on the genital tract of both sexes. The hormones differ in their action on the secondary sex characters (cock's-comb test). Loewe and others (A., 1931, 1097) omitted to take the authors' units and doses into account. Injections of cholesterol and ergosterol (5—10 mg.) produce oestrus, and hence the effects produced by

bile and faeces may be due to these substances rather than to a hormone. W. McC.

Castrated rats for the assay of testicular hormone. V. KORENCHESKY (Biochem. J., 1932, 26, 1300—1305).—The average variations in the wt. of retroperineal fat, sexual and endocrine organs, as calc. per unit of body-wt., are not great in the castrated male rat of the same degree of sexual maturity. S. S. Z.

Response of castrated male rats to the injection of testicular hormone. V. KORENCHESKY, M. DENNISON, and R. SCHALIT (Biochem. J., 1932, 26, 1306—1314).—In castrated rats the most sensitive organs suitable for the assay of testicular hormone are the atrophied prostate with seminal vesicles; the penis and thymus are less sensitive. The increase in wt. of the prostate with seminal vesicles is much greater in rats castrated before than after puberty, does not vary much in rats belonging to different litters, and is proportional to the increase of the dose of the injected hormone. S. S. Z.

Growth and cell-reserves in vitamin investigations. I. Essential considerations. II. Normal growth in the rat's rib. III. Histological distinction between scurvy and Moeller-Barlow disease and their causes. IV. Aplastic-consumptive deficiency disease. (a) Osseous changes with diets free from vitamins or from fat-soluble vitamins. V. Aplastic-consumptive deficiency disease. (b) Highly unsaturated fatty acids and their salts and the occurrence of the hæmophilia of scurvy. W. KOLLATH (Arch. exp. Path. Pharm., 1932, 167, 469—477, 478—506, 507—520, 521—537, 538—554).—I. Preliminary considerations in the study of diseases due to dietary deficiencies are discussed.

II. A detailed histology of the ossification in the rat's rib is given.

III. With true scurvy all formation of new bone or cartilage ceases, whereas in Moeller-Barlow disease such formation may occur.

IV. In order to obtain complete efficacy of fat-sol. vitamins it is necessary to fulfil certain, and as yet mainly unknown, conditions which may be studied histologically in the developing bone in the case of A and D, and in the testes and ovaries in the case of E.

V. The addition of linolenic acid (or its K salt) to a diet free from vitamins and unsaturated fatty acids initiates bleeding from the intestine and bone-marrow and accelerates the loss in wt. and the incidence or death. This effect, which is probably due to an action on membrane permeability, is inhibited by the presence of cotton-seed oil. F. O. H.

Vitamin content of dried figs and dates. M. ALI (Arch. Hyg., 1932, 107, 219—233; Chem. Zentr., 1932, i, 2199).—Dried dates contain little vitamin-B, and no -A, -C, or -D. Dried figs are relatively rich in vitamin-A, contain a moderate amount of -B, very little -C, and possibly a trace of -D. A. A. E.

Action of radioactive substances on vitamins. A. G. HOGAN, C. H. SHREWSBURY, G. F. BRECKENRIDGE, and W. S. RITCHIE (J. Nutrition, 1932, 5,

413—420).—Exposure to β -rays leads to the destruction of the vitamin-A of milk. Vitamins-B₁, -C, -D, and -B₂ are not affected by β - or γ -rays. A. G. P.

Evidence of the existence of a dietary principle stimulating general growth and lactation. L. W. MAPSON (Biochem. J., 1932, 26, 970—986).—The principle, "physin," which is present in ox-liver is not identical with any of the hitherto known accessory food factors and has a more marked effect on the growth rate of the male than the female rat. The stimulating effect on the growth rate after weaning is transmitted from a parent which has received the active substance in its diet to the first but not second generation fed solely on the synthetic diet. In these animals the growth acceleration is more prolonged than in those which received the liver directly. The average no. born to parents fed on liver is higher than in the case of control animals. "Physin" is present in autolysed liver, in acid aq. extracts of liver, especially when the liver is previously autolysed, and in 90% EtOH extracts. The ash of liver does not stimulate growth. S. S. Z.

Vitamin-A content of the liver of various animals. H. SIMONNET, A. BUSSON, and L. ASSELIN (Compt. rend. Soc. Biol., 1932, 109, 358—359; Chem. Zentr., 1932, i, 1921).—High vals. were obtained with the ox, and low with the guinea-pig. Other differences (e.g., dog) could be attributed to conditions of nutrition. A. A. E.

Carotene and vitamin-A. B. WOOLF and T. MOORE (Lancet, 1932, 223, 13—15).—A discussion. L. S. T.

Structure of vitamin-A. I. M. HEILBRON, R. A. MORTON, and E. T. WEBSTER (Biochem. J., 1932, 26, 1194—1196).—Treatment of the product obtained from a concentrate by the action of EtOH-HCl with Se at 300—330° gives a good yield of 1 : 6-C₁₀H₆Me₂. The latter compound is also obtained by dehydrogenating a vitamin-A concentrate with Se at 300—330°. Vitamin-A must therefore be a compound of a terpenoid nature and the richest concentrates must contain a substance possessing a constitution which as far as the 14th C atom must be identical with the constitution advanced by Karrer *et al.* (this vol., 200). S. S. Z.

Characteristics of highly active vitamin-A preparations. I. M. HEILBRON, R. N. HESLOP, R. A. MORTON, E. T. WEBSTER, J. L. REA, and J. C. DRUMMOND (Biochem. J., 1932, 26, 1178—1193).—After freeing the unsaponifiable matter of very active liver oils from sterols by cooling to -50°, it was distilled fractionally at a pressure below 0.0001 mm. The vitamin passed over without decomp. in a main fraction, b.p. 137—138°. Redistillation did not effect further purification. Distillation of concentrates from halibut, sturgeon, or mammalian liver oils yielded a main fraction which gave substantially the same vals. for the 328, 617, and 580 m μ bands. In spite of the const. very high potency of the fractions obtained from various sources, there are indications that they are not absolutely homogeneous. Karrer's chromatographic method of concn. (A., 1931, 1463; this vol., 200) has no advantage over the distillation procedure. A distilled concentrate from sturgeon-liver oil brought

about an improvement in the general condition of and a slow resumption of growth in rats on a vitamin-A-free diet in daily doses of 0.025×10^{-6} g. A dose of 0.05×10^{-6} g. effects a rapid cure of the eye disease. The distilled concentrate, C₂₀H₃₀O (non-cryst. monobenzoate, b.p. 188—198°), is hydrogenated fairly readily and has I val. 306—324. On treatment with O₃ it yields geronic acid. S. S. Z.

Reaction of fish-liver oils with antimony trichloride. F. ENDER (Biochem. J., 1932, 26, 1118—1123).—The blue colour obtained by treating a vitamin-A concentrate from halibut oil with SbCl₃ and CHCl₃ at -30° to -50° was decomposed with excess of cooled aq. KOH. By extracting this mixture with C₆H₆, a highly saturated reddish-yellow oil, "the chromogenic fraction" (I), was obtained which still reacted with SbCl₃, but was biologically inactive in daily doses of 0.01—1 mg., as was also (in daily doses of 0.002—0.02 mg.) the amorphous dry powder obtained by treating (I) with EtOH. The "non-chromogenic fraction" obtained from the reaction of the oil concentrate with SbCl₃ was biologically inactive in daily doses of 0.05 and 0.4 mg. The absorption bands of the original concentrate and (I) together with spectra of their reaction products with SbCl₃ are given. (I) did not give the selective absorption in the region of 328 m μ characteristic of vitamin-A. S. S. Z.

Isomerisation of carotene by means of antimony trichloride. A. E. GILLAM, I. M. HEILBRON, R. A. MORTON, and J. C. DRUMMOND (Biochem. J., 1932, 26, 1174—1177).—When the blue solution obtained by mixing SbCl₃ and carotene in CHCl₃ is poured into H₂O red crystals can be isolated from the CHCl₃ layer. The absorption spectrum of the recovered product both in the visible and ultra-violet regions is quite different from that of carotene. The properties of the substance agree with those of isocarotene. It is biologically inactive. S. S. Z.

Absorption spectra of substances derived from vitamin-A. J. R. EDISBURY, A. E. GILLAM, I. M. HEILBRON, and R. A. MORTON (Biochem. J., 1932, 26, 1164—1173).—By pouring the mixture of potent liver oils or their concentrates with SbCl₃ into much H₂O a product is recovered which still gives a blue or purple colour with SbCl₃; vitamin-A has, however, been partly decomposed with the appearance of narrow absorption bands. The wave-lengths at the max. of these bands are const. irrespective of whether rich or poor oils or whether concentrates are used, but the intensities vary approx. with the potency of the material. Absorption bands with similar max. can be obtained with greatly enhanced definition by the action of EtOH-HCl on rich concentrates, the intensity, persistence, rate of development, and permanence depending on the concn. of HCl. They are therefore probably due in both cases to products of decomp. Similar narrow bands together with a broad continuous band with its max. at 290 m μ are obtained in certain fractions in the slow high-vac. distillation of concentrates at about 180°. Prolonged heating at 120—125° in N₂ produces the narrow bands to only a very small extent, the main product exhibiting a max. at 290 m μ . At the b.p. in EtOH vitamin-A

is stable to prolonged exposure to a stream of O_2 . O_3 rapidly destroys vitamin-A with the formation of products with max. at 290 and 272 $m\mu$ in the very early stages. S. S. Z.

Use of 7-methylindole in the antimony trichloride colour test for vitamin-A. R. A. MORTON (Biochem. J., 1932, 26, 1197—1201).—7-Methylindole, which is practically transparent in the region 290—350 $m\mu$ and does not interact with vitamin-A before the addition of $SbCl_3$, inhibits the capacity of vitamin-A-containing substances to give a blue colour with $SbCl_3$. S. S. Z.

Comparison of colorimetric, spectrographic, and biological methods for the determination of vitamin-A. R. J. NORRIS (Bull. Basic Sci. Res., 1931, 3, 249—256).—The physical tests of cod-liver oil showed fairly good correlation, but the results deviated from those of the biological tests, sometimes by amounts considerably greater than the probable biological error. Only biological tests are trustworthy. CH. ABS.

Transmission of vitamin-A from parents to young in mammals. W. J. DANN (Biochem. J., 1932, 26, 1072—1080).—Only a small amount of vitamin-A, which is not influenced by the amount of carotene in the mother's diet during gestation, is present in the liver of the rat or rabbit at birth. This amount increases two- or three-fold in the suckling or even more if the nursing mother receives extra carotene. There is a limit to this increase and to the amount of vitamin-A that passes into the milk. S. S. Z.

Influence of vitamin-A deficiency on male rats. M. M. SAMPSON and V. KORENCHESKY (Biochem. J., 1932, 26, 1322—1339).—The organs and their functions are affected in male rats on a vitamin-A-deficient diet both by the decrease in the food intake and by some other influence of the deficiency. At the stage of vitamin-A depletion at which the rats were killed, about 2/5 of the deficiency in body-wt. seemed to be due to the decreased food intake, whilst the loss of the remaining 3/5 was caused by some other direct influence of the deficiency. These proportions are reversed for the fat deposition. Wt. for wt. a vitamin-A-deficient diet produces a much smaller increase in body-wt. than a complete diet. S. S. Z.

Absorption of nitrogen and of fat from the alimentary canal of rats kept on a vitamin-A-deficient diet. M. M. SAMPSON, M. DENNISON, and V. KORENCHESKY (Biochem. J., 1932, 26, 1315—1321).—The intake of food in proportion to body-wt. of rats on the deficient diet during the period of checking or cessation of growth was even larger than that consumed by the rats on a complete diet. During the same period the absorption of N and of fat was not appreciably altered. In the last period there was a decrease in the intake and absorption of the food. During the whole period of observation the nitrogenous metabolism increased. S. S. Z.

New technique for the preparation of vitamin-A-free caseinogen. M. T. POTTER (Science, 1932, 76, 195—196).—Vitamin-A-free caseinogen can be

prepared by heating powdered commercial caseinogen spread in thin layers at 110° for 7 days. L. S. T.

International standard for vitamin-B. H. CHICK and H. M. JACKSON (Biochem. J., 1932, 26, 1223—1226).—This adsorption product on fuller's earth from an acid aq. extract of rice polishings is active in a daily rat dose of about 10 mg. and is stable for one year when stored either at room temp., at 37°, or in a refrigerator. Its vitamin-B₆ content is negligible. S. S. Z.

Ultra-violet absorption spectra of certain preparations containing vitamin-B. F. F. HEYROTH and J. R. LOOFBOUROW (Bull. Basic Sci. Res., 1931, 3, 237—248).—The spectra resemble those of purines and pyrimidines previously examined, particularly those irradiated with ultra-violet light from which short waves are excluded (cf. A., 1931, 1308). CH. ABS.

Independence of vitamin-B₁ deficiency and inanition. A. P. MEIKLEJOHN, R. PASSMORE, and R. A. PETERS (Proc. Roy. Soc., 1932, B, 111, 391—395).—The brains of pigeons suffering from vitamin-B₁ deficiency and before death treated with small quantities of B₁ extracts show a greater O_2 uptake in presence of lactate than do the brains of untreated animals. The results are independent of the general state of nutrition, but depend on the nervous symptoms exhibited by the animals at death. W. O. K.

Oxidations in avitaminosis-B and in fasting. P. E. GALVAO and D. M. CARDOSA (Pflüger's Archiv, 1932, 229, 422—438; Chem. Zentr., 1932, i, 2602).—In pigeons, all oxidations (total gaseous metabolism; respiration and glutathione content of muscle and liver) are diminished in fasting, but not in avitaminosis with food intake. Tissue and total oxidations vary in the same sense. Glutathione is markedly diminished in both fasting and avitaminosis. Diminution of oxidation processes is attributed to lack of oxidisable substances. The oxidising power of the liver is in all cases unchanged. Its glutathione content is normal in avitaminosis, but considerably diminished in fasting. A. A. E.

Comparative action of 2:4-dinitrophenol on the thermogenesis of pigeons in a state of inanition, normal pigeons, pigeons deprived of vitamin-B, and those receiving an excess of carbohydrates. (MME.) L. RANDOIN and H. SEMONNET (Bull. Soc. Chim. biol., 1932, 14, 993—1010).—The above four groups of pigeons resist the hyperthermal effect of 2:4-dinitrophenol in the (decreasing) order given. Pigeons in a state of avitaminosis-B react hyperthermally to sudden intense cold. The results are considered to support the theory that avitaminosis is due to a disturbance of the metabolism of energy-producing substances. A. A. L.

Chemical identification of vitamin-C. L. J. HARRIS and J. R. M. INNES (Lancet, 1932, 223, 235—237).—The antiscorbutic action of a sample of Szent-Gyorgyi's hexuronic acid has been confirmed. 1 mg. of acid had an activity slightly > that of 1 c.c. of orange juice. Raw suprarenal cortex has a high antiscorbutic activity approx. proportional to its hexuronic acid content. L. S. T.

Vitamin formation in plants. A. I. VIRTANEN and S. VON HAUSEN (Suomen Kem., 1932, 5, B, 45).—The vitamin-C content of blossoming pea plants is max. when the quartz-sand in which they grow has p_H 6—6.5, and, with KNO_3 as source of N, is twice as great as with $(NH_4)_2SO_4$. Oats harvested just prior to blossoming are much poorer in vitamin-C, the content of which is not affected by the p_H of the quartz-sand or the nature of the N supply. A. C.

Vitamin-C content of various fodder plants. A. I. VIRTANEN, E. LUNDMARK, and E. PELTOLA (Suomen Kem., 1932, 5, B, 45—46).—The vitamin-C content of grasses has been determined by titrating the reducing substance with 2 : 6-dichlorophenolindophenol. Significant variations are not observed in weekly cuttings, and the following figures represent the no. of c.c. of 0.001M reagent equiv. to 10 g. of fodder. Purple clover 22—35, hybrid clover 49—65, cocks'-foot 20—23, meadow fescue 26—38, red fescue 43, meadow grass 20—24, timothy 36. After 6—8 months' acid preservation "A.I.V." fodder has a val. of 10—20 (50—100 on dry wt.), and the val. for dry hay determined in spring is only 0—1. Guinea-pigs are fully protected from scurvy by daily doses of 3 g. of fresh purple clover or 3 g. of "A.I.V." prepared from a clover-rich grass. A. C.

Determination of vitamin-D in the line test by measurement. R. S. MORGAN (Biochem. J., 1932, 26, 1144—1154).—The area of new calcification, as shown on magnified camera-lucida drawings of the bone sections, is measured. The healing is proportional to the log. of the dose of vitamin-D. The chief source of error is the variable response of litter mates to a given dose of vitamin. S. S. Z.

Mode of action of irradiated ergosterol on the normal organism. J. WARKANY (Wien. klin. Woch., 1932, 45, 206—208; Chem. Zentr., 1932, i, 1922).—In rats a dose of 30—50 mg. produced marked phosphaturia, which apparently causes renal injury. A. A. E.

Production of non-fatal vascular sclerosis in rabbits by means of viosterol (irradiated ergosterol). T. D. SPIES (Arch. Int. Med., 1932, 50, 443—449).—Viosterol administered in toxic but non-fatal doses to rabbits produced extensive damage, associated with Ca deposition, in the aorta, lungs, and kidneys. W. O. K.

Effects on dogs of large doses of calciferol (vitamin-D). H. H. DALE, A. MARBLE, and H. P. MARKS (Proc. Roy. Soc., 1932, B, 111, 522—537; cf. this vol. 434).—Calciferol in excessive doses has the same toxic action as the crude product from the irradiation of ergosterol both by the intravenous and oral routes. Complete parathyroidectomy has no effect on the fatal intoxication. There is no evidence that vitamin-D in excessive doses acts by promoting secretion of the parathyroid hormone or by rendering the organism more responsive to its action. H. G. R.

Rise of blood-calcium of the dog after treatment with irradiated ergosterol. Variability of commercial preparations. J. CHEYMOL and A. QUINQUAUD (J. Pharm. Chim., 1932, [viii], 16, 161—

165).—Of three commercial preps. of irradiated ergosterol, one was inactive. The other two were active, but not equally so. W. O. K.

Milk, blood, and excreta of cows given moderate and excessive amounts of irradiated yeast or ergosterol. A. F. HESS, R. F. LIGHT, C. N. FREY, and J. GROSS (J. Biol. Chem., 1932, 97, 369—377).—Cows fed daily with irradiated yeast (60,000 units of vitamin-D and a high content of vitamin-B₁) yield a milk rich in vitamin-D, but only normal in -B₁. The P, Ca, and ash of the milk and the inorg. P and Ca of the serum remain normal, but all these were increased by excessive doses of irradiated ergosterol, and vitamin-D is also detectable in the blood (1 unit per 1.5 g.). With cows receiving 300 g. of irradiated yeast daily, about 25% of the vitamin-D ingested is excreted with the faeces, whilst none appears in the urine. Excessive dosage of irradiated ergosterol for long periods does not cause any lesion of cellular structure and the bone-ash remains normal. The greater is the production of milk the greater is the abs. content of the vitamin. F. O. H.

Role of vitamin-D in the nutrition of the dairy calf. I. W. RUPEL, G. BOHSTEDT, and E. B. HART (Proc. Amer. Soc. Animal Produc., 1932, 24, 137—141).—Rickets, with low blood-serum-Ca and -P, follows withholding of vitamin-D. CH. ABS.

Parathyroid and vitamin-D; influence on bones and growth. M. A. RANSON (Semana med., 1932, I, 1424—1425).—Simultaneous treatment causes more rapid development without hypercalcification of other organs. CH. ABS.

Effect of deprivation of vitamin-E on the lactating rat. J. MORELLE (Compt. rend. Soc. Biol., 1931, 108, 804—805; Chem. Zentr., 1932, i, 1681).—Paralysis is induced in the suckling young. A. A. E.

Respiratory quotients of succulent plants. T. A. BENNET-CLARK (Sci. Proc. Roy. Dublin Soc., 1932, 20, 293—299).—Variations in the O₂ intake and CO₂ output of darkened leaves of *Sedum praealtum* are recorded. High vals. for the R.Q. indicate that the disappearance of malic acid is not due to its oxidation, but the acid forms a definite link in the C cycle of succulent plants. A. G. P.

Automatically recording the oxygen intake of living tissues. T. A. BENNET-CLARK (Sci. Proc. Roy. Dublin Soc., 1932, 20, 281—291).—Apparatus is described in which the time taken for plant-tissue to absorb a definite vol. of O₂ is recorded automatically. The effective unit measured is 0.36 c.c. of O₂. An atm. of const. composition is maintained around the tissue. A. G. P.

Plant respiration. I. Course of respiration of *Lathyrus odoratus* during germination of the seed and the early development of the seedling. W. STILES and W. LEACH (Proc. Roy. Soc., 1932, B, 111, 338—355).—The output of CO₂ from a single germinating seed of the sweet pea measured by the katharometer exhibits 5 distinct phases: (1) a fairly rapid increase in respiration rate as the seed absorbs H₂O, (2) a period characterised by const. respiration

rate of very variable duration which continues until the seed-coat is ruptured, (3) a very rapid rise in respiration rate following the rupture of the testas, (4) a period of approx. const. respiration rate, and (5) a phase of slowly diminishing respiration rate. Removal of the testas largely eliminates phase 2. The decline of respiration in phase 5 is probably due to the particular experimental conditions tending to decrease the transpiration rate in the older seedlings and so to reduce the rate of conveyance of respirable material from the cotyledons to the growing parts.

W. O. K.

Temperature characteristic for the anaerobic production of carbon dioxide by germinating seeds of *Lupinus albus*. P. S. FANG (J. Gen. Physiol., 1932, 16, 65—73).—The mean temp. characteristic between 7.5° and 18° is 21,500 g.-cal., which is slightly but probably not significantly lower than the val. 23,500 for aerobic CO₂ production.

W. O. K.

Metabolism of algæ. I. Influence of potassium cyanide and methylene-blue on the respiration of green algæ. A. WATANABE (Acta Phytochim., 1932, 6, 315—335).—Although both KCN and methylene-blue increase the respiration of *Chlorella ellipsoidea*, their combined action is not additive. Glucose increases the respiration fourfold (with certain other algæ this accelerating action is, however, much less), but this increase is strongly inhibited by KCN. The accelerating action of thionine is less than that of methylene-blue on *Chlorella*, but with *Ulva lactuca* that of the former is double that of the latter.

F. O. H.

Gas content of algæ. Gas contained in *Enteromorpha compressa*, i Ag. Z. DANIN (Atti R. Accad. Lincei, 1932, [vi], 15, 831—834).—The young algæ behave like all the other species examined (A., 1930, 1072; 1931, 1198) but the % of O₂ produced is greater, owing either to greater activity of the chloroplast or to greater permeability to the other gases.

T. H. P.

Carbohydrates in the bulb of *Allium scorodoprasum*, L. II. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1931, 7, 1067—1069).—The bulb contains scorodose. The leaves did not give Selivanov's reaction. Starch was not present in either. There is more reducing sugar in the leaves than in the bulb.

CH. ABS.

Carbohydrates in the bulb of *Narcissus tazetta*, L., var. *chinensis*, Roem. I. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1931, 7, 1061—1066).—The rapidly dried (100°) bulb contained: H₂O 6.12, Et₂O-sol. 0.62, total sol. carbohydrates 82.16, total N 0.82, pentose 2.38, ash 2.29, crude fibre 2.88%; galactan and inulin were absent. The carbohydrate in the cold H₂O extract was a glucomannan ("suisen-glucomannan"), decomp. 212°, $[\alpha]_D^{20} +320^\circ$, which does not reduce Fehling's solution. Hydrolysis by dil. acid affords glucose and mannose (1:2); it was partly hydrolysed by snail (*Eulota*) extract, but not by diastase, emulsin, or malt extract.

CH. ABS.

Properties of starch from tropical and temperate climates. J. B. MCNAIR (Science, 1932, 76, 83).—Corrections of previous statements (this vol.,

663) are made. Starches and glycerides from plants grown in temperate climates have higher I vals. than those from tropical plants. The low m.p. of temperate glycerides correspond with the low gelatinisation temp. of the starches.

L. S. T.

A polysaccharide from the pollen of timothy grass (*Phleum pratense*). G. A. C. GOUGH (Biochem. J., 1932, 26, 1291—1294).—The polysaccharide, which on hydrolysis with acids yielded L-arabinose, galactose, and a non-reducing acid, was prepared by pptn. with basic Pb acetate at alkaline reaction from the digested pollen, after clearing with Pb(OAc)₂, and by fractional pptn. with EtOH and MeOH of the decomposed basic Pb fraction.

S. S. Z.

Pentosan content of *Kleinia articulata*. H. EVANS (Biochem. J., 1932, 26, 1095—1100).—*K. articulata* contains pentosan, which is present to only a small extent in solution in the cell-sap, similar to that found in other succulents.

S. S. Z.

Quince-seed mucilage. A. G. RENTREW and L. H. CRETCHER (J. Biol. Chem., 1932, 97, 503—510).—Quince-seed gum on hydrolysis with 0.5N-H₂SO₄ leaves an insol. residue (approx. one third) of α -, β -, and γ -cellulose. The hydrolysate contains, in addition to L-arabinose, a mixture of methylated and non-methylated aldobionic acids which, on further hydrolysis, yield hexuronic acid and xylose.

F. O. H.

Occurrence of sugar alcohols in marine algæ. II. Sorbitol. P. HAAS and T. G. HILL (Biochem. J., 1932, 26, 987—990; cf. this vol., 101).—Sorbitol was isolated as the CHPh₃ and Ac₆ derivatives from *Bostrychia scorpioides*.

S. S. Z.

Glucosides from tobacco leaves. I. K. YAMAFUJI (J. Agric. Chem. Soc. Japan, 1932, 8, 404—410).—*Tabacinin* (0.02%), sinters at 175°, decomp. 227°, gives in EtOH solution a green colour with FeCl₃. Acid hydrolysis affords glycuronic acid. *Tabacilin* (0.4—0.5%) on hydrolysis affords nicotine and glucose.

CH. ABS.

Reducing and non-reducing sugars and pentosan in red and white ginseng. Y. OSHIMA and S. NOMURA (J. Chosen Med. Assoc., 1931, 21, 558—561).—Radix primaria of white and red ginseng contain, respectively, 58.05 and 43.17% of total sugar and radices fibrillæ of white 39.34% (reducing sugars 0.93, 6.35, 0.45%). The percentages of pentosan are 6.40, 8.47, 9.03, and of cellulose 5.33, 9.36, 9.14.

CH. ABS.

Inorganic salts in Chosen ginseng. II. S. NOMURA and Y. OSHIMA (J. Chosen Med. Assoc., 1931, 21, 553—557).—Dry radices fibrillæ of white *Panax ginseng*, C. A. Mey, and of red ginseng, respectively, contain ash 6.14, 6.16%; SO₄ 0.537, 0.486; P₂O₅ 1.650, 1.635; Fe₂O₃ 0.092, 0.159; Al₂O₃ 0.125, 0.119; CaO 0.528, 0.466; MgO 0.052, 0.048; SiO₂ 0.131, 0.192; Mn trace, trace.

CH. ABS.

Acidic constituents of jute fibre. J. K. CHOWDHURY and M. N. MITRA (J. Indian Chem. Soc., 1932, 9, 291—296).—The fibre is boiled with 0.5% NaOH, delignified with ClO₂, and then extracted with aq. NH₃ (17%) at 45°; the resulting extract contains

glycogen and glycuronic, galacturonic, and mucic acids. Extraction of the delignified fibre with 0.5% $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at 85–90° yields pectin; the pectic acid, m.p. 233–235° (decomp.) (darkens at 195–197°), isolated by Candlin and Schryver's method (A., 1928, 1162), is hydrolysed by $\text{N-H}_2\text{SO}_4$ at 125–130° to arabinose, galactose, and galacturonic acid, and by 2.5% H_2SO_4 to the two sugars. H. B.

Relationship between natural uronic acids, pentoses, and pentosans. H. FRANKEN (Biochem. Z., 1932, 250, 53–60).—Xylose is detected as a decarboxylation product of glycuronic acid on boiling with 2% H_2SO_4 . Arabinose is detected on boiling galacturonic acid with either dil. H_2SO_4 , HF, or $\text{H}_2\text{C}_2\text{O}_4$. The amount of pentose is much smaller than corresponds with the CO_2 liberated. P. W. C.

Determination of the acids of plant tissue. I. Nitric acid. G. W. PUCHER, H. B. VICKERY, and A. J. WAKEMAN (J. Biol. Chem., 1932, 97, 605–615).—The powdered, air-dried material is treated with 4N- H_2SO_4 to p_{H} 0.7–0.9 and extracted with Et_2O . Aq. NaOH is added to the extract, Et_2O removed by distillation, and NO_3^- in the residue determined by reduction followed by Nesslerisation, or by pptn. with nitron. F. O. H.

Catechin in the fruit of *Areca catechu*, Lin. R. YAMAMOTO and T. MURAOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 142–143).—The fruit contains *d*-catechin. R. S. C.

Occurrence of lycopene in several tropical fruits (*Erythroxolon novogranatense*, *Actinophleus macarthurii*, and *Ptychosperma elegans*). J. ZIMMERMANN (Rec. trav. chim., 1932, 51, 1001–1003).—The isolation of lycopene is described. J. W. B.

Carotene in mango fruit (*Mangifera indica*, Lin.). R. YAMAMOTO, Y. OSIMA, and T. GOMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 122–126).—The fresh pulp of mango fruit contains H_2O 81.7, citric acid 0.5, glucose 1.5, fructose 4.9, sucrose 5.5, crude fibre 0.5, N 0.1, ash 0.5, and Et_2O -sol. substances 1.3%. The dried pulp contains 0.1179 g. of carotene (α - and β -), and 0.0785 g. of esterified and 0.0156 g. of free xanthophyll per kg., but these quantities vary with the variety and ripeness of the fruit. R. S. C.

Carotene from the fruits of *Mangifera indica*, Lin. II. R. YAMAMOTO and G. KAWAKAMI (J. Agric. Chem. Soc. Japan, 1932, 8, 391–393).—Carotene, m.p. 179°, possibly a mixture of α - and β -, from the mango fruit cured avitaminosis-A in rats. CH. ABS.

Carotenoids in fresh tea leaves and fermented tea. R. YAMAMOTO and T. MURAOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 127–131).—Dried tea leaves (1 kg.) of the following varieties contain α -carotene and xanthophyll in the amounts stated: fresh Formosa 0.1751 and 0.4544 g.; fermenting Formosa 0.1571 and 0.4237 g.; Touchang 0.1681 and 0.4257 g.; Oolong 0.0784 and 0.2441 g.; black 0.0715 and 0.3686 g.; green 0.01571 and 0.4175 g. R. S. C.

Carotene content of ten varieties of carrots. C. E. BILLS and F. G. McDONALD (Science, 1932, 76,

108).—Data for white, yellow, and orange garden and field carrots are recorded. Garden varieties contain the largest amount of carotene, but traces occur even in white field carrots. L. S. T.

Organic bases of soya bean. K. SASAKI (J. Agric. Chem. Soc. Japan, 1932, 8, 417–420).—Korean soya bean (1930) contained H_2O 11.2, crude fat 16.6, total N 7.03, protein-N 6.48, non-protein-N 0.55%. 5 kg. afforded adenine (picrate) 1.40, guanine 0.31, histidine (dichloride) 0.62, arginine (nitrate) 9.55, choline (Au salt) 25.36, trigonelline (HCl) 0.33, and an unidentified base (from the lysine fraction; m.p. 214°; Pt salt, m.p. 235°; picrate, m.p. 206–208°), 0.80 g. CH. ABS.

Contents of the rhizomes of *Curcuma domestica* (Temoe Lawak). H. DIETERLE and P. KAISER (Arch. Pharm., 1932, 270, 413–418).—These contain *l*-camphor, *l*-cycloisoprenemyrcene, $[\alpha]_D -10.59^\circ$, and curcumin. R. S. C.

Existence and distribution of caffeine and theobromine in the organs of the guarana (*Paullinia cupana*). G. BERTRAND and P. DE B. CARNEIRO (Ann. Inst. Pasteur., 1932, 49, 381–386).—The leaves and stem bark of guarana contain much theobromine (I) and caffeine (II), the flowers and flower-stalks much (I), but only traces of (II); the seeds, stem wood, and roots contain (II) but no (I). W. O. K.

Alkaloids of Chinese drug *Pei-Mu*, *Fritillaria Roylei*. T. Q. CHOU and K. K. CHEN (Chinese J. Physiol., 1932, 6, 265–270).—From the corms of *F. Roylei* have been isolated two cryst. alkaloids: *peimine*, $\text{C}_{19}\text{H}_{30}\text{O}_2\text{N}$, m.p. 223°, optically inactive (*hydrochloride*, m.p. 295°; *hydrobromide*, m.p. 288°), and *peiminine*, $\text{C}_{18}\text{H}_{28}\text{O}_2\text{N}$, m.p. 135°, $[\alpha]_D^{25} -62.5^\circ$ (*hydrochloride*, m.p. 295°; *hydrobromide*, m.p. 292°). They differ in both mol. formulæ and properties from verticine and verticilline (cf. A., 1930, 227). R. N. C.

Strychnine-brucine ratio of *Nux vomica* and the relative potency of these alkaloids. R. W. MORRISON and A. R. BLISS, jun. (J. Amer. Pharm. Assoc., 1932, 21, 648–659, 753–760).—The total alkaloid content of *Nux vomica* (2.000–2.483% in 8 samples, av. 2.272%) is fairly uniform. The average strychnine-brucine ratio of 6 samples was 44–56, one was 49–51, and another 54–46, and these proportions were fairly well maintained in the preps. made from the crude drugs. Failing the double determination of total alkaloid and strychnine, the strychnine content is a more satisfactory standard than the present total alkaloid. E. H. S.

Trimethylamine from spores of *Tilletia laevis*, the stinking smut of wheat. W. F. HANNA, H. B. VICKERY, and G. W. PUCHER (J. Biol. Chem., 1932, 97, 351–358).—The contents of total volatile base and NH_3 in spores of *T. laevis* and *T. tritici* were determined. The NH_3 content varied from 0.054 to 0.143%. NMe_3 was isolated from the spores of *T. laevis* (0.0036–0.012%) but could not be detected in those of *T. tritici*. F. O. H.

Active substances in pollens of *Gramineae*. I. Occurrence of a histamine-like substance in

pollen of *Secale cereale*. C. E. BENJAMINS (Z. Immunität., 1931, 72, 189—211; Chem. Zentr., 1932, i, 2337).—Only rye among the *Gramineæ* pollens contains a substance completely identical in physiological properties with histamine. A. A. E.

Seeds of *Erythrina variegata* var. *orientalis* (L.), Merrill. J. MARANON (Philippine J. Sci., 1932, 48, 563—580).—A morphological and chemical study. Et_2O extracts from the seed a fatty oil (15.91%), EtOH an alkaloid (2.5%), identified as hypaphorine (A., 1911, i, 668), 0.1 g. of which is not toxic to guinea-pigs. A. C.

Oil of bittersweet seed. C. BARKENBUS and C. F. KREWSON (J. Amer. Chem. Soc., 1932, 54, 3993—3997).—Extraction of bittersweet (*Celastrus scandens*) seeds with light petroleum, Et_2O , and 95% EtOH gives 36.06, 46.72, and 53.22%, respectively, of extractives. The extracted meal contains H_2O 3.05, ash 2.88, protein 18.94, crude fibre 9.14, free invert sugar 0.49, sugar by inversion 1.6, pentosans 5.87, and starch 0.68%. The oil, extracted by Et_2O , has d_{20}^{20} 0.9772, n_D^{20} 1.4815, I val. (Hanus) 121.5, SCN-I val. 69.96, sap. val. 297.07, Reichert-Meissl val. 70.86, acid val. 3.98, Ac val. 147.5, unsaponifiable matter 2.96%, and contains glycerides of linoleic 38.46, linolenic 21.03, palmitic 8.42, stearic 1.88, and sol. acids (as AcOH) 15.67%; it is not known whether these acids occur as glycerides. The volatile acids contain HCO_2H and a little hexoic acid.

C. J. W. (b)

Natural occurrence of methyl *n*-octyl ketone. A. S. PFAU (Helv. Chim. Acta, 1932, 15, 1267—1270).—Spanish and Algerian oil of rue contains small amounts of Me *n*-octyl ketone (I), m.p. 2°, b.p. 89°/10 mm., oxidised by HOI to nonoic acid (*p*-phenylphenacyl ester, m.p. 71°). The m.p. 14° given (A., 1925, i, 514) for (I) is erroneous. The natural occurrence of a ketone with an even no. of C atoms is remarkable, but (I) is related to undecic acid, which also occurs in nature.

R. S. C.

Saponin content of the juice and leaf of the agave plant, Maguey, Manso Fino. H. D. JONES, G. N. FURBECK, and R. COLORADO (J. Amer. Pharm. Assoc., 1932, 21, 787—793).—The saponin, $[\text{C}_{32}\text{H}_{49}\text{O}_{16}]$; Ca 0.41% from the juice and the dry leaves is described. It has some hæmolytic action and on injection produces diarrhoea.

E. H. S.

Cultivated *Meriandra*. A. M. BORSALINO IN SEMERIA (L'Ind. Chimica, 1932, 7, 1205—1208).—The leaves of *M. Benghalensis* grown in Italy are similar in composition to those of the African plant, but differ by containing Mn in the ash. T. H. P.

"Diagnostic wood" of perennial plants (vines) in relation to production. M. E. VINET (Compt. rend. Acad. Agric. France, 1932, 18, 804—814).—The sum of the % of N, P_2O_5 , and K_2O in the "diagnostic wood" (bases of ripened shoots) of vines varies directly with sugar production in the fruit. There is a close proportionality between % of K and sugar production. In general, the PO_4 content of the wood varies directly and the N content inversely with the no. of grapes produced. A. G. P.

Determination of cellulose in soil. J. A. DAJI (Biochem. J., 1932, 26, 1275—1280).—The soil from which lignin has been removed is treated with dil. alkali and acid and then with a solution of NaOCl in the cold. The cellulose is extracted from the residue with Schweitzer's reagent, pptd. with EtOH , and determined by loss of wt. on ignition. S. S. Z.

Localisation of essential oils and pitch resins in pines. G. V. FIGULEVSKI (Bull. Inst. Pin, 1932, 33, 206—210). J. L. D.

Phosphatides of forage grasses. I. Cocksfoot. J. A. B. SMITH and A. C. CHIBNALL (Biochem. J., 1932, 26, 1342—1357).—Considerable phosphatide decomp. takes place during rapid drying of the grass. The presence of lecithin, cephalin, and the Mg or Ca salt of phosphatidic acid has been established. Linoleic and linolenic acids are among the constituent fatty acids of the phosphatides. Oleic acid is absent from this fraction as well as from the glyceride fatty acids. The ratio of saturated to unsaturated acids is <1. S. S. Z.

Nitrogenous nutrition of plants. A. I. VIR-TANEN (Suomen Kem., 1932, 5, 67—74).—In sterile cultures of const. p_{H} aspartic acid was a satisfactory N source for legumes, but not for cereals. The latter utilised asparagine freely. N compounds obtained by diffusion from root nodules of legumes were utilisable by *Gramineæ*. A. G. P.

Arginine metabolism and production of urea in higher plants. G. KLEIN and K. TAUBÖCK (Biochem. Z., 1932, 251, 10—50; cf. this vol., 101).—By means of a modification of the procedure of Weber (A., 1930, 755) micro-determinations of the free and combined arginine of plants can be made. The species and part of the plant and also the stage of growth affect the amounts greatly. In conifers the content of arginine is high and it plays an unusual part in the metabolism. The urea found in higher plants is probably produced by enzymic degradation of arginine and of similar substances. In the seeds of some species during germination much of the arginine is consumed, in those of others it is liberated from combination but scarcely consumed at all at this stage, whilst in most cases there is moderate consumption and liberation when germination occurs. W. McC.

Choline metabolism in plants. I. G. KLEIN and H. LINSE (Biochem. Z., 1932, 250, 220—253).—A method is described for determination of small amounts of choline and lecithin in terms of the NMe_3 liberated on treatment with conc. NaOH , and applied to the determination of the choline contents of a no. of lecithin preps. and of the EtOH extracts of various organs of a large no. of plants. The total choline content of the seeds of the latter amounts to 0.01—0.10% of the fresh wt. except for the *Leguminosæ*, which contain about twice this amount. The total, lecithin-, and free choline contents of a no. of plants during germination were determined. Etiolated seedlings contain more H_2O -sol. (free) choline and less lecithin-choline than green seedlings. The total, lecithin-, and especially the free choline contents of the seedling and of the cotyledon increase during

germination, the cotyledon (*Zea mays*) being often deprived of lecithin-choline in favour of the seedling.

P. W. C.

Utilisation of atmospheric nitrogen by germinating seeds. II. Germinating legumes in presence of alkaloids. N. VITA (Biochem. Z., 1932, 252, 278—291).—Caffeine and strychnine nitrate (1—2% solution) stimulate the utilisation of atm. N_2 by lupins, horse-beans, and peas. The action reaches a characteristic optimum according to the type of seed, the concn. of alkaloid, and the O_2 content of the surrounding atm. (increasing with decreased O_2 content).

P. W. C.

Seasonal changes in the composition of the insoluble nitrogen fraction in the current year shoots of Bartlett pear. A. S. MULAY (Plant Physiol., 1932, 7, 323—327).—The insol. N of bark and wood, respectively, consists approx. of NH_2 -N, 40—50, 40; basic N, 20, 12; melanin-N, 10—15, 14; amide-N, 7—9, 10; humin-N, 4—6, 4; EtOH-insol. N, 2, 8; residual N, 5—10, 12%. Seasonal variations in the bark are small, there being an increase in amide- and humin-N at the expense of basic and residual N in the early growing season and a slight fall in NH_2 - and a rise in residual N as growth proceeds. In the wood the N distribution is fairly const. except from June to August, when there is a marked decrease in NH_2 - and an increase in melanin-N. The residual N tends to increase after actual growth ceases.

A. G. P.

Carbohydrate exchange in nodule-bearing and nodule-free soya beans. E. RUFFER (Z. Pflanz. Düng., 1932, 24A, 129—167).—N fixation by nodule bacteria is largely dependent on the available carbohydrate supply in the plant. Plants grown under sterile conditions with generous N manuring had a lower N content than those inoculated with bacteria but receiving no fertiliser, although the initial intake of N was more rapid. Inoculated plants showed greater assimilation in the early growth stages and a consequent increase in sugar and starch contents. In later stages the carbohydrate content fell below that of sterile plants as a result of utilisation by the nodule organisms.

A. G. P.

Diurnal changes in the temporary accumulation of starch in leaves of green plants. P. P. STANESCU, A. ARONESCU, and I. G. MIHAILESCU (Bull. Acad. Sci. Roumaine, 1932, 15, 80—83).—No relationship exists between the commencement of starch accumulation and exposure of the plant to light. Diurnal changes vary with the type of plant, and in different leaves of the same plant. Day-to-day variations are considerable.

A. G. P.

Relations between carbohydrates and growth rate in the wild oat, *Avena fatua*. E. C. McCARTY (Oscas. Pap. Riverside Jun. Coll., California, 1932, 6, No. 1, 1—32).—The "food march" is inversely proportional to the meristem activity and to the increase in dry wt. The inverse ratio seems to be a fundamental relationship in the growth and development of annual as well as of perennial grasses.

CH. ABS.

Changes in composition of sunflower seeds with sowing time. S. RUSHKOVSKI (Masloboino Zhir. Delo, 1930, No. 9—10, 43—56).—Loss of H_2O by ripe seeds is lower with late than with early sowing; the % hulls in ripe seeds is independent of sowing time. The sol. carbohydrates (of which 50% is reducing) decrease during ripening from 37.5% to 4.5% and are independent of sowing time. The oil content decreases, and the kernel-protein is 10% lower, with late sowing. The hull-protein decreases from 12% to 3—5% with ripening, and is independent of sowing time. The hull-cellulose is higher and -ash lower with early sowing.

CH. ABS.

Use of expressed sap in determining the composition of maize tissue. J. D. SAYRE and V. H. MORRIS (Plant Physiol., 1932, 7, 261—272; cf. A., 1931, 775).—In successive portions of the expressed sap of maize obtained by steadily increasing pressure the concns. of total and reducing sugars, sucrose, NO_3 , and inorg. PO_4 remain const. The total solids, total N and P (which may include colloidal material) tend to decrease as the pressure rises. The composition of maize tissue with respect to any constituent existing in true solution in the sap may be determined from analyses of the expressed sap. The sucrose content of maize leaves is decreased by freezing the tissue, but not by grinding it.

A. G. P.

Hydrogen-ion concentration and Fe content of tracheal sap from green and chlorotic pear trees. J. OSERKOWSKY (Plant Physiol., 1932, 7, 253—259).— $[H^+]$ and $[Fe^{+++}]$ are high in the early part of the growing season, but the period of high $[Fe^{+++}]$ is shorter than that of high $[H^+]$. No significant difference exists between the $[H^+]$ or $[Fe^{+++}]$ of green and chlorotic branches from the same orchard.

A. G. P.

Protoplasmic potentials in *Halicystis*. II. Effects of potassium on two species with different saps. L. R. BLINKS (J. Gen. Physiol., 1932, 16, 147—156).—The p.d. between the cell-sap of *H. ovalis* (I) and the sea- H_2O in which it is immersed (at 8.1 and 15—20°) exceeds the corresponding figure for *H. Osterhoutii* (II) by about 12 mv. Experiments in which the K content of the surrounding sea- H_2O was varied and in which artificial sap containing K was used as immersion liquid, as well as others in which the K content of the sap in (II) was raised to a level equal to that of (I) (0.3M), indicate that the difference disappears when the difference in K content is balanced or abolished. It is therefore unlikely that the accumulation of KCl in (I) is due to the different mobility of the ions in the protoplasm of the species.

W. O. K.

Kinetics of penetration. IV. Diffusion against a growing potential gradient in models. W. J. V. OSTERHOUT (J. Gen. Physiol., 1932, 16, 157—163).—In a model consisting of (I) an aq. solution of K guaiacolate, (III) dil. $KHCO_3$ solution through which CO_2 is bubbled separated by (II) a guaiacol-phenol mixture containing K guaiacolate, the K migrates from (I) to (III), whilst a potential is set up opposing the movement. The conditions are analogous to those which probably obtain in

certain living cells in which K is accumulated in the sap. W. O. K.

Organic phosphorus compounds in plants and animals. III. Exosmosis of inorganic and organic phosphorus from the cells of plants. H. MAGISTRIS (Biochem. Z., 1932, 253, 64—80; cf. A., 1930, 260).—III. Below 10° the P which passes into the dialysate from vegetables (peas, beans, beet) is almost entirely inorg., but as the temp. is raised (to 30—35°) the amounts of total, org., and inorg. P which dialyse increase. At const. temp. the P which first passes out is chiefly inorg., but after about 10 hr. the amount of org. P which dialyses increases, whilst that of inorg. P decreases. Increase in the amount or renewal of the H₂O used, or irradiation (especially with ultra-violet rays) before or during dialysis, increases the amount of P which dialyses. CaCl₂ in the H₂O irreversibly reduces the amount of P (especially org. P) which dialyses, but KCl and MgCl₂ first increase, then greatly decrease, this amount. The action of KCl is reversible. The dialysis of inorg. P is greatly, that of org. P completely, inhibited, irreversibly, by heavy metal salts [Pb(OAc)₂, HgCl₂, Cu(NO₃)₂, AlCl₃, ZnSO₄, NiSO₄]. Very low concns. of mineral acid increase, higher concns. decrease, and CO₂ and H₂S greatly and reversibly increase, the dialysis of inorg. and org. P, and it is also increased, apparently in proportion to concn., by org. acids. NH₃ also reversibly increases the dialysis of P, but the investigation of the effect of other alkalis is complicated by their destructive action on the cells. Some of the results of Zaleski and Mordkin (A., 1928, 1061) have been confirmed.

W. McC.

Phosphorus compounds of plants. VI. Solubility of compounds of horse-bean meal and phytin-protein complexes. E. MNICH (Bull. Acad. Polonaise, 1931, B, 123—147).—The p_H of the medium determines the proportion of phytin and protein in combination. The p_H at which the concn. of P compounds in solution is min. corresponds with the initial stages of the formation of phytin-protein complexes; with increasing acidity (up to 0.1% HCl) the amount of bound protein increases. Decomp. of the complexes takes place only at a p_H at which denaturation of the protein occurs, the limits of such complex formation being approx. from p_H 6.7 to 1% HCl.

P. G. M.

Absorption of the solute from aqueous solutions by the grain of wheat. R. BROWN (Ann. Bot., 1932, 46, 571—582).—Data showing the rate of absorption of H₂O, NaCl, HCl, and I are recorded. The nature of factors influencing the semipermeable system is discussed.

A. G. P.

Isoelectric point of plant-cell nuclei. G. YAMAHARA (Proc. Imp. Acad. Tokyo, 1932, 8, 315—317).—The isoelectric point of nuclei of cells from the anther of *Lilium tigrinum* is 3.8—3.9.

P. W. C.

Iron, manganese, copper, zinc, and iodine contents of some important forage crops. J. S. MCHARGUE, W. R. ROY, and J. G. PELPHELY (J. Amer. Soc. Agron., 1932, 84, 562—565).—Considerable differences are recorded in the amounts

of Fe, Mn, Cu, Zn, and I in crops. In general, species having a high proportion of any one element contain unusually low amounts of the others. Liming tends to reduce the Mn contents of crops. A. G. P.

Factors affecting the distribution of iron in plants. C. H. ROGERS and J. W. SHIVE (Plant Physiol., 1932, 7, 227—252).—Plants in which the composite tissue fluids are of high p_H have very low sol. and high total Fe contents. Those with tissue fluids of low p_H have high sol. and low total Fe. The p_H range over which Fe is pptd. in plant tissues is wider than that of inorg. systems. Diurnal changes in the p_H of tissue fluids resulting from variation of light intensity are associated with corresponding changes in the proportion of sol. Fe. Accumulation of pptd. Fe is greatest in tissues of high p_H lying adjacent to others of low p_H . In plants in which the tissues are uniformly of low p_H , Fe does not accumulate and sol. Fe is evenly distributed throughout the tissues. Translocation of Fe from root to leaf occurs principally in the xylem.

A. G. P.

Occurrence of small amounts of iodine and fluorine in the organism. II. A. MAYRHOFER, C. SCHNEIDER, and A. WASITZKY (Biochem. Z., 1932, 251, 70—86; cf. A., 1929, 478).—By employing another method for the destruction of org. matter the I determination is improved. A description of two methods and an apparatus for the micro-determination of F in org. material is given. The I and F contents of spinach, lettuce, onions, beans, lentils, tea, coffee, and rice (and in some cases of EtOH extracts of these foods) have been determined. Tobacco, tomatoes, and potatoes contain I but no F and cucumber contains only traces of F. In some of the foods the F content is < the I content.

W. McC.

Variability of the chemical composition of plants. N. N. IVANOV (Biochem. Z., 1932, 250, 430—447).—Analytical figures are given in order to emphasise the variability of the protein, fat, carbohydrate, alkaloid, vitamin, etc. contents of plants with the type and strain of plant, the manuring, the climatic conditions (humidity, temp.), and the degree of growth, ripening, and storage.

P. W. C.

Effect of fertilisers on the chlorine content of the sap of maize plants. N. A. PETTINGER (J. Agric. Res., 1932, 44, 919—931).—The Cl content and the [H⁺] of the sap are increased when Cl-containing fertilisers are used, KCl exerting a residual effect even after 15 years. Fertilisers containing S cause little if any accumulation of SO₄ in the sap.

W. G. E.

Effect of thallium on growth of tobacco plants. J. E. McMURTREY, jun. (Science, 1932, 76, 86).—With 1 p.p.m. of Tl, toxicity is shown as a series of effects which has many of the characteristic symptoms of the typical frecking disease of tobacco.

L. S. T.

Radioactivity in plant physiology. D. MONTER (Compt. rend., 1932, 195, 582—584).—The action of radioactive substances on growth, from germination to final development of the plant, can be represented by a smooth curve, indicating a complete parallelism with animal physiology.

H. G. R.

Premature flowering in grapefruit from X-rayed seeds. C. N. MOORE and C. P. HASKINS (Science, 1932, 76, 167—168).—Grapefruit seedlings show premature flowering after exposure to radiations from a H₂O-cooled W-target Coolidge tube.

L. S. T.

Pipette manipulator. G. P. C. WANG (Chinese Med. J., 1932, 46, 607—608).—This manipulator works on the principle of a mechanical syringe, avoiding operation by the mouth.

H. G. R.

Simple apparatus for absorbing substances from the expired air of laboratory animals. W. MORSE (J. Lab. Clin. Med., 1931, 17, 282—283).

CH. ABS.

Micro-analysis of gases. J. A. CAMPBELL (Nature, 1932, 130, 240).—Krogh's method can be applied to gases from animal tissues by using glycerol containing 20% of H₂O.

L. S. T.

Determination of alkali by electrodialysis. C. O. OLDFELDT (Biochem. Z., 1932, 251, 235—245).—The apparatus and method for determination of total alkali in small amounts of tissue by titration of the cathode fluid are described; they have been used successfully for a series of salt solutions and mixtures thereof. The method is finally applied to blood, cat's liver, and urine before and after ashing.

P. W. C.

Micro-determination of magnesium in biological material. K. LANG (Biochem. Z., 1932, 253, 215—217; cf. A., 1928, 145).—After removal of protein and of Ca the Mg (0.001—0.002 mg. per c.c. of serum can be determined) is pptd. with tropæolin-OO, the ppt. (C₃₆H₂₈O₆N₆S₂Mg) dissolved in conc. H₂SO₄, and the Mg content of the solution determined colorimetrically. The error is <5%. The method can be applied gravimetrically in macro-analysis.

W. McC.

Copper and iron in chemistry and biology. A. QUARTAROLI (Annali Chim. Appl., 1932, 22, 517—543).—The co-activation of Fe and Cu in oxidation processes is shown in the ashing of plant materials. Tobaccos of high Fe and Cu content are easily ashed. The mechanism of Fe and Cu co-activation is studied and from these reactions a catalytic method for the determination of traces of Cu (up to 0.0001 mg.) is developed. The method is applied to the determination of Cu in blood, in the body, in food-stuffs, and to the study of the ratio Fe/Cu in the diet.

O. F. L.

Colorimetric micro-determination of copper in organic substances. W. D. McFARLANE (Biochem. J., 1932, 26, 1022—1033).—The coloured Cu salt of diethyldithiocarbamic acid is quantitatively extracted from aq. solution by amyl alcohol, the colour becoming intensified in the latter solvent. The depth of the colour is directly proportional to the amount of Cu present provided the range of Cu concns. is not too great. In alkaline pyrophosphate solution Cu may be determined in the presence of Fe. Previous oxidation of CuS in the cold with saturated Br-H₂O and 10% H₂SO₄ does not interfere with the colour

reaction. Procedures for the determination of Cu in biological materials are given.

S. S. Z.

Determination of iron in organic substances. I. Microcolorimetry as ferric thiocyanate. II. Potentiometric titration with titanous sulphate. W. D. McFARLANE (Biochem. J., 1932, 26, 1034—1049).—I. In Kennedy's method (A., 1927, 987) when quantities of Fe ranging from 0.007 to 0.022 mg. are determined, the red colour of Fe(CNS)₃ is not proportional to the concn. of Fe. It is possible to correct for this deviation so that 0.014 mg. of Fe can be accurately determined.

II. Methods are described by means of which 0.15 mg. of Fe can be determined in org. substances.

S. S. Z.

Gravimetric micro-determination of sulphur in biological material. H. WAELSCH and G. KLEPETAR (Z. physiol. Chem., 1932, 241, 47—56).—The method depends on ashing in an alkaline Benedict-Denis mixture [Cu(NO₃)₂, NaCl, NH₄NO₃, and Na₂CO₃ to p_H 7.2] and pptn. as BaSO₄.

J. H. B.

Iodometric micro-method for determination of chloride. N. BEREND (Biochem. Z., 1932, 252, 362—365).—After pptn. of the Cl with AgNO₃ and of the excess of AgNO₃ with KIO₃, the excess of KIO₃ is determined in the filtrate iodometrically. The mean error is $\pm 10^{-6}$ g.

P. W. C.

Circulation of iodine in nature. B. BLEYER, J. SCHWAIBOLD, and B. HARDER (Biochem. Z., 1932, 251, 87—100).—With the help of an apparatus described the I content of the following materials has been determined: air, snow, and rain in Munich (under varying meteorological and seasonal conditions); Bavarian deep spring water and river water; sewage from Munich. Very great variations were found.

W. McC.

Copper reduction values of mannose under certain fixed conditions. P. H. MOORE, R. W. LLOYD, and G. E. BURGET (J. Biol. Chem., 1932, 97, 345—350).—Mannose (I), admixed with proteins from intestinal contents, can be determined by reduction of Benedict's solution to Cu₂O under definite conditions and determination of the Cu in the ppt. by a modification of Peters' electrolytic method. Other methods are inaccurate or inapplicable. A table of Cu equivs. for (I) is given.

R. S. C.

Determination of residual nitrogen by direct Nesslerisation. A. LUBLIN (Klin. Woch., 1932, 11, 110—110; Chem. Zentr., 1932, i, 1557).—A simplification of Folin's method.

L. S. T.

Decomposition of rufanates, flavianates, picrates, and picrolonates by means of wool. H. MÜLLER (Z. physiol. Chem., 1932, 209, 207—210).—Ppts. of org. bases with substances capable of dyeing wool-fibre are decomposed on treatment with wool in neutral or alkaline solution at low temp.; the dye is absorbed and the base liberated. The method is specially suitable for biologically active bases.

J. H. B.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

DECEMBER, 1932.

General, Physical, and Inorganic Chemistry.

Series and term values in the arc spectrum of tellurium. J. E. RUEBY (Physical Rev., 1932, [ii], 41, 588—594; cf. this vol., 668).—The region λ 3750—11,287 was photographed. Full data and classifications are tabulated. The ionising potential was 8.96 volts. N. M. B.

Optical dissociation of iodine and enhancement of predissociation by collisions. L. A. TURNER (Physical Rev., 1932, [ii], 41, 627—634).—In the region 2100—1514, absorption by the atoms of light of wave-lengths 1830, 1783, 1642, 1618, 1583, and 1515 Å. was found, the lines arising from transitions to the normal state of the atom. A predissociation effect, enhanced by collisions, is described and interpreted. N. M. B.

Collisions of the first and second kind in the positive column of a caesium discharge. F. L. MOHLER (Bur. Stand. J. Res., 1932, 9, 493—508).—Previous measurements (*ibid.*, 95) lead to the conclusion that the no. of excited atoms in the first excited state nearly equals the no. which would exist in equilibrium at the electron temp. T_e . With increasing current, the electron concn. and the no. of collisions of the first and the second kinds increase greatly and the life of the excited states is reduced. With increasing pressure, the electron temp. and the concn. of excited atoms decrease, whilst their no. increases. E. S. H.

Light yield in helium, mercury, and nitrogen spectra excited by electron collision. T. THIEME (Z. Physik, 1932, 78, 412—422).—The relative intensity of 16 H α and 13 H γ lines was determined for exciting electrons of 9—400 volts. Measurements on N $_2$ showed that the laws for the excitation function of at. spectra apply to mol. spectra. A. B. D. C.

Nuclear spin and magnetic moment of Li 7 . L. P. GRANATH (Physical Rev., 1932, [ii], 42, 44—51).—From measurements on the hyperfine structure of λ 5485 the nuclear spin of Li 7 is $3/2$, and the nuclear magnetic moment is 3.29 times the theoretical val. for the proton. N. M. B.

Products of dissociation in nitrogen. J. KAPLAN (Physical Rev., 1932, [ii], 42, 97—100).—The products of dissociation of the known triplet states are determined from 4 regions of predissociation in the triplet band systems. N. M. B.

Influence of collisions on the time of decay of Na resonance radiation. F. DUSCHINSKY (Z. Physik, 1932, 78, 586—602).—The time of decay

of Na resonance radiation is decreased by addition of N $_2$, which extinguishes the fluorescence, but not by He, which only broadens the resonance lines. Rise of temp. increases the time of decay. A. B. D. C.

Further doublets of As v. A. S. RAO (Nature, 1932, 130, 630). L. S. T.

Spark spectrum of arsenic. M. RAM (Indian J. Physics, 1932, 7, 299—305).—Data for 130 lines in the region 5651.29—3780.80 Å. are tabulated. N. M. B.

Interferometric measurements in the spectrum of krypton. C. V. JACKSON (Proc. Roy. Soc., 1932, A, 138, 147—153).—The wave-lengths of the 10 bright violet lines of the first spectrum of Kr have been measured with an accuracy of about 0.001 Å., by interferometric comparison with the primary standard. The agreement with previous measurements by Humphries on the No scale (A., 1931, 7) is good. This group of lines appears to be suitable as a scale for spectroscopic purposes. It is situated in a convenient part of the spectrum, and the lines are suitably spaced and about twice as sharp as those of No. L. L. B.

Intensities of components of hyperfine structure of the more intense lines of the visible spectrum of Hg I. Hyperfine structure of the term (Hg 199) 7^3D_2 . J. GILLES (Compt. rend., 1932, 195, 579—580).—The hyperfine structures of the lines 5790.66, 5769.60, 5790, 4077, and the triplet 6^3P-7^3S of Hg 199 have been investigated, and the intensities of their components determined. The structure of the term 7^3D_2 is discussed. C. A. S.

Series in the complex spectrum of singly-ionised mercury, Hg II. T. S. SUBBARAYA (Z. Physik, 1932, 78, 541—554). A. B. D. C.

Singlet principal series of mercury. Y. ISHIDA and S. HIYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 78—82).—Term classifications are corrected by examination of Stark effect patterns. N. M. B.

Determination of some spectral properties of element 87. H. YAGODA (J. Amer. Chem. Soc., 1932, 54, 3074—3080).—The ionisation potential and doublet separations of the principal series spectrum have been evaluated by several independent methods. The weighted average val. of the ionisation potential is approx. 4.11+0.2 volts. In spectrographic detection of element 87, an intense line of approx. wave-length 4260+100 Å. is to be expected. H. S. H. (c)

Cold electric arc in vacuum. F. H. NEWMAN (Phil. Mag., 1932, [vii], 14, 712—718; cf. A., 1926, 1069).—The conditions for maintaining arcs with electrodes of Hg, Na, or K, and their spectra, have been investigated. H. J. E.

Spectroscopic investigation of some metal electrodes in vacuum arcs. F. H. NEWMAN (Phil. Mag., 1932, [vii], 14, 718—725).—Additional observations with cathodes of Hg, Na, and K are recorded. H. J. E.

Numerical values of atomic constants and X-ray terms. H. R. ROBINSON (Phil. Mag., 1932, [vii], 14, 605—612).—A crit. review of recent literature. H. J. E.

Fine structure in X-ray absorption spectra. J. D. HANAWALT (J. Franklin Inst., 1932, 214, 569—584).—The fine structure of absorption edges in X-ray spectra of vapours and solids is discussed, especially in connexion with Kronig's theory based on the quantum mechanics of electrons in crystal lattices. This theory explains experimental observations and the close relation that exists between the nature of the fine structure and that of the crystal structure of the substance. A. J. M.

X-Ray diffraction from calcite for wavelengths 1.5—5 Å. L. G. PARRATT (Physical Rev., 1932, [ii], 41, 561—576).—Expressions for the coeffs. of reflexion, % reflexion, and width of line are evaluated for calcite for six lines in the region 1.54—5 Å., and are in agreement with experiment. N. M. B.

K-Satellites. O. R. FORD (Physical Rev., 1932, [ii], 41, 577—587).—A survey of the α -satellites from Ge to Mg, and the β -satellites from Cu to Cl, shows new lines and resolutions of components. New series $K\beta^{IV}$ for Sc, Ca, and K and $K\beta^V$ for Ca, K, and Cl were found. N. M. B.

Influence of lattice binding on the K_α lines of carbon. M. RENNIGER (Z. Physik, 1932, 78, 510—520).—The shape of the 44.6 Å. line of C was investigated for graphite, diamond, and carborundum; carborundum gives the sharpest line, and graphite the least symmetrical. A. B. D. C.

Intensity ratios in the L-region of rare earths. G. VON HEVESY and E. ALEXANDER (Z. Physik, 1932, 78, 576—579).—The ratio of intensity for neighbouring rare earths of the L_α and L_β lines, when plotted against at. no., gives a curve similar to that of paramagnetism. A. B. D. C.

Ionisation of neon and argon by positive alkali ions of energies from 650 to 2000 volts. J. C. MORZON (Physical Rev., 1942, [ii], 41, 605—612).—A new type of apparatus allowed investigation with accelerating potentials up to 2000 volts. N. M. B.

Ionising action of neon atoms rendered metastable by resonance radiation. F. M. PENNING (Z. Physik, 1932, 78, 454—469).—Addition of 0.003% of A to Ne at 40 mm. pressure and illuminated with resonance radiation increased the current passing between electrodes 24 times, due to ionisation of A atoms by metastable Ne atoms. A. B. D. C.

Photo-electric properties of alkali metal films as a function of their thickness. J. J. BRADY (Physical Rev., 1932, [ii], 41, 613—626).—A mol. beam was used to deposit computed nos. of alkali metal atoms on a Ag surface. The max. threshold, the film thickness of its occurrence, and the thickness for max. total photo-electric emission, in mol. layers were, respectively, K, 5800 Å., 3.0, 12.4; Rb, 6200 Å., 1.5, 5.0; Cs, 6600 Å., 1.5, 5.0. Na showed some anomalous effects. N. M. B.

Thermionic and photo-electric work functions of molybdenum. L. A. DU BRIDGE and W. W. ROEHR (Physical Rev., 1932, [ii], 42, 52—57).—Photo-electric and thermionic data for outgassed Mo in const. equilibrium condition gave the val. 4.15 ± 0.02 volts for the work function. N. M. B.

Electric current from glowing cathodes in gases and vapours at atmospheric pressure. M. RUHNKE (Ann. Physik, 1932, [v], 14, 881—904).—The dependence of current intensity on electrode potential, distance between electrodes, temp. of cathode, and the nature of the gases adsorbed was investigated, using a W cathode for Hg vapour, H₂, and mixtures of N₂ and H₂. W. R. A.

Electron emission of metals under the influence of X-rays. H. KÜSTNER (Ann. Physik, 1932, [v], 14, 857—880).—Mathematical. W. R. A.

Radiation from caesium and other metals bombarded by slow electrons. C. BOECKNER (Bur. Stand. J. Res., 1932, 9, 413—418).—The abs. intensity and intensity wave-length distribution of the radiation emitted by Cs, Cr, Ni, Mo, and W, bombarded by slow electrons, is similar in each case. Radiation is much more intense from contaminated surfaces than from clean surfaces. The radiation is probably analogous to the continuous X-rays and not due to the excitation of characteristic electron levels. J. W. S.

Analogy between the Dirac electron and the electromagnetic wave: magnetic moment and moment of rotation of the electron. L. DE BROGLIE (Compt. rend., 1932, 195, 536—537, 577—578).—Mathematical. C. A. S.

Impacts of fast electrons and magnetic neutrons. J. F. CARLSON and J. R. OPPENHEIMER (Physical Rev., 1932, [ii], 41, 763—792).—Mathematical. The impacts of two free electrons, a fast electron, and a magnetic neutron, the energy transfers, range, and ionising power of the primary electron, and the no. and nature of the impacts of a neutron are considered. N. M. B.

Electron microscope. M. KNOLL and E. RUSKA (Z. Physik, 1932, 78, 318—339).—Formation of images by electron and ion beams is discussed, the possible "lens" systems being the pinhole camera, magnetic fields, electrostatic fields between electrodes, and electrostatic fields of space charge. A. B. D. C.

Investigation of the distribution of emission from glowing cathodes with the magnetic electron microscope. M. KNOLL, F. G. HOUTERMANS, and W. SCHULZE (Z. Physik, 1932, 78, 340—362).—Photographs are reproduced showing the

distribution of emission centres on cathodes, and points of intense emission are shown to be surrounded by negative space charge. A. B. D. C.

Inelastic electron scattering in gases. I. C. B. O. MOHR and F. H. NICOLL (Proc. Roy. Soc., 1932, A, 138, 229—244).—Experiments are described on the angular distribution of the inelastic scattering for the case of electrons which have lost energy in raising the atom to the most probable excited state. The investigations were carried out in He, A, and Hg vapour over the angular range 20—160°, using electrons with incident energies between 21 and 196 volts. In the case of A and Hg vapour, the scattering curves show maxima and minima at large angles and are similar to the corresponding elastic curves, whilst at the lower voltages in Hg vapour the resemblance gradually disappears. The results suggest that it is merely the "size" of the atom which is fundamentally important in the explanation of the inelastic, as well as the elastic, scattering of electrons by the heavier atoms. L. L. B.

Scattering of slow electrons. II. E. FEENBERG (Physical Rev., 1932, [ii], 42, 17—32; of this vol., 553).—Mathematical. The equations for scattering in He and the inert gases are considered. The former gives good agreement with experiment at the resonance potential; discrepancy at low potentials is due to neglected at. distortion. N. M. B.

Absorption of radiation originating from a beam of electrons in helium. Electron excitation function for the sharp series of ortho-helium. L. R. MAXWELL (J. Franklin Inst., 1932, 214, 533—542).—The fact that absorption takes place in excited He from the non-metastable 2P and 2p states, as well as from the metastable 2S and 2s levels, is confirmed. Absorption for higher series members is also shown; diffuse series lines are more easily absorbed than the sharp series lines for all the terms of the series. A. J. M.

Reflexion of fast electrons by single crystals. H. RAETHER (Z. Physik, 1932, 78, 527—538).—The resolving power of the crystal grating parallel to a beam of electrons is always small, the effective thickness of the crystal being $<10^{-5}$ cm.; this limiting thickness and the deduction of inner potentials are discussed. A. B. D. C.

Electron diffusion, electron attachment, and ageing of negative ions in commercial nitrogen at atmospheric pressure. J. ZELENY (J. Franklin Inst., 1932, 214, 513—532).—An answer to criticism by Loeb and Bradbury (this vol., 317). New evidence is given for the variation in size and mobility of ions formed in commercial N₂ with age. A. J. M.

Ionisation of helium, neon, and argon under impact of their own atoms and positive ions. C. J. BRASEFIELD (Physical Rev., 1932, [ii], 42, 11—16).—The no. of electrons liberated from neutral rare-gas atoms under impact was measured as a function of the kinetic energy of the impinging particles; curves show the relative efficiency of atoms and positive ions. N. M. B.

Mobility of alkali ions in gases. C. F. POWELL and L. BRATA (Proc. Roy. Soc., 1932, A, 138, 117—

132).—Previous work (this vol., 670) has been extended to include Li ions and the gases Kr, Xe, N₂, and H₂. In addition, the four-gauze method is applied to (a) an investigation of the clustering of impurity mols. around the simple alkali ions; (b) an attempt to detect the two isotopes of Li by the difference in their mobility; and (c) an unsuccessful search for the missing element no. 87 in samarskite. The results in A, Kr, and Xe are expressed by $k=0.55/[\sqrt{\rho(D-1)}](1+m/M)^{1/2}$ (cm., sec., unit e.s. field), where ρ is the gas density at n.t.p., D its dielectric field const., m and M are the masses of the gas atom and ion, respectively. If the factor 0.55 is replaced by a term A , this relation is identical with those deduced by Langevin and Hassé. L. L. B.

Emission of positive ions from hot tungsten. P. B. MOON (Proc. Camb. Phil. Soc., 1932, 28, 490—496).—Results of measurements of the positive ion currents emitted by W in the temp. range 3000—3200° abs. are in agreement with vals. calc. from the Saha equation. The work function associated with the ionic evaporation lies between 10 and 11 electron-volts. N. M. B.

Reflexion of thallium, lead, and antimony atoms from sodium chloride crystals. J. M. B. KELLOGG (Physical Rev., 1932, [ii], 41, 635—640).—Tl and Pb are in part scattered and in part specularly reflected; Sb shows reflexion deviating from the specular, which may be explained by the interchange of momentum between the incident particle and the crystal. N. M. B.

Polarisation of light originating from moving and stationary particles of hydrogen canal rays. (Miss) W. A. LUB (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 826—837).

Determination of at. wt. of osmium. R. GILCHRIST (Bur. Stand. J. Res., 1932, 9, 279—290).—A method for the extraction and purification of Os is described. The at. wt. obtained from the ratio (NH₄)₂OsCl₆:Os is 191.53 and that from the ratio (NH₄)₂OsBr₆:Os is 191.57. (NH₄)₂OsCl₆ and (NH₄)₂OsBr₆ have d^{25}_{20} 2.93 and 4.09, respectively. J. W. S.

Atomic mass of potassium. I. End-point of potassium chloride-silver titration. C. R. JOHNSON and G. W. LOW, jun. (J. Physical Chem., 1932, 36, 2390—2394).—Both potentiometric and nephelometric analyses have been made of KNO₃-HNO₃ solutions saturated with AgCl. The potentiometric titration method is applicable in at. mass measurements, and avoids liquid junction and activity difficulties. C. T. S. (c)

Isotopes of uranium. T. R. WILKINS and W. M. RAYTON (Nature, 1932, 130, 475—476).—Evidence of several isotopes of U (from Colorado carnotite) which emit α -rays has been obtained. L. S. T.

Isotopic weight of H². K. T. BAINBRIDGE (Physical Rev., 1932, [ii], 42, 1—10; cf. Urey, this vol., 554).—The mass of neutral H² was 2.01351 ± 0.00006 , and 2.01351 ± 0.00018 relative to He, and O¹⁶=16, respectively. The equiv. packing fraction was 0.675%. The structure of the nucleus and

interpretation of lines in the mass spectra are discussed. N. M. B.

Photochemical separation of isotopes. W. KUHN and H. MARTIN (*Naturwiss.*, 1932, 20, 772).—On irradiation of COCl_2 with light of wave-length 2816-179 Å. from an Al arc (filtered through $\text{Cl}_2 + \text{Br}$ in CCl_4 , barbituric acid in H_2O , and CS_2 in C_6H_{14}), the Cl. liberated shows slight excess of Cl^{35} .

J. W. S.

Isotopy. F. PANETH (*Z. Elektrochem.*, 1932, 38, 496-504).—A review. G. Hertz has prepared, by diffusion for only 8 hr., a 1 c.c. sample of Ne in which the ratio $\text{Ne}^{20} : \text{Ne}^{22}$ is 1:1 (normally 9:1); the lightest fraction obtained contained only 1% of Ne^{22} .

H. F. G.

Relation between the periodic system and chemical classifications. I. N. LONGINESOU (*Bul. Chim. Soc. Romane*, 1931, 34. Reprint, 4 pp.).—Similarities between the periodic system and electrochemical, thermochemical, photochemical, and analytical classifications of the elements are discussed.

J. W. S.

Ionising power of artificial H-rays. K. DIEBNER (*Z. Physik*, 1932, 77, 581-600).—H-rays were obtained by bombardment of Al and F with α -rays, and the expression $v^3 - a(R-x)$ was found to give the velocity in terms of range for ranges between 3 and 33 cm.; in the formula $K = K_0(R-x)^{2/3}$, relating total ionisation with range, K_0 is 2.06×10^4 for CO_2 , or approx. 1/4 that for α -rays. The sp. ionisation near the end of an H-ray path rises to seven times that at a range of 50 cm. A. B. D. C.

Natural hydrogen rays. K. PHILIPP [with L. MEYNER] (*Z. Elektrochem.*, 1932, 38, 545).—The range of the H-rays emitted from a thin film of paraffin on bombardment with α -rays ($2.9-3.4 \times 10^6$ volts) varies according to the third power of the velocity. The branching effect observed in the Wilson chamber with Be neutrons has been found to occur also with neutrons derived from B and Li.

H. F. G.

Early days of radioactivity. (LORD) RUTHERFORD (*Z. Elektrochem.*, 1932, 38, 476-480).—A lecture.

H. F. G.

Development of research on radioactivity, and its influence on related subjects. S. MEYER (*Z. Elektrochem.*, 1932, 38, 480-488).—A lecture.

H. F. G.

Radioactivity and elementary chemical processes. O. HAHN (*Z. Elektrochem.*, 1932, 38, 511-518).—A review, dealing mainly with applications of radioactive phenomena in the study of pptn. processes, mixed crystal systems, and adsorption, and in the investigation of structure by the emanation method.

H. F. G.

Relation of polonium and thorium-B to other metals. G. TAMMANN (*Z. Elektrochem.*, 1932, 38, 530-532).—The photographic method of studying the distribution of a radioactive element in an alloy is described. When Cu, Ag, Sb, Bi, Zn, Cd, Sn, or Te containing Po crystallise, the Po separates on the surfaces of the nuclei. The solubility of Po in these metals is extremely small: $10^{-10}\%$ in Te, and

$5.28 \times 10^{-10}\%$ in Bi. Th-B disperses homogeneously in Pb, but is insol. in other metals, even when 5-10% Pb is present.

H. F. G.

Neutron. J. CHADWICK (*Z. Elektrochem.*, 1932, 38, 546).—A note of recent work.

H. F. G.

Possible existence of multiply-charged particles of mass one. M. DELBRUCK (*Nature*, 1932, 130, 593).—Theoretical. It is suggested that the particle of mass 1 may have arbitrary, positive, and negative vals. of its charge.

L. S. T.

Enfeeblement of nuclear radiation from beryllium in material screens. J. THIBAUD and F. D. LA TOUR (*Compt. rend.*, 1932, 195, 655-657; cf. this vol., 672).—The log I_x/x curve is convex to the axis of x only if the aperture closed by the Pb screen is small; with a large aperture it is concave. This is attributed to dispersion by the Pb, the less penetrating neutrons being most strongly dispersed. To determine the coeff. of extinction, μ , a narrow aperture, 2.5-3.0 cm., must be used; this gives for recoil atoms producing 8000-10,000 pairs of ions the approx. relation $\mu = 0.3\sqrt{x}$, a result explicable either by the neutrons having a continuous spectrum of velocities or by their consisting of two principal components of coeff. $\mu_1 = 0.040$ and $\mu_2 = 0.065$. The particles producing $>22,000$ pairs of ions (N nuclei) are unaffected by thicknesses $>7-8$ cm. Pb; for greater thicknesses their no. falls rapidly. Extinction in Hg is similar to that in Pb, but for that in medium and light elements the curve is almost a straight line. $\mu_{\text{at.}}$ for screens of Sn, Fe, S, and Al containing the same nos. of atoms shows little variation with at. no.

C. A. S.

α -Rays and research on atomics. H. GEIGER (*Z. Elektrochem.*, 1932, 38, 488-490).—A survey.

H. F. G.

Ranges of α -particles from polonium, uranium I, and uranium II with the Wilson chamber. F. N. D. KURIE (*Physical Rev.*, 1932, [ii], 41, 701-707).—Using a new method, the ranges were 3.690 \pm 0.005, 2.58 \pm 0.015, and 3.11 \pm 0.01 cm., respectively.

N. M. B.

Energy distribution curves of the disintegration electrons. B. W. SARGENT (*Proc. Camb. Phil. Soc.*, 1932, 28, 538-553).—A method for calculating the absorption curve of β -rays forming a continuous spectrum is developed, and gives satisfactory agreement when applied to available data. Distribution curves with momentum of the β -rays from Ac-C'', U-X., Th-C, and Th-C'' are found.

N. M. B.

Significance of β - and γ -rays for research on atomics. (FRL.) L. MEYNER (*Z. Elektrochem.*, 1932, 38, 490).—A note of the difficulties of correlating quantitatively an α - or β -ray change with the state of excitation of the atom, of explaining the continuous energy distribution of emitted nuclear electrons, and the scattering of short wave-length radiation.

H. F. G.

Theory of emission of β -rays by radioactive nuclei. A. SCHIDLOF and H. SAINI (*Helv. phys. Acta*, 1932, 5, 73-91; *Chem. Zentr.*, 1932, ii, 15).

Numerical calculation of scattering correction of γ -ray absorption measurements. G. T. P. TARRANT (Proc. Camb. Phil. Soc., 1932, 28, 475—489).

Distinction between neutrons and γ -rays. H. BECKER and W. BOTHE (Naturwiss., 1932, 20, 757—758).—Experiments are described by which neutrons and γ -rays can be distinguished by using a tube containing paraffin and utilising the radiation from Be excited by α -rays from Po. W. R. A.

Spectrum of the solar corona. T. L. DE BRUIJN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 286—294).—The three red coronal lines 6776, 6704, and 6374 Å., and the green line 5303 Å. are shown, by a crit. examination of available data, to be due to neutral O. M. S. B.

Visible spectrum of Northern lights. L. VEGARD (Z. Physik, 1932, 78, 567—575).—A large-aperture prism spectrometer revealed several new lines, the most important appearing beyond 6000 Å. A. B. D. C.

Spectrum of cosmic radiation. A. S. SKAPSKI (Nature, 1932, 130, 472—473). L. S. T.

Spectrum of cosmic radiation. A. W. CONWAY (Nature, 1932, 130, 581; cf. preceding abstract). L. S. T.

Interpretation of cosmic-ray phenomena. T. H. JOHNSON (Physical Rev., 1932, [ii], 41, 545—552).—Schindler's data (cf. this vol., 5) on the transition effect is interpreted on the assumption that the equilibrium between the primary radiation and its secondary corpuscular rays is different in different media. Absorption coeffs. in Pb, Fe, and air are calc. N. M. B.

Dissociation of hydrogen molecules by collision with optically excited xenon atoms. H. R. CALVERT (Z. Physik, 1932, 78, 479—485).—Excited Xe atoms dissociate H_2 , indicating that no intermediate product is required for this sensitised reaction. A. B. D. C.

Penetration of atoms by photons. V. POSEJPAL (J. Phys. Radium, 1932, [vii], 3, 390—407).—Theoretical. The propagation of photons in a hypothetical corpuscular ether permeating the atom is investigated, and deductions are compared with various experimental data. N. M. B.

Relativistic Thomas-Fermi atom. M. S. VALARTA and N. ROSEN (Physical Rev., 1932, [ii], 41, 708—712).—A solution of the equation for inner at. potential and charge distribution is applied to the case of Hg. N. M. B.

Nuclear structure. E. G. JONES (Nature, 1932, 130, 580; cf. this vol., 894).—Quantised spins and orbital momenta appear to be associated with neutrons and protons in the nucleus. A model built on certain further assumptions accounts for all the observed moments of the nuclei up to O^{16} . L. S. T.

Analytic atomic wave functions. J. C. SLATER (Physical Rev., 1932, [ii], 42, 33—43).—Mathematical. N. M. B.

Fundamental particles. R. M. LANGER (Science, 1932, 76, 294—295).—The electron and the Dirac

magnetic pole can be regarded as fundamental particles. The photon is considered to be a combination of an ordinary and a negative energy electron, whilst the neutron is built from a positive and negative magnetic pole. The proton is a combination of a neutron and a positive electron. L. S. T.

Most probable values of e , e/m , and h . K. SHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 97—121).—Available data are reviewed critically. The val. of e must be revised by correcting for the coeff. of viscosity of air; the X-ray val. of e gives consistent vals. of h by eight methods. The most probable fully corrected vals. are: $e=(4.803\pm0.004)\times10^{-10}$; $e/m=(1.7605\pm0.0010)\times10^7$; $h=(6.624\pm0.007)\times10^{-27}$. N. M. B.

Band spectrum of chromic oxide. C. GHOSH (Z. Physik, 1932, 78, 521—526).—CrO bands between 7100 and 4800 Å. were investigated; the heat of dissociation of the lower electronic state is 3.78 volts. A. B. D. C.

Rotational analysis of some CO_2 emission bands. I. R. F. SCHMID (Physical Rev., 1932, [ii], 41, 732—750).—Full data are tabulated for the P and R branches composing the red degraded bands at λ 3254, 3377, 3511, 3534, 3839, 3247, 3370, 3503, 3545, and 3674 Å. The lines of the first five bands show staggering; none shows Zeeman effect. N. M. B.

Spectra of the alkali halide vapours. H. BEUTLER and H. LEVI (Z. Elektrochem., 1932, 38, 589—591).—The absorption spectra (2300—7000 Å.) at 1270°, emission spectra between Ni electrodes in an atm. of He or Ne, and chemiluminescence spectra produced when a stream of halogen enters a vessel containing the vapour of the metal have been determined. A new NaI absorption band system between 3050 and 5000 Å. is reported. H. F. G.

Absorption spectrum of nitrous oxide and heat of dissociation of nitrogen. A. K. DUTTA (Proc. Roy. Soc., 1932, A, 138, 84—91).—Gaseous N_2O shows continuous absorption, beginning at 2750 Å., corresponding with 104.0 kg.-cal. Assuming the photochemical reaction to be $N_2O+h\nu=NO+N$, the heat of dissociation of N_2 is calc. to be 8.7 volts. A second absorption, indicating photochemical decomp. of N_2O into NO and excited N atoms, is expected near 1840 Å. Previous work on the heat of dissociation of N_2 is discussed. L. L. B.

Absorption spectrum of nitrogen dioxide. A. HERRMANN (Ann. Physik, 1932, [v], 15, 89—108).—The absorption spectrum of NO_2 has been mapped afresh from 2491 to 2459 Å. The effect of an electric field on the spectrum and that of PhCl was investigated. There was no effect up to 36,000 volts per cm. The bands in the neighbourhood of 2459 Å. do not change their sharpness with temp. between -15° and 500° , nor appreciably by addition of another gas up to 3 atm. pressure. A. J. M.

Near ultra-violet bands of silicon chloride. A. C. DATTA (Z. Physik, 1932, 78, 486—491).—The heat of dissociation for the lower level associated with these bands is 4.9 volts. A. B. D. C.

Absorption spectra of the samarium ion in solids. I. Absorption by large single crystals of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$. II. Conglomerate absorption of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ and a partial energy level diagram of the Sm^{+++} ion as it exists in crystalline $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$. F. H. SPEDDING and R. S. BEAR (Physical Rev., 1932, [ii], 42, 58—75, 76—85).—Full data for absorption lines and bands at 20°, 78°, 112°, and 298° abs. are tabulated. The influence of temp. on the positions of lines and multiplets and on the width and intensity of lines is explained by three direct effects of temp. change on the crystal.

II. Additional lines from conglomerates of crystal fragments are reported for 20°, 78°, 169°, and 298° abs., and with those above are used to establish the existence of lower energy levels. N. M. B.

Absorption of substituted benzenes. I. Chlorine series. H. CONRAD-BELLROTH (Z. physikal. Chem., 1932, B, 19, 76—83).—The ultra-violet absorption of all the Cl-derivatives of C_6H_6 in hexane solution has been measured. With increase in the no. of substituents the spectra shift towards the visible. All the spectra exhibit three strong bands, from which two nuclear frequencies are deducible. In a group of isomerides two absorb at almost the same place and have about the same extinction in the strongest band, whereas the absorption of the third, the 1:4, 1:2:4, or 1:2:4:5 derivative, is nearer the visible; extinction in the strongest band is much greater than for the others. R. C.

Influence of substitution on the absorption and reactivity of the carbonyl group. W. HEROLD (Z. Elektrochem., 1932, 38, 633).—Previous work (this vol., 461) has been extended to solutions of various aldehydes, halogenated and hydroxylated ketones, esters, acid chlorides, and amides in H_2O and alcohols. In all cases when two groups attached to the CO group are positive, in the alternating polarity sense, the normal CO band at 32,000—36,000 cm^{-1} is observed; if one group is negative, the carbonyl band at >40,000 cm^{-1} appears instead, whilst with two negative groups the absorption lies beyond the range of quartz. When one positive and one negative group are present, there is no change with time of the absorption spectrum, i.e., no semiacetal type of compound is formed by union with the solvent. Chloroacetamide shows gradual change of the absorption with time. H. F. G.

Photochemical changes of histidine and histamine. J. P. BECKER (Pflüger's Archiv, 1931, 228, 751—754; Chem. Zentr., 1932, i, 2959).—The absorption curves are too close for spectro-analytical use. Glyoxalylethyl alcohol and glyoxalyl-lactic acid produce similar curves. A. A. E.

Absorption distribution in solutions with two absorbing constituents. K. WEBER [with E. DRESNER and B. AGRAS] (Z. physikal. Chem., 1932, B, 19, 30—34).—The validity of the absorption distribution formula (A., 1930, 288) has been demonstrated experimentally, the extinction of fluorescence by mol. collisions in fluorescing systems being taken into consideration. R. C.

New isotopic effect. L. GOLDSTEIN (Compt. rend., 1932, 195, 703—706).—Theoretical. The total isotopic effect on the Raman spectrum of a compound AB, where B consists of two isotopes, B' and B'' , B' being more abundant, is $\Delta\nu_R = (\rho^2 - 1)(\nu_R/2 - \nu_{m'})$, where ρ^2 is the product of the reduced masses of the isotopic mols. and $\nu_{R'}$, $\nu_{m'}$ are respectively the vibrational and rotational frequencies of AB' (cf. A., 1931, 1353). C. A. S.

Production of infra-red spectra with electric fields. E. U. CONDON (Physical Rev., 1932, [ii], 41, 759—762).—The occurrence and intensities of a mol. spectra effect in a strong electric field, analogous to the Stark at. effect, are considered mathematically. N. M. B.

Simplified registering infra-red spectrometer. C. LEISS (Z. Physik, 1932, 78, 704—706).

A. B. D. C.

Infra-red arc spectra photographed with xenocyanine. M. F. MEGGERS and C. C. KIESS (Bur. Stand. J. Res., 1932, 9, 309—326).—Using xenocyanine-sensitised plates, the infra-red arc spectra of Ti, Fe, Co, Ni, and Zr have been measured over the wave-length range 8000—11,000 Å. Most of these lines are interpreted as combinations of previously known terms of the neutral atom. A new Ti term α^3D has been identified. Ti and Fe form suitable comparison spectra for wave-length measurements in the region investigated. J. W. S.

Infra-red spectrum of water and the change of polymerisation caused by dissolved salts. R. SUHRMANN (Z. Elektrochem., 1932, 38, 627—628).—The dissociation of complex H_2O mols. produced on addition of sol. salts varies, not according to the degree of hydration of the ions of the salt, but in the order of the ionic vols. Certain salts, e.g., alkali halides, cause the bands to become sharper but only slightly displaced, whilst others (MgSO_4) cause flattening and the appearance of a new band at 1.4—1.8 μ . Acids and alkalis produce considerable flattening and strong absorption above 1.4 μ . H^+ and OH^- unite with the more strongly dissociated $(\text{H}_2\text{O})_n$ mols. H. F. G.

Absorption of carbon tetrachloride in the infra-red. C. SCHAUFFER and R. KERN (Z. Physik, 1932, 78, 609—629).—38 bands observed in the spectrum of CCl_4 between 1 and 22 μ are expressed as harmonic and combination frequencies of the four Raman bands at 215, 304.5, 439.5, 757.5, and 792.5 cm^{-1} . The intensities of the bands are discussed. A. B. D. C.

Raman effect in solutions of cupric salts. A. DA SILVEIRA (Compt. rend., 1932, 195, 652—653; cf. this vol., 1075).—Solutions of CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ show respectively a new line at 450 cm^{-1} with a triplet around 1110, attributed to SO_4^{--} (a case of destruction of degeneration), and lines closely resembling those of $\text{Ca}(\text{NO}_3)_2$. C. A. S.

Raman and infra-red spectra of carbon dioxide. A. LANGSETH and J. R. NIELSEN (Z. physikal. Chem., 1932, B, 19, 35—46).—Mecke's interpretation of the Raman spectrum of CO_2 (this vol., 559) is unacceptable; Fermi's theory (A., 1931, 1111) satisfactorily accounts for the two strong lines. The

Raman spectrum of gaseous CO_2 has proved to be more complex than had been supposed, several weak lines being present in addition to the two strong lines. The moments of inertia of the mol. in the excited states corresponding with the two latter have been calc. A partial energy diagram of the CO_2 mol. is reproduced. R. C.

Raman effect in molecules and crystals. E. FERMI (Mem. R. Accad. Italia, 1932, 3, [Chim.], 5—22).—Exceptions to the ordinary selection laws for the Raman effect in polyat. mols. are discussed for the case of CO_2 . The weak continuous Raman spectrum of NaCl and the spectrum of CaCO_3 can also be explained. O. J. W.

Raman spectra of iodides. I. Phosphonium iodide and methyl iodide. N. G. PAI (Indian J. Physics, 1932, 7, 285—297).—The lines for PH_4I are 930, 1040, 1113, 1259, 1416, 2304, and 2370 cm^{-1} , attributed to the PH_4 ionic group distorted by the I ions. Lines for MeI are 524, 895, 1028, 1242, 1434, 1760, 2050, 2461, 2557, 2796, 2849, 2950, and 3050 cm^{-1} ; correlation with infra-red absorption data is given. N. M. B.

Raman effect. Allenic hydrocarbons. Preparation of α -dimethylallene. M. BOURGUEL and L. PIAUX (Bull. Soc. chim., 1932, [iv], 51, 1041—1062).—The characteristic of the Raman spectra of allene, and methyl-, propyl-, butyl-, and α -dimethylallenes is a strong line at about 1100 (cf. this vol., 109). The Raman spectra of β -methyl- Δ^2 -butene (I) (alone and admixed with β -methyl- Δ^2 -butene), isoprene (II), and β -bromo- γ -methyl- Δ^2 -butene (III) are also given. The Raman spectrum of the product, b.p. 35—36.5°, obtained in about 25% yield [together with (III)] from β - γ -dibromo- β -methylbutane (IV) and quinoline shows that it is a mixture of (I) and (II); (I) results by elimination of 2 Br (not 2 HBr) from (IV). H. B.

Specific heat and dissociation of simple hydrocarbons. R. RUEDY (Canad. J. Res., 1932, 7, 328—336).—The vals. of C_p for CH_4 , C_2H_4 , and C_2H_2 calc. from the Raman and infra-red spectra agree with experimental data. The calc. heat of dissociation of CH_4 into CH_3 and H is 101 g.-cal. per mol., whilst thermochemical data indicate 110—130 g.-cal. The no. of collisions in which the energy could be transferred from mol. to mol. is too small to account for the dissociation of CH_4 into CH_3 and H when passed through a SiO_2 tube at 1000°. Dissociation into CH_2 and H_2 is probable. The fact that a mol. remains in any given vibrational state for a finite time is important in the elucidation of thermal decomp., the investigation of the velocity of ultrasonic waves in gases being of val. in this connexion. The possible modes of vibration in the C_2H_6 , C_2H_4 , and C_2H_2 mols. are considered. D. R. D.

Resonance fluorescence of benzene. G. B. KISTIAKOWSKY and M. NELLES (Physical Rev., 1932, [ii], 41, 595—604).—The fluorescence of C_6H_6 vapour, excited by the 2536 Å. Hg line, for the pressure range 25—0.01 mm. is described and interpreted. Full data are tabulated; vibrational frequencies found for the normal mol. are: 160, 793(?), 988, 1200, 1354, 1663, and 3139 cm^{-1} . N. M. B.

Theory of fluorescence extinction. K. WEBER (Z. physikal. Chem., 1932, B, 19, 22—29).—Experimental evidence against Baur's desensitisation theory (this vol., 578) is described. Electrolytes both extinguish the fluorescence of pinakryptol-yellow and cause pptn. There is no direct connexion between these two effects, for extinction by chlorides, unlike pptn., is almost independent of the cation, and pptn. is retarded by org. and inorg. deactivators. R. C.

Luminescence of solid nitrogen. J. KAPLAN (Physical Rev., 1932, [ii], 42, 86—96).—An explanation is proposed for the radiations observed by McLennan in the luminescence of solid N. N. M. B.

Colour of silver as a function of its surface nature. A. KUTZELNIGG (Kolloid-Z., 1932, 61, 48—50).—With repetition of reflexions, caused by looser packing of the crystallites, the colour of Ag passes from mirror-like silver, through matt-white, yellowish-grey, brownish-black, to black. A yellowish colour can be recognised photometrically in all these forms. E. S. H.

Photo-electric method for detecting Gurtwitsch's mitogenetic rays. L. PETRI (Atti R. Accad. Lincei, 1932, [vi], 15, 919—925).—Very short ultra-violet waves are emitted by living, but not by dead, vegetable matter. D. R. D.

Becquerel effect on selenium electrodes. M. VOLMER and W. MOLL (Z. physikal. Chem., 1932, 161, 401—410).—The effect on a Pt electrode thinly coated with Se and exposed to monochromatic light is a max. at a potential near that of the dropping electrode, the quantum yield then agreeing approx. with the principle of photochemical equivalence. The photo-electric current is accompanied by the formation of H_2Se in approx. the amount required by Faraday's law if the Se were univalent. The primary process is probably $\text{Se} + \text{H}^+ + \ominus = \text{HSe}$, the electron being released from within the Se, followed by $2\text{HSe} = \text{Se} + \text{H}_2\text{Se}$. A Becquerel effect has been detected in a Pt electrode thinly coated with S. R. C.

Emission mechanism of oxide cathodes. H. KNEPKAMP and C. NEBEL (Wiss. Veroff. Siemens-Konz., 1932, 11, No. 2, 75—87).—An oscillograph method was used to study the change of activity with time of a BaO cathode. The change in activity is to be ascribed to the varying surface covered with O atom-dipoles. A. J. M.

Nature of spontaneous currents on illumination of various detector substances. F. WAIBEL (Z. Physik, 1932, 78, 423—429).—Semi-conductors act as detectors through thermal effects, and not through barrier layer photo-effects. A. B. D. C.

New experiments on the photo-electric effect. Q. MAJORANA (Rend. Accad. Sci. Ist. Bologna, 1931, 35, 62—72; cf. this vol., 898).—The photo-electric effect produced when a metal, e.g., Zn, and other metals are illuminated by the light of a Hg-vapour lamp can be demonstrated by the attraction of the metal towards a positively-charged silvered quartz thread or Al needle. No movement of thread or

needle occurs when they are negative with respect to the metal. O. J. W.

Crystal photo-effect in clear zinc blende. H. DEMBER (Naturwiss., 1932, 20, 758).—The effect has been observed in raising the temp. to 365°.

W. R. A.

Photographic study of growth of electrolytic striations. R. TAFT and O. R. BINGHAM (J. Physical Chem., 1932, 36, 2446—2454).—The striations of Cu deposited in presence of gum arabic have been studied. The formation and growth of the striæ are explained by assuming adsorption of a gum arabic-copper hydroxide complex on the surfaces of the electro-deposited Cu crystals. Gum arabic increases the cathode polarisation of Cu.

R. H. C. (c)

Electrical conductivity of deformed rock-salt crystals. Z. GYULAI (Z. Physik, 1932, 78, 630—638).—Sudden compression of NaCl in the form of pastilles causes a sudden increase in conductivity; at high temp. NaCl has a large diminishing conductivity. These changes indicate that the conductivity of NaCl has a stable and a labile component, the labile component appearing on mechanical deformation of the crystal.

A. B. D. C.

Variation with temperature of dielectric constant and density of nitrobenzene in vicinity of m.p. H. BRAUNE and W. GIERTZ (Z. physikal. Chem., 1932, 161, 389—394).—Wolfke and Mazur's observations (this vol., 329), suggesting transition in the liquid phase, could not be confirmed. R. C.

Dipole moments and molecular structure. III. Oxychlorides of sulphur. J. W. SMITH (Proc. Roy. Soc., 1932, A, 138, 154—161).—The mol. polarisations and refractions of SOCl_2 and SO_2Cl_2 have been calc. from data derived from measurements of the dielectric consts. and densities of C_6H_6 solutions of the two chlorides at 25° and 45°, and the vals. of n^{15} and d^{15} for the same solutions. The electric moments calc. from the change in the mol. polarisation with temp. are 1.38 and 1.64×10^{-18} , respectively, whilst those calc. from the mol. polarisation at 25° and the mol. refraction are 1.58 and 1.86×10^{-18} , respectively. The discrepancy indicates either that the dipole moments increase with rise of temp., or that the at. polarisations of these mols. are high. L. L. B.

Variation of dielectric constant with temperature. II. Electric moments in the ethylene halides. E. W. GREENE and J. W. WILLIAMS (Physical Rev., 1932, [ii], 42, 119—140).—Theoretical expressions for free rotation are discussed. Dielectric const. and density measurements at various temp. by a new method are recorded for $\text{C}_2\text{H}_4\text{Cl}_2$ and $\text{C}_2\text{H}_4\text{Br}_2$ vapour, and are used to calculate the electric moments. The vals. deviate at lower, and converge at higher, temp. N. M. B.

Oxygen valency angle and structure of glucose and related compounds. H. HUBBERT and J. S. ALLEN (J. Amer. Chem. Soc., 1932, 54, 4115—4116).—The electric moment and O valency angle are: ethylene oxide 1.88, 77°; propylene oxide, 1.88, 77°; trimethylene oxide 2.01, 102°; tetrahydrofuran

1.71, 105°; tetrahydropyran 1.87, 88°. The "normal" O valency angle is $90 \pm 5^\circ$. From these results the pyranose ring of carbohydrates and related compounds represents a "strainless" puckered ring system and the furanose ring structure a strained flat ring. C. J. W. (c)

Molecular and atomic volumes. XLII. Revision of the densities of the aluminium halides. W. BILTZ [with O. HULSMANN]. XLIII. Densities of crystalline nitric, sulphuric, and phosphoric acids, and related substances at low temperature. W. BILTZ and O. HULSMANN (Z. anorg. Chem., 1932, 207, 371—376, 377—384).—XLII. Data are recorded for AlCl_3 , AlBr_3 , and AlI_3 at 18° to -180°; the zero mol. vols. are 53.3, 78.0 (lit. 83.88), and 98.3 (lit. 102—103), respectively. No evidence could be obtained for the existence of two forms of AlCl_3 .

XLIII. Data are recorded for HNO_3 , SO_2 , SO_3 , H_2SO_4 , SeO_2 , P_2O_5 , HPO_3 , H_3PO_4 , I_2O_5 , and HIO_3 , and the zero mol. vols. are given. The calc. val. for O is 10.9. The mol. vol. of vitreous P_2O_5 is smaller than that of the cryst. form. SO_2 and SO_3 have approx. the same mol. vol. From vol. relationships the oxy-acids cannot be regarded as hydrates of the corresponding oxides. H. F. G.

Influence of molybdates on rotatory power of xylose. E. DARMOIS and (Mlle.) M. MURGIER (Compt. rend., 1932, 195, 707—709).—Addition of varying proportions of MoO_3 and NaOH to aq. xylose has a much greater effect on the rotatory power than in the case of glucose, but indicates the existence of the similar compound, $\text{NaHMoO}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}_5$ (cf. A., 1921, i, 498; 1931, 939). The equilibrium const. at 20° for xylose+molybdate complex is 0.10. C. A. S.

Magnetic birefringence in solutions of sodium chloride and sodium bromate. S. W. CHINCHALKAR (Indian J. Physics, 1932, 7, 317—321).—A feeble negative magnetic birefringence is shown. N. M. B.

Electronic structures of polyatomic molecules and valency. II. Quantum theory of the double linking. R. S. MULLIKEN (Physical Rev., 1932, [ii], 41, 751—758; cf. this vol., 902).—The structure, in terms of mol. orbitals, and formation from two excited CH_2 radicals of C_2H_2 and its derivatives, the $\text{C}\equiv\text{N}$, $\text{N}\equiv\text{N}$, $\text{C}\equiv\text{C}$, $\text{O}\equiv\text{O}$, and $\text{BH}_3\cdot\text{BH}_3$ groups are discussed. The *cis trans* change by ultra-violet light is explained by the variation of the angles of the planes of the CH_2 radicals. N. M. B.

Chemistry in space. S. SUGDEN (Nature, 1932, 130, 567).—A summary of the application of the electronic theory of valency to the tetrahedral atom model and of the problem of the optical activity of living matter. L. S. T.

Modified ionic states in crystals. C. P. SNOW and F. I. G. RAWLINS (Proc. Camb. Phil. Soc., 1932, 28, 522—530).—The band spectra of Cr and some other transitional elements contain lines which must be of ionic or quasi-ionic origin, and can be explained as due to inter-combination transitions, in agree-

ment with theoretical intensity conditions, which apply also to the case of the rare-earth spectra.

N. M. B.

Nature of chemical linking. IV. **Energy of single linkings and relative electronegativity of atoms.** L. PAULING (J. Amer. Chem. Soc., 1932, 54, 3570—3582; cf. this vol., 561).—Extreme ionic and normal covalent linkings are defined. The energy of 21 single linkings can be calc. from data for heats of formation and combustion of gaseous mols. on certain assumptions. Deviations from additivity of the energies of normal covalent linkings (*ibid.*, 901) are positive for all linkings but one, and increase with the ionic character of the linking. Vals. of the energy of 20 linkings for which experimental data are not available are predicted.

G. M. M. (c)

Quantum theory of double linking. R. S. MULLIKEN (J. Amer. Chem. Soc., 1932, 54, 4111—4112).—Preliminary note.

C. J. W. (c)

Electron affinity of free radicals. IV. **Compounds not aromatic hydrocarbons.** H. E. BENT, M. DORFMAN, and W. F. BRUCE (J. Amer. Chem. Soc., 1932, 54, 3250—3258; cf. this vol., 680).— ΔF is the same for the addition of Na to diphenylanisylmethyl or CPh_3 . ΔF for the addition of Na to 9-chloro-10-phenanthroxyl is more negative than for C-free radicals. Pentaphenylcyclopentadienyl, tri-*p*-anisylmethyl, and α -diphenyl- β -trinitrophenylhydrazyl do not form additive compounds when treated with 1% Na amalgam.

R. H. F. (c)

Electronic constitution of some simple and complex derivatives of copper in relation to their magnetic properties. S. S. BHATNAGAR, B. SINGH, and A. GHANI (Indian J. Physics, 1932, 7, 323—330).—Susceptibilities in the solid and liquid state are given for Cu acetate, propionate, butyrate, valerate, hexoate, acetylacetonate, acetylacetate, and dimethylglyoxime, and for bisethylenediamminocupric nitrate, thiosulphate, and hypophosphite. The compound, when the central atom or ion contains completed sub-groups, has zero magnetic moment and is diamagnetic, and where the sub-groups are incompletely filled it is paramagnetic.

N. M. B.

Affinity capacity, affinity, and electroaffinity. G. URBAIN (J. Chim. phys., 1932, 29, 325—338).—A lecture.

J. G. A. G.

Reversible processes in a magnetic material with strong inner tension. R. BECKER (Wiss. Veroff. Siemens-Konz., 1932, 11, No. 2, 1—11).—Mathematical.

A. J. M.

Mechanism and experimental determination of magnetic multiplets. R. FORRER and J. MARTAK (J. Phys. Radium, 1932, [vii], 3, 408—436).—The multiplets were investigated by a study of hysteresis cycles of Fe, Ni, and Co. Ni shows a doublet, Fe two types of triplet, and Co a quadruplet. The deformation by intense fields, orientation, and inversion of the multiplets are described.

N. M. B.

Relation between the electric and diamagnetic susceptibilities of monatomic gases. J. P. VINTI

(Physical Rev., 1932, [ii], 41, 813—817; cf. Kirkwood, this vol., 215).—Mathematical.

N. M. B.

Variation of the principal magnetic susceptibilities of certain paramagnetic crystals with temperature. B. W. BARTLETT (Physical Rev., 1932, [ii], 41, 818—832).—The Curie and Weiss consts. for the temp. range 60° to -45° were determined for $CoSO_4 \cdot 7H_2O$, and for 5 crystals of the series $MR_2(SO_4)_2 \cdot 6H_2O$, where $M=Co$, Cu , or Ni , and $R=NH_4$ or K , using EtOH as solvent for the auxiliary paramagnetic salt at low temp. The Curie const. showed small, and the Weiss const. considerable, variation; both decreased progressively with change of metal ion $Co \rightarrow Ni \rightarrow Cu$. The effect of the change $NH_4 \rightarrow K$ was slight.

N. M. B.

Magnetic behaviour of bivalent copper, nickel, and cobalt compounds. W. KLEMM and W. SCHUTH (Z. Elektrochem., 1932, 38, 621).—The magnetic properties of the halides, oxides, sulphides, and selenides indicate that the tendency to the formation of metallic-type compounds increases with increasing ionisation potential of the cations. There is no abrupt change of magnetic behaviour on passing from highly complex salts to simple binary compounds.

H. F. G.

Change of paramagnetic susceptibility due to absorption of light. D. M. BOSE and P. K. RAHA (Nature, 1932, 130, 544).—Absorption of light increases the paramagnetic susceptibility of $CrCl_3$ solution (cf. A., 1931, 670).

L. S. T.

Diamagnetism of molecules. D. P. RAY-CHAUDHURI (Nature, 1932, 130, 579—580).—As a first approximation for diat. homopolar mols. the loss in diamagnetism on mol. formation is proportional to the binding energy.

L. S. T.

Magnetic properties of isotropic ferromagnetic substances. R. GANS (Ann. Physik, 1932, [v], 15, 28—44).—Mathematical.

A. J. M.

Magnetic susceptibility of carbamides, isocarbamides, and sulphamide. G. DEVOTO (Atti R. Accad. Lincei, 1932, [vi], 15, 973—976).—The magnetic susceptibility and sp. gr. of the following solid compounds have been measured: $R \cdot CO \cdot NH_2$ (where $R=NH_2$, $NHMe$, $NHEt$, $NHPr$, and NMe_3), $CO(NHMe)_2$, $CO(NEt_2)_2$, $NH_2C(NH_2) \cdot OMe$, $NH_2C(NH_2) \cdot OEt$, and $SO_2(NH_2)_2$. Isomeric compounds have almost identical susceptibilities.

D. R. D.

Growth of metal crystals in metal vapour. II. M. STRAUMANN (Z. physikal. Chem., 1932, B, 19, 63—75; cf. A., 1931, 1115).—In the sublimation of Zn in a H_2 atm. at < 4 mm. pressure, small crystals are formed, the habit of which agrees with Stranski's theory (cf. this vol., 986). The crystals have no definite orientation relative to the glass on which they are deposited. On rapid sublimation in a high vac. a coherent film is formed instead of a cryst. powder. Apparently no dimorphic regular form of Zn exists.

R. C.

Swelling of graphite. H. THIELE (Z. anorg. Chem., 1932, 207, 340—352).—Some samples of graphite exhibited pronounced unilateral swelling

when moistened with HNO_3 and heated. The phenomenon is due to union of the laminae at the edges, with the production of a concertina-shaped mass. It is inhibited by pressure. No oxidation of the C occurs during the swelling, and the nature of the gas filling the spaces between the laminae is of no significance. Fuming H_2SO_4 , anhyd. FeCl_3 , and Br produce the effect, which in the case of the last-named is to some extent reversible. H. F. G.

Geometrical method of determining the crystal axes of single-crystal wires. B. CHALMERS (Phil. Mag., 1932, [vii], 14, 612—616).—The specimen is stretched, and the axes are calc. from measurements made on the surface markings accompanying glide. H. J. E.

Diffraction of X-rays by liquid metals. J. T. RANDALL and H. P. ROOKSBY (Nature, 1932, 130, 473—474).—Liquid Na, K, Rb, and Cs diffract X-rays in one main direction, giving a single narrow band the spacing of which is approx. equal to that of the strongest line in the corresponding solid. L. S. T.

Distribution of crystal lattice in stretched aluminium. Y. TANI (J. Fac. Eng. Tokyo, 1932, 20, 133—146).

Lattice dimensions of niobium, tantalum, and some niobates and tantalates. L. L. QUILL (Z. anorg. Chem., 1932, 208, 257—272).—The following consts. have been determined for Nb and Ta (tempered at 800°), NaNbO_3 , NaTaO_3 , KNbO_3 , and KTaO_3 , in the order named: a 3.299, 3.298, 3.889, 3.881, 4.005, 3.981, all ± 0.002 Å.; d_{calc} 8.575, 16.69, 4.609, 7.141, 4.634, 7.022. F. L. U.

X-Ray examination of lanthanum, cerium, and neodymium. L. L. QUILL (Z. anorg. Chem., 1932, 208, 273—281).—La (hexagonal) has a 3.75 ± 0.010 , c 6.06 ± 0.030 Å., d_{calc} 6.194. Ce, face-centred cubic, a 5.143 ± 0.004 Å., d_{calc} 6.799. Nd, hexagonal close-packed, a 3.66 ± 0.010 , c 5.88 ± 0.030 Å., d_{calc} 6.991. F. L. U.

Precision measurements of lattice constants by the powder method. M. C. NEUBURGER [with G. MASING] (Z. Elektrochem., 1932, 38, 631—632).—The error caused by incomplete parallelism of the X-rays used is noted; it may be obviated by a method of calibration due to F. Regler. By using a calibration curve derived from 4 rock-salt powder diagrams, the total error may be reduced to 0.01%. Be has a 2.680 ± 0.0002 , c 3.5942 ± 0.0003 Å., d_{calc} 1.857. H. F. G.

Structure of electrodeposited metals. II. L. B. HUNT (J. Physical Chem., 1932, 36, 2259—2271). E. H. (c)

Charge distribution in ions and the grating constant of rubidium bromide according to the statistical method. H. JENSEN (Z. Physik, 1932, 77, 722—745).—A detailed application of a method previously described (Lenz, this vol., 1078); repulsive forces in these lattices are due to superposition of electric charge clouds, and consequent increase in the kinetic energy of the mol. Fermi gas, rather than to electrostatic repulsions. A. B. D. C.

Transformation of β -quartz into cristobalite. A. N. SCHUKAREV (J. Gen. Chem. Russ., 1932, 2, 231—237).—Not < 2 mols. of β -quartz take part in the reaction of transformation into cristobalite.

R. T.

Crystal structure of potassium dithionate. M. L. HUGGINS and G. O. FRANK (Amer. Min., 1931, 16, 580—591).— $\text{K}_2\text{S}_2\text{O}_6$ has a 9.82, c 6.36 Å.; space-group D_2^h . $\text{Rb}_2\text{S}_2\text{O}_6$ has a 10.0, c 6.3 Å. Both are hexagonal (trigonal trapezohedral). CH. ABS.

X-Ray examination of chrome ores. I. Lattice dimensions. II. Theoretical densities. G. L. CLARK and A. ALLY (Amer. Min., 1932, 17, 66—74).—Vals. of a vary inversely with the Al_2O_3 content; $d_{\text{calc.}} = d_{\text{obs.}} \pm 1.3\%$. CH. ABS.

X-Ray study of the polymorphism of normal saturated fatty acids. F. D. LA TOUR (Ann. Physique, 1932, [x], 18, 199—284).—The monoclinic acids with an even no. of C atoms from C_{12} to C_{18} show α and β forms, the transition temp. $\beta \rightarrow \alpha$ varying, as a function of the no. of C atoms, similarly to m.p. Transition points for oriented layers differ from those for whole crystals. Similar dimorphism is shown by the first members (malonic, succinic, and glutaric) of the di-acid series, and for the higher di-acids with an odd no. of C atoms. Full data are tabulated. N. M. B.

Crystallographic examination of α' -di-*p*-tolyl-acetone. H. L. PROTOWSKI (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 1—7).—The monoclinic crystals have $a:b:c = 1.4373:1:5.6247$, β $116^\circ 50'$; n_D 1.65. R. T.

Crystalline structure of α -methylxyloside. E. G. COX (J.C.S., 1932, 2535—2543).—Comparison of the lattice consts. of this compound with those of β -methylxyloside and α -xylose indicates close relationship. The mol. arrangement of α -methylxyloside is discussed. The pyranose sugar ring is probably not completely planar or of *trans*-strainless form. A. J. M.

Thermo-electromotive force between magnetic and non-magnetic iron. T. KOUSMINE (Helv. phys. Acta, 1931, 4, 364—366; Chem. Zentr., 1932, i, 3390).

Non-conducting modifications of metals. J. KRAMER and H. ZAHN (Naturwiss., 1932, 43, 792).—By cathode sputtering or by distillation under suitable conditions, Fe, Ni, Pt, Zn, Cd, Sn, Sb, and probably W can be obtained in forms of abnormally low conductivity which are stable only below a certain temp. characteristic of each metal. D. R. D.

Magnetic effects in iron crystals. A. G. HILL (Phil. Mag., 1932, [vii], 14, 599—604).—Between -190° and 162° the magnetisation curve is linear for fields below 2 gauss, and non-linear for fields up to 20 gauss. The magnetic lag is greater at lower temp. H. J. E.

Effect of strain on magnetostriction and magnetisation in nickel. C. W. HEAPS (Physical Rev., 1932, [ii], 42, 108—118).—Large discontinuities in the magnetisation curve and small Barkhausen

jumps may be due to magnetic instability produced in small regions by local strains. N. M. B.

Magnetostriction and magnetisation of single crystals of the iron-nickel series. F. LICHTENBERGER (Ann. Physik, 1932, [v], 15, 45—71).—The magnetisation curves and magnetostrictions of single crystals of the Fe-Ni series of various compositions were determined. The unique position occupied by "permalloy" is discussed. It seems to be due to the fact that its composition is approx. the mean of that at which the direction of easiest magnetisation changes (71% Ni), that at which the polycryst. magnetostriction disappears (83% Ni), and that at which there is equal magnetostriction in all directions (85.5% Ni). A. J. M.

Influence of impurities on the cohesion limits and on the ultra-microscopic sol formation of synthetic rock-salt crystals. III. Addition of heavy metal chlorides. W. METAG. IV. Density determinations for pure salt crystals and for rock-salt with heavy metal impurities. J. KOHLER (Z. Physik, 1932, 78, 363—374, 375—382).—III. Increase in strength of crystals is always due to impurity in the disperse phase. Doubly-charged foreign cations give a greater increase in strength than singly-charged.

IV. A displacement method was used to determine the densities of NaCl, KCl, and KBr to an accuracy of 0.01%; the method can be used to determine impurities. A. B. D. C.

Plastic extension of α -iron crystals. W. FAHRENHORST and E. SCHMIDT (Z. Physik, 1932, 78, 383—394).—Stretching of Fe was studied at room temp. and at -185° ; crystallographic translation with $T=\{123\}$ and $t=[111]$ is the probable mechanism. A. B. D. C.

Incidence of lattice distortion and orientation in cold-rolled metals. W. A. WOOD (Phil. Mag., 1932, [vii], 14, 656—665).—The degree of distortion of Cu, an alloy 70% Ni, 25% Fe, 5% Cu, Fe-Al (4% Al), and Fe-Si (4% Si) initially increases rapidly with reduction in thickness of the metal, reaching a const. val., characteristic of the metal and unchanged by further reduction. Lattice distortion, when it occurs, reaches a max. val. before preferred orientation appears. H. J. E.

Mechanism of the allotropic transformation of cobalt and thallium. U. DEHLINGER (Metallwirt., 1932, 11, 223—225; Chem. Zentr., 1932, i, 3150).—The hexagonal lattice is converted at 231° into a face-centred cubic lattice; conditions of the change are discussed. A. A. E.

Influence of impurities on the transformation point of liquid allotropic modifications. S. DOBINSKI (Nature, 1932, 130, 662—663).—A theoretical treatment of the possible effects of slight impurities in relation to recent work on PhNO_2 (cf. this vol., 1081). L. S. T.

Thermal variations in the mol. wt. of halogens. A. JOUNIAUX (Bull. Soc. chim., 1932, [iv], 51, 1062—1069).—A review of published data from which may be deduced the mol. wt. of Cl_2 , Br_2 , and I_2 at different temp. D. R. D.

Mol. wt. in different states of aggregation. I. G. ANTONOFF (J. Physical Chem., 1932, 36, 2406—2436).—It is concluded theoretically that all systems exerting outwardly the same pressure at the same temp. are equimol., irrespective of their states of aggregation. Accordingly, two or more phases in thermal equilibrium have the same mol. density. From the mol. wt. of the vapour of a pure substance the degree of association in another phase is calc. as the ratio of the densities of the two phases. The mol. wt. of a liquid attains high vals. at low temp. Liquid and vapour densities vary with temp. in a discontinuous manner. Between any two successive discontinuities the curves follow a single equation the consts. of which vary for different portions of the curve. At temp. of discontinuity the degree of association is a whole, simple no., showing that association takes place according to the law of multiple proportions, and consists of a no. of successive reactions. At discontinuities the liquid consists of only one kind of mol. The mol. wt. of a solid at its m.p. can be calc. from the ratio of the densities of the solid and liquid phases. R. H. C. (c)

Electrical resistance and the critical point of mercury. F. BIRCH (Physical Rev., 1932, [ii], 41, 641—648).—Relative resistance, and instantaneous pressure and temp. coeffs. in the regions 0 — 1200° and 1 — 4000 atm. are given. All vals. increase with rise of temp. and decrease with rise of pressure. The crit. consts. are $1460 \pm 20^\circ$, and 1640 ± 50 kg. per sq. cm. N. M. B.

Theory of thermoelectricity. B. BRUZZ (Z. Elektrochem., 1932, 38, 777—779).—In the thermodynamic treatment of the Thomson theory with reference to thermoelectric effects in metallic and electrolytic systems (Peltier and Seebeck effects), use is made of the postulate previously employed (this vol., 123) according to which the heats of reaction in a stationary system represent latent (secondary) heat. M. S. B.

Superconductivity with alternating currents of high frequency. J. C. McLENNAN, A. C. BURTON, A. PITT, and J. O. WILHELM (Proc. Roy. Soc., 1932, A, 138, 245—258).—Observations have been made on the resistance of a conductor at low temp. when both a.c. (frequency 12×10^6) and d.c. are flowing simultaneously. The crit. points for the high-frequency and d.c. resistances are the same, and the position of this common crit. point on the temp. scale is determined by the ratio d.c./a.c. Two effects have thus been established, viz., the depression of the crit. point for the a.c. resistance by the application of high-frequency currents, and the raising of the crit. point for the high-frequency resistance in the presence of a d.c.

Increase in thermo-electric force of oxides by the use of multiple oxide systems. F. FISCHER, K. DEHN, and H. SUSTMANN (Ann. Physik, 1932, [v], 15, 109—126).—The increase of thermo-electric force is determined for various oxide systems up to five components. The greatest e.m.f. is obtained with a 5-oxide system. The increase may be due to reduction of resistance, or higher e.m.f. of mixed crystals of different oxides. A. J. M.

Conduction of heat of lead-thallium alloy at low temperatures. W. J. DE HAAS and H. BREMMER (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 323—328).—The thermal resistance of the superconducting alloy, $PbTl_2$, below its transition point 4.09° abs., increases linearly with rise of temp. for magnetic fields $<$ the threshold val. for the alloy and remains practically const. when that val. has been reached. This behaviour is not in accordance with that of pure metals. An explanation is based on the possible non-homogeneity of the alloy. M. S. B.

Halides of the rare earths. VI. Terbium and erbium groups. G. JANTSCH, H. JAWUREK, N. SKALLA, and H. GAVALOVSKI (Z. anorg. Chem., 1932, 207, 353—367).—The following m.p. are recorded: $GdCl_3$ $609^\circ \pm 2^\circ$; $GdBr_3$ $765-786^\circ$; GdI_3 $926^\circ \pm 2^\circ$; $DyCl_3$ $654^\circ \pm 2^\circ$; $DyBr_3$ $881^\circ \pm 2^\circ$; DyI_3 $955^\circ \pm 5^\circ$; $HoCl_3$ $718^\circ \pm 2^\circ$; $HoBr_3$ $914^\circ \pm 4^\circ$; HoI_3 $1010^\circ \pm 10^\circ$; $ErCl_3$ $774^\circ \pm 2^\circ$; $ErBr_3$ $950^\circ \pm 10^\circ$; ErI_3 $1020^\circ \pm 10^\circ$; YCl_3 $721^\circ \pm 2^\circ$; YBr_3 $904^\circ \pm 3^\circ$; YI_3 $1000^\circ \pm 10^\circ$. With increasing at. no. there is a min. in the m.p. of the chlorides at $TbCl_3$; for the iodides the min. is at PrI_3 . Beyond Nd the m.p. falls in the order iodide, bromide, chloride, but for La, Ce, and Pr the chloride has the highest m.p. The connexion between these relationships and the crystal structure and form is discussed. The iodides of Ga, Dy, Ho, Er, and Y begin to sublime without decomp. at $650-700^\circ/0.03$ mm., and even at $800-850^\circ$ no I is liberated. H. F. G.

Variation of the m.p. and volume of carbon tetrachloride with thermal pre-treatment. W. BRULL (Z. Elektrochem., 1932, 38, 601—611).—The m.p. of CCl_4 increases (by up to 0.5°) with rise of the temp. at which the material has previously been maintained and with reduction of the time which elapses after cooling commences; the lowest m.p. is observed by maintaining the liquid for several hr. at -20° . The rate of cooling has little influence on the reading if the total time of cooling is const. The normal val. is approached slowly by any given specimen, the rate of change being accelerated by certain substances, e.g., anhyd. $CuSO_4$, but not by H_2O . The sp. vol. of the specimen at just above the m.p. is the smaller (by up to 0.05%) the higher is the temp. of pre-treatment. Ordinary solid CCl_4 undergoes a change of sp. vol. (up to 3.6%) with time, and on melting, the liquid also has an abnormal sp. vol. (1.7% max.). It is suggested that in normal liquid CCl_4 two forms are present, the exothermic form amounting to about 3 mol.-% of the total, and that two allotropic modifications exist in the solid state. H. F. G.

M.p. in very narrow capillaries. P. KUBELKA (Z. Elektrochem., 1932, 38, 611—614).—Theoretical. The f.p. of a liquid may be influenced by surface forces at the crystal-liquid, crystal-vapour, and liquid-vapour interfaces. The case of liquid-vapour forces is considered in detail in its application to the f.p. of a liquid adsorbed by an inert porous material; f.p. depressions of as much as 100° may be anticipated for liquids in contact with active C. H. F. G.

Melting of dissociable compounds. A. TIAN (Bull. Soc. chim., 1932, [iv], 51, 1088—1089).—It is

shown theoretically that the addition of a small quantity of either of its dissociation products to a dissociating compound has no effect on its m.p. The effect of dissociation is to lower the m.p. below the normal val. Consequences of these facts are considered. D. R. D.

[Nitrosyl and nitryl fluorides] NOF and NO_2F . O. RUFF, W. MENZEL, and W. NEUMANN (Z. anorg. Chem., 1932, 208, 293—303).—Physical consts. have been redetermined on carefully purified materials. NOF, m.p. -132.5° , b.p. -59.9° , d_{400} $1.919-0.00278T$; NO_2F , m.p. -166° , b.p. -72.4° , d_{400} $2.143-0.00323T$. V.p. were also determined. Chemical properties are described. F. L. U.

Relations between b.p. and chemical constitution. IV. Energy relations. Sublimation. Heat of dissociation. K. BILLIG (Svensk Kem. Tidskr., 1932, 44, 235—241; cf. this vol., 901).—Trouton's rule is derived, assuming that the b.p. is proportional to the true mol. wt. of the associated liquid in the neighbourhood of the b.p. The energy val. of the linking between the O atoms in $(H_2O)_n$, calc. from the heat of vaporisation of H_2O , is 7.8 kg.-cal., in agreement with the val. calc. for the similar linking in liquid HCO_2H ; the corresponding val. for $(MeOH)_2$ is 9.2 kg.-cal. Assuming that the heat of sublimation is proportional to the degree of association, Forerand's law is derived. Similar considerations are applied to the thermal dissociation of a series of ammoniates of $CaCl_2$ and the carbonates of H, Ag, Ca, Ba, and Na. The general inference is that the heat of vaporisation, sublimation, or thermal dissociation is directly proportional to the mol. wt. in the ideal gaseous or dissolved state, multiplied by the degree of association or other attractive property of the mols. E. S. H.

Correction for incomplete thermal insulation in measurements of small heat capacities. W. H. KEESOM and J. A. KOK (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 294—300).—An accurate method is described for correcting for heat exchange with the surroundings in the measurement of small heat capacities, by Nernst and Eucken's method, at the lowest liquid He temp. M. S. B.

Specific heat of liquid helium. W. H. KEESOM and K. CRUSIUS (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 307—320).—The sp. heat curve for liquid He under saturation pressure rises from 1.4° to 2.19° abs., where there is a sharp max. (at heat approx. 9 g.-cal.); it then falls quickly to a flat min. at approx. 2.6° abs. and again rises very slowly (cf. Dana and Onnes, A., 1927, 101) to 4.1° abs., the limit of the range examined. Measurements of sp. heat at const. vol. have also been made between 2.96° and 4.007° abs. M. S. B.

Specific heat of silver from 1.35° to 20.3° abs. W. H. KEESOM and J. A. KOK (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 301—306).—The at. heat of Ag increases from 0.000254 g.-cal. at 1.35° abs. to 0.3995 g.-cal. at 20° abs. The val. of θ for Ag is almost const. in the liquid-solid H range; it reaches a max. at 5.4° abs. ($\theta=226$) and decreases below this temp. to θ 165 at 1.35° abs. The at. heat

curves of Zn and Ag intersect so that below 14° abs. Ag has a larger at. heat than Zn. M. S. B.

Exact measurement of the specific heat of solid substances at high temperatures. V. Cooling correction of the metal calorimeter in exact high-temperature calorimetry. F. M. JAEGER, E. ROSENBOHM, and J. A. BOTTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 347—352).—The conditions have been determined for making the leakage modulus of a metal calorimeter as small and const. as possible. M. S. B.

Exact measurements of the specific heats of solid substances between 0° and 1625° . VI. Neumann-Joule-Kopp-Regnault law concerning the molecular heat of chemical compounds as a function of the atomic heats. F. M. JAEGER and J. A. BOTTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 352—362).—The mol. heat of PtSn is less than the sum of the at. heats of Pt and Sn at the same temp. and the difference increases approx. linearly with rise of temp. At 20° it is 4.54% and at 200° 8.70%. This contradicts the law of the additive character of at. heats. The sp. heat of white Sn at 0° is 0.05393 and of PtSn 0.03836. X-Ray data for PtSn are given: a_0 4.103, c_0 5.428 Å. The compound is hexagonal and the cell contains 2 mols. M. S. B.

Vapour pressure of liquid water that has recently been frozen. A. W. C. MENZIES (Proc. Nat. Acad. Sci., 1932, 18, 567—568).—The v.p. of H_2O which has reached equilibrium temp. of 25° and 3.5° 10 min. after having been frozen does not differ by more than 0.05 mm. from that of H_2O cooled directly from 100° . O. J. W.

Vapour pressure of sodium. E. THIELE (Ann. Physik, 1932, [v], 14, 937—970).—The v.p. of Na was determined between 614° and 771° abs., using an improved streaming method and employing vac.-distilled Na. The partial pressures of the Na atoms and the Na mols. were calculated; the heat of dissociation is 16,800 g.-cal. The heat of vaporisation of Na atoms at 0° abs. is $26,200 \pm 130$ g.-cal., and the chemical const. of Na is 0.85 ± 0.10 . W. R. A.

Vapour pressures and vapour densities of beryllium and zirconium halides. W. FISCHER and O. RAHLS (Z. Elektrochem., 1932, 38, 592).—The following m.p., sublimation temp., and heats of sublimation in kg.-cal. are recorded: $BeCl_2$ 405° , —, 29; $BeBr_2$ 487° , 470° , 31; BeI_2 480° , 480° , 28; $ZrCl_4$ 436° , 332° , 26; $ZrBr_4$ 449° , 356° , 27; ZrI_4 499° , 430° , 30. For the Zr halides the v.d. accord with the unimol. formula; $BeBr_2$ exists as Be_2Br_4 at low temp. (20% in saturated vapour at the b.p.). The Be halides react with SiO_2 ; $ZrCl_4$ and $AlCl_3$ react slightly, and TiF_4 reacts very rapidly; Zr and Al bromides and iodides do not react. H. F. G.

Behaviour of certain organic materials when heated to 650° at an initial pressure of 1000 kg. per sq. cm. G. TAMMANN and A. RUHENBECK (Z. anorg. Chem., 1932, 207, 368—370).—Pressure-temp. curves have been determined for various hydrocarbons, alcohols, and ethers. In all cases the pressure shows at first a linear increase with

rise of temp.; at higher temp. the pressure either (a) rises more rapidly ($EtOH$, Et_2O , $C_6H_5Me_3$, etc.); (b) rises more slowly ($PhMe$, Ph_2 , stilbene, etc.); or (c) passes through a max. and then rises rapidly (C_6H_6 , $C_{10}H_8$, anthracene, etc.). H. F. G.

Relation between [specific] volume of saturated vapour and capillary properties of liquids. N. A. KOLOSOVSKI and B. N. GREBENSCHTSCHIKOV (J. Gen. Chem. Russ., 1932, 2, 189—192).—It is shown theoretically that $\sigma d_1/d_2 = \text{const.} = 0.0688$; σ is the surface tension of a liquid at the b.p., and d_1 and d_2 are respectively the relative densities of the liquid and of its saturated vapour. This equation is verified for a no. of non-associated liquids, but does not hold for associated liquids. R. T.

Compressibility of liquid helium at 2.7° abs. W. H. KEESOM and K. CLUSIUS (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 320—322).—A preliminary determination at 2.71° abs. and a pressure of 5—10 kg. per sq. cm. gave vals. of the order of $7-8 \times 10^{-8}$ sq. cm. per kg., which is greater than the compressibility of any other liquid hitherto measured. The val. for lower pressures obtained by extrapolation is in satisfactory agreement with the val. calc. from the expansion coeff. and the difference between the sp. heats at const. pressure and const. vol. M. S. B.

Viscosity of a fluid containing small drops of another fluid. G. I. TAYLOR (Proc. Roy. Soc., 1932, A, 138, 41—48).—Mathematical. Einstein's expression for the viscosity of a fluid containing small solid spheres in suspension is extended to liquids containing small drops of another liquid in suspension. An expression is derived for the size of the largest drop that can exist in a fluid undergoing distortion at a given rate. L. L. B.

Diffusion of metals in solid lead. W. SEITH and J. G. LAIRD (Z. Metallk., 1932, 24, 193—196).—The rate of diffusion (D) of Ag, Bi, Ti, and Sn in Pb is given by the expression $D = Ae^{-Q/RT}$. At 285° the diffusion consts. are Ag 0.79×10^{-2} , Bi 3.8×10^{-5} , Ti 2.7×10^{-5} , Sn 1.4×10^{-5} , and Pb 6×10^{-6} (sq. cm., day). Hence the rate of diffusion decreases with increasing similarity between the metal and Pb. A spectrographic method of measuring the rate of diffusion of one metal into another is described. A. R. P.

Diffusion of metals in the solid state. V. Diffusion and corrosion of Cu-Ni alloys. G. GRUBE and A. JEDELE (Z. Elektrochem., 1932, 38, 799—807).—A rod of Ni electrolytically plated with Cu and a rod of Cu plated with Ni were heated in an atm. of H_2 at 1000° and 1025° and the amount of diffusion was determined. Ni diffuses into Cu more rapidly than Cu into Ni. The diffusion coeff. of Ni into Cu increases with increasing depth of penetration or with increasing concn. of Cu in the mixed crystals. The opposite is the case for the diffusion coeff. of Cu into Ni. The diffusion coeff. of Cu into Ni is reduced to about one third by the presence in the latter of 0.5% Mn. In a solution of 0.146M- $(NH_4)_2CO_3$ and 0.148M- H_2O_2 at 20° Ni-Cu alloys containing < 30 at.-% of Ni are attacked. Alloys

of higher Ni concn. are completely resistant. In 4*N*-H₂SO₄ containing 0.5*M*-KClO₃ at 25° both components dissolve at all concns. and between 75 and 80 at.-% Ni corrosion increases very rapidly with increasing Ni concn. This is apparently due to the fact that the magnetic α -mixed crystals are more readily attacked than the non-magnetic β -mixed crystals. M. S. B.

Liquid sodium amalgams. G. R. PARANJPE and R. M. JOSHI (J. Physical Chem., 1932, 36, 2474—2482).—The literature indicates that these amalgams are sols of Na in Hg with micelles of the composition (Na_x)Hg_y. To define an amalgam, the method of prep., age, and previous history are necessary.

C. T. S. (c)

X-Ray study of electrolytic Fe-Ni alloys. K. IWASE and N. NASU (Bull. Chem. Soc. Japan, 1932, 7, 305—314).—X-Ray diagrams for mixtures of Fe and Ni deposited from sulphate solutions show that both α and γ solid solutions are present at concns. of 14—58% Ni. The X-ray lines are diffuse and the lattice consts. of both α and γ solutions pass through a max. with increasing Ni concn. It is suggested that each metal generally forms its own crystal lattice during deposition and that solid solutions are subsequently formed by diffusion. A. G.

Structure and chemical composition of some metallic alloys. N. PARRAVANO and V. CAGLIOTI (Mem. R. Accad. Italia, 1932, 3, [Chim.], 5—21).—X-Ray data for the system Zn-Mn up to 33 at.-% Mn show that the hexagonal ϵ phase, like the ϵ phases of brasses, is stable from 24 to 33% Mn at room temp. and from 24 to 12.5% Mn at higher temp. It contains 2 atoms in the unit cell: α varies from 2.754 (33% Mn) to 2.764 Å. (12.5% Mn). The γ phase has a body-centred cubic structure, with 52 atoms per unit cell, and is analogous to the γ phases of brasses: α 9.11 Å. It exists in the region 22.21—8.09% Mn at room temp. only. The alloys with 11.07—8.094% Mn also show lines of a γ' or β' phase, which has not been completely identified. The η phase consists of a 1—2% solution of Mn in Zn and is unstable. Formulae for the various intermetallic compounds are proposed. O. J. W.

General laws governing the changes in the structure and properties [of metals] during transformation processes. G. SACHS (Z. Metallk., 1932, 24, 241—247).—A review of recent work and theories on the mechanism of the breakdown of solid solutions with the formation or separation of intermetallic compounds. A. R. P.

Transformations in the gold-copper system and their theoretical importance in the study of transformations in solid metals. L. GRAF (Z. Metallk., 1932, 24, 248—253).—The AuCu and AuCu₃ transformations in Au-Cu alloys take place slowly in polycryst. aggregates and are two-phase reactions, whereas in single crystals they take place rapidly as single-phase reactions. The AuCu transformation takes place in two stages, in the first of which the lattice symmetry changes from cubic to tetragonal, and in the second the atoms regroup themselves from random orientation into a regularly oriented

lattice; the first change occurs rapidly and completely, whereas the second is much slower, so that it is possible to arrest the transformation in an intermediate stage characterised by a tetragonal lattice with heterogeneously distributed regularly oriented fields. In this state the alloy AuCu has an electrical resistance 25% greater than, and a tensile strength about double that of, the fully-transformed alloy. The first stage in the transformation is attributed to changes in the state of the free valency electrons in the lattice, and the second stage to thermodynamic conditions. The fact that larger crystals undergo transformation more readily than smaller crystals indicates a definite connexion between the mechanism of the two stages; a theoretical explanation of this is given. A. R. P.

Cause of the austenite-martensite transition at room temperature. E. SCHEIL (Z. Elektrochem., 1932, 38, 554—557).—The γ - α -Fe transition at low temp. is not due to thermal displacement of atoms, and cannot be induced by the operation of shear stresses set up, e.g., during quenching, since the initial temp. is not altered on stressing a fine-cryst. specimen. It is probably due to the existence of a mechanically unstable condition, this view being supported by the diminution of elasticity at the transition temp. H. F. G.

Ternary system silver-copper-phosphorus. H. MOSER, K. W. FRÖHLICH, and E. RAUB (Z. anorg. Chem., 1932, 208, 225—237).—The binary systems Cu-P and Ag-P and the ternary system have been investigated by micrographic and thermal methods. There is no indication of the reported existence of Cu₅P₂. Cu₃P and Cu are not miscible in the solid state, but systems containing 14—26% P are homogeneous. When Ag-P mixtures containing >2% P are melted in a closed tube two liquid layers are formed. Under normal atm. pressure not more than 1.45% of P can be retained as phosphide. Ag and AgP₂ form a eutectic, whereas AgP₂ and AgP₃ give mixed crystals over a wide range. Ternary systems with varying ratios of Cu : P are described.

F. L. U.

Relation between magnetic properties, especially coercive force, and structure of alloys, and the development of new types of magnetic alloys. W. KÖSTER (Z. Elektrochem., 1932, 38, 549—553).—The finer is the structure, the greater is the coercive force. Measurements with various C and alloy steels, and the influence of tempering on the hysteresis loop, are described; the systematic development of new alloys is also discussed.

H. F. G.

Determination of the shape and arrangement of ferromagnetic precipitations by means of the magnetic balance. E. GEROLD (Z. Metallk., 1932, 24, 255—257).—If the curves for longitudinal and transverse magnetisation of a non-magnetic metal containing segregations of a magnetic constituent coincide, it follows that the latter exists in separate particles completely surrounded by the non-metallic ground mass; this occurs, e.g., in Cu with 2% Fe. If the curves do not coincide, then the magnetic phase exists as tenuous films, forming a network throughout

the ground mass. After rolling alloys of the first type the magnetic inclusions are elongated and the magnetic properties are no longer isotropic.

A. R. P.

Van der Waals forces between tetrahalide molecules. J. H. HILDEBRAND and J. M. CARTER (J. Amer. Chem. Soc., 1932, 54, 3592—3603).—The expansion on mixing has been measured for various binary mixtures of tetrahalides. $(\partial P/\partial T)_T$ has been measured for the pure liquids and mixtures and $(\partial E/\partial V)_T$ calc. The latter is very nearly a pure vol. function. J. V. V. (c)

Refractive index of liquid mixtures with acetic acid as a component. N. A. PUSHIN and P. G. MATAVULJ (Z. physikal. Chem., 1932, 161, 341—345).—Binary systems of AcOH with various amines have been examined. In all cases n exceeds the val. calc. by the mixture rule, the excess being a max. at a composition which corresponds with a simple mol. ratio and often represents a known solid compound. R. C.

Specific heat of aqueous sulphuric acid. A. SOKOLIK (J. Gen. Chem. Russ., 1932, 2, 311—316).—The sp. heat (C) of the system $H_2SO_4-H_2O$ has been measured at 60° and 80°. The results obtained, together with those of other authors, indicate that C for $H_2SO_4.H_2O$ obeys the simple mixture rule; for all other mixtures C is higher, due to formation of other hydrates. R. T.

Thermochemical examination of solutions. II. Specific heat of aqueous ethylene glycol at various temperatures. M. B. NEUMAN and I. A. KURLIANKIN (J. Gen. Chem. Russ., 1932, 2, 317—321).—The sp. heat (C) of aq. $(CH_2OH)_2$ is a linear function of temp.; that of $(CH_2OH)_2$ is given by $C=0.5388+0.00112T$. R. T.

Vapour pressures of the system ethyl alcohol-ethyl acetate. W. MUND and G. HEIM (Bull. Soc. chim. Belg., 1932, 41, 349—376).—An apparatus fitted with a glass spring manometer for the determination of the v.p. of mixtures is described, the vol. of the vapour phase being very small in order to avoid change in the composition of the liquid. The v.p. of EtOH, EtOAc, and binary mixtures of these have been determined over the range 0—100°. The results agree well with those of previous investigators. D. R. D.

Partial pressures and refractivities of binary mixtures of benzene and some of its polar derivatives. A. R. MARTIN and B. COLLIE (J.C.S., 1932, 2658—2665).—Data are given for mixtures of C_6H_6 with PhCl, PhBr, NH_2Ph , PhOMe, PhCN, and PhOH (refractivities only), and correlated with the dipole moment and mol. radius of the polar mol. D. R. D.

Fractionation of liquid binary mixtures. II. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1932, 12, 655—661).—When both components of a mixture are unassociated or are associated to the same degree, the quotient p_A/p_B , where p_A and p_B are the v.p. of the more (A) and the less volatile component (B), respectively, rises with fall in temp.; this increase in p_A/p_B is usually more marked when A is unassociated and

B is associated. In the latter case p_A/p_B may increase, remain const., or diminish with fall in temp. R. T.

Striae in chemical processes. V. System methyl alcohol-acetone; employment of the "visual method." H. ALBER (Z. anal. Chem., 1932, 90, 87—99).—The "visual method" (cf. A., 1931, 1263) has been employed successfully in obtaining pure samples of MeOH and COMe₂, and in determining the n and distillation curves for mixtures. The latter agree well with previous results and indicate the existence of a const.-boiling mixture at 87% and probably at 95% COMe₂. M. S. B.

Equilibria between three and four liquids at room temperature. E. JÄNECKE (Z. Elektrochem., 1932, 38, 583—588).—The miscibilities of H_2O and 18 org. liquids, taken in pairs, and of the various binary and ternary mixtures with pure H_2O and with aq. solutions of K_2CO_3 , K_3PO_4 , NH_3 , etc., have been determined qualitatively. Seven groups of liquids, forming in all 54 three-layer mixtures, and two groups forming 24 four-layer mixtures are described. All these mixtures contain aq. NH_3 , an inorg. salt, and two org. liquids. The theory of miscibility is discussed. H. F. G.

Mixed crystals of Ca_3SiO_4 and Mn_3SiO_4 . W. L. C. GREER (Amer. Min., 1932, 17, 135—142).—The compounds form mixed crystals in all proportions; n decreases regularly with decrease in the latter. Ca may replace Mn at least up to 50% in the orthosilicates. CH. ABS.

Solubility of hydrogen and helium in liquid ammonia. V. V. IPATIEV and V. P. THEODOROVITSCH (J. Gen. Chem. Russ., 1932, 2, 305—310).—The solubility (S)-temp. curve of H_2 in liquid NH_3 is a straight line, whilst that of He is convex to the temp. axis; in both cases S increases with rise of temp. The S -pressure curves are in both cases rectilinear. H_2 is about three times as sol. as He. R. T.

Liquid ammonia as a solvent. I. Solubility of inorganic salts at 25°. H. HUNT (J. Amer. Chem. Soc., 1932, 54, 3509—3512).—The data for a no. of salts are recorded. E. R. S. (c)

Solubility of alkali halides in acetone. A. LANNUNG (Z. physikal. Chem., 1932, 161, 255—268).—The solubilities have been determined at 18° and 37°. The conductivity of F' in COMe₂ at infinite dilution at 18° is 96. The H_2O or MeOH content of COMe₂ may be determined from the conductivity of a saturated solution of NaCl. R. C.

Effect of water and alcohols on solubility of salts in acetone. A. LANNUNG (Z. physikal. Chem., 1932, 161, 269—278).—The influence of H_2O and alcohols on the solubility of NaCl, and of H_2O on the solubility of various alkali salts, has been determined at 18°. The results for salts which form hydrates are interpreted, and a method of determining the activity coeff. of H_2O in COMe₂ from v.-p. and solubility data is described. R. C.

Different solubilities of optical antipodes in active solvents. E. SCHRÖER (Z. Elektrochem., 1932, 38, 595—596).—The aq. extract of a solution of α -mandelic acid in d -carvone is dextrorotatory, the

acid recovered from the carvone being laevorotatory. The reverse effect is observed when *l*-carvone is used as the solvent. The approx. partition coeffs. K_d and K_l are 4.991 and 5.007, respectively. H. F. G.

Solubility of barium hydroxide in dilute solutions of sodium hydroxide. S. M. NEALE and W. A. STRINGFELLOW (Trans. Faraday Soc., 1932, 28, 765—766).—Data for 0—1.84*N*-NaOH are recorded. J. G. A. G.

Influence of valency on activity. Solubility of cerium iodate in aqueous solutions of certain electrolytes. J. CHLOUPEK, V. DANEŠ, and B. A. DANEŠOVA (Chem. Listy, 1932, 26, 531—533).—The solubility of $\text{Ce}(\text{IO}_3)_3$ is increased by the presence of KNO_3 , K_2SO_4 , MgSO_4 , or MgCl_2 . R. T.

Isodimorphism of formates. F. LEWINTERÓWNA (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 21—48).—The solubility of mixed crystals of Cu and Mn, Cu and Zn, and Cu and Cd formates ($2\text{H}_2\text{O}$) differs from that calc. from Retger's rule, and the three systems correspond with Roozeboom's 4th type. The partition coeff. is not in general const. R. T.

Equilibrium between mixed crystals of nickelous and manganous nitrate, and of nickelous and zinc nitrate hexahydrates and their saturated solutions. T. KOEPEŁÓWNA (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 8—20).—The solubility data for mixed crystals of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ correspond with Roozeboom's 5th type; those for $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ correspond with the 1st type. The solubility of the mixed crystals is not the arithmetic mean of that of the constituent salts. Nernst's distribution law is followed when one of the constituents is present in low concn. The results indicate that the mixed crystals are solid solutions. R. T.

Equilibrium of mixed crystals of ferrous and cupric sulphates and of cupric and cobaltous nitrates with their saturated solutions. W. SCHREŃZŁOWA (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 131—146).—Solubility measurements indicate that the pairs $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ - $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are isodimorphous; these pairs are of Roozeboom's 5th and 4th types, respectively. The partition coeff. is in both cases variable. The solubility of the mixed crystals is not the arithmetic mean of that of their constituent salts. R. T.

Crystallisation of ammonium chloride with cadmium chloride. A. SWARYCZEWSKI (Bull. Acad. Polonaise, 1932, A, 128—144).—The crystallisation of solutions of NH_4Cl alone and with the addition of 0.05, 0.2, and 1.0 wt.-% CdCl_2 has been followed by analysing the solution (kept at const. temp.) at regular time intervals. Periodic curves were obtained, indicating alternate dissolution and crystallisation processes. Photomicrographs of the mixed crystals reveal a zonal structure, which probably corresponds with the periodicity of crystallisation. The solubility of NH_4Cl is not markedly influenced by the presence of CdCl_2 , but the rates of crystallisation and of dissolution are thereby reduced. The distribution of Cd^{++} between the crystals and the solution depends

both on the composition of the solution and on the conditions of crystallisation; with increasing rate of crystallisation the crystals become richer in Cd^{++} . The existence of the compound $4\text{NH}_4\text{Cl} \cdot \text{CdCl}_2$ in the mixed crystals is not supported by determinations of n , and X-ray evidence fails to establish a new compound. E. S. H.

Periodic precipitation of silver salts. (MLLE.) S. VEIL (Compt. rend., 1932, 195, 606—608).—Liesegang rings formed by drops of aq. AgNO_3 on gelatin impregnated with K chromate, phosphate, or arsenate are described. Rings obtained by reversal of the electrolytes do not show the secondary microscopic stratification (cf. A., 1920, ii, 26). C. A. S.

Partition of saturated fatty acids between water and toluene. N. A. KOLOSOVSKI and I. MEGENINE (MESHENIN) (Bull. Soc. chim., 1932, [iv], 51, 1000—1004, and J. Gen. Chem. Russ., 1932, 2, 197—201).—Data are given for HCO_2H , AcOH , and EtCO_2H , at 25°. D. R. D.

Capillary chemistry. R. DUBRISAY and R. ARDITTI (Bull. Soc. chim., 1932, [iv], 51, 1199—1202).—Certain substances in solution may be separated by taking advantage of their unequal distribution between the liquid and a foam formed on the surface by bubbling CO_2 or N_2 through the solution. In this way mixtures of Na laurate with Na oleate, stearate, or arachidate, and of night-blue with basic fuchsin, have been separated into their constituents, and commercial oleic acid has been purified. D. R. D.

Distribution of radioactive substances between solid crystalline and liquid phases. VIII. Distribution of radium-*D* (lead) and a mixture of radium-*D* and radium between crystalline barium nitrate or chloride and its saturated aqueous solution at 0° and 25°. A. POLESITSKI (Z. physikal. Chem., 1932, 161, 325—335; cf. this vol., 14).—The distribution of $\text{Ra-D}(\text{NO}_3)_2$ between $\text{Ba}(\text{NO}_3)_2$ and its solution follows Nernst's distribution law, the distribution ratio changing in favour of the liquid phase as the temp. rises. The same is true of the distribution of Ra-DCl_2 between $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and solution if the Ra-D concn. lies within the miscibility limits of BaCl_2 and PbCl_2 . If $\text{Ra-D}(\text{NO}_3)_2$ and $\text{Ra}(\text{NO}_3)_2$ are simultaneously distributed between $\text{Ba}(\text{NO}_3)_2$ and its solution or RaCl_2 and Ra-DCl_2 between $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and its solution each salt distributes itself as if the other were absent. R. C.

Laws governing isomorphous separation of small amounts of substances with crystallising salts. H. KADING, R. MUMBRAUER, and N. RIEHL (Z. physikal. Chem., 1932, 161, 362—372).—By steady evaporation of a saturated solution or rapid crystallisation of a supersaturated solution the distribution of the substance present in small amount between the solution and crystals may be represented by a logarithmic formula (cf. A., 1925, ii, 381), but the crystals are not homogeneous. By the slow crystallisation of supersaturated solutions, which gives homogeneous crystals, and by prolonged stirring after rapid crystallisation of a supersaturated solution systems are obtained for which the Nernst distribution law is

valid; the concns. should preferably be expressed in wt.-% (cf. A., 1931, 1225). R. C.

Adsorption of carbon dioxide, ethylene, and hydrogen on pyrophoric iron and gold powder. A. MAGNUS and R. KLAR (Z. physikal. Chem., 1932, 161, 241—254).—At 0°, 20°, and 40° the isotherms for CO₂ and C₂H₄ on Au deviate slightly and that for C₂H₄ on Fe deviates considerably from the isotherms for the same gases on C (this vol., 223); this is ascribed to the presence on Au and Fe of active centres. Au and Fe continue to sorb H₂ slowly for a long time, and no reproducible adsorption isotherms have been obtained. R. C.

Adsorption of ionium by manganese [dioxide]. A. PYLKOFF (J. Chim. phys., 1932, 29, 430—435).—Io and its isotope U-X₁ are pptd. simultaneously with MnO₂, which is a better adsorbent than CeO₂. E. S. H.

Adsorption of sugars by charcoal. F. HAYASHI (J. Biochem. Japan, 1932, 16, 1—16).—Mineral acids do not increase the adsorption of glucose by blood C (cf. A., 1929, 133). With increasing mol. wt. of the sugar there is increased adsorption. Surface-active substances (MeOH, EtOH, PrOH, BuⁿOH, COMe₂, AcOH, PhOH) produce an inhibiting effect which is inversely proportional to the normal adsorption. Conditions for the separation of glucose and sucrose by adsorption are given. F. O. H.

Effect of chemical and physical factors on activity of charcoal. III, IV. E. V. ALEXEEVSKI and J. S. PIKAZIN (J. Gen. Chem. Russ., 1932, 2, 327—334, 335—340).—III. The adsorptive properties of birch C saturated with 0.1N and N alkalis (Na, K, Li, NH₄, Ba, Ca, and Sr hydroxides) and then heated at 450° under reduced pressure are practically the same as those of the original C for C₆H₆ vapour, for C₂H₂, and for aq. iso-C₅H₁₁OH and PhOH. The adsorptive capacity of the C is augmented for CCl₃·NO₂ vapour, as a result of catalytic decomp. of the adsorbate, with liberation of fresh active surfaces.

IV. Treatment of C with NH₄X (X=Cl, CO₃, C₂O₄, OAc, SO₄, MoO₄, tartrate, S₂O₈, NO₃, H₂PO₄, and ClO₄) leads to only insignificant changes in its adsorptive properties; in the case of salts of NH₄ with non-volatile acids the product binds more alkali from solutions than does the original C. C treated with NH₄CNS is largely inactivated. R. T.

Swelling of charcoal. II. Factors controlling the expansion caused by water, benzene, and pyridine vapours. D. H. BANGHAM, N. FAKHOURY, and A. F. MOHAMED (Proc. Roy. Soc., 1932, A, 138, 162—183; cf. A., 1931, 160).—Details are given of an apparatus for measuring the expansion of a pinewood charcoal rod in contact with the vapours of C₆H₆, C₅H₅N, and H₂O. It is assumed that the expansion is a measure of the pressure in the surface phase and from this it is shown that the Gibbs equation is approx. valid over a wide pressure range for C₆H₆ and C₅H₅N, but not for H₂O. At low pressures the adsorption of C₆H₆ and C₅H₅N is a complex phenomenon involving two distinct processes: the first causes a large expansion of the charcoal and consists in the formation of a two-dimensional film, the second is accompanied by

a contraction and is accelerated by heat. In the case of H₂O vapour, the "mol. expansion" curves between 0 and 23.5° are similar in form to the *p-v* graph of a gas undergoing condensation by isothermal compression, but the surface phase is the less condensible the higher is the temp. At -30° the surface vapour phase condenses to form a solid film. L. L. B.

Adsorption. Methods of obtaining saturated vapours. L. J. BURRAGE (Chem. News, 1932, 145, 206—211).—Methods and apparatus whereby a stream of air can be saturated with the vapour of H₂O or org. liquids at definite pressures are described. E. S. H.

Heats of adsorption of hydrogen and carbon monoxide on copper. R. A. BEEBE (Trans. Faraday Soc., 1932, 28, 761—765).—By using a single-junction thermocouple in direct contact with the reduced Cu granules it is found that adsorption of the initial portions of CO does not occur uniformly throughout the catalyst, but in successive layers. The adsorption of H₂ for the entire range and that of CO for the later portions is approx. uniform and the heats of adsorption are independent of the quantity of gas already adsorbed. Non-uniform adsorption may account for discrepancies between recorded heats of adsorption. J. G. A. G.

Remarkable reaction of nitrous oxide adsorbed on charcoal. L. MEYER (Naturwiss., 1932, 43, 791).—Below 0° the adsorption of N₂O by activated C is a reversible physical change, but at higher temp. decomp. occurs. N₂ is liberated and the O remains adsorbed, being held probably by the free valencies of the C atoms. The velocity of decomp. is almost independent of the temp. The reaction may be used to measure the active surface of the C, since it ceases when the surface has become covered with a monat. layer of O. D. R. D.

Increase in hygroscopicity of potassium chlorate in presence of traces of potassium chloride. O. J. DRUETZKA (Bull. Soc. Chim. Yougoslav., 1932, 3, 105—107).—KClO₃ containing 3% KCl is as hygroscopic as pure KCl. R. T.

Kinetics of adsorption by porous powders from solutions of substances of high mol. wt. V. B. ILJIN and N. N. SHELECHOVTZEVA (J. Gen. Chem. Russ., 1932, 2, 436—441).—The velocity of adsorption of Me-violet (A) from aq. solution by blood C is greater for 0.1% than for 0.04% solutions, and is greater when A is added to suspensions of C than when dry C is added to solutions of A. The adsorption coeff. diminishes with increasing concn. of A and with time. R. T.

Adsorption of paraffin vapours by water. Significance of Traube's rule. H. CASSEL and M. FORMSTECHE (Kolloid-Z., 1932, 61, 18—26).—The surface tension, π , of H₂O against the vapours of *n*-C₄H₁₀, -C₆H₁₄, and -C₇H₁₆ has been measured at 0° and 12°. The curves relating π to v.p., *p*, are convex towards the *p* axis and can be expressed by $\log p - A + \log \pi + \beta\pi/2.3RT - \log(1 + \alpha\pi)$, where *A*, α , and β are consts. This form indicates a mol. attractive force. The paraffins have a limited solubility in the adsorption layer. The heats of

adsorption, calc. from the temp. coeffs., are of the order of magnitude of heats of condensation. The data show that Traube's rule is valid for paraffins, supporting the view that the mols. lie with their flat surfaces against the H₂O. The behaviour of the corresponding fatty acids and alcohols is discussed.

E. S. H.

Adsorption and complex compounds of sucrose with surface-active substances; their destruction and displacement of equilibrium by micro-flotation. D. TALMUD and P. POCHIL (Kolloid-Z., 1932, 61, 101—111).—The existence of adsorption compounds of sucrose with colloiddally disperse, surface-active substances, and of complex compounds of sucrose with mol. disperse, surface-active substances, and semi-colloids has been established by comparing the velocity of dialysis of the mixtures with that of the components. The compounds are readily destroyed by acids or alkalis, and also by dialysis, when the surface-active substance is not dialysable. A micro-flotation method is also described for the separation of the sucrose, whatever the nature of the surface-active substance. This process has been applied to the purification of molasses and increases the yield of sucrose obtained therefrom by crystallisation.

E. S. H.

Thermodynamics of surface phenomena. N. BARBULESCU (J. Chim. phys., 1932, 29, 418—429).—Theoretical.

E. S. H.

Wetting experiments with hydrophilic and hydrophobic powders in a system of two immiscible liquids. I. E. BERL and B. SCHMITT (Kolloid-Z., 1932, 61, 80—90).—The conditions for the wetting and flotation of powders in a system of H₂O and C₆H₆ in presence of a flotation agent are examined theoretically. With Pb glance and Zn blende the amount of the agent (K Et xanthate or Na oleate) required to cause phase reversal is directly proportional to the surface of the powder. Pb glance readily oxidises to PbSO₄ at corners and edges of the finely-divided material, thus producing a more hydrophilic powder. The effect of addition agents, such as K₂CrO₄, Na₂CO₃, or KCN, has been investigated and is interpreted in terms of the change in the direction of hydrophobic or hydrophilic properties due to adsorption.

E. S. H.

Surface tension of the surface of contact of benzene solution of palmitic acid and aqueous solution of sodium hydroxide or barium hydroxide. L. GAY and M. DONNET (J. Chim. phys., 1932, 29, 385—402).—The interfacial tension has been examined with reference to the concn. of both solutions. All the curves show a sharp break, named the "Adam point," which represents the formation of an "epiphase" or two-dimensional phase of the corresponding soap at the surface of separation. In the case of Ba(OH)₂ solutions, the curves show two more breaks. The first of these, the "Marcelin point," corresponds with the initial formation of a three-dimensional soap phase from the epiphase, and the second point indicates the completion of this phase.

E. S. H.

Effect of neutral salts on properties of solutions of non-electrolytes. III. Surface tension

of solutions of salts in mixtures of organic liquids and water. P. P. KOZAKIEVITSCH and M. M. LOMIKOVSKAYA (J. Gen. Chem. Russ., 1932, 2, 238—248).—The surface tension (σ)-EtOH concn. curves of the systems aq. EtOH-MX (M=Li or Na, X=Cl, Br, or I) pass through a max.; this effect is ascribed to combination of salt with EtOH. The influence of the halides increases in the order Cl, Br, I. NaHSO₃ increases the σ of aq. COMe₂, owing to combination with COMe₂, and AgNO₃ has a similar action in aq. NH₂Ph.

R. T.

Present status of theories of solution with special reference to the problem of the solubility of non-electrolytes. H. L. WARD (Washington Univ. Stud. Sci. Tech., 1932, [ii], No. 6, 61—79).—A discussion.

CH. ABS.

Molecular size of dissolved silicic acids. E. GRUNER and J. ELÖD (Z. anorg. Chem., 1932, 208, 317—320; cf. A., 1931, 1021).—The f.p. depression of solutions of silicic acid prepared by Willstätter's method has been determined. When the results are corrected for the potentiometrically determined activity of the accompanying HCl, instead of for its amount as found by analysis, it is found that the solutions contain pure monosilicic acid.

F. L. U.

Density of solutions of sodium, potassium, and sodium bromide in liquid ammonia. W. C. JOHNSON and A. W. MEYER (J. Amer. Chem. Soc., 1932, 54, 3621—3628).—Vals. of d for solutions of various concns. are recorded.

E. R. S. (c)

Viscosity of strong electrolyte solutions according to electrostatic theory. H. FALKENHAGEN and E. L. VERNON (Phil. Mag., 1932, [vii], 14, 537—565).—Theoretical. The original central-symmetric electric density of the ionic atm. is deformed when a velocity gradient exists in a solution. The related shearing force has been calc. to give a term proportional to the sq. root of the concn. γ , which is additive to the viscosity, $\eta_r = \eta_0(1 + A\sqrt{\gamma})$. A has been calc. as a function of T , of the dielectric const., of the viscosity η_0 of the pure solvent, and of the nos., valencies, and mobilities of the ions, together with certain general consts.

H. J. E.

Distribution of suspended particles under gravity. C. M. McDOWELL and F. L. USHER (Proc. Roy. Soc., 1932, A, 138, 133—146).—Recent observations on the distribution of the particles of colloidal systems under the influence of gravity have led to results greatly at variance with earlier work. The work of Porter and Hedges (A., 1923, ii, 743) and of Barkas (A., 1925, ii, 289) is criticised on the ground of inadequate temp. control and failure to reach a state of equilibrium. A method of measuring the distribution of particles of colloidal Au over a range of 1 cm., the suspension being maintained at a temp. varying by $>0.001^\circ$ per hr., is described. Perrin's law is found to hold over a range of 0.9 cm. from the surface and up to a concn. of 10^{12} particles per c.c.

L. L. B.

Sedimentation of clays. E. W. KANNING, R. J. HARTMAN, and F. CHILDS (J. Physical Chem., 1932, 36, 2369—2382).—The size of the particles of various Indiana clays has been calc. from the velocity

of fall of particles, indicated by the sedimentation in definite time intervals. C. T. S. (c)

Orientation and deformation of disperse particles in streaming liquids. W. HALLER (Kolloid-Z., 1932, 61, 26—41).—A mathematical treatment of the orientation of anisodimensional particles and of the deformation of non-solid particles under the influence of streaming. Two opposing factors are considered in orientation, viz., the streaming of the liquid and the Brownian movement of the particles. Deformation is considered in relation to the form, elasticity, and internal friction of the particles. Published data indicate that the streaming double refraction of sols such as V_2O_5 is in accordance with the theory developed for the orientation of anisodimensional particles, whilst the behaviour of lyophilic colloids (myosin) is in agreement with the deformation theory. E. S. H.

Determination of size, form, and solvation of macro-molecules. G. V. SCHULZ (Z. physikal. Chem., 1932, 161, 441—462; cf. this vol., 993).—Theoretical. The relative viscosity of fresh rubber solutions agrees with the val. calc. by Eizenschitz' equation, using the osmotic sp. solvation vol. and assuming that the dissolved mols. are thread mols. stretched out to their full length. These latter are highly solvated. In hemicolloidal solutions for which Staudinger's relation is valid (this vol., 121) there is only slight solvation, owing to the high osmotic pressure. In the ageing of rubber or gelatin solutions the long mols. disintegrate; this is followed by changes in the solvation, and finally the fragments come to lie side by side in bundles, apparently held together by principal valencies. In general, the osmotically measured solvation vol. is equal to the true solvation vol. R. C.

Structure of colloidal particles. II. Kinetics of formation of atacamite sols. S. M. LIEPATOV, E. J. VINITZKAYA, and A. A. MOROZOV (J. Gen. Chem. Russ., 1932, 2, 260—270).—The duration of the induction period preceding the formation of sols of $[Cu(OH)_2Cu](OH)Cl$ from aq. $Cu(OAc)_2$ and $NaCl$ varies inversely with the relative concn. of $NaCl$. The process consists of three stages: chemical reaction between $Cu(OAc)_2$ and $NaCl$, formation of nuclei, and aggregation of nuclei, with consequent flocculation. The conductivity of the systems falls continuously; this is ascribed to the low velocity of the chemical reaction, and not to adsorption of ions on the coagulate. R. T.

Extension double refraction of colloids in solution. W. KUHN (Z. physikal. Chem., 1932, 161, 427—440; cf. this vol., 993).—A suspension of optically isotropic elongated particles which become doubly refracting as a result of extension or compression exhibits double refraction when a flow gradient is set up in it. The flow double refraction of rubber, gelatin, and polystyrene solutions is accounted for in this way, which shows that the dispersed particles are not linear, but are coiled up in such a way as to be effectively isotropic. The ratio of length to thickness of the particles deduced from the streaming double refraction agrees with the val. deduced from the

viscosity by means of an equation which takes into account a pronounced Brownian motion. R. C.

Calculation of the mol. wt. of a polar colloid from the data for the dispersion of its aqueous solution. B. M. BLOCH and J. ERRERA (Physikal. Z., 1932, 33, 767—769).—Theoretical. W. R. A.

Fowweather's gold sol. W. HERRMANN (Klin. Woeh., 1932, 11, 902—903; Chem. Zentr., 1932, ii, 187).—In the photo-reduction of $KAuCl_4$ by $K_2C_2O_4$ in the cold, freshly distilled H_2O and freshly prepared $K_2C_2O_4$ solution must be used. A. A. E.

So-called colloidal carbon from carbohydrates and sulphuric acid. B. L. VANZETTI (Rend. Sem. Fac. Sci. Univ. Cagliari, 1931, 1, 49—50; Chem. Zentr., 1932, i, 3393).—When sucrose, glucose, fructose, and cellulose in H_2O are slowly treated with H_2SO_4 , a brown or black coagulum separates after some days from the dark, apparently colloidal, solution, the supernatant liquid becoming first light yellow and then colourless. Later the supernatant liquid shows no Tyndall effect, but a blue fluorescence. Small quantities of H_2S are produced. After 2—3 months the solution is converted into a black gelatinous mass, which after washing with H_2O and drying forms a hard mass. The aq. extracts afford oxidation products. A. A. E.

Exchange reactions and structure of the micelles of stannic acid sols. R. WINTGEN (Kolloid-Z., 1932, 61, 1—18; cf. A., 1931, 909).—When SnO_2 sols, peptised by $NaOH$, are treated with electrolytes which form insol. or sparingly sol. stannates, an irreversible coagulum is formed. Turbidity is first produced when the amount of added electrolyte is equiv. to the amount of $NaOH$ in the micelles; complete flocculation occurs when the amount of electrolyte is equiv. to the total $NaOH$ in both the micelles and the dispersion medium. Electrolytes which form sol. stannates produce a reversible coagulum and in this case the points of incipient turbidity and of complete coagulation depend, not on the amount added, but on the concn. A quant. investigation of the ion exchanges involved in the formation of the irreversible coagula shows that the equivalence noted does not indicate that discharge of the particles begins when the exchange of Na^+ for other cations is complete. Exchange reactions occur even when the electrolyte causes no visible change in the colloid. Assuming the sol. particles to be approx. spherical, secondary aggregates, it is inferred that the average micelle has 14,850 charges and consists of 370 primary particles, each containing 2800 mols. of SnO_2 and 100 atoms of Na . E. S. H.

Does cellulose acetate dissolve molecularly in organic liquids? I. SAKURADA and S. LEE (Kolloid-Z., 1932, 61, 50—54).—Measurements of the viscosity of different preps. of cellulose acetate in a mixture of $CHCl_3$ and C_6H_6 are not in agreement with the view (A., 1930, 1414) that the substance is mol. dispersed. E. S. H.

Starches and the colloidal state. M. CATOIEE (Ann. Inst. Pasteur, 1932, 49, 500—537).—A detailed discussion of the colloidal state with special reference to micellar complexes and the chemical composition of

starch in particular. Natural starch is to be considered as consisting of biological micelles, which in turn consist of chemical micelles; the latter are polymericides of organo-mineral complexes. P. G. M.

Coagulation of casein and albumin sols by alcohols at different p_H . B. JIRGENSONS (Kolloid-Z., 1932, 61, 41—46; cf. A., 1931, 1368).—In the coagulation of casein sols by MeOH, EtOH, and BuⁿOH, with increasing concn. of alcohol the turbidity increases to a max. and then decreases to a sharp min., after which it increases again. The positions of the max. and min. vary with the particular alcohol, but in general the max. lies at 12—35 vol.-% and the min. at 40—60 vol.-%. The max. bears a linear relation to the dielectric const. of the alcohol and varies with p_H . The behaviour of the alcohols towards albumin sols is similar. With BuⁿOH the max. is displaced in the direction of higher concn. of alcohol when the p_H is lowered, but less change is produced in the other alcohols. The existence of labile, strongly polar, alcohol-H₂O complexes is inferred. E. S. H.

Application of physico-chemical analysis to the study of peptisation. I. Peptisation of pea proteins. A. DUMANSKI, E. G. ANTONOVITSCH, and A. B. SILAEV (J. Gen. Chem. Russ., 1932, 2, 297—304).—Less protein is extracted from pea meal when the vol. of H₂O is increased; this is attributed to dilution of peptising electrolytes. Max. peptisation of pea globulin is obtained with 10% NaCl, which yields solutions containing 2.42% of globulin; the max. globulin concn. does not exceed 0.3% with KCl, 0.93% with BaCl₂, 0.5% with NaOH, and 0.2% with HCl. R. T.

Silicic acid gels. II. Time of setting as a function of temperature. C. B. HURD and P. S. MILLER (J. Physical Chem., 1932, 36, 2194—2204; cf. this vol., 464).—Solutions of water-glass with the ratio SiO₂:Na₂O varying from 1.58 to 3.86 were treated with AcOH at 273—328.8° abs. The graph of log. setting time against 1/temp. (abs.) is a straight line for all the water-glasses except the one containing the most alkali. From the graphs the average "heat of activation" for the reaction leading to the setting of silicic acid gel is 16,640 g.-cal. Gel formation probably occurs by elimination of H₂O from two OH groups of neighbouring silicic acid mols. J. W. P. (c)

Variations in extinction coefficients during course of jelly formation. S. PRAKASH (J. Physical Chem., 1932, 36, 2483—2496; cf. A., 1930, 1369).—Variations in the extinction coeff., k , during jelly formation were studied with Fe^{III}, Cr^{III}, Al, and Zr hydroxides, Th, Sn^{IV}, and Ce^{IV} arsenates, Sn₃(PO₄)₄, Th, Fe^{III}, and Zr molybdates, Zr borate, and mercurithiosalicylic acid. The jellies may be perfectly transparent, with no change in K , or opalescent at the point of setting, but finally become opaque before or at the point of setting. C. T. S. (c)

Gelation of sucrose with metal hydroxides. W. COITOF (Kolloid-Z., 1932, 61, 54—68).—Gels are formed by the interaction of KOH with CaCl₂, SrCl₂, or BaCl₂ in presence of sucrose. Gelation does not occur until the mol. ratio Ca(OH)₂:sucrose exceeds

3:2, but with Sr(OH)₂ the mass gels when the ratio is 1:1. With Ba(OH)₂ the mol. ratio must exceed 1:1. In general, excess of KOH aids gelation and excess of the chloride has the reverse effect. Gelation is more difficult with increasing dilution of the components. The presence of increasing quantities of sucrose causes pptd. alkali hydroxides to assume a more transparent, soft, and sol. form, until gels are produced at the ratios given. The microscopical and ultramicroscopical appearance of these gels, prepared in different ways, is described. E. S. H.

Kinetics of the sol-gel transformation. I. Relation between concentration of coagulating electrolyte and setting period of jellies. S. PRAKASH and H. L. DUBE (Z. anorg. Chem., 1932, 208, 163—168).—Times of setting of sols of FeAsO₄, ZrO₃, CeO₂, and Cr arsenate (negative or positive) are related to the concn. of electrolyte by the expression $t=ac$ in which a and b are const. in any given experiment. F. L. U.

Isoelectric point of serum-globulin as determined by cataphoresis. F. O. HOWITT and E. B. R. PRIDEAUX.—See this vol., 1271.

Isoelectric point of collagen. M. SHIMIDZU (Collegium, 1932, 794—798).—The isoelectric point of hide collagen as determined by means of Fe and Au sols is p_H 4.69. D. W.

Isoelectric point of silk. M. HARRIS (Bur. Stand. J. Res., 1932, 9, 557—560).—Colloidal solutions prepared by dissolving silk fibroin in 50% aq. LiBr and dialysing were mixed with buffers and a small amount of quartz powder was added. Electrophoretic measurements with these systems indicate an isoelectric point at p_H 2.5. E. S. H.

Colloid chemistry of gluten. H. L. B. DE JONG (Trans. Faraday Soc., 1932, 28, 798—812).—The isoelectric point of gliadin is p_H 6.5—6.6 and that of glutenin is 5.4—5.3. The deviations from the additive law on mixing gliadin and glutenin indicate complex formation, in which the gliadin part is always positively charged and the glutenin part negatively charged. The components appear to retain their charges in the complex, whilst their degree of solvation is changed. Complex formation is limited to the region between the isoelectric points and is a max. at a definite p_H , which depends on the ratio of the two proteins and on the electrolytes present. The complex is comparable with natural gluten. E. S. H.

Effect of ammonia and amines on viscosity of collodions. P. PASCAL and J. GREVY (Compt. rend., 1932, 195, 726—729).—Addition of increasing amounts (10—200 mg. per 100 g. of solution) of NH₃ to a 4% (by wt.) solution of unstabilised industrial cellulose nitrate in 65:35 Et₂O-EtOH (99.3%) gives rise at first to a large increase in the viscosity, followed by a decrease to vals. much below the viscosity of the original solution. Equiv. amounts of NH₂Me, NHMe₂, and NH₂Et have similar but more marked effect, whilst that of NMe₃ is still greater, causing pptn. of part of the cellulose nitrate. Aromatic bases have little effect. C. A. S.

Solvation of rubber sols. J. LENS (Rec. trav. chim., 1932, 51, 971—980).—V.-p. lowering has been measured in sols of pure and crude rubber in CCl_4 , CHCl_3 , C_6H_6 , MeOH , EtOH , and COMe_2 . The results are discussed from the point of view of solvation. Solvation of particles in one of the first three solvents is greatly reduced by addition of one of the last three. In the case of octyl alcohol a sudden decrease of solvation occurs at about 42° when the sol is cooled. The system rubber-solvent is considered to have more than two components. F. L. U.

Complex coacervation. XII. Coacervation of hydrophilic sols with dyes. H. G. B. DE JONG and J. LENS. **XIII. Auto-complex coacervation of tryptaflavine.** H. G. B. DE JONG and F. A. MENALDA (Biochem. Z., 1932, 254, 15—34, 35—46; cf. this vol., 807).—XII. Coacervation occurs either when a basic dye acts on a negative hydrophilic sol or when an acid dye acts on a positive hydrophilic sol. The combination gum arabic-tryptaflavine exhibits complex coacervation probably of the mixed type III—IV (complex and auto-complex coacervation). Gelatin-Na picrate exhibits auto-complex coacervation, the picrate ion being adsorbed between the positive ionogenic positions on the surface of the particles. The behaviour of the combination positive gelatin-tropæolin-O is more complicated.

XIII. In its behaviour towards solutions of neutral salts containing multivalent anions [$\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_4\text{P}_2\text{O}_7$, $\text{CH}(\text{SO}_3\text{K})_3$, Na citrate] and in the formation of films at the interface when CHCl_3 is added, tryptaflavine acts to some extent as a hydrophilic colloid. The droplets which separate from solution on addition of $\text{Na}_4\text{P}_2\text{O}_7$ indicate auto-complex coacervation, but when $\text{CH}(\text{SO}_3\text{K})_3$ is added the material which separates is solid and it is not certain that such coacervates are produced. The auto-complex coacervation in tryptaflavine solutions does not occur unless a certain concn. of the dye is attained and is almost or completely prevented by suitable non-electrolytes (carbamide, urethane, chloral hydrate, NH_2Ac , resorcinol, pyrogallol, glucose) or by rise in temp. W. McC.

Applications of cryoscopic measurements to biological problems. F. F. NORD, O. M. VON RANKE-ABONYI, and G. WEISS (Z. Elektrochem., 1932, 38, 632).—The freezing of a complex lyophilic colloidal solution may cause both aggregation and breaking down of the particles, with resulting changes, possibly in different directions, of the viscosity and surface tension of the solution. The influence of freezing on solutions of colloids capable of acting as emulsifying agents has been studied; the viscosity of gelatin and albumin emulsions is reduced, and that of Na oleate, gum arabic, and saponin emulsions is increased, after freezing. The stability of emulsions prepared with emulsifiers which have been frozen is somewhat higher than the normal. H. F. G.

Insulin. I. Cataphoresis of insulin alone and in presence of glucose: the question of an insulin-glucose reaction *in vitro*. F. O. HOWITT and E. B. R. PRIDEAUX.—See this vol., 1292.

Organic phosphorus compounds in plants and animals. III. Exosmosis of phosphorus from plant cells. IV. Effect of animal and vegetable lecithin on diffusion of acids and alkalis in gels. H. MAGISTRIS (Biochem. Z., 1932, 253, 64—80, 81—96).—III. See this vol., 1181.

IV. The diffusion of acids and of alkalis in gelatin and agar gels is accelerated by low concns. of cholesterol, but retarded by low concns. of various kinds of lecithin. With suitable proportions of the two substances the diffusion is unaffected. High concns. of cholesterol and of the lecithins retard the diffusion, the influence of the cholesterol, however, being less pronounced than that of the lecithins. The effects produced by the latter vary with their origin and methods of prep. Org. acids diffuse more rapidly than inorg. and alkali hydroxides more rapidly than alkaline-earth hydroxides. HBO_3 and NH_3 diffuse very readily; $\text{Sr}(\text{OH})_2$ more rapidly than $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$. The rate of diffusion of acids and alkalis is also affected by their concn. Within certain limits increase in concn. of mineral acid increases their rate of diffusion; at higher concns. the rate decreases. With org. acids the effect of concn. is less pronounced. In some cases the addition of lecithin ($>2\%$) produces visible alteration in the degree of dispersion of the gel.

W. McC.

Chemical equilibria of reactions between hydrocarbons. I. V. P. SHARKOVA and A. V. FROST. II. A. A. VEDENSKI and A. V. FROST (J. Gen. Chem. Russ., 1932, 2, 534—541, 542—552).—I. The equilibrium const. for $\text{C}_6\text{H}_6 + 3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12}$ is given by $\log K = 9590/T - 9.9194 \log T + 0.002285T + 8.566 \pm 0.084$.

II. The val. of $\log K$ for $2\text{C}_6\text{H}_6 \rightleftharpoons \text{Ph}_2 + \text{H}_2$ (I) is -0.83 ± 0.14 at 845° and -0.69 ± 0.11 at 920° ; for $\text{Ph}_2 + \text{C}_6\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_5\text{Ph} + \text{H}_2$ $\log K$ is -0.58 at 845° . Nernst's approx. formula for K is not applicable to reaction (I). R. T.

Methane equilibria from absolute entropies, and use of Ehrenfest symmetry number. A. R. GORDON and C. BARNES (J. Physical Chem., 1932, 36, 2601—2609).—The abs. entropy, S , and the heat capacity at const. pressure have been calc. for gaseous CH_4 at 300 — 1200° abs. The calc. vals. of $R \log_e K$ for $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$ at 600 — 700° abs. agree with experiment, and ΔS° and ΔF° have been derived for 298.1° abs. The vals. of $R \log_e K$ have been calc. for $\text{C}(\text{graphite}) + \text{CO}_2 = 2\text{CO}$ at 1123 — 1223° abs. The calc. vals. of $R \log_e K$ for $\text{C}(\text{graphite}) + 2\text{H}_2 = \text{CH}_4$ at 700 — 1200° abs. agree with experiment only at the lower temp. For CH_4 $\Delta F^\circ_{298.1}$ is $-12,490$. Geometrical symmetry is a sufficient, but not a necessary, condition for the existence of a symmetry no. If the use of a symmetry no. leads to a val. for the entropy in approx. agreement with the observed val. this affords no evidence for the shape of the mol. F. D. R. (c)

Free energy of enolisation in gaseous phase of substituted acetoacetic esters. J. B. CONANT and A. F. THOMPSON, jun. (J. Amer. Chem. Soc., 1932, 54, 4039—4047).—Measurements of the equilibrium const. of enolisation in the gaseous state show that there is a connexion between the structure of the

compound and the free energy of enolisation in the gaseous state. Comparison of the results with ΔF referred to the liquid equilibrium mixture or a dil. solution shows that the parallelism between structure and free energy is often obscured by solvent effects, which may be as large as 1 kg.-cal. A dil. hexane solution seems to approximate to the gaseous state in most instances, as far as free energy vals. are concerned, but the regularity is less marked; for ketonic esters and diketones a dil. hexane solution will probably yield results significant to ± 0.3 kg.-cal.

C. J. W. (c)

Equilibria in boric acid-diol-water system. II. N. VERMAAS (Rec. trav. chim., 1932, 51, 955—963; cf. this vol., 228).—In continuation of previous work, potentiometric titrations of OH-acids (HZ) with KBO₃ have been carried out. Vals. of K_1 ($= [H^+][BZ^-]/[HB][HZ]$), K_2 ($= [H^+][BZ_2^-]/[HB][HZ]^2$), and K_3 ($= [H^+][Z^-]/[HZ]$) have been calc. for α -hydroxyisobutyric, cyclopentanol- and cyclohexanol-2-carboxylic, methylethyl- and ethylpropyl-glycolic acids.

F. L. U.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. XV. Conversion of ions of monotungstic acid into those of hexatungstic acid with increase in hydrogen-ion concentration of solutions of alkali tungstate. K. F. JAHR and H. WITZMANN (Z. anorg. Chem., 1932, 208, 145—156; cf. this vol., 809).—Measurements of diffusion coeffs. of Na tungstate in solutions of different acidity show that transformation of mono- into hexa-tungstate ions occurs within the range p_H 6—8. No definite intermediate stage was recognised.

F. L. U.

Szyszkowski's neutral salt effect coefficient in the light of modern theories of electrolytes. A. SKAPSKI (Bull. Acad. Polonaise, 1932, A, 46—49).—Theoretical.

E. S. H.

Application of the differential tensimeter to the measurement of dissociation tensions. Dissociation of ammonium salts. M. CENTNERSZWER and S. KOWALSKI (Bull. Acad. Polonaise, 1932, A, 50—64).—An apparatus for measuring the v.p. or dissociation pressure of solid substances in a given atm. is described. The v.p. and dissociation of NH₄Cl and NH₄Br in air have been measured over a range of temp.; the influence of excess of the dissociation products is in accordance with mass action. The heats of dissociation calc. with the aid of Nernst's equation are in approx. agreement with experimental vals.

E. S. H.

Redetermination of thermal dissociation equilibria of inorganic compounds. III. Determination of dissociation equilibrium of calcium hydroxide by means of high-temperature vacuum balance. S. TAMARU and K. SIOMI (Z. physikal. Chem., 1932, 161, 421—426; cf. this vol., 468).—The dissociation pressure has been determined at 405—500°.

R. C.

Water vapour equilibrium over tungsten and its oxides. L. WOHLER, Z. SHIBATA, and R. KUNST (Z. Elektrochem., 1932, 38, 808—812).—The coeff. $K_1 = [H_2O]/[H_2]$ for the system W₂O₅—WO₃ varies with

the proportions of the two oxides present, indicating that they form a solid solution. This explains the fact that W₂O₅ is never obtained pure by the reduction of WO₃, 2—3% of WO₃ always remaining. The corresponding vals. K_2 and K_3 for the systems W₂O₅—WO₂ and WO₂—W, respectively, were found to be const. as previously observed (A., 1923, ii, 471), and thus WO₂ is easily obtained pure by reduction. Neither W₂O₁₁ (cf. A., 1931, 447, 583), nor any oxide other than W₂O₅, was found between WO₂ and WO₃.

M. S. B.

Dissociation of synthetic crystalline manganese oxides. F. KRÜLL (Z. anorg. Chem., 1932, 208, 134—144).—The dissociation of cryst. MnO₂ in O₂ at 1 atm. begins at 500—550°. Mn₂O₃ decomposes at 900—950° into Mn₃O₄, which is stable at 1000°. Mn₃O₄ thus prepared absorbs O₂ at 900° to form Mn₂O₃, which in turn is slowly converted into MnO₂ at 500°. In all cases the partial pressure of O₂ was maintained const. at 1 atm. Rates of decomp. and of recombination were measured.

F. L. U.

Dissociation of manganese spar and manganese carbonate. J. KRUSTINSONS (Z. Elektrochem., 1932, 38, 780—783).—Dissociation of Mn spar at 1 atm. is observable at 407.5°, but can be completed only at approx. 700° when the CO₂ pressure is 485 mm. By heating the product to a still higher temp. practically no further dissociation is obtained. The results can be explained by the formation of a solid solution of MnO and MnCO₃. The heat of dissociation calc. from Nernst's formula is 25.39 g.-cal. Some CO₂ is given up by artificial MnCO₃ between 30° and 130°, but is re-absorbed on cooling. Actual dissociation begins only at 270°/1 atm. and is not complete until a temp. of 480° is reached, when the CO₂ pressure is 680 mm. The form of the dissociation curve is best explained by the formation of intermediate products. No CO due to reduction of CO₂ by MnO has been observed.

M. S. B.

System calcium oxide-phosphorus pentoxide. G. TRÖMEL [with H. SCHNEIDERHÖHN] (Mitt. Kaiser Wilh.-Inst. Eisenforsch., 1932, 14, 25—36; Chem. Zentr., 1932, i, 3025—3026).—In addition to the meta-, pyro-, and ortho-phosphates, 4CaO.P₂O₅ is formed; oxyapatite, 10CaO.3P₂O₅, was not observed.

A. A. E.

Equilibrium diagrams of binary systems with acetic acid and amines as components. N. A. PUSHIN and I. I. RIKOVSKI (Z. physikal. Chem., 1932, 161, 336—340).—F.-p. diagrams show that AcOH combines only in equimol. proportions with C₆H₅N, piperidine, quinoline, and NHPh.NH₂, but with NH₂Ph forms only a diacetate.

R. C.

Binary systems. I. System *as-o*-xylidine-carbonic acid. F. E. C. SCHEFFER and J. SMITTENBERG (Rec. trav. chim., 1932, 51, 1008—1011; cf. A., 1931, 310).—Phase equilibria for the system *o*-4-xylidine—CO₂ are shown in a *p-t* diagram. Metastable unmixing occurs over a considerable range. The system belongs to the type H₂S—NH₃.

F. L. U.

Freezing of solutions as a method of investigation in pure chemistry. IX. Mixtures con-

taining phenylglycollic and phenylaminoacetic acids. J. TIMMERMANS and K. MOTIUK (Bull. Soc. chim. Belg., 1932, 41, 399—411).—The methods previously described (A., 1931, 676) show that no compounds are formed in the systems: *d*- or *l*-phenylglycollic acid-*l*-malic acid; *d*- or *l*-phenylglycollic acid-*l*-chlorosuccinic acid; *d*- or *l*-phenylglycollic acid-*l*-asparagine; *d*-phenylglycollic acid-*d*- or *l*-tartaric acid; *l*-phenylglycollic acid-*l*-phenylglycine. *d*-Phenylglycollic acid, however, forms an equimol. compound with *l*-phenylglycine.

D. R. D.

Ternary system composed of the nitrates of potassium, sodium, and lead. K. LAYBOURN and W. M. MADGIN (J.C.S., 1932, 2582—2589).— KNO_3 and NaNO_3 form a continuous series of solid solutions. $\text{KNO}_3\text{-Pb(NO}_3)_2$ and $\text{NaNO}_3\text{-Pb(NO}_3)_2$ form simple eutectic systems, whilst the complete system $\text{KNO}_3\text{-NaNO}_3\text{-Pb(NO}_3)_2$ has one ternary eutectic, no compounds being formed.

D. R. D.

Polytherms of ternary systems containing water, an alkali sulphate, and a sulphate of the vitriol type. VI. A. BENRATH. VII. A. BENRATH and W. THEIMANN (Z. anorg. Chem., 1932, 208, 169—176, 177—193; cf. this vol., 229).—VI. Solid phases have been characterised and their solubilities determined between 0° and 100° for systems containing sulphates of K+Co , $\text{NH}_4\text{+Co}$, Rb+Co , K+Ni , $\text{NH}_4\text{+Ni}$, Ti+Ni , and Rb+Ni .

VII. Similar data have been obtained for sulphates of Ti+Co , $\text{NH}_4\text{+Mg}$, $\text{NH}_4\text{+Cd}$, and Na+Cd . Formation of the double salts $\text{CdSO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ and $3\text{CdSO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot 5\text{H}_2\text{O}$ was observed.

F. L. U.

Equilibria $\text{Pb+SnCl}_2 \rightleftharpoons \text{PbCl}_2\text{+Sn}$ and $\text{Cd+PbCl}_2 \rightleftharpoons \text{CdCl}_2\text{+Pb}$ in melts. Applicability of the ideal mass-action law. F. KORBER and W. OELSEN (Z. Elektrochem., 1932, 38, 557—563).—Contrary to the report of Lorenz, the equilibria at $500\text{--}600^\circ$ conform to the ideal law of mass action, but if the mixtures are not cooled with sufficient rapidity, e.g., by pouring on to a Cu block, large deviations are observed. The equilibrium const. for the system Pb+SnCl_2 is 3.45 ± 0.45 at 600° and 5.6 ± 0.7 at 500° ; the calc. heat of reaction is $5.6\text{--}7$ kg.-cal. per mol. as compared with $3.7\text{--}4.9$ calc. from the heats of formation of the chlorides. No evidence could be obtained of a transition in the Sn-rich mixtures, as reported by Lorenz. For the system Cd+PbCl_2 the equilibrium const. at 600° is 37.5 ± 5.5 ; the temp. coeff. is very large, the calc. heat of reaction being 7.85 kg.-cal. per mol. The heat of reaction between Cd and SnCl_2 is 11.7 kg.-cal. per mol. The apparent applicability of the mass-action law to heterogeneous systems of this type is discussed.

H. F. G.

Thermal decomposition of zinc and cadmium carbonates in an atmosphere of water vapour. A. LEHRMAN and N. SPEAR (J. Physical Chem., 1932, 36, 2664—2669).—No equilibrium is reached with CdCO_3 , but with ZnCO_3 and H_2O vapour at 1 atm., equilibrium is rapidly attained.

F. D. R. (c)

Thermodynamics of lead bromide. J. Y. CANN and R. A. SUMNER (J. Physical Chem., 1932, 36, 2615—2620).—For the reaction $\text{Pb(s)} + 2\text{AgBr(s)} = \text{PbBr}_2\text{(s)} + 2\text{Ag(s)}$ e.m.f. measurements give $\Delta F_{298.1}^\circ = -16258$; $\Delta S_{298.1}^\circ = -12.599$; $\Delta H_{298.1}^\circ = -20014$. From these vals. other data are calc. F. D. R. (c)

Nitrogen compounds of germanium. II. Equilibrium in system $\text{Ge-NH}_3\text{-Ge}_3\text{N}_4\text{-H}_2$. Dissociation of germanic nitride. G. H. MOREY and W. C. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 3603—3610).—Equilibrium data for the reaction $3\text{Ge} + 4\text{NH}_3 = \text{Ge}_3\text{N}_4 + 6\text{H}_2$ are recorded. ΔH at $883\text{--}937^\circ$ abs. is $155,600$ g.-cal. According to NH_3 equilibrium data, the equilibrium const. of the reaction $\text{Ge}_3\text{N}_4 = 3\text{Ge} + 2\text{N}_2$ varies from 19.63 at 883° to 0.650 at 937° . ΔH for $883\text{--}937^\circ$ is $-102,000$ g.-cal.

J. V. V. (c)

Polyiodides in benzonitrile. J. H. MARTIN (J.C.S., 1932, 2640—2643).—The compounds $\text{KI}_3\cdot 2\text{PhCN}$, m.p. 53° , $\text{NaI}_3\cdot 2\text{PhCN}$, m.p. 67° , $\text{LiI}_3\cdot 4\text{PhCN}$, m.p. 92.5° , $\text{HI}_3\cdot 4\text{PhCN}$, m.p. 97° , and $\text{LiI}_3\cdot 4\text{C}_6\text{H}_4\text{Me-CN}$ have been obtained by crystallisation from solutions of the corresponding monoiodides and I in the appropriate nitrile. The dissociation pressure increases with the at. wt. of the metal, and RbI_3 and CsI_3 do not combine with PhCN. No similar compounds could be prepared using MeCN or $\text{CH}_2\text{Ph-CN}$. PhCN extracts KI and I_2 in equimol. proportions from a solution of I in aq. KI.

D. R. D.

Equilibria in reduction [oxidation, and carburisation] processes in iron [XI]. R. SCHENCK (Z. anorg. Chem., 1932, 208, 255—256; cf. this vol., 811).—A correction.

F. L. U.

Study of aqueous solutions at high temperatures. I, II. E. I. AGHUMOV and B. B. VASILIEV (J. Gen. Chem. Russ., 1932, 2, 271—281, 282—289).—I. Methods and apparatus for the determination of solubility of salts at high temp. are described.

II. Equilibrium diagrams for $\text{KCl-NaCl-MgCl}_2\text{-H}_2\text{O}$ at 125° , 150° , 200° , and 265° are given. R. T.

Solvent properties of soap solutions. III. System sodium oleate-sodium chloride-water-ethyl acetate. E. L. SMITH (J. Physical Chem., 1932, 36, 2455—2473; cf. this vol., 802).—At 25° the system Na oleate- $\text{NaCl-H}_2\text{O}$ has one more degree of freedom than is allowed by the phase rule, since the solubility of Na oleate curd fibres is a function of their diameter. Na oleate, EtOAc , and H_2O yield six phases: isotropic Na oleate solution, middle soap, neat soap, curd soap, wet EtOAc , and vapour. Na oleate, NaCl , and EtOAc are almost immiscible. The quaternary system yields six phases: neat soap, curd soap, NaCl , brine, EtOAc , and vapour. The proportion of soap in the colloidal state can be calc. approx. from the data.

C. T. S. (c)

Entropies of some simple polyatomic gases calculated from spectral data. R. M. BADGER and S. WOO (J. Amer. Chem. Soc., 1932, 54, 3523).—The entropies of CO_2 , N_2O , HCN , and C_2H_2 at 298.2° abs. have been calc. The "virtual" entropies (those to be compared with calorimetric data) are 51.07 ,

52.58, 48.23, and 48.00 E.U., respectively. The corresponding abs. entropies are 51.07, 56.94, 51.79, and 50.75. J. B. A. (c)

Internal effect in thermodynamic transformations. V. NJEGOVAN (Arh. Hemiju, 1932, 6, 154—161).—Mathematical. R. T.

Heat of formation of hydrogen chloride. H. VON WARTENBERG and K. HANISCH (Z. physikal. Chem., 1932, 161, 463—469).—The val. 21.89 ± 0.01 kg.-cal. at 24° has been obtained by direct synthesis. R. C.

Calorimetric method for determining the intrinsic energy of a gas as a function of the pressure. E. W. WASHBURN (Bur. Stand. J. Res., 1932, 9, 521—528).—A method for determining the change in internal energy of a gas ($\pm < 1$ g.-cal. for a litre bomb) under pressure is suggested. A known mass of gas is compressed in a bomb at a known pressure and allowed to expand slowly to atm. pressure; the bomb is immersed in a calorimeter and the cooling effect is compensated by electrical heating. E. S. H.

Free energy, entropy, and heat of formation of iron carbide (Fe_3C). C. P. YAP and C. L. LEE (Trans. Faraday Soc., 1932, 28, 788—797).—The following data are obtained for the reaction $3\alpha\text{-Fe} + \text{C} = \text{Fe}_3\text{C}$ at 25° : free energy 9300, heat of formation 12,300, entropy of formation 9.9, abs. entropy 31.8 g.-cal. per mol. Fe_3C is stable above 750° . E. S. H.

Heats of combustion of the chloroacetic acids and their esters. E. SCHJANBERG (Svensk Kem. Tidskr., 1932, 44, 227—231).—Data are recorded for acetic, mono-, di-, and tri-chloroacetic acids, their Pr^a , Pr^b , Bu^a , Bu^b , and isoamyl esters, and for the Me, Et, and allyl chloroacetates. The difference in the series mono-, di-, and tri-chloroacetic esters, and in the series Et, Pr, etc., is not const. Calculation of the energy of decomp. of the C-Cl linking gives vals. which also show no constancy; in some series, e.g., the Bu and allyl esters, the vals. increase with the Cl content, but diminish in others, e.g., the Et and Pr^b esters. H. F. H.

Concentration at which heats of dilution are measured in the calorimetric method. V. K. LA MER and I. A. COWPERTWAITE (J. Amer. Chem. Soc., 1932, 54, 4114—4115).—The vals. recorded by Lange and Robinson (Chemical Reviews, 1931, 9, 89) for heats of dilution, whilst probably correct for the final concns., do not constitute measured vals., but depend on the validity of the Debye-Hückel theory. C. J. W. (c)

Electric conductivity of solutions of alkali metals in liquid ammonia. L. FARKAS (Z. physikal. Chem., 1932, 161, 355—361).—The variation with concn. of the electron conductivity may be explained by supposing that the electrons undergo "non-mechanical" transitions from one alkali metal atom to another in the direction of the field, and that the alkali metal atoms in the solution are arrayed in a regular manner as in a crystal lattice, the interat. distance varying with the concn. This theory leads to results in agreement with published data for solutions of Na in NH_3 . R. C.

Conductivity of salts and alkalis in sucrose solutions. E. LANDT [with C. BODEA and SAALMAN] (Z. Elektrochem., 1932, 38, 630—631).—The vals. of the product of λ_∞ and the viscosity for solutions of NaCl, KCl, and BaCl_2 in saturated sucrose solution are 618.7, 727.7, and 508.1, respectively, at 20° . Decrease of hydration of the ions does not alone suffice to explain the abnormal conductivity. Walden's rule is increasingly valid for solutions of NET_4 picrate as the temp. is raised from 35° to 50° . It is probable that in sucrose solutions there exist large aggregates of solvent and solute mols. which are responsible for the high viscosity and act as obstacles to the movements of ions. The mobility of an ion is depressed the more, the larger is the ion. Kohlrausch's law is valid for all the solutions studied, but the Debye-Hückel-Onsager theory is only qualitatively applicable to sucrose solutions. Sucrose behaves as a dibasic acid in solutions containing $\text{Ca}(\text{OH})_2$ etc.; it is not correct to assume that in such solutions the conductivities of the "sucrate" and of the alkali are independent of the sucrose concn. H. F. G.

Conductivity data of aqueous mixtures of hydrogen peroxide and organic acids. II. W. H. HATCHER and E. C. POWELL (Canad. J. Res., 1932, 7, 270—282).—On adding H_2O_2 to aq. org. acids (HCO_2H , AcOH , EtCO_2H , succinic and monopersuccinic acids), there is a fall in conductivity due to formation of non-ionised complexes of the type $\text{RCO}_2\text{H} \cdot \text{H}_2\text{O}_2$. These eliminate H_2O slowly, forming the ordinary peracids, RCOO_2H , the H of which is not ionisable. It is shown conductometrically and by titration with alkali and phenolphthalein that monopersuccinic acid is monobasic. D. R. D.

Electrochemistry of ethereal solutions. VI. Conductivity of ethereal solutions in connexion with complex formation. M. USSANOVITSCH. VII. System antimony trichloride-ethyl ether. M. USSANOVITSCH and F. TERPUGOV (J. Gen. Chem. Russ., 1932, 2, 443—446, 447—454).—VI. Halides of As or Sb which give non-conducting solutions in org. solvents form compounds with the latter of a different type from the oxonium compounds present in conducting solutions.

VII. Conductivity curves for the system $\text{SbCl}_3\text{-Et}_2\text{O}$ are given for 0— 100° . The max. sp. conductivity is 2.6 for 95% SbCl_3 . The decomp. potential is 0.97 volt. The electrolyte is $\text{Et}_2\text{O} \cdot 2\text{SbCl}_3$. R. T.

Explanation of certain secondary phenomena in the determination of hydration of ions. J. BABOROVSKÝ (Chem. Listy, 1932, 26, 474—476).—The discrepancies between the vals. for electrolytic transport of H_2O and the transport nos. of ions found for aq. H, alkali, and alkaline-earth halides are due not to electro-osmotic factors, but to reduction of the mobility of the anion by the parchment membrane used, and to dehydration of the latter by the electrolytes at higher concn. R. T.

Theory of surface conductivity. J. J. BIKERMAN (Z. Elektrochem., 1932, 38, 763—764).—McBain and Dubois' objection to Smoluchowski's expression for surface conductivity (A., 1931, 1121), on the ground that the double layer would be too thin to exist, is

based on an error in the val. taken for the dielectric const. The surface conductivity measurements of White, Urban, and van Atta (this vol., 699) give a much larger val. for the double layer. M. S. B.

Similar electrical conductivity of moving and stationary surfaces: the Laing paradox. R. DUBOIS (Z. Elektrochem., 1932, 38, 764—769).—Surface conductivity is to be ascribed to (1) the conductivity of the solid walls and (2) the conductivity due to the mobile ions of the electrical double layer. (1) depends on the excess free charge of the solid walls and (2) is the numerical sum of the ionic charges in the double layer, independent of sign. At the isoelectric point the part due to (1) is zero, but that due to (2) has a finite val., which explains the surface conductivity observed by Briggs at the isoelectric point (A., 1928, 713). Calculations from available data indicate that the conductivity of the solid walls forms 13—46% of the total surface conductivity. The effective mobility of the ions attached to the walls is as great as, or even considerably greater than, that of ordinary dissolved ions. Smoluchowski's equation for surface conductivity is incorrect, since it leads to a val. for the thickness of the double layer of < at. dimensions (cf. preceding abstract). M. S. B.

Thermo-electric behaviour of tungsten, molybdenum, and tantalum. A. SCHULZE (Z. Metallk., 1932, 24, 206).—The e.m.f. of the Pt-Mo couple rises from 1.22 mv. at 100° to 10.6 at 500°, 29.40 at 1000°, and 42.73 mv. at 1300°. The corresponding figures for the Pt-W couple are 0.77, 8.89, 28.28, and 43.04 mv., and for the Pt-Ta couple 0.42, 4.41, 15.42, and 25.40 mv. Below 0° the e.m.f. is of opposite sign and passes through a min. at about -150°. The e.m.f. of the W-Mo couple rises to a max. of 2 mv. at 600° and then falls smoothly to zero at 1200°, whilst that of the Ta-W couple is 0.35 at 100°, 4.75 at 500°, 12.86 at 1000°, and 17.64 mv. at 1300°. A. R. P.

Calomel electrode. I. Dependence of electrode potential on lapse of days and on temperature. II. Junction potential between a concentrated and a dilute potassium chloride solution. M. HIRAKI (Acta Schol. Med. Kioto, 1922, 14, 300—316, 288—299).—I. The potential of a freshly-prepared HgCl electrode is stabilised in about 2 weeks, independently of the concn. of the KCl or of the purity of the materials used. Between 5° and 40° equilibrium is attained in 30—40 min. Temp. coeffs. of 0.1*N*-, 3.5*N*-, and saturated HgCl electrodes are recorded.

II. When dil. and conc. KCl solutions are brought into contact in an agar medium, the equilibrium diffusion potential is attained in 30—40 min.; the variation is <0.1 mv. CH. ABS.

Standard electrode potentials of Ag-AgCl and calomel electrodes and single potentials of calomel electrodes. H. M. SPENCER (J. Amer. Chem. Soc., 1932, 54, 3647—3648).—From Randall and Young's data $E_{298.1}^{\circ}$ for Ag-AgCl is -0.2222₁ volt, compared with -0.2223 volt by Carmody's extrapolation. If Gerke's val. of 0.0455 volt is taken for the difference between the HgCl and Ag-AgCl elec-

trodes, for the HgCl electrode is 0.2677 volt. On this basis the single potentials for calomel electrodes with various concns. of KCl are calc. Correcting for liquid junction potential, the "normal HgCl electrode" val. is -0.2800 volt. R. H. C. (c)

Causes of the hydrogen effect. IV. L. WOLF [with L. PENJKOVA-USPENSKAJA] (Z. Elektrochem., 1932, 38, 622—627; cf. this vol., 586).—The fall of p_H during use of the H electrode is due to replacement of the H in the outer surface of the electrical double layer on the Pt by cations from the electrolyte. The magnitude of the H effect varies with the area of the Pt electrode; an electrode transferred from one solution to another does not show the effect a second time, unless washed. No effect is observed unless Pt-black and H are present simultaneously.

H. F. G.

Electrochemical behaviour of aluminium. III. R. MÜLLER (Z. anorg. Chem., 1932, 208, 304—312; cf. A., 1920, 1105).—When AlBr₃ is dissolved in a large amount of C₅H₅N 220.9 kg.-cal. are evolved, of which about 99.9% is heat of formation of AlBr₃·3C₅H₅N, the remainder being heat of dissolution of the solvate. With PhCN 44 kg.-cal. are evolved, due to formation of AlBr₃·4PhCN, which dissolves in excess of PhCN without measurable thermal effect. Electrode potentials of (amalgamated) Al in a saturated solution of AlBr₃ in C₅H₅N, in the eutectic mixture (13.15% C₅H₅N), and in PhCN saturated with AlBr₃ are, respectively, 0.87, 0.33, and 0.52 volt negative to H. All these vals. are much lower than those calc. on the assumption that the potential is determined by the process Al → Al⁺⁺⁺. F. L. U.

Electrometric studies of the precipitation of hydroxides. VII. Glass-electrode titrations of mercuric salt solutions. H. T. S. BRITTON and (Miss) B. M. WILSON (J.C.S., 1932, 2550—2557).—The p_H at which HgO is pptd. on running aq. NaOH into aq. Hg⁺⁺ salts varies from salt to salt, owing to the varying degrees of ionisation and complex ion formation. Hg(ClO₄)₂ is considerably ionised, but not appreciably hydrolysed, HgSO₄ and Hg(NO₃)₂ suffer considerable ionisation and appreciable hydrolysis, whereas HgCl₂, HgBr₂, Hg(CN)₂, Hg(NO₂)₂, and Hg(OAc)₂ are weak electrolytes. Pptn. occurs when the solubility product [Hg⁺⁺][OH⁻]² = 10⁻²⁶ is reached. Addition of KX (X=halogen) to aq. HgX₂ raises the p_H at which pptn. occurs, owing to formation of HgX₄²⁻. HgI₄²⁻ is not affected by NaOH.

D. R. D.

Theory of glass electrode. II. Glass as a water electrode. M. DOLE (J. Amer. Chem. Soc., 1932, 54, 3095—3105; cf. this vol., 700).—The failure of the glass electrode to act as a perfect H electrode in strongly acid solutions is explained on the assumption that H⁺ migrates through the glass with 1 mol. of H₂O of hydration. This theory indicates that the glass electrode will not act like a H electrode in non-aq. solutions. M. D. (c)

Influence of formation of complexes on attainment of equilibrium in certain oxidation-reduction systems. W. F. JAKÓB and M. R. REZNAR (Chem. Listy, 1932, 26, 461—466).— E_H for mixtures

of aq. $[H_2(MoO)_6]H_5(NH_4)_3$ and $NH_4[Mo_2O_7 \cdot MoO_4(OH)_2]$ has been measured at p_H 3.4–5.2. The E_H-p_H curve is not rectilinear, pointing to possible reaction between oxidation-reduction complexes and H^+ , with consequent activity changes.

R. T.

Potentiometric study of Scholl's anthroxyl radicals. L. F. FIESER and W. Y. YOUNG (J. Amer. Chem. Soc., 1932, 54, 4095–4100).—These radicals (A., 1931, 846) form, with their reductants, fairly stable oxidation-reduction systems, the potentials of which have been measured. In dil. acid solution the reductant of the radical is formed by the intramol. condensation of the corresponding α -aroylanthrahydroquinone.

C. J. W. (c)

Electrokinetic potential of porcelain diaphragms. A. VASIČEK (Chem. Listy, 1932, 26, 503–507).—Electro-osmotic measurements of the electrokinetic potential (P_e) of an unglazed porcelain diaphragm in aq. KCl are not in agreement with those obtained by the filtration potential method, owing to electrolytic transport, which becomes considerable in conc. solutions. The P_e -dilution curve rises linearly from 0.02N- to a max. at 0.002N-KCl, below which it gradually falls.

R. T.

Electro-osmosis at porcelain diaphragms in aqueous potassium chloride. J. VELÍSEK and A. VASIČEK (Chem. Listy, 1932, 26, 507–512).—The electro-osmotic potential of a porcelain diaphragm has a max. val. of 42 mv. in 0.002N-KCl. The diaphragm used has much larger pores than kaolin diaphragms.

R. T.

Electro-osmosis with a ceramic diaphragm in aqueous solutions of some alkali halides. J. VELÍSEK and A. VASIČEK (Coll. Czech. Chem. Comm., 1932, 4, 428–443; cf. A., 1931, 434).—Electro-osmotic measurements have been made for aq. solutions of LiCl, NaCl, KCl, KBr, and KI at concns. of 0.00005–1.0N, using a porcelain diaphragm. The electro-kinetic potential curve shows a max. for LiCl, NaCl, and KCl, but not for KBr and KI. At medium concns. electro-osmotic transport is nearly the same for all electrolytes investigated. J. W. S.

Variation of the electrokinetic potential with the chemical composition of the diaphragm. N. SCHONFELDT (Z. Elektrochem., 1932, 38, 628–630).—The electrokinetic potential ζ of sintered Al_2O_3 diaphragms containing up to 95% of SiO_2 , BeO , or $AlPO_4$ in 0.05% KCl solutions has been measured. ζ varies, differently in each case, with the percentage composition of the diaphragm, and similar variations are observed with diaphragms consisting of a mixture of coarse and fine Al_2O_3 . There is apparently no relation between ζ and the composition of the diaphragm.

H. F. G.

Electrokinetic phenomena. IX. Electrophoresis and electro-osmosis. H. A. ABRAMSON (J. Gen. Physiol., 1932, 16, 1–3).—For surfaces coated with purified cryst. horse serum-albumin, the ratio of the electro-osmotic mobility to the electrophoretic mobility is approx. unity. This result confirms the theory of Henry (A., 1931, 1232).

W. O. K.

Technique of electro-osmotic measurements. P. I. ANDRIANOV (Kolloid-Z., 1932, 61, 46–47).—A modified form of the apparatus of Harkavitsch (A., 1929, 265) is described.

E. S. H.

Overvoltage. V. Moving-coil oscillograph system for study of overvoltage and transfer resistance. A. L. FERGUSON and G. M. CHEN (J. Physical Chem., 1932, 36, 2437–2445; cf. this vol., 701).—An oscillograph-commutator system is described for use in the study of transient electrode phenomena. Oscillograms for charging and discharging intervals are given and a direct comparison of the polarisation potentials as determined simultaneously by the commutator and direct methods is obtained. Previous results with the commutator-potentiometer system are confirmed. R. H. C. (c)

Effect of applied voltage on electrolysis in residual current range. G. H. DAMON (J. Physical Chem., 1932, 36, 2497–2503).—Below 0.5 volt the residual current is practically independent of voltage, but above 0.5 volt increases rapidly with the voltage. For the higher voltages it is greater in air than in vac.

R. H. C. (c)

Electrochemical periodicities. M. LIGNANA (Nature, 1932, 130, 474).—A cell with a Cu anode and 25% H_2SO_4 as electrolyte in which the ratio of e.m.f. to circuit resistance has a certain crit. val. shows periodic variations of the current which flows through it. The effect is due to the alternate formation and destruction of a thin anodic layer, analogous to that responsible for the passivity of metal electrodes.

L. S. T.

Depth distribution of current in electrolytic cells. O. BUSSE (Z. Elektrochem., 1932, 38, 783–793).—Measurements of the thickness of the electrolytically deposited layer of metal on the cathode, and direct measurement of c.d. at a divided cathode, do not give satisfactory results. Concordant results are obtained by the following methods: (1) fall in c.d., measured by changes in wt., along a divided bent cathode; (2) potential fall at different parts of the surface of a bent cathode by means of a test electrode; (3) tracing of equipotential lines through the electrolyte by a test electrode. Vals. of $\gamma - E_b/\alpha$ are recorded, where E_b is the e.m.f. of the bath and α is obtained from $z = w^2$, z being the potential at a point in the bath at a distance u from the anode. A bath with a high γ val. gives the most favourable results. It is obtained at low temp., high c.d., and low electrical conductivity.

M. S. B.

Theory of passivity phenomena. XVI. Properties of natural coating of iron after various kinds of mechanical treatment. W. J. MÜLLER and W. MACHU (Z. physikal. Chem., 1932, 161, 411–420).—The pore area in the coating is greater if the metal has been rubbed only with coarse emery paper or has received the highest polish than if it has been treated only with moderately fine emery paper. The thickness of the film, judged by its resistance, is independent of such mechanical treatment. R. C.

Topochemistry of corrosion and passivity. III. E. PIETSCH [with E. JOSEPHY, B. GROSSE-EGGBRECHT, and W. ROMAN] (Korrosion u. Metall-

schutz, 1932, 8, 57—66; Chem. Zentr., 1932, ii, 117—118; cf. this vol., 128).—It is probable that the processes involved in the dissolution of the material, following adsorption, are associated with an exchange of electric charge. This is significant for the chemical, but not for the adsorption, process. In the case of Pt-Zn in dil. H_2SO_4 , SO_4^{--} is adsorbed on the Zn and H on the Pt at the Pt-Zn phase boundary; the two negative charges liberated by the formation of the $[\text{Zn}^{++}\text{SO}_4^{--}]$ complex in the Zn lattice pass by way of the Pt to 2H^+ and discharge these to H_2 . This, having relatively to H a small adsorption potential, leaves the surface, whilst the $[\text{Zn}^{++}\text{SO}_4^{--}]$ complex, being unstable in the lattice, passes into solution. A. A. E.

Passivity of gold. W. J. SHUTT and A. WALTON (Trans. Faraday Soc., 1932, 28, 740—752; cf. A., 1930, 1527).—The potential changes accompanying the spontaneous reactivation of a passivated Au anode in 0.125–4*N*-HCl have been investigated by an improved method at temp. between 15° and 65.5°. The interruption of the passivating current is followed instantaneously by an abrupt fall of potential to an almost const. val. A subsequent small inflexion is followed by a slow voltage drop which terminates in a sudden fall to the normal potential of active Au. The "total time of recovery," θ , varies considerably with c.d. at high rates of stirring, and the temp. coeff. of θ is of the order of that required by a chemical reaction rather than of physical processes. θ is increased by dissolved Cl_2 and by decreasing $[\text{HCl}]$. For HCl-KCl mixtures, $\theta = k/[\text{H}^+] + \theta_{\text{Cl}}$, where θ_{Cl} decreases rapidly with $[\text{Cl}^-]$, with passivating c.d., and with increased stirring, and k is approx. const. The time required for cathodic reduction increases with passivating current, duration of passivity, and less efficient stirring. Passivation of Au in H_2SO_4 was investigated, and the thickness of the oxide film in HCl and H_2SO_4 is shown to be only uni- or bi-mol. A mechanism consistent with the results is developed. The first stage in the reactivation is independent of acid content, but proceeds at a rate approx. proportional to $[\text{Cl}^-]^2$ and involves the interaction of a peroxide with Cl^- to produce Cl_2 and Au_2O_3 , which subsequently dissolves at a velocity governed by $[\text{H}^+]$. J. G. A. G.

Passivation of tantalum in non-aqueous solvents. A. Methyl, ethyl, propyl, butyl, and *iso*-amyl alcohols. P. SCHUPP (Z. Elektrochem., 1932, 38, 774—777).—The valve action of Ta in alcohols is similar to that in H_2O . The max. e.m.f. is very low in MeOH and increases with the mol. wt. of the alcohol. The low vals. do not, however, represent true max., but are due to oxidation of the alcohol by anodic O instead of formation of Ta_2O_5 . The thickness of the oxide layer depends only on the voltage employed and is proportional to it. Its val. is the same in alcohols as found by Günther-Schulze in H_2O (A., 1931, 546, 1130). $\text{Ca}(\text{NO}_3)_2$ was used as electrolyte. M. S. B.

Bronsted's kinetic equation and Debye's theory. A. MUSIL (Monatsh., 1932, 61, 229—273).—A theoretical interpretation of the divergences from the classical laws of chemical kinetics in the alkaline

hydrolysis of esters is based on Bronsted's kinetic equation and Debye's theory. J. W. S.

General considerations in connexion with the chain-reaction theory. N. N. SEMENOV (Trans. Faraday Soc., 1932, 28, 818—822).—A theoretical discussion, emphasising the role of free energy in chemical kinetics and ascribing secondary importance to temp., concn., catalysts, etc. E. S. H.

Inert gas effects in chain reactions. H. W. MELVILLE (Trans. Faraday Soc., 1932, 28, 814—818).—A discussion of the effects of foreign gases on chain reactions between O_2 and H_2 , CH_4 , PH_3 , H_2S , CS_2 , and P_4 , respectively, reveals regularities, which are in accordance with the theory developed. The inert gas has a greater accelerating influence on reactions which involve the oxidation of light mols. The mass of the chain carrier mols. appears to increase with increasing mass of the mol. of combustible substance. E. S. H.

Function of the solvent in unimolecular reactions. M. MAGAT (Z. Elektrochem., 1932, 38, 619).—The influence of the solvent may be due to the formation of swarms containing solute and solvent mols. H. F. G.

Thermal dissociation. I, II. M. F. STRUNNIKOV (J. Gen. Chem. Russ., 1932, 2, 140—153, 154—165).—I. Theoretical. Reactions are preceded by dissociation with formation of free valencies, or by the production of additional valencies, this applying to all substrates present.

II. Examples of the above processes are given, and catalysis is considered from this point of view.

Rate of dissociation of nitrogen tetroxide. C. E. TEETER, jun. (J. Amer. Chem. Soc., 1932, 54, 4111).—Richards and Reid's results for the velocity coeff. (this vol., 916) could not be confirmed. Velocity coeffs. calc. from Einstein's original equations may be 20% too low. C. J. W. (c)

Thermal decomposition of methane. L. S. KASSEL (J. Amer. Chem. Soc., 1932, 54, 3949—3961).—The decomp. in quartz bulbs at 700—850° is initially unimol. and homogeneous. Under some conditions there is an induction period. The primary process is probably the formation of CH_2 and H_2 with a rate coeff. of $5 \times 10^{11} e^{-79385/RT}$ and the next step the combination of CH_2 and CH_4 to give C_2H_6 . H_2 greatly retards the decomp., which is accounted for by supposing C_2H_6 to lose H in successive steps to C_2H_5 , C_2H_4 , and C, all the steps being reversible. L. P. H. (c)

Energy exchanges between unlike molecules. Decomposition of methyl ether, ethyl ether, acetone, and their binary mixtures. L. S. KASSEL (J. Amer. Chem. Soc., 1932, 54, 3641—3647).—Contrary to Steacie's observation (this vol., 576, 701), mixtures of Et_2O with Me_2O or COMe_2 decompose at a rate which indicates that the transfer of internal energy occurs about as readily between unlike as between like mols. H. A. B. (c)

Homogeneous thermal polymerisation of Δ^2 -butadiene. W. E. VAUGHAN (J. Amer. Chem. Soc., 1932, 54, 3863—3876).—The reaction at 720—

1.5 mm. and 326–436° follows the second-order equation over the greater portion of the association. The rate is expressible by $\log k = -568_0(1/T) + 7.67_3$.

W. E. V. (c)

Kinetics of the oxidation of gaseous acetaldehyde. W. H. HATCHER, E. W. R. STEACIE, and F. HOWLAND (Canad. J. Res., 1932, 7, 149–161).—The velocity of reaction in MeCHO-O_2 mixtures at 60–120° has been studied by observing the pressure change at const. vol. During the somewhat lengthy induction period, CO_2 , H_2O , and HCO_2H are the main products, whilst in later stages of the reaction peroxides and their oxidation products are formed. An increase of the surface in contact with the reacting mixture increases the induction period. The main reaction is of the chain type, the chains commencing, and to some extent ending, at the walls of the vessel; its order varies from about 1.7 at 60–100° to 1.47 at 120°. The heat of activation is 8.7 ± 0.7 kg.-cal. Bodenstein's views on the reaction, and particularly his opinion that the induction period is due to the effect of inhibitors derived from stop-cock grease, do not accord with the results obtained. H. F. G.

Mechanism of the initiation and propagation of detonation in solid explosives. W. TAYLOR and A. WEALE (Proc. Roy. Soc., 1932, A, 133, 92–116).—An investigation has been made of the conditions whereby a thin layer of explosive can be initiated to explosive decomp. by percussive forces of the same order of magnitude as those present in the shock waves associated with detonations. Ignitions may be caused by impacts with insufficient energy to raise the sample of explosive to the ignition temp. The temp. variation of the ignition process has been studied and an exponential relation found, suggestive of a surface activation mechanism.

L. L. B.

Photographic studies of detonation of explosives. T. URBANSKI (Rocz. Chem., 1932, 12, 715–769).—Photographs of detonation of picric acid (I) and of cellulose nitrate (II), taken at intervals of 0.0001 sec., indicate that the primary flame consists of blue, green, red, and infra-red rays, whilst blue rays are absent from the secondary flame, representing reaction between the products of explosion. In both flames the intensity of the rays increases in the order blue, green, red. The primary flame consists of a central core, with a rosette of rays around it; with time, these rays form a series of rings, of the shape of truncated cones. The non-luminous products of detonation of (II), but not of (I), re-emit light on contact with Cu. The duration of the primary flame is 0.0004–0.0005 sec., respectively, for (I) and (II); the duration of emission of green and red light by the secondary flame is, respectively, 0.0008 and 0.001 sec. for (I). R. T.

Kinetics of reaction of potassium permanganate with hydrogen peroxide in acid solutions. II. W. LIMANOWSKI (Rocz. Chem., 1932, 12, 638–650).—The velocity of reduction of KMnO_4 by excess of H_2O_2 in presence of H_2SO_4 , HNO_3 , or H_3PO_4 is given by $dx/dt = k_1b(1-x) + k_2ax(1-x)$, where x is the relative fall in concn. of KMnO_4 , a its initial concn., and b that of H_2O_2 . KMnO_4 is simultaneously

reduced by H_2O_2 and by Mn^{++} ; alkali metal phosphates and fluorides catalyse the latter but not the former reaction. H^+ in low concn. retard, and in higher concn. accelerate, reaction. The process of reduction of Mn^{VII} to Mn^{II} is practically instantaneous. The temp. coeff. of the reaction between KMnO_4 and H_2O_2 is 2.06, and of that between KMnO_4 and Mn^{++} 1.52, over the range 0–20°. In low concn. of H_2O_2 and acids, glass and SiO_2 catalyse the reaction. R. T.

Kinetics of the [thermal] iodine-oxalate reaction. R. O. GRIFFITH and A. MCKEOWN (Trans. Faraday Soc., 1932, 28, 752–760; cf. this vol., 702; A., 1924, ii, 327; 1925, ii, 141).—The data obtained at temp. between 40° and 60° with $M/100$ — $M/1500$ I and $M/6$ — $M/12$ Na and K oxalate in $M/5$ — $M/1000$ KI are consistent with the reaction $\text{Na}_2\text{C}_2\text{O}_4 + \text{I}_2 \rightarrow 2\text{NaI} + 2\text{CO}_2$, proceeding by way of two simultaneous and independent processes. The velocity coeff. of the process unimol. with respect to I_2 has the temp. coeff. 9.4 and the crit. increment of the rate-determining step $\text{HOI} + \text{HC}_2\text{O}_4' \rightarrow \text{H}_2\text{O} + 2\text{CO}_2 + \text{I}'$ is 18,550 g.-cal. The following is suggested for the process semi-mol. with respect to I_2 : (a) $\text{I}_2 \rightleftharpoons 2\text{I}$, (b) $\text{I}_2 + \text{I}' \rightleftharpoons \text{I}_3'$, (c) $\text{I} + \text{C}_2\text{O}_4' \rightarrow \text{I}' + \text{C}_2\text{O}_4'$, and (d) $\text{C}_2\text{O}_4' + \text{I}_2 \rightarrow 2\text{CO}_2 + \text{I} + \text{I}'$; the crit. increment of (c) is computed to be 17,800 g.-cal. approx. There is no evidence for a reaction between $\text{HC}_2\text{O}_4'$ and I atoms. J. G. A. G.

Velocity of esterification of alcohols in acetic acid. A. KAILAN and R. RAFF (Monatsh., 1932, 61, 116–142).—The velocities of esterification at 25° of Pr^nOH , Pr^sOH , Bu^nOH , Bu^sOH , *sec.*- and *tert.*-butyl, *n*-amyl, and *n*-octyl alcohols, pentan- β - and - γ -ol, γ -methylbutan- α -ol (containing 20.8% of *l*- β -methylbutan- α -ol), and octan- β -ol in AcOH containing "0.112 mol." and "1.1 mol." H_2O per kg. of 100% acid, have been determined (cf. A., 1929, 655). In presence of HCl as catalyst the velocity is increased by a higher initial H_2O content, but in its absence the reverse is the case; in the former case it is approx. proportional to the HCl content. The influence of the catalyst is the more marked the higher is the velocity coeff. In the drier AcOH in presence of HCl , where the steric effect is most marked, the velocity coeff. of the *n*-primary alcohols is approx. 10 times that of the corresponding *n*- β -OH-compounds, and decreases steadily to C_4 , further elongation of the chain being without effect. In branched-chain alcohols the vals. are the lower the nearer is the OH group to the position of branching.

H. A. P.

Velocity and mechanism of racemisation. I. Rochelle salt. A. N. CAMPBELL and A. J. R. CAMPBELL (J. Amer. Chem. Soc., 1932, 54, 3834–3841).—The rate of inactivation of Na K tartrate when heated with NaOH has been measured. The interpretation of the experimental results is rendered difficult by the formation of a levorotatory complex. The evidence for the existence of this complex depends on the sign of rotation, $[\text{OH}']$, and a phase theory study of the system Na K tartrate- H_2O - NaOH . S. L. (c)

Ester formation in glycerol and ethyl alcohol. A. KAILAN and P. ULICNY (Monatsh., 1932, 61, 169—

188).—The velocities of esterification of *n*- and *iso*-valeric, *n*-hexoic, *n*-octoic, and benzoic acids in glycerol, and of *o*-, *m*-, and *p*-toluic acids in EtOH, under the influence of HCl, and of *n*-valeric acid in glycerol with H₂SO₄ as catalyst, have been measured at 25° (cf. A., 1930, 710). With carefully dried starting materials the velocity coeffs. for a unimol. reaction are in all cases proportional to the HCl concn., but in the initial presence of H₂O this is so only in the case of the aliphatic acids in glycerol. The vals. for *o*-, *m*-, and *p*-toluic acids are in the ratio 1 : 3.28 : 3.02.

H. A. P.

Kinetics of reaction between bromoacetate and thiosulphate ions at great dilutions. A. N. KAPPANNA and H. W. PATWARDHAN (Rec. trav. chim., 1932, 51, 379—382; cf. A., 1929, 516).—Repetition of previous work over a wider range of temp. (30—90°) confirms the validity of the Bronsted-Debye theory as applied to this reaction, contrary to the results obtained by La Mer (A., 1930, 168). The energy of activation of the reacting ions is calc. to be 15,680 g.-cal.

F. L. U.

Rates of hydrolysis to betaines of some quaternary bases of α -aminonitriles. Quaternary ammonium bases. T. D. STEWART and K. KORPI (J. Amer. Chem. Soc., 1932, 54, 3977—3988).—The alkaline hydrolysis of quaternary ammonium substituted MeCN to the betaine cannot be represented as a simple second-order reaction between positive and negative ions. In presence of excess of OH⁻ the rate is proportional to [NH₄⁺]^{1.3} and to [OH⁻]^{1.3-1.8}. When the concns. are equal the sum of the indices is about 2.4. These relations are unchanged by changes in salt concn., temp., and the homologue.

C. J. W. (c)

Study of kinetic processes on metal surfaces by radioactive methods. O. ERBACHER (Z. Elektrochem., 1932, 38, 532—535).—The deposition of radioactive elements on "noble" metals, either by forming a H₂ film on the latter or by using a solution in which the metal dissolves with formation of a complex ion, is described. Interchange of ions between a metal and an equilibrium solution of its ions is reduced by pretreatment of the electrode, but the effect always extends below the surface layer of atoms. Interchange between an electrode and ions of another metal, such as occurs with Ni in a solution containing Ni²⁺ and Bi³⁺, may be reduced by pretreatment to such an extent that only the surface layer is involved. If a single layer of a radioactive element be deposited in this manner on a surface of a metal, the abs. extent of the surface may be determined. With polished, roughened, and platinised Pt the active surfaces are in the ratio 1 : 10 : 100.

H. F. G.

Velocity of dissolution of marble in acids. II. W. JACEK (Bull. Acad. Polonaise, 1932, A, 65—73; cf. A., 1931, 1242).—The velocity of dissolution of a marble sphere in HCl increases proportionally to the concn. at low concns. only. A max. velocity is reached as the concn. of HCl is increased, after which the velocity falls greatly. This behaviour is considered to be due to the covering of the marble surface by bubbles of CO₂.

E. S. H.

Inflammation temperature of activated carbons. E. BERL and E. WEINGARTNER (Z. physikal. Chem., 1932, 161, 315—324).—The inflammation temp., *T*, is generally the lower the more highly developed is the surface. *T* rises with increase in the degree of graphitisation, measured by decrease in the sp. resistance of the C. Some CO₂ appears at temp. a little below *T*, which suggests that *T* is the min. temp. at which corrosion of the surface is sufficiently great to start combustion.

R. C.

Velocity and equilibrium constants of the reaction between carbon and ferrous oxide in the production of steel. H. SCHENK, W. RIESS, and E. O. BRÜGGEMANN (Z. Elektrochem., 1932, 38, 562—568).—The reaction FeO + C → CO + Fe has been studied by determining by Hertzy's method of adding Al to the melt the FeO content of steel produced in commercial furnaces (15,000—60,000 kg.). The $d[C]/dt - [FeO][C]$ curves for 0.14—0.5% C steels are linear, but the apparent velocity coeffs. vary with [C]. If, however, the concn. of free C, and not that of total C, be considered, it may be assumed that *k*₁ is independent of [C], and the calc. val. of *k*₁ is then 0.418. The combined C is probably present as (Fe₃C)₆. The velocity coeff. *k*₂ = 0.458 × 10⁴ [Fe]_{free}, where Fe_{free} is the percentage of uncombined Fe calc. by taking log *D* - 7.43, *D* being the dissociation const. of (Fe₃C)₆.

H. F. G.

Temperature increment of the velocity of heterogeneous reactions. V. Reactions of salts rich in oxygen. K. FISCHBECK and K. SCHNAIDT (Z. Elektrochem., 1932, 38, 769—773).—The temp. increment of the reaction velocity of KMnO₄ with H₂ is 11.5—13.8 kg.-cal. and with CO 11.5—14.4 kg.-cal., the val. increasing with the proportion of KMnO₄ decomp. The corresponding vals. for KIO₃ are 20.4—22.0 and 36.3 kg.-cal., respectively.

M. S. B.

Active oxides. LIV. Rate of decomposition of zinc carbonate into zinc oxide and carbon dioxide. G. F. HÜTTIG, A. MELLER, and E. LEHMANN (Z. physikal. Chem., 1932, B, 19, 1—21).—At 415—460° the velocity passes through a max., attained when the ZnO-ZnCO₃ interface has reached a max., and after this point is equal to *kn*^{2/3}, *n* being the proportion of undecomposed ZnCO₃, from which it is concluded that decomp. begins at the surface of the crystals and progresses inwards at a uniform rate, and that the ZnCO₃ mols. at the interface have a much greater rate of decomp. than the others. *k* varies with the temp., *T*, according to the equation log *k* = *A*/*T* + *B*. The rate of the reaction ZnO + CO₂ → ZnCO₃ is proportional to the CO₂ pressure and to *n*^{2/3}. The reaction velocities are also affected by the total activity of the solid phase, which depends on the age of the ZnO, and is a max. when *n* is about 0.6. To secure ZnO of max. activity the CO₂ pressure in the gas phase should be high, the reaction temp. low, and the rate of reaction as great as possible.

R. C.

Oxidation of substances in colloidal solution. S. A. VOSNESSENSKI and I. M. TZINN (J. Gen. Chem. Russ., 1932, 2, 491—501).—Aq. suspensions of S are rapidly oxidised by Cl₂ and Br, but not by I. The

velocity of oxidation is diminished in the presence of Na_2SO_4 or NaHSO_4 ; kaolin and $\text{Fe}(\text{OH})_3$ have no action, $\text{Al}(\text{OH})_3$ reduces only the initial velocity of reaction, whilst powdered alabaster and protective colloids (lumiens) considerably retard reaction.

R. T.

Influence of high concentrations of salts on velocity of oxidation of suspensions of sulphur by bromine. S. A. VOSNESSENSKI and I. M. TZINK (J. Gen. Chem. Russ., 1932, 2, 502—503).— NaCl (1—4*N*) inhibits oxidation of S by Br to a greater extent than do equiv. concns. of LiCl ; this is ascribed to the greater hydration of Li^+ and to its capacity for giving rise to aquo-acids.

R. T.

Velocity of dissolution of oxygen in water and in solutions of substances reacting with it. Influence of liquid surface films on velocity. S. A. VOSNESSENSKI and L. A. KLUTSCHAEV (J. Gen. Chem. Russ., 1932, 2, 506—514).—The initial velocity of dissolution (v_0) of O_2 in aq. Na_2SO_3 is const., and is unaffected by stirring. In pure H_2O v_0 is the same as for aq. Na_2SO_3 ; with time, the velocity increases, and has a max. final val. in 0.3—0.8*N*- Na_2SO_3 . The val. of v_0 is unaffected by surface films of liquid paraffin, paraffin oil, or kerosene $>5\ \mu$ thick, but after 1 hr. such films cause retardation of reaction. Films $<10\ \mu$ thick retard reaction from the beginning.

R. T.

Open-air corrosion of copper. III. W. H. J. VERNON.—Sec B., 1932, 940.

Catalytic action of water vapour in combustion of carbon monoxide. H. PASSAUER (Z. physikal. Chem., 1932, 161, 299—304).—The rate of combustion of a moist CO-air mixture is the same as that of a dry CO-air mixture containing CO_2 and H_2 in amounts such as would furnish the same amount of H_2O by the water-gas reaction. It thus appears that the catalysis of the combustion of CO by H_2O depends on the water-gas reaction. The decomp. of the H_2O probably occurs in the preheating zone, but is incomplete if the air-CO mixture contains $>$ about 3% H_2O .

R. C.

Use of an electrode to study irreversible reactions: the polymerisation of acetaldehyde. V. HNZIDA and D. J. BROWN (J. Physical Chem., 1932, 36, 2842—2843).—The polymerisation of MeCHO can be followed by observing the change of p.d. of solutions of MeCHO against a standard electrode. The results indicate that H^+ has a preserving effect, which is proportional to its concn., whilst Cl^- appears to catalyse the polymerisation proportionally to its concn.

E. S. H.

Catalytic decomposition of hydrogen peroxide by iodine-iodide couple. II, III. Rate of oxidation in neutral and in acid solution of hydrogen peroxide by iodine. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1932, 54, 3499—3508; cf. this vol., 818).—One of the steps in the oxidation of H_2O_2 by I_2 which determines the rate has been isolated by measuring the rate of O_2 evolution from approx. neutral solutions, saturated with I_2 , the most probable mechanism being $\text{IO}^+ + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{I}^+ + \text{O}_2$. At 25° the sp. reaction const., is in such agreement

with the val. deduced from the steady state measurements as to show that the hydrolysis equilibrium of I_2 is always established in the $\text{I}_2\text{--I}^+\text{--H}_2\text{O}_2$ reaction system. By measuring the O_2 evolution from acid solutions in the presence of TI^+ a second rate-determining step has been isolated, probably $\text{HIO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{H}^+ + \text{I}^+ + \text{O}_2$. At 25° k agrees with the val. deduced from steady state measurements. It is concluded that the reaction system can be interpreted in terms of the three compensating reactions within the wide range of experimental conditions over which the corresponding rate laws have been definitely established.

H. F. J. (c)

Role of ozone as an oxidation catalyst. III. Chemical reactivity of ozone in the absence of oxygen in the ozonolysis of benzaldehyde and sodium sulphite. E. BRINER and H. BIEDERMANN (Helv. Chim. Acta, 1932, 15, 1227—1234; cf. this vol., 235).—When PhCHO and Na_2SO_3 are oxidised by $\text{O}_3\text{--O}_2\text{--N}_2$ mixtures of different proportions, (a) the total oxidation taking place falls from 300 and 112% to 44 and 40%, respectively (with regard to the amount of O_3 decomposed), and (b) the amount of BzO_2H formed falls to nearly 0, as the amount of O_2 is decreased from 99 to 0.5%. In absence of O_2 , O_3 reacts by decomp. to $\text{O}_2 + \text{O}$; therefore, efficiencies above 33% [not 100% (*loc. cit.*)] indicate that the O_3 has catalysed oxidation by O_2 . (b) proves that per-acids are formed by O_3 and not by O_2 . The catalytic action of O_3 is shown only in oxidations which occur spontaneously even in absence of O_3 . Possible mechanisms of the catalysis are discussed.

R. S. C.

Crystal structure and catalytic activity of carbon. U. HOFMANN and W. LEMOKE (Z. anorg. Chem., 1932, 208, 194—212; cf. this vol., 16).—The adsorptive capacities of technical active charcoals, of soots, and of graphites, and their catalytic activity in promoting the combination of H_2 and Br, are closely parallel and depend on the total accessible surface of graphite crystals. "Activation" by heating in CO_2 at 950° increases the adsorptive power and catalytic activity of prepared charcoals and soots by enlarging the pores and thus making a larger surface accessible, whereas it diminishes the catalytic efficiency of retort C or Ceylon graphite by preferentially destroying the smallest crystals. The heat of activation of the HBr synthesis is the same whether catalysed by Ceylon graphite or by "supranorit."

Catalysis of reaction between solids. IV. Decomposition of stannic oxide by radiation from radium. S. TAMARU and K. OTIAI (Z. physikal. Chem., 1932, 161, 346—354; cf. this vol., 705).—As a result of exposure to the radiation from Ra, SnO_2 becomes able to catalyse the formation of stannate from SnO_2 and CaO in the same way as SnO . SnO can be isolated from it by vac.-sublimation, but no metallic Sn is present. Ultra-violet light has no action on SnO_2 .

R. C.

Catalytic hydrogenation and polymerisation. C. SCHUSTER (Z. Elektrochem., 1932, 38, 614—618).—Various kinds of active C serve as catalysts for the hydrogenation of adsorbed olefines (C_2H_4 —

C_5H_{10}). Traces of Ni on the C produce proportionate increases of the velocity coeff. of the reaction. The velocity decreases rapidly with increase of mol. wt. of the hydrocarbon. For Δ^2 -butylene the rate is proportional to $p^{1.5}$, p being the C_4H_8 pressure, whereas for C_2H_4 it is independent of the concn. The heat of activation ranges between 3600 and 6800 g.-cal. During hydrogenation of C_2H_4 , Δ^2 -butylene is formed; the velocity of polymerisation is proportional to the C_2H_4 concn., and the heat of activation is about 5000 g.-cal. H. F. G.

Nickel [prepared] by the Raney process as a catalyst of hydrogenation. L. W. COVERT and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 4116—4117).—By a modification of this process (B., 1927, 606), a Ni catalyst active at low temp. and pressures is obtained. $COMe_3$ is completely hydrogenated after 11.2 hr. at 23° and 2—3 atm. pressure, and mesityl oxide and $CH_3Ac \cdot CO_2Et$ behave similarly. Complete hydrogenation occurs at room temp. and 110 atm. with $PhCHO$, $MeCHO$, $CHPh \cdot CH \cdot CHO$, $(NPh)_2$, and $CH_2Ph \cdot CN$. C. J. W. (c)

Reaction between nitrous oxide and hydrogen on platinum. H. CASSEL and E. GLÜCKAUF (Z. physikal. Chem., 1932, B, 19, 47—62).—The reaction has been investigated at 600—1400° abs. in presence of an excess of H_2 and under 10^{-3} mm. pressure. Up to 775° the only reaction is $N_2O_{ads.} + (H_2)_{gas} \rightarrow N_2_{gas} + H_2O_{ads.}$, and the relative reaction velocity, G , remains const. during the reaction. When the temp., T , rises above about 775° G falls abruptly, and in the course of reaction passes through a min. At this temp. the partial pressure of O_2 formed by the thermal decomp. of the N_2O has become sufficient to form on the Pt surface an oxide film on which the catalysed reactions occur with diminished velocity, being also retarded by adsorbed O (cf. this vol., 1073). As T rises, the min. in G during the reaction becomes less and less pronounced, and disappears at about 1250° , the dominant reaction now being $H_2_{gas} + O_{ads.} \rightarrow H_2O_{ads.}$ R. C.

Vapour-phase catalytic oxidation of hydrocarbons. T. J. WILKEN-JORDEN.—See B., 1932, 927.

Catalytic decomposition of germane. T. R. HOGNESS and W. C. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 3583—3592).—The rate of decomp. on a Ge surface at 283 — 374° is proportional to $p^{1/3}$, where p is the pressure of the undissociated GeH_4 . H_2 inhibits the decomp. at lower temp. The heat of activation is 39.7 ± 2 kg.-cal. per mol. The results are discussed in terms of Langmuir's adsorption theory. J. V. V. (c)

Reactions between gas and solid. VI. Azotation of calcium carbide and the effect of catalysts on its velocity. T. AONO (Bull. Chem. Soc. Japan, 1932, 7, 287—297).—The optimal quantity of CaF_2 necessary to produce the max. velocity of azotation is a function of the temp. as well as of the quantity of carbide. The reaction between CaC_2 and N_2 is also accelerated by active C and hence probably by C formed in the reaction. A. G.

Dissociation of gypsum in presence of catalysts. I. E. ADADUROV and V. P. PLIGUNOV (J. Appl. Chem., Russia, 1932, 5, 149—156).—Displacement of SO_3 by SiO_2 is not a chemical, but a catalytic, reaction; the action of Al_2O_3 , Fe_2O_3 , and Cr_2O_3 is similar to that of SiO_2 , the quantity having little effect on the yield of SO_3 . CH. ABS.

Heat of activation of thermal dissociation of gypsum in presence of catalysts. I. E. ADADUROV (J. Appl. Chem., Russia, 1932, 5, 157—162).—Since the heat of activation at 700 — 900° is only 9500 g.-cal. per mol., the decomp. must depend on intramol. rearrangements. At 900 — 1100° the process is catalytic. CH. ABS.

Catalytic decomposition of carbon disulphide by steam and hydrogen. K. BUNTE and F. LORENZ (Gas- u. Wasserfach, 1932, 75, 765—771, 787—791).— MoS_3 and a mixture of U sulphides are efficient catalysts for the reactions $CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$ and $CS_2 + 4H_2 \rightarrow 2H_2S + CH_4$. The corresponding oxides may be used, but they are converted into sulphides during the reaction; there is thus no poisoning of the catalyst, and C is not deposited, as the working temp. can be kept low. The influence of temp., concn., and streaming velocity has been examined; at 400° the U sulphide catalyst gives 100% efficiency. N_2 , NH_3 , and heavy hydrocarbons found in coal gas have practically no influence on the reactions, but the presence of CO has a slight, favourable influence. The addition of alkali to the catalyst is feebly activating at high temp., but has the reverse effect at low temp. E. S. H.

Influence of catalyst of a primary reaction on the velocity of a secondary one. S. A. IVLEV (J. Gen. Chem. Russ., 1932, 2, 504—505).—The oxidation of peat humins by $HOCl$ is accelerated by addition of $CoCl_2$, which catalyses the decomp. of $HOCl$. R. T.

Anodes for zinc plating. G. B. HOGABOOM and A. K. GRAHAM.—See B., 1932, 986.

Deposition of bright zinc-cadmium alloys from cyanide baths. C. J. WERNLUND.—See B., 1932, 987.

Cadmium plating. C. M. HOFF.—See B., 1932, 986.

Electrolytic cadmium plating. F. PIETRAFESA and C. LUCIANI.—See B., 1932, 942.

Electrolytic manganese dioxide. G. W. NICHOLS.—See B., 1932, 991.

Preparation of manganese dioxide by electrolysis. V. P. ILINSKI and N. P. LAPIN.—See B., 1932, 979.

Preparation of manganese dioxide by electrolysis with alternating current. N. KAMEYAMA and H. IIDA.—See B., 1932, 1028.

Electrolysis of fused acetates and propionates. G. B. MOORHOUSE (Trans. Faraday Soc., 1932, 28, 766—776).—A fused mixture of Li, Na, and K acetates was electrolysed at 200° between a bright Pt anode and a Pb cathode in the apparatus described. The main products were CO_2 and C_2H_6 .

with small quantities of CO , CH_4 , H_2 , C_2H_4 , and MeOAc . The yield of CH_4 and CO was increased and that of C_2H_6 decreased by adding H_2O to the electrolyte. The chief products of the electrolysis of a fused mixture of Li and Na propionates at 230° were CO_2 , C_4H_{10} , C_2H_4 , C_2H_6 , with some CO , H_2 , and EtCO_2Et . The most probable mechanism of the Kolbe synthesis is the interaction of discharged ions. Mechanisms for the formation of the by-products are suggested. The Kolbe synthesis is fairly good with C anodes, but with Pt -black and Au the yields are poor with acetate and moderate with propionate.

J. G. A. G.

Relation between Kolbe's reaction and hydrogen-ion concentration. VII. Mechanism of Kolbe's reaction. H. R. MATSUDA (Bull. Chem. Soc. Japan, 1932, 7, 297—305).— EtCO_2H is formed during the electrolysis of EtCO_2H .

A. G.

Decomposition and synthesis of ammonia under the action of alpha rays. J. C. JUNGERS (Bull. Soc. chim. Belg., 1932, 41, 377—398; cf. A., 1931, 580).—When pure NH_3 at 25° is irradiated with α -rays from Rn , $M/I = 1.16(1 - 0.157\sqrt{q})$, where M = no. of mols. decomposed, I = no. of pairs of ions formed, and q = no. of millicuries \times vol. of reaction chamber. The addition of N_2 to the NH_3 does not alter the val. of M/I until the mixture contains $<1\%$ of NH_3 , but the addition of H_2 causes a rapid fall in M/I .

D. R. D.

Photochemical studies. XIV. Decomposition of nitrous oxide sensitised by mercury vapour. W. M. MANNING and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1932, 54, 3907—3917).—The total reaction between excited Hg and N_2O may be represented $\text{Hg} + \text{N}_2\text{O} \rightarrow \text{HgO} + \text{N}_2$. Two possible primary steps are the production of an excited O atom and a N_2 mol., or a normal N atom and a NO mol. Velocity measurements indicate that the N_2O mol. has a very large effective cross-section in its interaction with excited Hg .

W. E. V. (c)

Quantum efficiency of photochemical decomposition of potassium persulphate. R. H. CRIST (J. Amer. Chem. Soc., 1932, 54, 3939—3942; cf. A., 1927, 323, 428).—The quantum efficiency is unity for neutral and alkaline solutions. The effect of KCl , HCl , $\text{KCl} + \text{H}_2\text{SO}_4$, and $\text{HgCl}_2 + \text{H}_2\text{SO}_4$ has been investigated. A capillary Hg arc may be improved by deflexion with a magnet.

G. M. M. (c)

Photolysis of octacyanides of quadrivalent molybdenum. G. A. BARBIERI (Rend. Accad. Sci. Ist. Bologna, 1931, 35, 93—97; cf. A., 1931, 1255).—Exposure to sunlight for several hr. of a conc. solution of the yellow salt $\text{Na}_4\text{Mo}^{\text{IV}}(\text{CN})_8 \cdot \text{C}_6\text{H}_{12}\text{N}_4 \cdot 3\text{H}_2\text{O}$ containing excess of hexamethylenetetramine gave blue crystals of $\text{Na}_3[\text{Mo}^{\text{IV}}(\text{H}_2\text{O})(\text{OH})_2(\text{CN})_5] \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 3\text{H}_2\text{O}$, showing that the substitution of CN by OH in the photolysis of the complex $[\text{Mo}^{\text{IV}}(\text{CN})_8]$ is preceded by the replacement of 1 mol. KCN by 1 mol. H_2O , as in the photolysis of ferrocyanides. The blue compound, in conc. solution with a large excess of NaOH , gave reddish-violet crystals of $\text{Na}_4[\text{Mo}^{\text{IV}}(\text{OH})_4(\text{CN})_4] \cdot 6\text{H}_2\text{O}$, whereas the unsubstituted $[\text{Mo}(\text{CN})_8]$ is stable to alkalis. A conc. solution of this compound, treated

with a large excess of NaOAc and $\text{C}_6\text{H}_{12}\text{N}_4$, gave violet crystals of $2\text{Na}_3[\text{Mo}^{\text{IV}}(\text{H}_2\text{O})(\text{OH})_3(\text{CN})_4] \cdot 3\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{SH}_2\text{O}$ (cf. A., 1928, 159).

O. J. W.

Action of heat and of ultra-violet rays on mercury fulminate. M. PATRY and P. LAFFITTE (Bull. Soc. chim., 1932, [iv], 51, 1205—1212).—Below 139.5° $\text{HgC}_2\text{N}_2\text{O}_2$ decomposes slowly, evolving CO_2 and becoming successively brown, yellow, and white. Above 172° it explodes. Between these temp. the results depend on the pressure, explosion occurring more readily with higher pressure. PbEt_4 facilitates explosion. Under the action of light from a Hg -vapour lamp, $\text{HgC}_2\text{N}_2\text{O}_2$ is converted into a black isomeride or polymeride, which is not so readily detonated as the ordinary form, although more inflammable and more easily decomposed by heat.

D. R. D.

Concentration at emulsification and grain size [in photographic emulsions]. LUPPO-CRAMER (Z. wiss. Phot., 1932, 31, 179—181).—Photomicrographs show that the size of the grains in a AgBr - AgI emulsion increases as the H_2O content at emulsification is decreased. The effect is less marked in emulsions containing only AgBr .

J. L.

Photoanisotropic effect (Weigert effect) with dyes. I. T. KONDO (Z. wiss. Phot., 1932, 31, 153—167).—1700 dyes have been tested, both in gelatin and in collodion emulsions; in 450 cases the Weigert effect has been detected (cf. A., 1929, 871). Nearly all the dyes giving the effect are brown, red, yellow, or intermediate between these in colour. The amount of the effect varies greatly with the method of prep. of the sensitive layers. A trace of moisture destroys the dichroism. The dyes are not always sensitive in both gelatin and collodion emulsions. The majority of the dyes show no certain double refraction; a few dyes (all yellow), showing dichroism in both emulsions, also show strong double refraction in one emulsion only. The effect is reversible by exposure to light polarised in the plane at right angles to that of the initial exposure.

J. L.

Effect of intensity and underlying fogs on the latent image. F. E. POINDEXTER and L. E. JAMES (J. Opt. Soc. Amer., 1932, 22, 525—536).—Using fast plates, reciprocity failure is greatest for low intensities of illumination. Exposure to low-intensity white light after exposure to a stronger white light, or exposure to white light after red light, is more efficient than the reverse order of exposures. This effect is not found when using two intensities of the same coloured light, in the case of certain narrow bands of green and red light. These results are discussed in support of the photomechanical (crystal shattering) hypothesis of the formation of the latent image. No change in the latent image with the time between exposure and development has been found.

J. L.

Photographic emulsion; variables in sensitisation by dyes. B. H. CARROLL and D. HUBBARD (Bur. Stand. J. Res., 1932, 9, 529—545).—The relative spectral sensitisation of photographic emulsions by dyes (erythrosin, pinacyanol, pinaverdol, and pinaflavol) increases slowly with the concn. of the dye and is affected only slightly by the formation of

sensitivity nuclei (e.g., from allylthiocarbamide), which increase greatly the abs. sensitivity to any wave-length. The effect of $[H^+]$ is sp. for the dye and is $<$ that of $[Ag^+]$. In general, sensitisation increases with increasing $[Ag^+]$; sp. effects are explained by supposing that spectral sensitisation depends on adsorption of the ion of the dye by the oppositely-charged ion of the $AgCl$ lattice. Changes in adsorption of basic dyes may be sufficient to counteract the general trend when a certain excess of Ag^+ is reached.

E. S. H.

Action of ultra-violet light on ethane. W. KEMULA, S. MRAZEK, and S. TOŁŁOCZKO (Chem. Listy, 1932, 26, 466—473).— C_2H_6 yields C_4H_{10} , C_6H_{14} , and C_8H_{18} , together with traces of CH_4 , on irradiation with ultra-violet light in presence of Hg vapour. The proportion of C_4H_{10} in the product varies directly with the rate of flow and the pressure, and inversely with the temp. of the receiver. Both the linkings C-C and C-H undergo activation; the rate of activation is independent of the pressure and of the rate of flow, but depends exclusively on the intensity of irradiation.

R. T.

Oxidation of solutions of iodoform. R. DUBRISAY and G. EMSCHWILLER (Compt. rend., 1932, 195, 660—662).—A C_6H_6 solution of CHI_3 exposed to light is oxidised with formation of a little I and HI . Addition of small amounts of these substances to a solution kept in the dark produces the same result, thus explaining the photochemical after-effect. HI may be replaced by other mineral acids, but not by $AcOH$. In such solution with addition of HCl and I there is a varying period of induction, due probably to impurities in the solvent. Once started the reaction proceeds at a rate varying directly with $[CHI_3]$ and $[HCl]$, inversely with $[I]$. The nature of the solvent has much effect on the rate; oxidation occurs in C_6H_6 , C_6H_{14} , CCl_4 , and $COMc_2$, but not in Et_2O , CS_2 , or $PhMe$. Addition of certain substances, e.g., $PhOH$ or quinol, checks or inhibits oxidation (cf. A., 1925, ii, 595).

C. A. S.

Chlorine-sensitised photo-oxidation of tetrachloroethylene in carbon tetrachloride solution. R. G. DICKINSON and J. A. LEERMAKERS (J. Amer. Chem. Soc., 1932, 54, 3852—3862).—The photochemical chlorination of C_2Cl_4 in CCl_4 is strongly inhibited by O_2 . In presence of both O_2 and Cl_2 photosensitised oxidation to CCl_3COCl (87%) and $COCl_2$ occurs. With radiation of wave-length 4358 Å. the rate of oxidation in a uniformly illuminated layer is proportional to the first power of the intensity of the incident radiation and to the first power of $[Cl_2]$, is independent of $[O_2]$, and varies only slightly with $[C_2Cl_4]$, unless this is very high. The rate of oxidation has been measured at 3°, 20°, and 36°; the temp. coeff. of the yield is 1.20. The quantum yields have been determined.

L. K. (c)

Hydrolysis of acetone in ultra-violet light. M. QURESHI and N. A. TAHIR (J. Physical Chem., 1932, 36, 2670—2673).—The quantum efficiency varies from 0.13 to 0.14, for concns. of 0.05—0.5M. The ratio of the efficiencies at 30° and 40° is 1.41. The temp. coeff. is 1.52. The rate of hydrolysis is directly proportional to the intensity.

I. J. P. (c)

Photolysis of chloropicrin in aqueous solution. E. V. ALEXEEVSKI (J. Gen. Chem. Russ., 1932, 2, 341—344).—Aq. CCl_3NO_2 is decomposed by X-rays, and by voltaic arc and quartz-Hg vapour lamp illumination.

R. T.

Sensitised photolysis of azo-compounds by zinc oxide. I. FUKUSHIMA, M. HORIO, and M. OHMORI (J. Soc. Chem. Ind. Japan, 1932, 35, 398—399B).—In $EtOH-H_2O$ solution azobenzene in presence of ZnO is reduced photochemically almost quantitatively to hydrazobenzene in the absence of O_2 , but no detectable change occurs in presence of O_2 . Crystal-scarlet and *pp'*-hydroxyazobenzene, however, show simultaneous oxidation and reduction in light, the reaction being more rapid in presence of O_2 .

J. W. S.

Testing materials with γ -rays. N. RIEHL (Z. Elektrochem., 1932, 38, 548—549).—With 30 mg. of Ra or meso-Th and a distance of 30 cm. between the prep. and the plate an exposure of 2 (16) hr. is sufficient with a thickness of 10 (80) mm. of Fe; air inclusions totalling 1.5 (3) mm. may be detected in a thickness of 10 (80) mm. The method will not detect hair cracks etc. It does not require complicated apparatus, and has other advantages over the X-ray method when dealing with thick castings or dense materials (Pb).

H. F. G.

Effect of supersonic radiation on bromothymol-blue. A. R. OLSON and N. B. GARDEN (J. Amer. Chem. Soc., 1932, 54, 3617—3620; cf. A., 1929, 523; this vol., 480).—The inhomogeneity of commercial bromothymol-blue is responsible for conflicting reports on the effect of supersonic radiations. Proof is given that $[H^+]$ changes on destruction of the indicator.

H. F. J. (c)

Behaviour of a grainless emulsion towards α -particles. M. BLAU and H. WANBACHER (Monatsh., 1932, 61, 99—106).—The sensitivity of a "grainless" (Luppo-Cramer) $AgBr$ emulsion to α -particles, as measured by the rate of darkening on exposure, is much less than is expected from its sensitivity to visible light and is not proportional to the intensity of radiation. Contrary to expectation, the emulsion is desensitised by $NaNO_2$ and, to a smaller extent, by $NaHSO_3$, but is sensitised normally by NaN_3 . It is suggested that the strong ionising action of the α -particles may lead not only to a photochemical decomp. of the $NaNO_2$, but also to formation of Ag^+ from the Ag set free and combination of this with NO_2^- or O ions.

H. A. P.

Preparation of atomic hydrogen for organic preparative purposes. H. KROEPFELIN and E. VOGEL (Naturwiss., 1932, 45, 821).—4 litres per hr. of strongly activated H_2 may be obtained with the apparatus described. Activation is effected by means of a heated W spiral.

D. R. D.

Iodochlorides of the alkali and alkaline-earth metals; structure and constitution. M. G. DE CELIS and E. MOLES (Anal. Fis. Quím., 1932, 30, 540—551).— KCl_4I may be obtained in good yield by passing Cl_2 through a slightly acidified mixture of KCl (9 g.), H_2O (5 g.), and I (10 g.) at 60° until all the I has dissolved; the solution is then heated

at 70°, when crystals separate on continuing the passage of Cl_2 . $\text{NaCl}_4\text{I} \cdot 2\text{H}_2\text{O}$ and $\text{LiCl}_4\text{I} \cdot 4\text{H}_2\text{O}$, and the Ca, Sr, and Mg salts (all $+8\text{H}_2\text{O}$) may be prepared by the same procedure. The d of these compounds have been determined; the mol. vols. conform to the additive law ($\text{MCl}_4 + \text{ICl}_3 + \gamma\text{H}_2\text{O}$). H. F. G.

Oxidation of aqueous alkali sulphite solution by cupric salt in presence of pyridine. P. BAUMGARTEN (Ber., 1932, 65, [B], 1637—1645).—Oxidation of alkali sulphite solution by CuSO_4 in presence of $\text{C}_5\text{H}_5\text{N}$ affords a 60% yield of *N*-pyridiniumsulphonic acid (I), $2\text{Cu}^{++} + \text{SO}_3^{--} + \text{C}_5\text{H}_5\text{N} = 2\text{Cu}^+ + \text{C}_5\text{H}_5\text{N}^+ - \text{SO}_3\text{O}$. About 30% of sulphite is converted into sulphate, $2\text{Cu}^{++} + \text{SO}_3^{--} + \text{H}_2\text{O} = 2\text{Cu}^+ + \text{H}_2\text{SO}_4$, and the remaining 10% into dithionate, $2\text{SO}_3^{--} + 2\text{Cu}^{++} = \text{S}_2\text{O}_6^{--} + 2\text{Cu}^+$. Reaction is quant. with CuSO_4 and Na_2SO_3 in the ratio 2 : 1. (I) is determined by transformation by NaOH into the Na salt of glutacetaldehyde (converted into the corresponding dianil hydrochloride) and $\text{NH}_2 \cdot \text{SO}_3\text{H}$ (determined as H_2SO_4 after treatment with HNO_3) or by decomp. with NH_3 into $\text{C}_5\text{H}_5\text{N}$ and $\text{NH}_2 \cdot \text{SO}_3\text{NH}_4$ (determined as BaSO_4). The formation of SO_3 as a step in the oxidation is postulated. H. W.

Polyiodides of rubidium. I. Iodine and rubidium iodide. T. R. BRIGGS and E. S. PATTERSON (J. Physical Chem., 1932, 36, 2621—2624; cf. A., 1930, 1521, 1522).—In the system $\text{RbI}-\text{I}_2$ from 60° to the b.p. of the saturated liquid phase (238°) the only solid phases are I_2 , RbI , and RbI_3 (m.p., incongruent, 188°); there is no indication of the existence of higher polyiodides. L. F. A. (c)

Possibility of following recrystallisation of silver by colour reaction with ferric chloride. Properties of silver chloride layer formed by superficial action of ferric chloride on silver. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1932, 61, 189—198, 199—205).—Immersion of Ag sheet in aq. FeCl_3 (20%) results in the formation of a coloured film of AgCl (identified by m.p., solubility in $\text{Na}_2\text{S}_2\text{O}_3$, NH_3 , etc.), accompanied by an increase in wt. which reaches a max. in a few sec. The film, which can be removed by HNO_3 , is stable in diffused daylight, but is darkened by direct sunlight or ultra-violet light to a brownish-grey independent of its original colour; this change is due to decomp. into Ag and Cl_2 . It is also reduced to Ag by base metals. The colour and wt. of the film are influenced markedly by pre-treatment (heat or cold-working) of the metal. Min. brightness occurs with previous heating at 100° or 600—650°, and the wt. of AgCl film formed under comparable conditions falls rapidly as the temp. of pre-treatment is raised from 500° to the m.p. Etching with HNO_3 (d 1.33) before immersion into FeCl_3 gives a brighter shade if treatment has been carried out below 660°, and otherwise a duller shade. Cryst. Ag, like cold-worked, gives deeper shades. It is suggested that the variations in colour are a function of size of grain and, to some extent, of orientation of the crystallites. H. A. P.

Ammonium, potassium, and sodium silver thiosulphates. III. Sodium silver thiosulphate. G. SPACU and J. G. MURGULESCU (Z. anorg. Chem.,

1932, 208, 157—162; cf. this vol., 1007).—The existence of the following compounds has been established by potentiometric titration of $\text{Na}_2\text{S}_2\text{O}_3$ with AgNO_3 , supplemented by analyses: $[\text{Ag}_4(\text{S}_2\text{O}_3)_3]\text{Na}_2 \cdot 4\text{H}_2\text{O}$; $[\text{AgS}_2\text{O}_3]\text{Na}$; $[\text{AgS}_2\text{O}_3]\text{Na} \cdot \text{H}_2\text{O}$; $[\text{Ag}_2(\text{S}_2\text{O}_3)_3]\text{Na}_4 \cdot 2\text{H}_2\text{O}$; $[\text{Ag}(\text{S}_2\text{O}_3)_2]\text{Na}_3 \cdot 2\text{H}_2\text{O}$. The second and fourth are not new. F. L. U.

Silver ferrites. VI. Mechanism of formation of Bohm's goethite and influence of hydrogen concentration on the ageing of orthoferric hydroxide at high temperatures. A. KRAUSE, H. LAKOSCIUKÓWNA, and J. CICHOWSKI (Z. anorg. Chem., 1932, 208, 282—292; cf. this vol., 805).— $\text{Fe}(\text{OH})_3$ is insol. in 2*N*- NaOH or KOH at temp. up to 150°, but > 0.2 g. of orthoferric hydroxide, α - or γ - FeOOH is dissolved by 100 c.c. of 18*N*- NaOH at its b.p. On cooling, a white cryst. Na ferrite separates. Hydrolysis occurs on dilution and $\text{Fe}(\text{OH})_3$ is pptd. Conc. solutions of KOH dissolve only traces of the hydroxide, and the solutions are unstable. Products of hydrolysis of Na ferrite were proved by the Ag ferrite method to be polyorthohydroxides. Dehydration is greatly influenced by $[\text{H}^+]$, and is most marked in presence of 0.01*N*- NaOH . The mechanism of ageing of the orthohydroxide is discussed. F. L. U.

New hydrates of magnesium perchlorate. Their structural relation to known forms of hydrated perchloric acids and properties as intensive dehydrating agents. G. F. SMITH, O. W. REES, and V. R. HARDY (J. Amer. Chem. Soc., 1932, 54, 3513—3523).—Di- and tetra-aquo-perchlorates of Mg are described. The heats of hydration of the Mg perchlorates have been measured. That of the anhyd. salt is 33,000 g.-cal. per mol. X-Ray powder diagrams are different for each hydrate. H. F. J. (c)

Preparation of phosphorescent substances. V. Calcium, strontium, and barium sulphides. N. F. ZHIROV (J. Appl. Chem., Russia, 1932, 5, 177—192).—The use of the following secondary solvents has been investigated: SrWO_4 shifts the spectrum towards the red ($\text{CaS} > \text{SrS} > \text{BaS}$), the intensity being max. at 25% SrWO_4 ; BaWO_4 is less satisfactory ($\text{Ba} > \text{Sr} > \text{Ca}$); MgWO_4 shifts it towards the violet and increases the intensity ($\text{Sr} > \text{Ba} > \text{Ca}$); BeWO_4 shifts slightly towards the violet ($\text{Sr} > \text{Ba} > \text{Ca}$) and increases the intensity ($\text{Sr} > \text{Ca} > \text{Ba}$); $\text{Al}_2(\text{WO}_4)_3$ is valueless; $\text{Ca}_3(\text{PO}_4)_2$ shifts towards the violet ($\text{Ba} > \text{Sr} > \text{Ca}$), and $\text{Sr}_3(\text{PO}_4)_2$ ($\text{Ca} > \text{Ba} > \text{Sr}$) and $\text{Ba}_3(\text{PO}_4)_2$ ($\text{Sr} > \text{Ba} = \text{Ca}$) towards the red. The optimal concn. of phosphates is 20—50%. CH. ABS.

Molecular transformations of calcium sulphate at high temperatures. P. N. LASCHTSCHENKO and A. I. MOROZOVA (J. Appl. Chem., Russia, 1932, 5, 15—24).—At 450° CaSO_4 loses its ability to combine with H_2O , and at $> 650^\circ$ it is converted into a form different from anhydrite. Dissociation commences at 1020—1080°. CH. ABS.

Reaction of the alkaline-earth metals with nitrogen. A. VON ANTROPOFF [with H. KLINGEBIEL and K. H. KRÜGER] (Z. Elektrochem., 1932, 38,

588—589).—Na, and probably also NaOH, in Ca accelerates the reaction with N_2 , not catalytically, but by its action in converting the Ca_3N_2 film into a porous form. Microscopical observations show the Na droplets to be absorbed by the Ca_3N_2 film, with the production of yellowish-brown rings and cracks in the film. Traces of A retard the reaction, as the A becomes conc. in the pores of the Ca_3N_2 , but after evacuating the vessel the initial velocity is readily reattained; Na vapour produces a similar effect. Ba and Sr exhibit no reduction of reactivity towards N_2 at high temp., and the same is true of the reactivity of Ca towards H_2 . H. F. G.

Calcium phosphates and silicophosphates. F. KORBER and G. TROMEL (Z. Elektrochem., 1932, 38, 578—582).—Largely a review of published work. Pure $Ca_3P_2O_8$ and $Ca_4P_2O_9$ have been prepared. Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is extremely stable, being formed in moist air at 1100° , and by pptn. from aq. solution. In Ca-rich mixtures containing CaO , P_2O_5 , and SiO_2 , the compounds $9CaO, P_2O_5, 3SiO_2$ and $5CaO, P_2O_5, SiO_2$ exist at high temp.; α - $3CaO, P_2O_5$ exhibits an extended miscibility region in the ternary diagram. H. F. G.

Calcium phosphates and apatite. A. SCHLEEDÉ, W. SCHMIDT, and H. KINDT (Z. Elektrochem., 1932, 38, 633—641).—On prolonged treatment with H_2O , di-, tri-, and tetra-calcium phosphates yield hydroxyapatite, $3Ca_3(PO_4)_2, Ca(OH)_2$. $5CaO, P_2O_5, SiO_2$, Thomas meal, and Rhenania phosphate, on the other hand, hydrolyse only very slowly. Practically all natural Ca phosphates are of the apatite structure. The X-ray diagram of $Ca_3(PO_4)_2$ prepared by pptn. exhibits the lines of apatite, and, less strongly, those of $CaHPO_4$, but after heating the material to 600 — 800° a characteristic diagram is obtained. Tetra-calcium phosphate of definite structure is obtainable only by rapid crystallisation from the fused state; slow cooling, in presence of H_2O vapour, results in the formation of hydroxyapatite and CaO ; $3Ca_3(PO_4)_2, CaO$ is not formed. Pure $3Ca_3(PO_4)_2, Ca(OH)_2$ may be prepared by boiling $Ca_3(PO_4)_2$ with $0.5N$ -KOH for many hr. and heating the washed product at 900° ; the temp. of decomp. into tri- and tetra-phosphate is $>1500^\circ$. H. F. G.

Hydrothermal synthesis of calcium aluminates and silicates from lime and alumina or kaolin. III. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 394—398B).—The hydrothermal reactions between CaO and raw or calcined kaolin in different proportions have been investigated comparatively under various conditions of pressure, temp., and time. J. W. S.

Effect of alkaline media on crystallisation of calcium aluminates and on the setting of aluminous cements. SEAILLES (Compt. rend., 1932, 195, 662—664).— Al_2O_3 and CaO in solution form $3CaO, Al_2O_3, nH_2O$ or $4CaO, Al_2O_3, 12H_2O$ according as the p_H is $>$ or < 12 , irrespective of the nature of the base present, the action of CaO not being sp. (cf. B., 1929, 173; A., 1930, 872). The detrimental effect of the presence of a small amount of CaO in aluminous cements is due to rapid conversion, when

p_H is > 12 , of the anhyd. CaO, Al_2O_3 into $4CaO, Al_2O_3, 12H_2O$ with pptn. of Al_2O_3 , a reaction occurring much more rapidly than the re-formation of CaO, Al_2O_3 . C. A. S.

Double salts of cadmium ferricyanide. F. ČUTA (Coll. Czech. Chem. Comm., 1932, 4, 400—411; cf. A., 1929, 1407).—The solubility of $Zn_3[Fe(CN)_6]_2$ and $Cd_3[Fe(CN)_6]_2$ in solutions of alkali chlorides is explained by supposing that the less dissociated $ZnCl_2$ and $CdCl_2$ liberated by double decomp. are held as complexes by the Cl^- . The following compounds are described: $CdKFe(CN)_6, 2KCl, 5H_2O$;

$CdNH_4Fe(CN)_6, 2NH_4Cl, 1.5H_2O$;

$LiCd_2[Fe(CN)_6]_3, 16H_2O$;

$Na_2Cd_5[Fe(CN)_6]_4, 20H_2O$;

$NH_4Cd_4[Fe(CN)_6]_3, NH_4Cl, 13H_2O$. J. W. S.

Action of carbon dioxide on barium at the ordinary temperature. P. REMY-GENNETE (Bull. Soc. chim., 1932, [iv], 51, 1029—1035).—When kept in an atm. of dry CO_2 , Ba is attacked superficially, owing to the reaction $5Ba + 2CO_2 = BaC_2 + 4BaO$. Ba may be preserved in vac. or in an atm. of A.

D. R. D.

Barium radium salts of high emanation. F. STRASSMANN (Z. Elektrochem., 1932, 38, 544).—The evolution of emanation from Ba salts containing Ra is not governed solely by the sp. surface, but varies also with the structure of the salt; thus for insol. fatty acid salts of large surface it increases with increase of the chain length. Widely differing results are obtained with substituted fatty acid salts, especially with cyclic compounds. For homologous and isomeric compounds the effect increases with decrease of d , whilst the hardness of the crystals also plays a part. Structure is, nevertheless, the most important factor. H. F. G.

Radiochemical methods in chemistry, physics, and biology. G. VON HEVESY (Z. Elektrochem., 1932, 38, 504—511).—A review, dealing particularly with applications of radioactive indicators. From measurements of the conductivity of PbI_2 , in conjunction with diffusion experiments, it is shown that at low temp. ($< 270^\circ$) the current is carried primarily by the I^- , but at higher temp. by the Pb^{++} . The heat of activation of the movement of the Pb ions in the lattice, calc. from measurements of the rate of diffusion, is 27 kg.-cal. per mol. H. F. G.

Action of ammonia and certain organic bases on calomel. R. VOYNNET (J. Pharm. Chim., 1932, [viii], 16, 344—350).— Hg_2Cl_2 is decomposed by NH_3 and most amines or their hydrochlorides with the formation of Hg and $HgCl_2$. The latter salt then combines with the reagent. Compounds with the bases indicated or their hydrochlorides have been obtained: $2CH_3Ph, NH_2, HCl, HgCl_2$; novocaine, $2C_{13}H_{27}O_2N_2, HCl, HgCl_2$; $NPhMe_2, HCl, HgCl_2$; cocaine, $C_{17}H_{21}O_4N, HCl, HgCl_2$; $3NH_2Ph, 2HgCl_2$ and $2NH_2Ph, HCl, HgCl_2$; $3C_5H_5N, 2HgCl_2$. The same compound is not obtained in all cases by the direct action of $HgCl_2$ on the base. NH_3 gives the known compound NH_2HgCl , whilst NH_4Cl gives a complex compound of Hg, Cl, and NH_3 , and not $HgCl_2$ as generally stated. The compound is sol. and gives the

reactions of Hg^{++} salts. The readiness with which the reaction takes place is less the less is the alkalinity of the base. The bearing of these reactions on the medicinal use of Hg_2Cl_2 is discussed. M. S. B.

Additive compounds of boron trichloride. A. STIEBER (Compt. rend., 1932, 195, 610—611).—On mixing BCl_3 and AsH_3 at -80° , or by passing H_2 through AsH_3 into BCl_3 at that temp., prisms of $\text{BCl}_3\cdot\text{AsH}_3$ are obtained; this dissociates at -40° , or if kept in a sealed tube at room temp. decomposes into BCl_3 , As, and H_2 . $\text{BCl}_3\cdot\text{PCl}_3$ is similarly obtained by the first method as a white solid which can be sublimed in needles, and reacts with COMe_2 to form a solid or a viscous liquid, according to temp. C. A. S.

Formation of the spinel Al_2ZnO_4 by reaction in the solid state. K. HILD (Z. physikal. Chem., 1932, 161, 305—314).—In the formation of the spinel by reaction of ZnO with Al_2O_3 reaction sets in at the interface at about 975° . Above about 1100° the magnitude and variation with temp. of the reaction velocity depend on the rate of diffusion of ZnO through the spinel. R. C.

Nitrogen compounds of gallium. I. Ammonates of gallium tribromide and gallium tri-iodide. II. Gallium trifluoride trihydrate and its reaction with ammonia. W. C. JOHNSON and J. B. PARSONS. III. Gallic nitride. W. C. JOHNSON, J. B. PARSONS, and M. C. CREW (J. Amer. Chem. Soc., 1932, 54, 2588—2595, 2651—2654).—I, II. Interaction of the anhyd. halides with liquid NH_3 gives the hexammonates, $\text{GaBr}_3\cdot 6\text{NH}_3$ and $\text{GaI}_3\cdot 6\text{NH}_3$, in which the NH_3 is replaceable by H_2O . $\text{GaF}_3\cdot 3\text{H}_2\text{O}$, a white powder, forms $\text{GaF}_3\cdot \text{H}_2\text{O}\cdot \text{NH}_3$ with liquid NH_3 .

III. Gallic nitride, GaN , obtained by interaction of NH_3 with Ga at 900° , sublimes above 800° and reacts with O_2 above 900° , forming Ga_2O_3 . L. F. A. (c)

Purification of carbon for spectroscopic purposes. G. HEYNE (Angew. Chem., 1932, 45, 612).—Very pure C is obtained by heating the material at 2000° in Cl_2 or in a $\text{N}_2\text{—CCl}_4$ mixture; the ultimate lines of B, and occasionally of Cu, alone are obtained in the spark spectrum. If heating at $2800\text{—}3000^\circ$ in $\text{N}_2\text{+H}_2$ is employed, lines of numerous other elements are observed. H. F. G.

Silicon hydride, monatomic or triatomic hydrogen. A. B. VAN CLEAVE and A. C. GRUBB (J. Physical Chem., 1932, 36, 2817—2818).—Polemic (cf. Schultze, this vol., 107). E. S. H.

Silicon fluorochlorides. W. C. SCHUMB and E. L. GAMBLE (J. Amer. Chem. Soc., 1932, 54, 3943—3949; cf. this vol., 482).—The compounds SiF_3Cl , b.p. -70.0° , m.p. -138° , and SiF_2Cl_2 , b.p. -31.7° , m.p. -144° , have been prepared by interaction of SiF_4 and Cl_2 , and the v.p. at -86° to -58° and at -78° to 16° , respectively, measured. They are readily hydrolysed to HCl , HF , H_4SiO_4 , and H_2SiF_6 . Indications of the existence of SiFCl_3 have been obtained. L. K. (c)

Modifications of lead chromate. H. WAGNER, R. HAUG, and M. ZIPFEL (Z. anorg. Chem., 1932, 208, 249—254; cf. this vol., 351).—Monoclinic PbCrO_4 free from the rhombic modification can be

prepared by pptg. an inorg. Pb salt with a large excess of CrO_4^{--} at $60\text{—}100^\circ$. The tetragonal variety, obtainable pure only by pyrogenic methods, can be prepared in the form of mixed crystals containing PbSO_4 and PbMoO_4 by pptn. A no. of mixed crystals with PbCrO_4 are described. X-Ray diagrams are given. F. L. U.

Preparation of active thorium precipitates. P. M. WOLF and N. RIEHL (Z. Elektrochem., 1932, 38, 543—544).—By employing a specially prepared ash-free C to adsorb the emanation, and depositing the active ppt. electrochemically on Pt by a method devised by Erbacher (unpublished) very pure Th-B preps. may be obtained in 75% yield. H. F. G.

Rediscovery of nitryl chloride. W. A. NOYES (J. Amer. Chem. Soc., 1932, 54, 3615—3617).—Schumacher and Sprenger's method of prep. (A., 1929, 1155) is the best. H. F. J. (c)

Reactions of compounds with even numbers of electrons. Nitrogen trichloride and nitrogen tetroxide. W. A. NOYES (J. Amer. Chem. Soc., 1932, 54, 3612—3614; cf. A., 1931, 52).—The interaction of NCl_3 dissolved in CHCl_3 and N_2O_4 at 0° to -35° gives N_2 , O_2 , N_2O , Cl_2 , NO_2Cl , and NOCl . The formation of NO is explained by supposing an initial covalency reaction in which the positive nitric oxide ion combines with the negative dichloride ion to form the same dichlorodinitrogen oxide which is formed by the interaction of NO and NCl_3 . N_2O is formed from this by the loss of Cl_2 . H. F. J. (c)

Phosphorus bromochlorides. T. MIELOBEDZKI (Chem. Listy, 1932, 26, 458—461).—A résumé of the work of the author and his collaborators on this subject. R. T.

Oxidation of phosphine by atmospheric oxygen in presence of hydrogen. I. N. BUSCHMAKIN, A. A. VEDENSKI, and A. V. FROST (J. Gen. Chem. Russ., 1932, 2, 415—420).— PH_3 is quantitatively converted at 300° into H_3PO_3 and H_3PO_4 by O_2 in presence of H_2 . Explosion does not take place if the proportion of PH_3 to H_2 is $< 1:11$ and if the PH_3 is free from traces of P or P_2H_4 . At 20° the reaction takes several days for completion, the velocity being proportional to the partial O_2 pressure, but independent of the partial PH_3 , H_2 , or N_2 pressures. R. T.

Reactions of vanadium carbide. S. E. OLDEHAM and W. P. FISHEL (J. Amer. Chem. Soc., 1932, 54, 3610—3612).—With gaseous HCl at 750° it forms CH_4 , H_2 , VCl_2 , and VCl_3 . It is insol. in aq. HCl , but sol. in hot oxidising acids, forming hydrated V_2O_5 . H. F. J. (c)

Preparation of pure hydrogen sulphide; system hydrogen sulphide-carbon dioxide in the interval $153\text{—}213^\circ$ abs. A. KLEMENC (Z. Elektrochem., 1932, 38, 592—595).—The only trustworthy method for the prep. of pure H_2S is that of direct synthesis; 100% yield may be obtained at a pumice surface at 600° . H_2S has m.p. -85.6° (lit. -82.9°), b.p. -60.7° , d_{100}^{100} 0.9883, d_{210}^{210} 0.9539; the v.p. has been determined between -66° and 120° . Calculation from the d of the synthetic H_2S yields 32.065 for the at. wt. of S, thus demonstrating

the purity of the material. Liquid H_2S and CO_2 are only partly miscible under 1 atm. total pressure; on cooling, the pure components separate. No compound is formed. The quadruple point is at -95.2° , 253.2 mm., and 9.79% CO_2 . H. F. G.

Preparation of dithionates by sulphonation of sulphites. P. BAUMGARTEN (Ber., 1932, 65, [B], 1645—1646).—Approx. 60% $\text{K}_2\text{S}_2\text{O}_7$ (17 g.) is added to $\text{K}_2\text{S}_2\text{O}_5$ (6.6 g.) and KHCO_3 (18 g.) in H_2O (75 c.c.) at 10° . After 0.5 hr. at 10° and 5 hr. at 20° the solution is heated, treated with excess of $\text{Ba}(\text{OH})_2$, and filtered. The filtrate when treated with CO_2 , filtered, and conc. yields $\text{K}_2\text{S}_2\text{O}_6$ in about 12% yield. Replacement of $\text{K}_2\text{S}_2\text{O}_7$ by *N*-pyridiniumsulphonic acid or trimethylsulphamic acid raises the yield to 80% or 92%, respectively. H. W.

Lead chamber process. II. Violet acid [SO_5NH_2]. (A). E. BERL and H. H. SAENGER. III. Violet acid. (B). E. BERL and K. WINNACKER (Z. anorg. Chem., 1932, 208, 113—123, 124—133; cf. B., 1931, 585).—II. Cathodic reduction of $\text{OH}\cdot\text{SO}_2\cdot\text{NO}_2$ dissolved in 98% H_2SO_4 gives rise to "violet acid" (SO_5NH_2), which is rapidly oxidised when the current is interrupted. It has also been made by allowing N_2O_4 and H_2O vapour to impinge on liquid SO_2 at -70° . When 100% H_2SO_4 or 15% oleum is in contact with NO at high pressure, violet acid is formed immediately. With 97% acid the action is slow, and with 85% undetectable.

III. A method of analysing violet acid has been devised and its formation from H_2SO_4 and NO studied. The proportion of H_2SO_4 transformed varies from 4% at 8 atm. to 59% at 190 atm. The reaction is reversible. The chemical behaviour of violet acid, which is regarded as an important intermediate product in the chamber process, is discussed. F. L. U.

Fluorine polyhalides. H. S. BOOTH, C. F. SWINEHART, and W. C. MORRIS (J. Physical Chem., 1932, 36, 2779—2788; cf. this vol., 823).—Structural formulae are suggested for compounds of the type MFICl_3 . E. S. H.

Dilute perchloric acid as oxidising agent. A. TRAVERS and SILICE (Compt. rend., 1932, 195, 709—710).—Dil. aq. HClO_4 oxidises under pressure at 260° . Thus whilst to oxidise Cr^{III} at the ordinary pressure < 65% acid is required, 20% acid acts rapidly at 260° in a sealed tube, and 5% acid effects partial oxidation. 65% aq. HClO_4 oxidises Cr^{III} but not Mn^{II} . C. A. S.

Transformation from rose to green manganous sulphide. G. LANDESEN (J. Physical Chem., 1932, 36, 2521—2522; cf. A., 1931, 1140).—Polemical. I. J. P. (c)

Transformation from rose to green manganous sulphide. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1932, 36, 2840—2841).—Polemical (cf. preceding abstract). E. S. H.

Reactions between hydriodic acid and highly insoluble compounds. E. R. CALEY (J. Amer. Chem. Soc., 1932, 54, 4112—4113; cf. this vol., 1100).—A note on the action of HI on the alkaline-earth sulphates, $\text{Cr}_2(\text{SO}_4)_3$, CrCl_3 , CrBr_3 , PbSO_4 ,

PbCrO_4 , Ag halides, and other complex insol. compounds. C. J. W. (c)

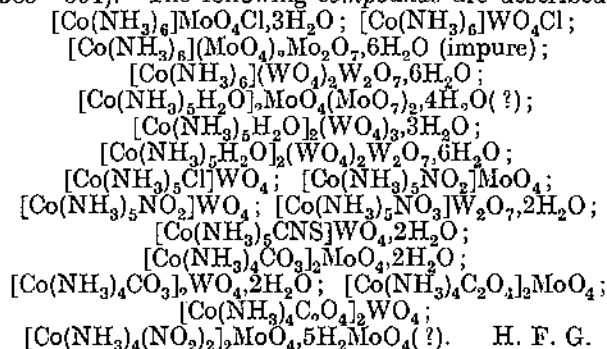
Metal carbonyls. W. HIEBER and co-workers. XVII. Volatile iron nitrosocarbonyl, $\text{Fe}(\text{CO})_5(\text{NO})$. J. S. ANDERSON (Z. anorg. Chem., 1932, 208, 238—248; cf. this vol., 920).— $\text{Fe}(\text{CO})_5(\text{NO})$ is formed by the action of NO on $\text{Fe}(\text{CO})_5$ dissolved in $\text{Fe}(\text{CO})_5$ at 60 – 100° , best at 95° . It can be separated from $\text{Fe}(\text{CO})_5$ by fractional distillation at -15° . It forms red crystals, m.p. 18.5° , d_4^{20} 1.56, b.p. (by extrapolation) 120° ; v.p. between 0° and 80° are given. The substance decomposes above 70° , and is rapidly oxidised by air or O_2 at room temp. Its relationship to other metal carbonyls is discussed. F. L. U.

Effect of hydrogen sulphide on corrosion of iron by salt solutions. S. C. BRITTON, T. P. HOAR, and U. R. EVANS.—See B., 1932, 1035.

Corrosive action of potassium (and other alkali) salt solutions on metals. I. Cast iron and lead. V. K. PERSHKE and G. I. CHUFAROV.—See B., 1932, 985.

Persulphatopentamminocobaltic sulphate. (MME.) R. DUVAL and C. DUVAL (Bull. Soc. chim., 1932, [iv], 51, 1035—1040).—A reply to Klément (A., 1931, 1140). Previous work on the above compound (A., 1931, 53) has been repeated and its structure confirmed. Klément's compound probably exists, but is distinct from that prepared by the authors. The Co in cobaltammines does not liberate I from aq. KI. D. R. D.

Molybdates and tungstates of complex cobaltammines. E. NEUSSER (Z. anorg. Chem., 1932, 207, 385—394).—The following compounds are described:



Analysis of small quantities of volatile material by determination of the vapour pressure and mol. wt. during distillation. B. G. ŠIMEK and R. KASSLER (J. Amer. Chem. Soc., 1932, 54, 3962—3969).—A method for ascertaining the behaviour of small quantities of material during distillation is described; temp. are measured in a tension eudiometer at 20 mm. It is possible to calculate the behaviour of a substance in a regular A.S.T.M. distillation or in the Kramer-Spülker method. The mean mol. wt. of the fractions may be determined simultaneously in the tension eudiometer. Tests are reported for C_6H_6 , 4 gasolines, and motor and commercial benzol. C. J. W. (b)

Systematic qualitative analysis of anions. E. W. FLOSDORF and C. M. HENRY (Ind. Eng. Chem.

[Anal.], 1932, 4, 434).—A scheme for the group separation of anions in qual. analysis is suggested.

E. S. H.

Systematic detection of anions. R. MONTEQUI (Anal. Fis. Quim., 1932, 30, 567—599).—Eight groups are recognised, containing respectively anions (1) directly detectable (CO_3^{2-} , OAc^-); (2) pptd. by KCl from AcOH solution; (3) pptd. by $\text{Zn}(\text{OAc})_2$ from AcOH solution; (4) pptd. from AcOH solution by $\text{Ca}(\text{OAc})_2$; (5) pptd. from neutral solution by Ca or Zn acetate; (6) pptd. by $\text{Ba}(\text{OAc})_2$ from AcOH solution; (7) pptd. by Ag^+ from HNO_3 solution; and (8) not already included. Full details are given of the group separations and of sp. tests for the anions.

H. F. G.

Radium rays as a means of examining solid materials. K. PRZIBRAM (Z. Elektrochem., 1932, 38, 490—496).—The coloration produced in certain salts by Becquerel-ray irradiation is of val. for identification, and serves also to provide information regarding the structure of the material. Application of the method to study of the recrystallisation velocity of compressed rock-salt shows that the velocity increases with increase of the degree of deformation, whilst the temp. coeff. diminishes. The inhibition of the recrystallisation by intensive irradiation indicates that the coloration involves those points which are primarily concerned with the beginning of the recrystallisation process.

H. F. G.

Rock sampling for chemical analysis. F. F. GROUT (Amer. J. Sci., 1932, [v], 24, 394—404).—Reasoned suggestions are made.

C. W. G.

Spectrographic detection of minute amounts [of elements]. W. SPATH (Monatsh., 1932, 61, 107—115).—An apparatus is described for the spectrographic detection of elements in which the following sensitivities were observed: (spark) 10^{-10} g. Cd, 10^{-10} g. Mn, 10^{-8} g. Tl, 10^{-7} g. Te, 10^{-7} g. As, 10^{-9} g. Li, 10^{-11} g. Sr; (arc) 10^{-10} g. Cd, 10^{-8} g. Mn, 10^{-9} g. Te, 10^{-9} g. Tl. The prep. of Ag sufficiently free from Cd for use as an electrode for its detection is described.

H. A. P.

Applications of the spectrograph in specific analysis and in the detection of vapours and suspended matter. F. WIRTH and E. GOLDSTEIN (Angew. Chem., 1932, 45, 641—646).—Details are given of the apparatus and procedure employed when using the quartz spectrograph in conjunction with the condensed W spark and the H discharge tube, and of the interpretation of the results. The determination of C_6H_6 , PhMe, etc. vapour in air by the direct method and by removal with EtOH is described in detail; 60—100 mg. of C_6H_6 per cu. m. of air may be detected. The sp. character of the results obtained by the spectrographic method, as compared with those given by refractometric and interferometric methods, is emphasised.

H. F. G.

Application of antimony and manganese electrodes to determination of $[\text{H}^+]$. I. I. SHUKOV and J. A. BOLTUNOV (J. Gen. Chem. Russ., 1932, 2, 407—414).—The p_{H} vals. of solutions containing org. acids as determined using Sb electrodes are considerably higher than when the H or quinhydrone electrode is used, whilst with Mn electrodes the

difference is so great as to render the results completely untrustworthy.

R. T.

Application of hydrogen and quinhydrone electrodes to mixed solvents. I. I. SHUKOV and I. G. VOROCHOBIN (J. Gen. Chem. Russ., 1932, 2, 399—406).—The p_{H} of buffer solutions containing EtOH, MeOH, or COMe_2 rises with the org. solvent content for both acid and alkaline solutions; this effect is not shown by glycerol. The p_{H} vals. given by H and glass electrodes are in all cases higher than those given by the quinhydrone electrode, which should not be applied to such solutions.

R. T.

Use of the antimony electrode in the determination of acidity. T. GYSINCK (Arch. Suikerind. Ned.-Indie, 1932, 711—749; Chem. Zentr., 1932, ii, 409).—Gentle stirring gives the most const. vals. Cast Sb electrodes are preferred; they give the most reproducible results shortly after prep. Sb deposited electrolytically on Pt wire rapidly loses reproducibility. p_{H} -c.m.f. curves consisted of two almost straight and practically parallel sections. Between p_{H} 7.12 and 8.17 there was an inflexion which might disappear with purer electrodes.

A. A. E.

Colorimetric determination of p_{H} of solutions containing chlorine or hypochlorites, and the stability of indicators. H. F. LEWIS and S. I. KUKOLICH.—See B., 1932, 1028.

Effect of manganese salts on acidimetric titrations in presence of methyl-orange. A. PERRET and A. M. KRAWCZYNSKI (Bull. Soc. chim., 1932, [iv], 51, 1014—1019).—On running aq. NaOH into an acid solution containing a Mn^{2+} salt and Me-orange, $\text{Mn}(\text{OH})_2$ is pptd. and oxidised by the air to manganous acid, which destroys the Me-orange. Titration in boiling solution in an atm. of H_2 inhibits this effect, but the best results are obtained by the addition of reducing agents, of which quinol is the most efficient. Co^{2+} does not interfere with Me-orange titrations.

D. R. D.

Detection of chloride in presence of cyanide. R. MONTEQUI and E. OTERO (Anal. Fis. Quim., 1932, 30, 564—566).—The reagent used is prepared by dissolving AgNO_3 (4.25 g.) and $\text{Hg}(\text{NO}_3)_2$ (2.7 g. $\text{HgO} + 10$ c.c. conc. HNO_3) in H_2O (to 50 c.c.); when it is added to a dil. solution containing Cl^- and CN^- , non-ionised $\text{Hg}(\text{CN})_2$ is formed, together with AgCl . The solution should contain $\pm 0.5\%$ of alkali cyanide, as otherwise an insol. complex is formed. The reagent will detect easily 0.2 mg. of NaCl in 5 c.c. of solution. It may be used in presence of $\text{Fe}(\text{CN})_6^{3-}$ and/or $\text{Fe}(\text{CN})_6^{4-}$, but preliminary pptn. with $2N\text{-Zn}(\text{OAc})_2$ is necessary.

H. F. G.

Micro-determination of perchlorate by titanous chloride. A. ROSENBERG (Z. anal. Chem., 1932, 90, 103—109).—The liquid is decomposed with sufficient conc. H_2SO_4 to give a 50% H_2SO_4 solution after addition of aq. TiCl_3 . When CO_2 has been allowed to pass for 15 min. a slight excess of 0.01N- FeCl_3 is added and the flask placed in boiling H_2O for 30 min. After cooling in ice- H_2O the solution is diluted with aq. CO_2 and, after addition of 5 c.c. of 40% KCNS, is titrated back with 0.01N- FeCl_3 . The

passage of CO_2 must be continued throughout the analysis. M. S. B.

Determination of iodine in cuprous iodide. A. ROUSSY.—See B., 1932, 980.

Use of metallic lithium in analysis of gases. Determination of nitrogen in inert gases. J. H. SEVERYNS, E. R. WILKINSON, and W. C. SCHUMB (Ind. Eng. Chem. [Anal.], 1932, 4, 371—373).—Molten Li reacts quantitatively with N_2 , O_2 , and H_2O vapour, giving non-volatile products. An apparatus which enables the purity of He to be calc. from the change in pressure when these gases are removed by electrically heated Li is described. E. S. H.

Selenium in determination of nitrogen by Kjeldahl method. J. TENNANT, H. L. HARRELL, and A. STULL (Ind. Eng. Chem. [Anal.], 1932, 4, 410).—Evidence is given to show that Se is a more efficient catalyst than CuSO_4 . E. S. H.

Detection of ammonia in the atmosphere. I. M. KORENMAN (Z. anal. Chem., 1932, 90, 115—118).—When filter-paper, soaked in a solution of certain freshly-diazotised amines, is exposed to air containing NH_3 , a colour is developed on the filter-paper. NH_2Ph , sulphanilic acid, benzidine, $\text{NHPh}\cdot\text{NH}_2$, Ursol DW and DS, α - and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, atoxyl, and *p*-nitroaniline (I) react; the sensitivity varies from 0.0025 mg. of NH_3 per litre for *p*-nitroaniline (red) to 0.07 mg. for α - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ (violet-red) and Ursol DS (rose-red). NPhEt_2 , NHPh_2 , m - $\text{C}_6\text{H}_4(\text{NH}_2)_2$, antipyrine, brucine, quinine, etc. do not react. Halogens inhibit the reaction, H_2S affects only Ursol DW, and SO_2 (I). $\text{C}_5\text{H}_5\text{N}$ has no effect on the reaction, but NH_2Ph or CH_2O inhibits it in the case of (I). M. S. B.

Microchemical reaction for ammonia and test for its presence in pyridine. I. M. KORENMAN (Z. anal. Chem., 1932, 90, 114—115).—If a little of a solution containing free NH_3 is placed at the bottom of a porcelain crucible covered with a glass from which hangs a drop of a solution containing a Cu salt and picric acid, characteristic greenish-yellow crystals of a compound of NH_3 , Cu, and picric acid can be observed under the microscope. The presence of $\text{C}_5\text{H}_5\text{N}$ does not interfere with the test. The limiting amount of NH_3 detected is 2 mg. M. S. B.

Simple apparatus for absorption of small amounts of gas: detection of nitric oxide with ferrous sulphate. K. TAUFEL and P. SADLER (Z. anal. Chem., 1932, 90, 20—23).—A micro-gas absorption apparatus suitable for the detection and determination of NH_3 , CO_2 , NO, etc. is described. For detection of traces of NO it is preferable to absorb the gas in conc. H_2SO_4 and then apply the brown ring test with FeSO_4 , rather than to absorb in FeSO_4 directly. J. W. S.

Polarographic studies with the dropping mercury cathode. XXVII. Electro-reduction and determination of nitrates and nitrites. M. TOKUOKA (Coll. Czech. Chem. Comm., 1932, 4, 444—455).—The reduction of nitrates and nitrites at the dropping Hg cathode has been studied polarographically from current-voltage curves. In neutral or

alkaline solution reduction occurs only in presence of bi- or ter-valent cations; in 0.1*N*- LaCl_3 the reduction potential is -1.2 volt (HgCl zero). SO_4^{2-} hinders the reaction. The increase of current caused by electro-reduction of NO_3^- is eight times the current depositing an equiv. amount of metallic cation. Hence NO_3^- takes up eight faradays to give NH_3 . The saturation currents due to reduction of NO_3^- and NO_2^- are proportional to their concn., whilst NO_2^- is decomposed by strong acids, yielding electro-reducible NO. Hence small quantities of NO_2^- and NO_3^- can be determined in this way. It is supposed that the strong field in the neighbourhood of the cathode splits the ions into elementary N^{5+} and N^{3+} ions, high-valency cations serving to drag the anions towards the cathode surface. J. W. S.

Diphenylbenzidine as a test for nitrates and nitrites. H. STROMBERG (Proc. Staff Mtgs. Mayo Clinic, 1932, 7, 254—256).—The specimen (free from proteins and Cl) is diluted and 1 c.c. (0.0002—0.0009 mg. N as NO_3^- or NO_2^-) is treated with 0.1 c.c. of NaCl solution (12.5 mg. per c.c.), 10 c.c. of the diphenylbenzidine solution (50 mg. in 200 c.c. H_2SO_4 diluted with 200 c.c. H_2O), and 10 c.c. of conc. H_2SO_4 . The glass-stoppered tubes are inverted twice, kept in ice for 20 min., allowed to reach room temp., and compared after 1.75 hr. with a standard (0.0005 mg. N as NO_3^-). CH. ABS.

Determination of phosphoric acid in the presence of pyrophosphoric acid. V. NJEGOVAN and V. MARJANOVIĆ (Chem. Listy, 1932, 26, 449—451).—The solution, containing 0.1—0.5 g. of P_2O_5 , is evaporated to dryness, and 5 c.c. each of H_2SO_4 and of saturated aq. MgSO_4 are added. The solution is then made alkaline to phenolphthalein by a mixture of conc. aq. NH_3 and 25% NH_4OAc , H_2O is added to 200 c.c., and, after heating 1 hr. at 100° , the cooled solution is filtered, and the residue of MgNH_4PO_4 is washed and ignited. An accuracy of 99.7% is obtained. R. T.

Phosphate determination in boiler water. A. SULFELAN.—See B., 1932, 963.

Determination of phosphoric acid with benzidine. F. UKRADIGA.—See B., 1932, 1027.

Identification of arsenic. M. SAUVÉ (Bull. Biol. Pharm., 1932, 280).—An apparatus is described for the identification of AsH_3 by means of the yellow stain obtained on paper moistened with aq. HgCl_2 . A. L.

Determination of arsenic. Iodometric acidimetric method. R. C. WILEY, J. P. BEWLEY, and R. IREY (Ind. Eng. Chem. [Anal.], 1932, 4, 396—397).—The As compound is converted into AsH_3 , which is absorbed by standard I solution. The residual I is titrated and the result checked by titrating the acids formed in the oxidation. It is possible to determine 0.00002 g. As. E. S. H.

Determination of boron spectroscopically. J. S. MCHARGUE and R. K. CALFEE (Ind. Eng. Chem. [Anal.], 1932, 4, 385—388).—The following procedure is suitable for determining the B content of plant and animal tissues. The material is ashed at or below 400° with excess of K_2CO_3 , and the ash dissolved in

aq. citric acid. B is converted into Me_3BO_3 by means of MeOH and H_3PO_4 , and the vapour is burned in O_2 in a special apparatus. The spectrum is viewed through a glass cell containing H_2O , to which a standard solution of KMnO_4 is added until the bright green band is eliminated. The method gives an accuracy of ± 0.0095 mg. on samples containing 0.05—0.3 mg. of B. E. S. H.

Displacement of end-point in titration of solutions of boric acid and mannitol-boric acid. F. L. HAHN, R. KLOCKMANN, and K. SCHULZ (Z. anorg. Chem., 1932, 208, 213—216; cf. A., 1928, 857).—The observation by van Liempt (A., 1920, ii, 331) that a very small proportion of mannitol (I) enables H_3BO_3 to be neutralised by the theoretical amount of NaOH was due to an error in determining the end-point. When due precautions are taken the excess alkali required decreases as the proportion of (I) increases. If CO_2 is present the amount of (I) necessary greatly exceeds its solubility, and better results are obtained with glycerol. F. L. U.

Determination of carbon dioxide in gas mixtures. Potentiometric method. P. W. WILSON, F. O. ORCUTT, and W. H. PETERSON (Ind. Eng. Chem. [Anal.], 1932, 4, 357—361).—The gas mixture is bubbled through about 10 c.c. of aq. Na_2CO_3 , the p_{H} of which is then determined by means of the glass electrode. The CO_2 is calc. from a calibration curve. The procedure is suitable for 0.03—7% CO_2 in the mixture and the error in rapid routine work is about 4%. Greater accuracy may be obtained by incorporating certain refinements. The method can be modified for use with a p_{H} colorimeter. E. S. H.

Apparatus for the determination of carbon dioxide. A. HANAK (Chem.-Ztg., 1932, 56, 672).—The apparatus comprises a conical decomp. flask (A) in the neck of which fits a bulb (B) for the dil. HCl , through the upper neck of which fits a second bulb (C) containing H_2SO_4 for drying the issuing gas. (C) has a long tube (D) passing through (B) into (A); the upper part of this tube terminates at the top of the inner bulb of (C), the lower end of which is provided with small holes to allow the gas to bubble through the acid from the inner to the outer bulb of (C). A small tube at the lower end of (D) communicates with a hole in the wall of (D) at the lower end of (B) so that by rotating (A) in one direction the HCl can be kept from running into (A) while the apparatus and contents are weighed and by rotating it in the other direction the HCl is allowed to fall on to the material being analysed. A. R. P.

Test paper for carbon disulphide. V. I. KUZNETZOV (Anilinokras. Prom., 1932, 2, No. 3, 1—2).—Paper treated with a solution of Cu or Co salt in excess of NHMe_2 , NH_4Et_2 , or $\text{C}_5\text{H}_{11}\text{N}$ becomes brown in presence of CS_2 or H_2S . For the detection of CS_2 in presence of H_2S a CN' solution is added, to exact decolorisation, to the Cu- NHMe_2 complex; this becomes yellow to brown with CS_2 , and remains colourless with H_2S , whilst with both the wet paper is coloured yellowish-green and becomes brown on

drying. The reagent detects 0.001 g. of CS_2 in 1 litre of air, and 1—2% of CS_2 in H_2S . CH. ABS.

New source of error in the separation of K_2PtCl_6 . R. STREBINGER and H. HOLZER (Z. anal. Chem., 1932, 90, 81—86).—In the analytical separation of K_2PtCl_6 by EtOH reduction takes place if the EtOH contains MeCHO . This is an important source of error in micro-analytical work where the amount of EtOH is relatively large. K_2PtI_6 , used in the colorimetric determination of Pt, is still more sensitive. The action is photochemical. M. S. B.

Visual conductivity titrations and measurements. G. JANDER and H. SCHORSTEIN (Angew. Chem., 1932, 45, 701—703).—With the aid of a sensitive a.c. galvanometer it is possible to titrate small amounts of substances in the presence of excess of electrolytes, e.g., 5 c.c. of 0.01N- NaI and 130 times as much NaNO_3 . Zn can be determined by adding to Na_2S and titrating excess of Na_2S with HCl . A. G.

Detection of silver in very dilute solutions by physical development. A. J. VELCULESCU (Z. anal. Chem., 1932, 90, 111—113).—One drop of very dil. aq. AgNO_3 to be tested is put on a marked spot on a piece of filter-paper, treated with 0.02M- KBr , and thoroughly washed, leaving the spot impregnated with AgBr . This is then treated with a developer of the following composition: 500 c.c. H_2O , 10 g. metol, and 50 g. citric acid, and to 50 c.c. of this mixture 2 c.c. of 0.1M- AgNO_3 are added immediately before use. The presence of AgBr on the filter-paper causes a considerable portion of Ag from the developer to be pptd. as metal, whether exposed to light or not. The limiting concn. which has been detected is 1 part in 10^7 , but it is possible that the dilution might be carried further. Free HNO_3 , but not H_2SO_4 , is detrimental. Pb has no effect even when its concn. is 2000 times that of Ag. Hg behaves similarly to Ag and so must be removed previously by heating. M. S. B.

Application of catalysis to the detection of certain cations. Silver and copper. Applications. G. DENIGES (Bull. Soc. chim., 1932, [iv], 51, 1096—1100).— 2×10^{-4} mg. of Ag^+ and 5×10^{-3} mg. of Cu^{++} in 10 c.c. of solution may be detected by the following tests, depending on their activity as catalysts in the oxidation of Mn^{++} to MnO_4^- . To 10 c.c. of the Ag solution are added 20 drops of H_2SO_4 , 2 drops of 0.4% $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, and 0.10 g. of $\text{K}_2\text{S}_2\text{O}_8$ or $\text{Na}_2\text{S}_2\text{O}_8$. On heating at 100° on a water-bath, the pink colour and characteristic absorption spectrum of MnO_4^- appear. Hg and Co produce a similar effect, but their catalytic activity is, respectively, 1/50 and 1/200 of that of Ag. The method may be applied to the detection of Ag in coinage etc., a minute drop of HNO_3 being placed on the metal and after 8—10 sec. washed off and the solution tested as above. The method can be used for the colorimetric determination of Ag. To test for Cu, to 10 c.c. of the solution are added 5 drops of 0.4% $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ and 5 drops of aq. NaOBr , prepared by dissolving 1 c.c. of Br in 30 c.c. of 3.3N- NaOH . The mixture is heated on the

water-bath for 2 min., cooled, and centrifuged to separate the MnO_2 ppt., when the colour of MnO_4^- can be seen in the clear solution. Ni and Co act similarly, but their activity is only 1/12 and 1/45, respectively, of that of Cu. The application to the analysis of natural waters and to the colorimetric determination of Cu is considered. D. R. D.

Composite reagent for calcium. G. J. COX and M. L. DODDS (Ind. Eng. Chem. [Anal.], 1932, 4, 361).— $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (200 g.) and NH_4Cl (500 g.) are dissolved in H_2O (3500 c.c.), and AcOH (1000 c.c.) and 0.4% Me-red (10 c.c.) are added, any ppt. formed being filtered off. The composite reagent is satisfactory for pptg. CaC_2O_4 from bone ash solutions. E. S. H.

Precipitation of calcium by potassium ferrocyanide. R. CHANDELLE (Bull. Soc. chim. Belg., 1932, 41, 420–429).—Ca salts give a ppt. on adding aq. $\text{K}_4\text{Fe}(\text{CN})_6$ in presence of a large excess of NH_4Cl or KCl . In the first case, the ppt. is $\text{Ca}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$; in the second, it is $\text{Ca}_2\text{Fe}(\text{CN})_6$. D. R. D.

Determination of radium in insoluble substances. A. KARL (Bull. Soc. chim., 1932, [iv], 51, 1023–1029).—The emanation method (this vol., 355) is described. D. R. D.

Beryllium. IV. Micro-qualitative analysis of beryllium. H. S. BOOTH and S. G. FRARY (J. Physical Chem., 1932, 36, 2641–2650).—Of existing micro-analytical methods, the K oxalate method is the most satisfactory, and the H_2PtCl_6 method satisfactory under certain conditions. The use of K malonate similarly to K oxalate, and of the basic acetate, recrystallised from glacial AcOH , as a confirmatory test are suggested. I. J. P. (c)

Rapid determination of small amounts of magnesium in presence of phosphates. W. E. THURN (Ind. Eng. Chem. [Anal.], 1932, 4, 426–427).—Mg is determined colorimetrically by the formation of a lake with curcumin in presence of NaOH . The colour is affected by PO_4^{3-} , but not by its amount; $\text{Ca}_3(\text{PO}_4)_2$ is dissolved, therefore, in the colour standard. E. S. H.

Determination of zinc in brass and other alloys by the oxalate-permanganate method. E. KNORRICK.—See B., 1932, 986.

Detection of cations of group IIb. A. SCHEINKMANN (Pharm. Zentr., 1932, 73, 681–682; cf. A., 1931, 1260).—The sulphides are dissolved in HCl and H_2O_2 , and Pb, Hg, and Bi pptd. with aq. NH_3 . The Pb and Hg are extracted with NH_4OAc and detected by the usual methods. The Bi in HNO_3 solution gives BiPO_4 with Na_2HPO_4 , or bismuthyl dichromate with $\text{K}_2\text{Cr}_2\text{O}_7$. The Na_2SnO_2 test for Bi is untrustworthy. Alternatively the $\text{Pb}(\text{OH})_2$, HgCINH_2 , and basic Bi salt are dissolved in NH_4OAc and AcOH . Pb is then detected as PbSO_4 , Hg with SnCl_2 , and Bi as above, $\text{K}_2\text{Cr}_2\text{O}_7$ being used only in the absence of Pb. Cd in a solution decolorised with KCN gives a yellow ring at its junction with an aq. H_2S layer. A. A. L.

Separation and determination of traces of lead in presence of small quantities of iron. J. H. HAMENCE (Analyst, 1932, 57, 622–626).—Fe is removed as $\text{Fe}(\text{CNS})_3$, which is extracted by equal vols. of Et_2O and amyl alcohol, and Pb is determined as PbS . If much SO_4 is present, Pb may be pptd. as PbSO_4 ; this is avoided by using smaller quantities or by the addition of NH_4OAc . NH_4 citrate is added to retain Ca in solution. T. McL.

Determination of thallium after oxidation with bromine. P. E. BROWNING (Ind. Eng. Chem. [Anal.], 1932, 4, 417).—Tl (0.1 mg. in 10 c.c.) can be detected by the dark coloration produced by adding Br and excess of NaOH . The presence of Fe, Mn, Co, or Ni interferes. The test may be made quant. by heating the ppt. at 150–200° and weighing as Ti_2O_3 . E. S. H.

[Copper zinc mercuriothiocyanate test for copper.] R. MONTEQUI (Anal. Fis. Quím., 1932, 30, 600).—A claim for priority. H. F. G.

Dry test for copper. B. BATSCHA (Z. physikal. Chem. Unterr., 1932, 45, 117–118; Chem. Zentr., 1932, ii, 411).—The manipulation of the borax bead test is discussed. A. A. E.

Determination of traces of mercury as comparable rings of mercuric iodide. A. DELAUNAY (Ann. Falsif., 1932, 25, 409–412).—Hg deposited on a brass or Au electrode is volatilised on to a cool portion of a hard glass tube (6 mm. diam.) in a current of air at a dull red heat. I is then passed over the Hg at 135–140° and the HgI_2 deposited in a further portion of the tube. Comparisons are made after the HgI_2 has turned red. T. McL.

Determination of metals in organic combination. D. L. TABERN and E. F. SHELBERG (Ind. Eng. Chem. [Anal.], 1932, 4, 401–403).—A mixture of $\text{H}_2\text{S}_2\text{O}_7$ and 30% H_2O_2 destroys rapidly all the org. matter in organometallic compounds of Hg, As, Sb, Bi, Au, Ag, and Ge. The metal is obtained in solution, generally as sulphate, and may be determined by the usual methods. E. S. H.

Separation of aluminium from zinc, using hydrazine carbonate. A. JILEK and J. VŘESTAL (Chem. Listy, 1932, 26, 497–503).—Al (> 0.1 g.) is doubly pptd. as double salt with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{CO}_3$, ignited, and weighed as Al_2O_3 . The mean error is $\pm 0.5\%$. R. T.

Separation of aluminium as phosphate in the presence of calcium phosphate, with special reference to the action of milk on aluminium. A. G. G. GWYER and N. D. PULLEN (Analyst, 1932, 57, 704–707).—A modification of Carnot's method is employed, the AlPO_4 being pptd. at p_{H} 4.0–4.5 in the presence of AcOH . Milk has no action on Al. T. McL.

Rapid analysis of manganate-permanganate mixtures. J. E. ORLOV (Z. anal. Chem., 1932, 90, 35–38).—The method suggested for analysis of mixtures containing KMnO_4 , K_2MnO_4 , MnO_2 , K_2CO_3 , and KOH consists in determination of (a) total oxidising constituents iodometrically; (b) of $\text{K}_2\text{CO}_3 + \text{KOH}$; (c) $\text{MnO}_4^- + \text{MnO}_4^{2-}$ by centrifuging with CaCl_2 and determining oxidising constituents in the

solution; (d) KOH by titration of alkali in the last solution; (e) the $\text{MnO}_4^-:\text{MnO}_4^{2-}$ ratio colorimetrically.

J. W. S.

Analytical chemistry of rhenium. VII. Detection and determination of small quantities of rhenium by the aid of potassium thiocyanate and stannous chloride. W. GEILMANN, F. W. WRIGGE, and F. WEIBKE (Z. anorg. Chem., 1932, 208, 217—224; cf. A., 1931, 328).—A yellow to orange-red coloration is produced when KCNS and SnCl_2 are added to a solution, acidified with HCl, containing a small quantity of a perrhenate. The colour can be conc. by extraction with Et_2O . The min. quantity of Re detectable is 5×10^{-7} g. in 10 c.c. The reaction has been used as the basis of a colorimetric method of determining Re, details of which are given.

F. L. U.

Analytical chemistry of rhenium. E. KRONMANN (Z. anal. Chem., 1932, 90, 31—34).—Re can be separated quantitatively from minerals by distillation of a conc. H_2SO_4 solution in a stream of air (for separation from W) or HCl (to separate from Mo). Apparatus is described.

J. W. S.

Iodometric determination of iron. A. V. FILOSOFOV and S. MELNIK (J. Appl. Chem., Russia, 1932, 5, 219—220).—2.7 g. KI per 0.1 g. Fe, and $\text{HCl} \geq 0.1N$ are recommended.

CH. ABS.

Determination and separation of cobalt as the cobaltic nitrosonaphthol compound. C. MAYR and F. FEIGL (Z. anal. Chem., 1932, 90, 15—19).—Co can be determined, even in presence of Ni, Zn, or Al, by pptn. with a 2% solution of 1-nitroso- β -naphthol in 50% AcOH. A solution containing 1—30 mg. Co as CoSO_4 , CoCl_2 , or $\text{Co(NO}_3)_2$ in 10—20 c.c. is made slightly acid and treated with 5—10 drops of "perhydrol" and then with 2N-NaOH until pptn. of Co(OH)_2 commences; 10—20 c.c. of AcOH are added, the ppt. is redissolved, and the solution diluted to 200 c.c. Co is pptd. by addition of 10—20 c.c. of the above reagent, the ppt. coagulated by boiling, and weighed in a Gooch crucible.

J. W. S.

Determination of cobalt, using dinitroresorcinol. O. TOMIČEK and K. KOMÁREK (Chem. Listy, 1932, 26, 515—520).—Pptn. of Co by Orndorff and Nichols' method (A., 1923, ii, 584) is not quant., and both the composition of the ppt. and the amount of Co remaining in solution depend on the conditions of pptn. and on the concn. of Co and of other substances present. Under certain conditions incomplete pptn. is masked by adsorption of dinitroresorcinol and alkali on the ppt., which ordinarily contains $\geq 80\%$ of Co dinitroresorcinol. Attempts at attaining quant. pptn. of Co by varying the conditions of reaction were unsuccessful.

R. T.

Spectro-identification of small quantities of nickel and chromium. A. J. DE A. GOUVEIA (Rev. Chim. pura appl., 1932, 5, 41—43; Chem. Zentr., 1932, ii, 412).—The detection of Ni (5476.9 Å.) is sensitive to 0.05% and that of Cr (5208.4, 5206.0, 5204.5 Å.) to 0.005% when SiO_2 is present.

A. A. E.

Volumetric determination of molybdenum by oxidation of quinque- to sexa-valent molyb-

denum by means of ceric sulphate or potassium permanganate. B. STEHLIK (Chem. Listy, 1932, 26, 533—537).—Mo is reduced to Mo^V by means of TiCl_3 , SnCl_2 , Pb, or Zn, 50% of conc. H_2SO_4 is added, and the hot solution is titrated with $\text{Ce(SO}_4)_2$ or KMnO_4 in presence of MnSO_4 and in an atm. of CO_2 , the end-point being determined potentiometrically.

R. T.

Colorimetric determination of traces of tungsten. F. FEIGL and P. KRUMHOLZ (Angew. Chem., 1932, 45, 674—675).—To 2 c.c. of the slightly alkaline tungstate solution (0.5—0.05N-NaOH) 5 drops of 25% KCNS solution are added, and 10% SnCl_2 (in conc. HCl) is added to make a total vol. of 5 c.c. The yellow colour is compared with a standard after 30 min. The error, when 10—100 microg. W is present, is about 3%. Molybdate, but not phosphate, interferes.

H. F. G.

Rapid method of dissolving lead alloys preparatory to determination of tin and antimony. B. S. EVANS.—See B., 1932, 941.

Separation of titanium from aluminium and certain elements of groups II and III by means of guanidine carbonate in presence of tartrate. A. JILEK and J. KOŘA (Coll. Czech. Chem. Comm., 1932, 4, 412—417; cf. this vol., 491).—Separation of Ti with guanidine carbonate is quant. in presence of an equal quantity of Al^{+++} , CrO_4^{--} , WO_4^{--} , MoO_4^{--} , UO_2^{++} , AsO_3^{--} , or Ti^+ , provided a boiling neutral dil. solution is used under conditions which are detailed.

J. W. S.

Determination of bismuth. C. MAHR (Z. anorg. Chem., 1932, 208, 313—316).—Bi is pptd. in acid solution by $\text{K}_2\text{Cr(CNS)}_6$ as red cryst. BiCr(CNS)_6 , the solubility of which in 0.1N- HNO_3 is 9.6 mg. per litre. The ppt. may be weighed, or the Cr determined volumetrically after oxidation to CrO_4^{--} . The method can be used in presence of compounds of Mo, Cr, Al, Fe, Zn, Mn, Ni, Co, Mg, alkaline earths, and alkalis.

F. L. U.

Separation of rhodium from iridium and the gravimetric determination of these metals. R. GILCHRIST (Bur. Stand. J. Res., 1932, 9, 547—556).—Salts of Rh and Ir are evaporated with H_2SO_4 to convert them into sulphates. Addition of TiCl_2 ppt. metallic Rh; two pptns. effect a quant. separation. Rh is redissolved in conc. H_2SO_4 , pptd. by H_2S , ignited in H_2 , and weighed as metal. Ti is removed from the filtrate by means of cupferron, two pptns. being necessary to eliminate contamination with Ir. Ir is determined in the filtrate by hydrolysing with NaHCO_3 . The pptd. $\text{IrO}_2 \cdot \text{aq.}$ is ignited in H_2 and weighed as metal.

E. S. H.

Calorimetric apparatus and the degree of accuracy attainable. S. DE WAARD (Chem. Weekblad, 1932, 29, 567—569).—An apparatus utilising electrical ignition is described. With BzOH results vary by $\pm 0.025\%$, and with paraffin by $\pm 0.0125\%$; it is suggested that the paraffin burns more uniformly. In determinations of the heat of combustion of coals, a tolerance of ± 40 kg.-cal. is proposed, owing to variations arising from incomplete combustion and from differences of the ash and H_2O contents and of the fineness of different samples.

H. F. G.

Vacuum-furnace design. K. K. KELLEY (Ind. Eng. Chem. [Anal.], 1932, 4, 391—392).—The apparatus described is designed for calorimetric measurements at high temp. At 1000° a vac. of 0.1 mm. may be maintained. E. S. H.

Modifications in the Haughton-Hanson thermostat. J. L. HAUGHTON (J. Sci. Instr., 1932, 9, 310—315).—Improvements of an apparatus previously described (B., 1917, 1039). C. W. G.

Device for increasing effectiveness of freezing mixtures. R. C. ARCHIBALD (J. Amer. Chem. Soc., 1932, 54, 3886—3887).—A wire screen holder keeps the NaCl on top and the ice below, to aid convection. In a test, -20° was reached within 30 min., and the temp. remained const. until the ice had melted. L. O. (c)

Adiabatic method for precise electrical calibration of thermometers. F. BARRY, H. W. WEBB, and A. K. SMITH (J. Amer. Chem. Soc., 1932, 54, 3785—3799).—The procedure depends on the precise maintenance of an adiabatic condition for a few hr., electrical heat being generated at a const. rate within the calorimeter. G. M. M. (c)

Self-rectifying demountable X-ray tube of high power. C. E. EDDY (J. Sci. Instr., 1932, 9, 354—358).—The tube, of the thermionic type, can be used with either a line or circular focus, and has readily detachable electrodes mounted on ground metal joints. The metal portions can be degassed. In intermittent use the tube will pass 10 millamp. at 95 kv. C. W. G.

Double-crystal X-ray vacuum spectrometer. L. G. FARRATT (Physical Rev., 1932, [ii], 41, 553—560).—An instrument for operation in a vac., designed to allow the study of soft X-rays, is described. N. M. B.

Metal X-ray tubes for characteristic radiation. C. J. KSANDA (Rev. Sci. Instr., 1932, [ii], 3, 531—534).—The main body is of stainless steel. The cathode is in a standard fitting for interchangeability. C. W. G.

Influence of refractive index on mounting media. W. MARSHALL (J. Roy. Micros. Soc., 1932, [iii], 52, 275—280).—Vals. of n (1.33—2.00) of a large no. of mounting media have been determined and the general usefulness of the mountants has been examined. The max. val. for a mountant for use in histology is about 1.70, and for vals. approaching this, specially computed objectives are desirable. Otherwise the ordinary laboratory microscope cannot be used with success. The effect of high n of the mountant is comparable with that of a thick cover-glass and the tube length has in consequence to be shortened. M. S. B.

Apparatus for taking photomicrographs. M. H. STOW (Science, 1932, 76, 277). L. S. T.

Modified apparatus for Raman effect. B. ANAND (J. Sci. Instr., 1932, 9, 324—325).—Further details of an apparatus previously described (this vol., 7) are given. C. W. G.

Measurements with the absolute colorimeter. A. THIEL and W. THIEL (Chem. Fabr., 1932, 409—

411).—The Leitz colorimeter operates on the Duboscq principle employing monochromatic light with a series of filters. Half of the beam passes through the solution to be tested and half through a standard neutral grey solution of known extinction power for light of any wave-length. The immersions in the two tubes are adjusted until the light intensities in the fields are equal, when the sp. extinction of the solution can be read directly from a scale. The instrument is also applicable to quant. measurements of turbidity and fluorescence. The "grey solution" supplied as standard should be kept in the dark and is permanent for at least 6 weeks. C. I.

Absolute colorimetric measurements. A. THIEL (Z. Elektrochem., 1932, 38, 621—622).—Abs. measurements may be effected by using Diehl's grey solution (Marburger Sitzungsber., 1931, 66, 55) in an ordinary colorimeter, together with suitable light filters. H. F. G.

Reproducible spintharometer for quantitative spectroscopy. A. OCCHIALINI and L. GALLINO (Atti R. Accad. Lincei, 1932, [vi], 15, 559—563).—A metal plate placed between two auxiliary wedge-shaped electrodes forms an easily reproducible electrode for the method of quant. spectroscopy previously described. O. J. W.

Regulation of temperature of water for refractometric measurements. V. ČVRK and T. KREMPASKY (Chem. Listy, 1932, 26, 522—525).—Apparatus for the continuous delivery of H_2O at const. temp. is described. R. T.

[Chemical] microscopy. G. L. KEENAN (J. Assoc. Off. Agric. Chem., 1932, 15, 626—629).—The solid substance is examined microscopically in ordinary light and in both parallel and convergent polarised light (crossed nicols) to determine whether it is singly- or doubly-refractive. n is then measured by immersion in suitable mixtures of mineral oil (n 1.490), $C_{10}H_7Cl$ (n 1.64), and CH_2I_2 (n 1.74); the line of contact between the solid and liquid disappears when their vals. of n are equal. J. G.

Illuminating device for use in experiments with filtered ultra-violet light. J. GRANT (J. Sci. Instr., 1932, 9, 359—360).—To obviate the difficulty of reading a burette when working in the dark with ultra-violet light, a weighted float containing acidified quinine is used. C. W. G.

Sputtering and manipulation of replica gratings. L. G. WILSON (J. Sci. Instr., 1932, 9, 360).—More brilliant spectra are obtained if the gratings are sputtered with Pt. C. W. G.

Vacuum-tube potentiometer for p_H measurement with glass electrodes. F. ROSEBURY (Ind. Eng. Chem. [Anal.], 1932, 4, 398—401).—The construction and operation of the apparatus are described. Galvanometer drift is negligible. An accuracy of ± 0.03 p_H is readily attainable. E. S. H.

Design of pressure ionisation chambers. J. H. WILLIAMS (Rev. Sci. Instr., 1932, [ii], 3, 586—592).—Constructional details of two metal ionisation chambers to be used at 30 and 60—100 atm., respectively, are given. C. W. G.

Distillation trap. E. S. WEST (Ind. Eng. Chem., [Anal.], 1932, 4, 445).—The trap may be used as a connecting bulb in Kjeldahl distillations.

E. S. H.

Laboratory extractor. H. G. TANNER (Ind. Eng. Chem. [Anal.], 1932, 4, 397).—An extractor is assembled from common laboratory apparatus.

E. S. H.

Large-capacity Soxhlet extractor and reflux condenser. A. E. CAMERON (Ind. Eng. Chem. [Anal.], 1932, 4, 394—395).—Modified apparatus is described.

E. S. H.

Static method for accurate vapour-pressure determination at high temperatures, and its application to the fixing of the hundred point on the temperature scale. H. MOSER (Ann. Physik, 1932, [v], 14, 790—808).—The construction of a glass membrane manometer and its application for the determination of v.p. in the neighbourhood of 100° or higher are described. It has been used to fix the 100° point of the temp. scale with an accuracy of $\pm 0.001^\circ$. The dependence of v.p. of H_2O on temp. in the neighbourhood of the b.p. has been determined.

A. J. M.

Low vapour-pressure gauge. K. NEWBURY and C. L. UTTERBACK (Rev. Sci. Instr., 1932, [ii], 3, 593—595).—Depression of the surface of a Hg column moves a float, causing rotation of a small mirror. The instrument is calibrated against a McLeod gauge.

C. W. G.

Accurate viscosimeter for volatile and hygroscopic liquids. E. N. DA C. ANDRADE and K. E. SPELLS (J. Sci. Instr., 1932, 9, 316—319).—A completely closed all-glass viscosimeter is described. Resetting is carried out by means of a magnetically actuated Fe plunger, which does not come into contact with the liquid.

C. W. G.

Apparatus for the determination of water by the xylene method. F. ECK (Glas. u. Appar., 1932, 13, 51—52; Chem. Zentr., 1932, i, 3469).

Improved micro-fractionating flask. H. ALBER (Z. anal. Chem., 1932, 90, 100—103).—A form of micro-fractionating flask, which is simple, durable, and easily cleaned, is described. The best results are obtained for quantities of liquid < 0.2 c.c. and the flask can also be employed for distillation under reduced pressure.

M. S. B.

Manufacture of glass apparatus for micro-chemical work. P. DE FONBRUNE (Compt. rend., 1932, 195, 706—707).—The essential points are: heating the glass on the microscope stage by a Pt-Ir wire with regulated electric current in a regulated current of air, with means for moving the glass or wire at any desired speed.

C. A. S.

Differential multiple condensation ebullioscope and its application. W. SWIENTOSLAWSKI (Chem. Listy, 1932, 26, 442—444).—The difference between the b.p. of an azeotropic mixture and the condensation point of its vapours varies at different levels of the rectifying column; by substituting a no. of columns in series, each fitted with a receiver for the condensate, which then passes through the succeeding column, information may be obtained

as to the nature of the components of an azeotropic mixture, and as to the degree of purity of a given liquid.

R. T.

Automatic percolator. L. E. WARREN (J. Assoc. Off. Agric. Chem., 1932, 15, 629—632).—The substance (e.g., drug) to be extracted is placed on a wad of cotton-wool in the bottom of a glass cylinder terminating in a capillary tube at the lower end, and is covered with washed sand. The shoulder of this cylinder rests on glass knobs at the base of an outer jacket, the lower constricted end of which encloses the capillary of the cylinder and passes through a cork into the extraction flask, the upper end being attached to a condenser.

J. G.

Rapid filtration apparatus. G. MÜLLER (Chem. Fabr., 1932, 339—341).—The apparatus is a modified vac. filter in which the paper is placed in a perforated porcelain cone.

E. S. H.

Aliquot and filter devices for analytical laboratories. T. M. SHAW (Ind. Eng. Chem. [Anal.], 1932, 4, 409—410).—A device for withdrawing an aliquot part from a suspension at any given depth is described. It is intended primarily for soil analysis. A rack for the simultaneous vac. filtration of several samples is described.

E. S. H.

Glass and quartz filters for handling gases. P. H. PRAUSNITZ (Ind. Eng. Chem. [Anal.], 1932, 4, 430—434).—The application of sintered glass and quartz filters to mercury traps, explosion safety-valves, dust filters, and gas-liquid reaction vessels is discussed.

E. S. H.

Baro-burette. III. Application to gas density determinations. H. S. BOOTH and K. S. WILLSON (Ind. Eng. Chem. [Anal.], 1932, 4, 427—429; cf. A., 1930, 885, 1151).—The d of gases may be determined by measuring the pressure, vol., and temp. of a small sample in the baro-burette and determining its wt. by adsorption and weighing in a tube filled with C. Results are given for O_2 and CCl_2F_2 .

E. S. H.

Use of the bromine water pipette in exact chemical analysis. G. R. SCHULTZE (Angew. Chem., 1932, 45, 573—575).—The only advantage the Br pipette has over the $KMnO_4$ pipette for determining olefines is its rapidity; in fact reasonably correct results are obtained with Br only with a short time of contact, a low temp., absence of direct light, and absence of O_2 in the gases. In sunlight and at temp. $> 25^\circ$ C_2H_6 and higher paraffins are fairly readily attacked by $Br-H_2O$.

A. R. P.

Comparative efficiencies of gas-washing bottles. S. HALBERSTADT (Ind. Eng. Chem. [Anal.], 1932, 4, 425—426; A., 1930, 1151).—The experiments show the superiority of glass-filter washers, particularly when the gaseous component to be absorbed is at a low concn. The spiral gas-washer can be employed only up to a max. velocity of 60 litres per hr., independently of the concn. of gas.

E. S. H.

Improved McLeod gauge and manometer. H. S. BOOTH (Ind. Eng. Chem. [Anal.], 1932, 4, 380—382).—Two modified forms of apparatus are

described, permitting the measurement of pressures from 760 to 0.00001 mm. E. S. H.

Modification of Poth's carbon dioxide generator. E. W. LOWE and W. S. GUTHMANN (Ind. Eng. Chem. [Anal.], 1932, 4, 440—441).—Undesirable features of the original apparatus (A., 1931, 706) are eliminated. E. S. H.

Esterification resin as a ground-joint lubricant. T. P. SAGER (Ind. Eng. Chem. [Anal.], 1932, 4, 388).—The resin obtained by heating 1 mol. of citric acid and 1.5 mols. of tetraethylene glycol together at 180—185° for 90 min. is insol. in both aromatic and aliphatic hydrocarbons and is a suitable lubricant for use in the distillation of these liquids. The resin is sol. in H_2O , EtOH, and $COMe_2$. E. S. H.

Collecting train for recovering traces of iodine from ashed samples. G. M. KARNs (Ind. Eng. Chem. [Anal.], 1932, 4, 375—377).—The products of combustion are led through a train of freezing tubes (ice and NaCl, and solid CO_2 and $COMe_2$) and Cottrell precipitators. E. S. H.

Mol. wt. micro-method. A. C. BRATTON, jun., and H. L. LOCHTE (Ind. Eng. Chem. [Anal.], 1932, 4, 365—367).—The principle of the apparatus described is that of the Victor Meyer method, using samples of 2—10 mg. To avoid measuring the vol. of vapour produced, the change in pressure at const. temp. before and after vaporisation is determined. The error is <2.5%. E. S. H.

Absorption tube. E. F. DEGERING (Ind. Eng. Chem. [Anal.], 1932, 4, 356).—A combination of Folin and Meyer absorption tubes provides a more efficient gas scrubber than either of these tubes separately, especially for high rates of gas flow. E. S. H.

Simple apparatus for carrying away corrosive or inflammable vapours in the laboratory. C. O. GUILLAUMIN (Bull. Soc. chim., 1932, [iv], 51, 1021—1023).—The vapours given off during a reaction or evaporation are sucked through an absorbing apparatus by means of a filter pump. D. R. D.

Laboratory apparatus. S. ROTHENFUSSER (Z. Unters. Lebensm., 1932, 64, 114—118).—A stand to hold a no. of separating funnels, a stand to hold a no. of burettes, a lamp for refractometers, and pocket apparatus for detection of heated milk by the Rothenfusser method are described. E. B. H.

Mercury traps. L. MARTON (Nature, 1932, 130, 739).—Glass-electrolysis is used to introduce clean Na into closed glass vessels to form a trap to prevent Hg vapour diffusing back into a vac. from a Hg pump. L. S. T.

Apparatus for automatic registration of dehydration with increasing temperature. S. SKRAMOVSKY (Chem. Listy, 1932, 26, 521—522).—The substance is suspended on the arm of a balance, which registers loss of wt. R. T.

Spectrophotometric development for biological and photochemical investigations. F. S. BRACKETT and E. D. McALISTER (Smithsonian Miscell. Coll., 1932, 87, 1—7).—A method and apparatus for investigating the effect of radiation on biological material, exposed to several wavelengths at the same time, are described, and illustrated for the Hg spectrum in the range 2500—3000 Å., and unicellular algæ. N. M. B.

Graphical method for converting atomic per cent. into weight per cent. A. ÖLANDER (Ind. Eng. Chem. [Anal.], 1932, 4, 438). E. S. H.

Geochemistry.

Salinity of the Rance at Chatelier determined by means of electric conductivity. P. CHAUCHARD (Compt. rend., 1932, 195, 621—623; cf. A., 1928, 147).—Using the method previously described, the salinity of the H_2O immediately above the tidal lock at Chatelier has been determined, showing the variations with tide and river flow, and the connexion between salinity and aquatic vegetation. C. A. S.

Natural waters containing radium and mesothorium. V. CHLOPIN and V. VERNADSKI (Z. Elektrochem., 1932, 38, 527—530).—A comprehensive survey has been made of the waters in the neighbourhood of petroleum and mineral deposits in the U.S.S.R. H_2O adjacent to petroleum has a high Ra content (2×10^{-11} to $1.8 \times 10^{-9}\%$), and usually considerable quantities of meso-Th-I and Th-X are present. U and Th are present in <1% of the equilibrium amounts. The minerals examined usually contained <10% of the quantity of Ra found in the H_2O . H. F. G.

Thermal springs of Sambor. S. S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1932, 3, 91—103).—The inorg. constituents of the waters of two springs

examined are practically pure Mg and Ca H carbonates, whilst a third spring contains also Na, K, $SO_4^{''}$, and Cl' . R. T.

Distribution of iodine in Alberta in relation to the prevalence of goitre. I. Iodine in water supplies. O. J. WALKER (Canad. J. Res., 1932, 7, 137—148).—The I content of the surface H_2O in Alberta is usually <1 in 10^9 , but in the H_2O from deep wells it ranges from 0 to 663 in 10^9 . There is no immediately apparent connexion between the I content of the H_2O supplies and the prevalence of goitre in different parts of the province. H. F. G.

Action of iodine on marine waters. G. DENIGES (Compt. rend., 1932, 195, 669—671).—Superiodised sea-water (5 samples), as also the inter-valvular H_2O of superiodised oysters (4 samples), contains 36—145 mg. of I per litre, of which 30—139.5 is in the form of I' and 0.5—9 in that of IO_3' , free I (17 mg. per litre) being found only once. Comparison of the interaction of I and H_2O , aq. NaCl, aq. $CaH_2(CO_3)_2$, and sea-water shows the action of the two last to be similar, 75% of the I forming I' and IO_3' in the approx. ratio 5:1, and 25% being

dissolved as I; this last is absorbed by animal or vegetable matter, alive or dead ($HX + 2I \rightarrow XI + HI$).

C. A. S.

Stability of the liquid carbon dioxide in the ocean. W. VERNADSKY (Nature, 1932, 130, 661—662).—A reply to criticism (this vol., 829).

L. S. T.

Geological structure of the potassium salt-beds of Stebnik. C. KUŹNIAK (Bull. Acad. Polonaise, 1932, A, 183—191).—Chemical analyses are given.

E. S. H.

Granophyry and porphyry from the Carpathians in the neighbourhood of Sanok. A. GAWET (Bull. Acad. Polonaise, 1932, A, 145—157).—Chemical and mineralogical analyses of these rocks are given.

E. S. H.

Tertiary dolomite of the Kerchensk Peninsula. S. V. KONSTANTOV (Min. Sibir., 1930, 5, 1081—1093).—The average composition is: CaO 31.7, MgO 18.14, R_2O_3 0.87, insol. residue 1.72%.

CH. ABS.

Ore deposits in south Osetii. F. I. ARRABOV (Min. Sibir., 1930, 5, 1036—1049).—The ore of the Karsman deposits contains: sphalerite 26.2, pyrite, 23.5, galena 6.5, arsenopyrite 1.5, calcite 17.2%, with small amounts of chalcopryrite and tennantite. Galena from Rasdaran-Kom contains Pb 30.91, Cu 0.06, Zn 0.14, Fe 0.62, Al_2O_3 4.06, TiO_2 trace, CaO 14.02, MgO 0.2, CO_2 12.22, SiO_2 29.42, S 4.21%. Pyrite ore from Moguta contains: pyrite 36.7, galena 7.8, sphalerite 4.4, chalcopryrite 0.5, siderite 17% (29% carbonate).

CH. ABS.

Geochemistry of rhenium. E. KRONMANN (Z. physikal. Chem., 1932, 161, 395—396).—It is probable that Re accumulates in rocks rich in C which also contains S (cf. A., 1931, 707).

R. C.

Radium content of some Hungarian rocks. S. S. DE FENÁLY (Amer. J. Sci., 1932, [v], 24, 306—310).—Samples of granite contained $1.43\text{--}3.69 \times 10^{-13}$, of andesite $1.64\text{--}2.38 \times 10^{-13}$, and of basalts $1.48\text{--}1.93 \times 10^{-12}$ g. Ra per g. of rock.

C. W. G.

Manganese minerals of a vein near Bald Knob, N. Carolina. C. S. ROSS and P. F. KERR (Amer. Min., 1932, 17, 1—18).—Alleganyite, d 4.020, orthorhombic, n_a 1.756, n_b 1.780, n_c 1.792, occurring as pink grains of $5MnO \cdot 2SiO_2$ in calcite, contained SiO_2 24.90, Al_2O_3 trace, FeO 1.40, MnO 70.35, MgO 2.16, CaO 0.74, total 99.55%. Galaxite, d 4.234, n 1.923, $MnO \cdot Al_2O_3$, black with a reddish-brown streak, contained SiO_2 0.96, TiO_2 trace, Al_2O_3 45.71, FeO 16.36, MnO 34.03, MgO 1.50, CaO and ZnO trace, total 98.56%. Mn-bearing calcite, tephroite, rhodonite, and spessartite are also described.

CH. ABS.

Pumpellyite from California. J. IRVING, M. VONSEN, and F. A. GONYER (Amer. Min., 1932, 17, 338—342).—Green and brown varieties are chemically similar. The formula $Ca_4R_6Si_6O_{23}(OH)_3 \cdot 2H_2O$, where $R = (Al : Mg + Fe = 5 : 1)$, is derived.

CH. ABS.

Gadolinite from Loughborough Township, Frontenac Co., Ontario. H. V. ELLSWORTH (Amer. Min., 1932, 17, 96—97).—The mineral, $n > 1.75$, d 4.101, contained SiO_2 25.97, ThO_2 0.14, $(Ce, La, Di)_2O_3$ 2.85, $(Yt, Er)_2O_3$ 46.47, Fe_2O_3 2.34, FeO 5.82, MnO

1.17, BeO 10.29, Al_2O_3 0.32, CaO 2.36, MgO 0.55, $Na_2O + K_2O$ 0.09, H_2O 1.23, P_2O_5 trace, UO, total 99.60%.

CH. ABS.

Ptilolite from Utah. W. T. SCHALLER (Amer. Min., 1932, 17, 125—127).—The mineral, $10SiO_2 \cdot Al_2O_3 \cdot (Ca, K_2, Na_2)O \cdot 7H_2O$, n_a 1.473, n_b 1.475, 1.478, contained SiO_2 07.35, Al_2O_3 11.49, CaO 3.87, K_2O 0.11, Na_2O 2.63, H_2O 5.13, $H_2O + 8.82$, total 99.40%.

CH. ABS.

Mordenite-tilolite group; clinoptilolite. W. T. SCHALLER (Amer. Min., 1932, 17, 128—134).—Three species are distinguished: mordenite, $9SiO_2 \cdot Al_2O_3 \cdot (Ca, K_2, Na_2)O \cdot 6H_2O$, monoclinic or triclinic; ptilolite, $10SiO_2 \cdot Al_2O_3 \cdot (Ca, K_2, Na_2)O \cdot 7H_2O$, orthorhombic; clinoptilolite, a dimorphous form of ptilolite, monoclinic tabular. Vals. of n are, respectively: α 1.472, 1.474, 1.476; β 1.474, 1.478, 1.479; γ 1.476, 1.480, 1.479.

CH. ABS.

Cesium biotite from Custer County, S. Dakota. F. L. HESS and J. J. FAHEY (Amer. Min., 1932, 17, 173—176).—The Cs biotite, d 3.10, n_a 1.573, n_b 1.620, n_c 1.620, contained SiO_2 36.97, TiO_2 2.64, Fe_2O_3 2.26, Al_2O_3 17.51, FeO 14.81, MnO 0.22, MgO 8.45, Li_2O 0.65, Na_2O 0.45, K_2O 8.04, Cs_2O 3.14, H_2O —0.32, $H_2O + 2.48$, F 3.17, less O for F 1.34, total 99.77%.

CH. ABS.

Montmorillonite or smectite as constituents of fuller's earth and bentonite. P. F. KERR (Amer. Min., 1932, 17, 192—198).—Montmorillonite and smectite are identical; the former term is preferred. European fuller's earth was formed by the alteration of volcanic ash, like bentonite.

CH. ABS.

Composition of cuprotungstite. W. T. SCHALLER (Amer. Min., 1932, 17, 234—237).—Analysis of material from Cave Creek, Arizona, indicates the formula $WO_3 \cdot 2CuO \cdot H_2O$.

CH. ABS.

Joaquinite. C. PALACHE and W. F. FOSHAG (Amer. Min., 1932, 17, 308—312).—Joaquinite is orthorhombic, $a : b : c = 0.919 : 1 : 2.14$; a 9.61, b 10.45, c 22.4 Å.; d 3.89; n_a 1.748, n_b 1.767, n_c 1.823; it contains SiO_2 35.27, TiO_2 29.53, FeO 3.41, BaO 23.91, CaO 0.27, MgO 0.07, ignition 0.47, Na_2O 4.47, total 97.40%, corresponding with $NaBa(Ti, Fe)_2Si_2O_{15}$. The unit cell contains 4 mols.

CH. ABS.

Sanbornite from Mariposa County, California. A. F. ROGERS (Amer. Min., 1932, 17, 161—172).—Sanbornite, trichinic $BaSi_2O_5$, has n_a 1.597, n_b 1.616, n_c 1.624.

CH. ABS.

Minerals from the rhodolite quarry near Franklin, North Carolina. E. P. HENDERSON (Amer. Min., 1931, 16, 563—568).—Gedrite, d 3.178, n_a 1.642, n_b 1.655, n_c 1.661, contains SiO_2 44.22, Al_2O_3 23.79, FeO 9.21, CaO 0.62, MgO 20.69, MnO 0.16, H_2O 1.42, Fe_2O_3 0.20, total 100.31%. Hypersethene, n_a 1.685, n_b 1.696, n_c 1.699, contains SiO_2 52.36, Al_2O_3 4.29, FeO 16.90, CaO 0.44, MgO 25.89, H_2O 0.34, total 100.22%. Rhodolite has n 1.758; biotite, FeO 5.78, Fe_2O_3 0.72%, has n_a 1.565, $n_b = n_c = 1.607$.

CH. ABS.

Triclinic manganiferous pyroxenes. N. SUNDRUS (Amer. Min., 1931, 16, 411—429, 488—518).—A

discussion of the composition and stability relationships of rhodonite, bustamite, fowlerite, Fe rhodonite, sobralite, and pyroxmangite. CH. ABS.

Negative crystal cavities of certain galenas and their brine content. M. J. BUEGER (Amer. Min., 1932, 17, 228—233). CH. ABS.

Uraninite from Huron Claim, Winnipeg River area, Manitoba. J. S. DELURY and H. V. ELLSWORTH (Amer. Min., 1931, 16, 569—575).—The uraninite (small cubic crystals in pink albite) is rich in Pb and Th; the high Pb ratio (0.260—0.265) indicates that it is the oldest uraninite known. CH. ABS.

Uraninite from Henry Township, Parry Sound district, Ontario. H. V. ELLSWORTH (Amer. Min., 1931, 16, 576—579).—The uraninite (d 8.173, Pb ratio 0.117) is associated with thucolite in pink perthitic microcline, and is in the second stage of alteration. CH. ABS.

X-Ray study of psilomelane and wad. L. S. RAMSDALL (Amer. Min., 1932, 17, 143—149).—Of the four types of pattern observed, one is arbitrarily selected as that of "true" psilomelane (I). (I) containing Ba and lithiophorite are distinct species. "(I)" may be either of the above, pyrolusite, braunite, or wad; "wad" may be pyrolusite or (I). CH. ABS.

Perthites. H. L. ALLING (Amer. Min., 1932, 17, 43—65).—Processes capable of forming perthitic feldspars are discussed. CH. ABS.

Determination of manganese in a rock from Miranda do Corvo. A. J. DE A. GOUVEIA (Rev. Chim. pura Appl., 1932, 5, 44—45; Chem. Zentr., 1932, ii, 412). CH. ABS.

Deuteric and later alterations of the uncomphagrite of Iron Hill, Colorado. E. S. LARSEN and E. A. GORANSON (Amer. Min., 1932, 17, 343—356).—The processes are discussed. Juanite, $10\text{CaO} \cdot 4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 11\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, has n_a 1.640, n_y 1.647; cebollite is orthorhombic, n_a 1.592, n_g 1.597, n_y 1.630. CH. ABS.

Solubility of cassiterite in distilled water. S. J. THUGUTT (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 122—133).—A sample of Bolivian cassiterite, containing SnO_2 93.36, TiO_2 0.49, Nb_2O_5 2.82, Ta_2O_5 3.71, and H_2O 0.39%, was heated with H_2O at 211—215°. The solution contained 0.00026% of dissolved substances, in colloidal solution. R. T.

Composition of pegmatic feldspars as a criterion of their hydrogenetic origin. E. ZANIEWSKA-CHLIPALSKA (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 49—81).—Klesow microcline has the composition: SiO_2 64.55, Al_2O_3 18.90, Fe_2O_3 0.33, BaO 0.20, CaO 0.32, K_2O 13.13, Na_2O 2.7, H_2O 0.38%. Feldspars of igneous origin have the ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2 = 1 : 6$; for those of pegmatitic origin it is $1 : < 6$. This indicates the hydrogenetic origin of such feldspars, which would have been deposited from colloidal solutions of igneous feldspar. R. T.

Composition of predazzite. M. KOLACZKOWSKA (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 149—165).—Predazzite is a mixture of calcite and brucite. R. T.

Epinatrolite, a component of hydronephelinite. S. J. THUGUTT (Arch. Min. Soc. Sci. Varsovie, 1932,

8, 141—144).—Hydronephelinite is a mixture of epinatrolite and hydrargyllite. R. T.

Microcline of Maczulanka (Volhynia) grey granite. E. S. LITMANOWICZÓWNA (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 82—130).—Maczulanka granite consists of quartz, biotite, acid oligoclase, and microcline, the crystallographic data for which are given. R. T.

Silver-tin deposits of Oruro, Bolivia. B. KOZŁOWSKI and S. JASKÓLSKI (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 1—121).—A detailed list of the minerals found in these deposits is given, together with crystallographic and analytical data. The minerals of the veins are partly of hydrothermal origin. R. T.

Phillipsite from the Pacific Ocean. S. J. THUGUTT (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 134—140).—Phillipsite is formed by hydrolysis of nepheline, with loss of 4 mols. of $\text{Na}_2\text{Al}_2\text{O}_6$. Its composition is $8\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 3\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 55\text{H}_2\text{O}$. The higher K content found by Murray and Renard (H.M.S. "Challenger" Rept., 1891) was due to their use of Thoulet's reagent for isolation of phillipsite. R. T.

Rocks of the gabbroid massif of the Bukk Mts., Hungary. S. VON SZENTPÉTERY (Chem. Erde, 1932, 7, 351—382).—Forty-one analyses of plutonic rocks ranging from peridotite to andesinite are tabulated and the mol. ratios plotted on diagrams for the purpose of showing the relation between the different types. L. J. S.

New type of Fe Al phosphate deposit in Brazil. F. BRANDT (Chem. Erde, 1932, 7, 383—425).—Phosphatised laterite overlying diabase contains small white to brown spherulites and "octahedra" (perhaps pseudomorphs after pyrite) which contain P_2O_5 25.7—36.4, SiO_2 0.2—1.7, TiO_2 0.8—2.0, Al_2O_3 24.5—33.4, Fe_2O_3 3.8—26.5, Na_2O 2.0—4.7, H_2O 16.9—19.1%; d 2.781—2.798 n 1.602—1.618. A formula $6\text{Al}_2\text{O}_3 \cdot 4\text{P}_2\text{O}_5 \cdot 17\text{H}_2\text{O}$ (differing from wavellite in containing less H_2O) is deduced and the mineral is named harbortite. At greater depths in the laterite there are tubular concretions of Al Fe phosphate, some of which is dufrenite. Analyses of materials from borings indicate that the phosphate was derived from the diabase. L. J. S.

Weathering of andesite from Java. E. BLANCK and E. VON OLDERSHAUSEN (Chem. Erde, 1932, 7, 426—433).—Analyses are given of the fresh rock, of material from different weathered zones, and of the resulting soil. L. J. S.

Cryoconite from the East Greenland pack-ice. E. BLANCK, H. POSER, and E. VON OLDERSHAUSEN (Chem. Erde, 1932, 7, 434—440).—Analyses of a fine grey dust collected from the surface and from pockets in the pack-ice gave SiO_2 61.12—64.24, Al_2O_3 15.19—15.70, Fe_2O_3 6.49—7.38, ignition loss 5.86—9.43, etc. L. J. S.

Synthesis of polianite, braunite, and hausmannite. F. KRULL (Chem. Erde, 1932, 7, 473—482).—Minutely (0.1 mm.) crystalline MnO_2 is best prepared by the slow decomp. of $\text{Mn}(\text{NO}_3)_2$ at 154°/20 mm.; Mn_2O_3 by heating cryst. MnO_2 in O_2 at 550°;

and Mn_3O_4 by heating pptd. MnO_2 in H_2 at 200° . The MnO_2 (d 4.94) and Mn_3O_4 (d 4.89) so obtained show the same microscopical characters and X-ray patterns as polianite and hausmannite, respectively, but artificial Mn_2O_3 (d 4.77) shows some differences from braunite. L. J. S.

New hexahedrite from Cerros del Buen Huerto, Chile. F. HEIDE, E. HERSCHKOWITZ, and E. PREUSS (Chem. Erde, 1932, 7, 483—502).—A polished section of this meteorite, d 7.822, shows one very prominent set of Neumann lines, nodules and plates of troilite with some enclosed daubreelite, and plates and needles of schreibersite arranged parallel to (100), (210), and (211), along which directions the mass can be broken. The following X-ray determinations were made: kamacite, body-centred cubic, a 2.859 Å.; troilite, hexagonal, a 3.439, c 5.855 Å.; schreibersite (rhabdite), body-centred tetragonal, a 9.013, c 4.424 Å., with 8 mols. $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$, $d(\text{calc.})$ 7.44; daubreelite, cubic with spinel structure, a 9.966, d 3.81 (calc. 3.87). Analysis of the kamacite with enclosed rhabdite needles gave Fe 93.75, Ni 5.43, Co 0.58, S 0.08, P 0.19=100.03. Spectroscopic analysis showed also Cr, V, Mo, Mn, Pt, Cu, Ag, Au, Zn?, Ga, Si, Ge, Sn, Pb. L. J. S.

Radioactivity and current geological problems. V. VERNADSKI (Z. Elektrochem., 1932, 38, 519—527).—A crit. review of the present state of knowledge of the geochemistry of Pb and of the distribution of radioactive elements in the earth's crust, and of the determination of geological time by the methods of radioactivity. H. F. G.

Minerals and Wood's light. A. ESTRAFALLACES (L'Ind. Chimica, 1932, 7, 1360—1366).—213 minerals were subjected to Wood's light and those showing fluorescence were examined spectroscopically. This fluorescence is not produced by monochromatic light and does not show a characteristic spectrum line or zone capable of identifying the mineral under examination. Two specimens of fluorite from the same locality gave different emissions. The observed emissions extend between 4000 Å. up to the vals. given, except for two specimens of topaz in which the emission varied between 4750 and 5600 Å. and 4600 and 6050 Å., respectively. O. F. L.

Metallic meteorite from Ogallala, Nebraska. H. H. NININGER (Amer. Min., 1932, 17, 221—225).—The meteorite (3300 g.) contains Fe 90.10, Ni 7.93%, with small amounts of Co, Cu, Cr, P, S, C, Si, and O. CH. ABS.

Petrological and mineralogical study of the under-clays of Illinois coal. V. T. ALLEN (J. Amer. Ceram. Soc., 1932, 15, 564—573).—The clays consist chiefly of potash beidellite purified before deposition in H_2O together with feldspars, muscovite, quartz, etc. in the warm Pennsylvanian period. Later leaching by soil-forming processes has removed the carbonates. J. A. S.

Metamorphosis of coals and the problem of artificial coalification. W. GROFF and H. BODE (Braunkohle, 1932, 31, 277—284, 299—302, 309—313; Chem. Zentr., 1932, ii, 150).—Cellulose, wood, humic acid, peat, and lignite were heated at 300°

at pressures up to 2000 atm.; in all cases the volatile constituents diminished and the fixed C increased. The H_2O content diminished towards vals. for bituminous coal. At 300° transformation into typical lignites, but not into bituminous coals, could be effected. The duration of the process is of secondary importance. A. A. E.

Genesis of coals. V. E. BERL and A. SCHMIDT. —See B., 1932, 917.

Formation of bituminous coal, mineral oil, and asphalt. E. BERL.—See B., 1932, 918.

Mechanical and chemical composition of loess and genetically related rocks. S. S. MOROZOV (Pedology, 1932, 27, 232—259).—A series of loesses from various parts of European Russia showed a complete absence of particles > 1 mm. in diameter, and a fair constancy in the amounts of the various other fractions present. The chemical composition of the individual fractions showed great similarity and suggests a single place of origin for all samples. This is probably the N.W. part of the U.S.S.R., the source of the Würm glacier. A. M.

Soil types from different climatic areas of S. Africa. F. BEHREND and K. UTESCHER (Z. Pflanz. Düng., 1932, 26A, 175—203).—Analytical data for a red loam and a black earth soil derived from the same parent rock are recorded. Differences between the two soils are attributable entirely to climatic conditions. A. G. P.

Role of forest (oak) in soil formation. N. N. STEPANOV (Pedology, 1932, 27, 163—177).—The invasion of chernozem steppe by oak forest results in a degradation of the soil; Ca^{++} and Mg^{++} are leached to lower horizons, H^+ taking their place, and there is an increase in soluble electrolytes in the A horizon. These changes are due to the litter of oak forest and its decomp. products. A. M.

Colours and signs for soil maps. L. I. PRASOLOV (Pedology, 1932, 27, 149—162).—Colours and symbols used for the soil maps of Russia are reproduced and their merits discussed. A. M.

Contradictory processes as a basis for genetic soil classification. N. P. RENEZOV (Pedology, 1932, 27, 178—211).—A philosophical discussion of soil classification giving a new scheme based on the differences in humus formation in different climates. A. M.

Role of organic matter in the classification of forest soils. M. F. MORGAN and H. A. LUNT (J. Amer. Soc. Agron., 1932, 24, 655—662).—The nature and distribution of org. matter in various soil types are examined. A. G. P.

Saline soils. L. POZDENA (Chem. Erde, 1932, 7, 441—472).—The alkaline (soda) soils of the western Hungarian plain are discussed in detail with many mechanical and chemical analyses. L. J. S.

Important soil profiles of southern Puerto Rico. J. THORP (Soil Sci., 1932, 34, 241—257).—Soils described are chernozem and chocolate-coloured clay pans with "alkali spots" in marshy coastal areas. Analyses, profile characteristics, and natural flora are recorded and discussed. A. G. P.

Organic Chemistry.

Natural classification of chemical compounds.

II. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1932, 2, 128—134; cf. A., 1931, 1357).—The "structural no." of a given mol. is a numerical expression giving the combination of atoms and at. groups which constitute the mol. By arranging isomeric compounds in accordance with their structural nos., the "normal geometrical series" is obtained which is the same for all classes of org. compounds, and is of the type $[R_2'R_n'']$, $[R_3'R_nR''']$, $[R_4'P_nR''']$, etc., the index of R showing the valency. Each member of the normal series can be the parent of a new series differently oriented, and is thus termed the top member. By plotting the physical consts. of the geometrical series of the top members for certain classes of org. compounds it is seen that complete analogies exist between the curves for different consts. and between the curves for the same const. of different classes of compounds arranged in normal geometrical series according to their structural nos. The conception is further developed and illustrated by three-dimensional space diagrams. Formulae can be developed to express the abs. b.p., d , and n in terms of the b.p. and at. nos. of neon, and the mol. nos. and symmetry of the mol. M. Z.

Natural classification of catalytic organic reactions. A. A. BALANDIN (J. Gen. Chem. Russ., 1932, 2, 166—182; cf. A., 1929, 1245).—Consideration is devoted to org. compounds containing C, H, and O, and possessing only single and double linkings, and in which there is no change of valency, the reactions being limited to those with doublet indices, i.e., in which two linkings only are broken and remade. All possible types of compounds are examined and grouped in nine classes. M. Z.

Synthesis, purification, and physical constants of the normal hydrocarbons from pentane to dodecane, of n -amyl bromide, and of n -nonyl bromide. B. J. MAIR (Bur. Stand. J. Res., 1932, 9, 457—472; cf. A., 1931, 792).—The b.p., f.p., and n_D^{20} for the n -paraffins C_5 to C_{12} and for n -amyl and n -nonyl bromide (preps. described) are accurately determined. n -Nonyl bromide is isolated in two forms, m.p. -29.06° and -30.71° . J. L. D.

Slow combustion of β -methyltricosane. S. LANDA and J. POKORNÝ (Coll. Czech. Chem. Comm., 1932, 4, 456—462, and Chem. Listy, 1932, 26, 512—515).—Slow combustion of β -methyltricosane (I) yields the following identified products: CH_3O , $MeCHO$, $EtCHO$, $MeOH$, and $COMe_2$; the $COMe_2$ originates from the $\cdot CHMe_2$ group of (I). The production of $COMe_2$ from natural paraffin (cf. A., 1930, 190) indicates the presence of branched-chain hydrocarbons. β -Methyltricosan- β -ol (phenylurethane, m.p. 86°) has m.p. 63° (cf. A., 1930, 1268). H. B.

Addition of hydroxyl groups to ethylallene. M. BOUYS (Bull. Soc. chim., 1932, [iv], 51, 1177—1178).— Δ^2 -Pentadiene shaken with aq. 10% $AgClO_3$ containing 0.15% of osmic acid gives a small amount of unstable material, b.p. $92-95^\circ/11$ mm., and

(mainly) acetylethylcarbinol, which is formed thus: $CH_3:C:CHEt + 2OH = CH_3:C(OH):CHEt \cdot OH \longrightarrow CHAcEt \cdot OH$. H. B.

Catalytic hydrogenation of unsaturated compounds. VI. *iso*Propyl- and phenyl-acetylene. S. V. LEBEDEV and V. J. SCHTERN (J. Gen. Chem. Russ., 1932, 2, 249—259).—Addition of H_2 to the ethylenic products of hydrogenation of C_2H_2 derivatives takes place simultaneously with their formation, the proportion of H_2 combining at a given moment with each component of the mixture depending on the relative concn. of $CR:CH$ to $CHR:CH_2$ ($R=Pr^i$ or Ph) and on the nature of R . R. T.

Acetylene polymerides and their derivatives.

III. Addition of hydrogen chloride to vinyl-acetylene. W. H. CAROTHERS, G. J. BERCNET, and A. M. COLLINS (J. Amer. Chem. Soc., 1932, 54, 4066—4070).—The initial product in the (1:4)-addition of HCl to $CH_2:C:CH:CH_2$ (I) is δ -chloro-*butadiene* (II), b.p. $87.7-88.1^\circ$, which readily undergoes isomerisation to chloroprene ($CH_2:CCl:CH:CH_2$) (III), which always constitutes a part of the reaction product. The Cl atom of (II) is very reactive; (II) does not react with maleic anhydride or with naphthoquinone, does not give a Cu^+ derivative, with O_3 it yields CH_2O and (after oxidation with $KMnO_4$) $CH_2Cl \cdot CO_2H$, with $KMnO_4$ gives $CH_2Cl \cdot CO_2H$, and with cold conc. H_2SO_4 affords δ -chlorobutan- β -one, b.p. $120-122^\circ/760$ mm. The formation of (II) is accelerated by certain salts. (III), which is the main product when the reaction is carried out in presence of $CuCl$, reacts further with HCl to give $\beta\delta$ -dichloro- Δ^2 -butene (IV), b.p. $53-54^\circ/50$ mm., $127-129^\circ/756$ mm. (II) is transformed into (III) by powdered KOH , by quinoline at $140-150^\circ$, by heat (290°) in presence of silica gel, and by hot dil. HCl ; the best conditions are heating with $CuCl$ in 18% HCl [(IV) is recovered unchanged under these conditions]. (IV) undergoes no change when heated at $50^\circ/6000$ atm. for 45 hr. (II) shows no tendency to polymerise. C. J. W. (b)

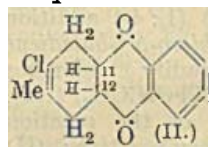
3-Nitrophthalimide as reagent for the identification of organic halogen compounds. P. P. T. SAH and T. S. MA (Ber., 1932, 65, [B], 1630—1633).—The alkyl halide is gradually heated under reflux to $120-200^\circ$ with *K* 3-nitrophthalimide (improved prep. of 3-nitrophthalic acid given). Reaction is discontinued when the mixture has become homogeneous and the cold product is boiled with H_2O to extract K halide and hydrolyse unchanged 3-nitrophthalimide. The following *N*-substituted 3-nitrophthalimides are described: *Me*, m.p. $112-113^\circ$; *Et*, m.p. $105-106^\circ$; *Pr^i*, m.p. $84-85^\circ$; *Bu^i*, m.p. $71-72^\circ$; *isoamyl*, m.p. $93-94^\circ$; *allyl*, m.p. $100-101^\circ$; β -bromoethyl, m.p. $115-116^\circ$; *CH_2Ph*, m.p. $142-143^\circ$; *p*-nitrobenzyl, m.p. $181-182^\circ$; *acetonyl*, m.p. $152-153^\circ$; *carbethoxymethyl*, m.p. $79-80^\circ$. H. W.

Oxidation of solutions of iodoform. R. DUBRISAY and G. EMSCHWILLER.—See this vol., 1215.

Photolysis of chloropicrin in aqueous solution. E. V. ALEXEEVSKI.—See this vol., 1215.

Synthesis of ethylene bromide from acetylene and hydrogen bromide. F. DE CARLI (Annali Chim. Appl., 1932, 22, 455—462).—Combination of C_2H_2 and HBr over $FeBr_3$ or $CuBr_2$ at 160—170° gives ethylene and ethylidene bromides (cf. A., 1931, 598), and a product shown by d , viscosity, m.p., and Br content to be a complex partly brominated mixture, from which CH_2Br-CH_2Br is not easily isolated. E. W. W.

New synthetic rubbers. II. Homologues of chloroprene and their polymerides. W. H. CAROTHERS and D. D. COFFMAN (J. Amer. Chem. Soc., 1932, 54, 4071—4076).— $CH_2:CMc:C:CH$, b.p. 34°, shaken with conc. HCl, CuCl, and NH_4Cl , gives 40% of β -chloro- γ -methyl- $\Delta^{\alpha\gamma}$ -butadiene (I), b.p. 37°/105 mm., 93°/760 mm. with polymerisation, which with α -naphthaquinone affords 2-chloro-3-methyl-1:4:11:12-



tetrahydroanthraquinone (II), m.p. 165—166°, oxidised by air in dil. EtOH-NaOH to 2-chloro-3-methylantraquinone, m.p. 214—215°. (I) polymerises very rapidly to a rubber-like polymeride, which after vulcanisation is less extensible than the corresponding product from chloroprene (B., 1932, 156). $CHMe:CMc:C:CH$ similarly gives 22% of β -chloro- γ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene, b.p. 57—60°/96 mm., converted (as above) into 2-chloro-3:4-dimethyl-1:4:11:12-tetrahydroanthraquinone, m.p. 107°, and thence into 2-chloro-3:4-dimethylantraquinone, m.p. 171—5°. This Cl-derivative polymerises very slowly; the product, even after vulcanisation, is soft and lacking in "nerve." 1-Ethynyl- Δ^1 -cyclohexene gives 32% of β -chloro- γ -tetramethylene- $\Delta^{\alpha\gamma}$ -butadiene [1- α -chloro-vinyl- Δ^1 -cyclohexene], b.p. 55—57°/1 mm., convertible into 2-chloro-3:4-tetramethylene-1:4:11:12-tetrahydroanthraquinone, m.p. 191—192°, and thence into 2-chloro-3:4-tetramethylantraquinone, m.p. 191—192°. This Cl-derivative also polymerises very slowly; the product is very soft, plastic, and sticky. Since butadiene, isoprene, and β -dimethylbutadiene do not differ greatly in the rate of their spontaneous polymerisation, this indicates that Me is not an activating group. The fact that chloroprene polymerises about 700 times as fast as isoprene illustrates the powerful activating effect of Cl in the β -position. The introduction of Me at C_γ does not greatly modify this effect, although the polymeride is somewhat less extensible; the introduction of a second Me at one of the terminal C atoms almost completely checks the activating effect of the Cl atom. C. J. W. (b)

Safe preparation of dichloroacetylene as lecture experiment. L. METZ (J. pr. Chem., 1932, [ii], 135, 142—144).— C_2Cl_2 is prepared without risk of explosion by interaction of dry KOH with $C_2H_2Cl_4$ in xylene in N_2 at 95—100°. An apparatus in which the spontaneous inflammation of C_2Cl_2 in air is demonstrated is described. H. A. P.

Oxidising properties of the halogenated dinitromethanes. A. E. KRETOV and N. N. MELNIKOV (J. Gen. Chem. Russ., 1932, 2, 202—207).—

Bromopicrin reacts with thiophenol or thiocresol to give the corresponding disulphides with evolution of oxides of N considerably more than in the case of chloropicrin. With KI, a complicated reaction takes place, Cl_4 , much free I, CO_2 , CO, N oxides, and N_2 being evolved. With alkali sulphides the reaction is also complicated, a mixture of COS, CS_2 , S, and alkali nitrite and halide being obtained, whilst CO, CO_2 , N_2 , and N oxides are evolved. With NaHS the reaction is still more complicated, since in addition to the products enumerated above, NH_3 and salts of HNO_3 are obtained. Mechanisms for the above various reaction schemes are suggested, and it is concluded that the halogenated dinitromethanes react as oxidising agents, attacking C atoms in the first instance. M. Z.

Reaction between *p*-nitrophenylcarbimide and some higher alcohols. W. J. HOPPENBROUWERS (Rec. trav. chim., 1932, 51, 951—954).—The following are thus prepared: *nonyl*, m.p. 104°, *undecyl*, m.p. 99.5°, *n-cetyl*, m.p. 117—118°, and *cholesteryl*, m.p. 204—205°, *p*-nitrophenylurethane. Myricyl alcohol and phytosterol react only with great difficulty and no derivative could be obtained from pentaerythritol. J. W. B.

Preparation of acetone-chloroform [$\alpha\alpha\alpha$ -trichloro-*tert*-butyl alcohol]. P. P. T. SAH, M. LEI, and S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 209—214).—The prep. is modified. R. S. C.

Dehydration of *tert*-carbinols containing a neopentyl system. I. Methylethyl-*tert*-butylcarbinol and dimethyl-*tert*-amylcarbinol. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1932, 54, 4011—4014).— $CMcEtBu:OH$, b.p. 76°/40 mm., obtained in 60% yield from $MgEtBr$ and $COMcBu$, refluxed with a trace of I, gives a mixture of 80% of $CMc_3:CMc:CHMe$, b.p. 109°/740 mm., and 20% of $CH_2:CMc:CMcEt$ (I), b.p. 106—106.7°/742 mm.; none of the olefine postulated by Clarke and Jones (A., 1912, i, 150) is found. Dehydration of dimethyl-*tert*-amylcarbinol gives mainly (I). C. J. W. (b)

Ether-esters of glycerol or ether-glycerides of shark-liver oil, *Scymnorhinus lichia*, Bonnaterre. E. ANDRE and A. BLOCH.—See this vol., 1275.

New catalysts for hydrolysis. Hydrolysis of diethyl ether. A. A. BALANDIN, N. I. SCHUJIKIN, M. P. NESVISHSKI, and T. K. KOSMINSKAJA (Ber., 1932, 65, [B], 1557—1561).—At 275—300°/100 atm., hydrolysis of Et_2O does not occur in presence of Al_2O_3 , Fe_2O_3 , or active C. With Al_2O_3 95%—NiO 5% (I) or Al_2O_3 90%—ZnO 10% extensive hydrolysis is observed; Al_2O_3 50%— Fe_2O_3 50% (II) and Al_2O_3 63%— Fe_2O_3 37% are also serviceable. With (I) and (II) decomp. of Et_2O with production of (?) C_2H_4 is observed, whereas gas is not formed with the other catalysts. H. W.

Ether-like compounds. VII. Preparation of the simpler, mixed formal. M. H. PALOMAA and K. K. KANTOLA (Ber., 1932, 65, [B], 1593—1598; cf. this vol., 833).—The requisite chloromethyl alkyl ether is added slowly and with agitation to an ice-cold mixture of the requisite alcohol and C_2H_5N and the mixture is boiled until the upper layer no longer

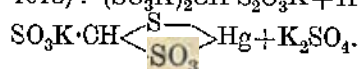
increases. This layer is washed, dried over K_2CO_3 , purified by Na, and fractionally distilled (apparatus described). The following compounds are described: *Me ethers*; ethoxymethyl (methylethylformal), b.p. 65.06—65.18°/744.6 mm.; *n-propoxymethyl*, b.p. 92.7°/761.3 mm.; *n-butoxymethyl*, b.p. 119.5°/760.9 mm.; *n-amyloxymethyl*, b.p. 144.5°/757.4 mm.; *n-hexyloxymethyl*, b.p. 167.7°/757.4 mm.; *Et ethers*; *n-propoxymethyl*, b.p. 113.4°/762.6 mm.; *n-butoxymethyl*, b.p. 137.6°/744.9 mm.; *n-amyloxymethyl*, b.p. 161.9°/757.4 mm.; *n-hexyloxymethyl*, b.p. 184.0°/760 mm.; *Prⁿ n-butyloxymethyl ether*, b.p. 160.2°/755 mm. H. W.

Esters of monofluorophosphoric acid. W. LANGE and G. VON KRUEGER (Ber., 1932, 65, [B], 1598—1601; cf. A., 1929, 662).—*Me₂ monofluorophosphate* (I), b.p. 150.1°/759 mm., is prepared from MeI and Ag_2PO_3F at 50°. Et_2PO_3F has b.p. 171.5—172°/757 mm. At 200°, the esters are unimol. (I) is readily hydrolysed by aq. alkali, whereas (II) is only slowly affected by KOH—EtOH, whereby it is ultimately transformed into dialkyl phosphate. The esters have very marked physiological action. H. W.

$\beta\beta$ -Dichloro- and $\beta\beta$ -dibromo-divinyl sulphoxides. A. E. KRETOV and S. M. KLIEGER (J. Gen. Chem. Russ., 1932, 2, 322—326).—Divinyl sulphoxide, prepared by the action of $NaHCO_3$ on $\beta\beta'$ -dichlorodiethyl sulphoxide, is chlorinated in EtOH to $\alpha\alpha'\beta\beta'$ -tetrachlorodiethyl sulphoxide, m.p. 122.5° (80—85% yield), converted into $\beta\beta'$ -dichlorodivinyl sulphoxide (A., 1926, 1224), b.p. 86—87°/10 mm., m.p. 15°. $\alpha\alpha'\beta\beta'$ -Tetrabromodiethyl sulphoxide, m.p. 120.8°, is similarly obtained (35—50% yield), and is converted by $NaHCO_3$ into $\beta\beta'$ -dibromodivinyl sulphoxide, m.p. 40.5—42° (75% yield). Neither this nor the Cl_2 -compound could be reduced. G. A. R. K.

Dithiomethionic acid. H. J. BACKER (Rec. trav. chim., 1932, 51, 981—987).—Oxidation of K or Ba thiolmethanedisulphonate with I in neutral aq. solution affords *di(thiolmethanedisulphonic) acid*, $[(SO_3H)_2CH\cdot S]_2 + 6H_2O$ (I) ($K_4 + 2H_2O$, Tl_4 , Ba , and *strychnine* + $6H_2O$ salts). The Pb , Ag , Cu , and Hg salts are unstable, decomp. of the Pb salt occurring thus: $2[Pb(O_3S)_2CH\cdot S]_2 \rightarrow Pb\{Pb(O_3S)_2CH\cdot S\}_2 + Pb\{SC(SO_3H)\cdot SO_3\}_2$, the second product not being isolated. Oxidation of (I) with Cl_2 in neutral aq. solution gives $CH(SO_3H)_3$, whilst H_2S is obtained by reduction with Zn. (I) is decomposed in presence of excess of alkali: $(I) + H_2O \rightarrow HS\cdot CH(SO_3H)_2$ (II) + $HO\cdot S\cdot CH(SO_3H)_2$ (III), (II) being isolated as its Tl salt, whilst (III) accounts for the yellow colour formed in the presence of alkalis, but is further decomposed thus: $(III) + KOH \rightarrow K_2SO_3 + OH\cdot SO\cdot SO_3K + H_2O$. J. W. B.

Reaction of potassium disulphomethanemonothiosulphate with mercuric oxide. H. J. BACKER (Rec. trav. chim., 1932, 51, 988—990).—That the acid previously designated thiolmethanetrithiosulphonic acid is actually *disulphomethanemonothiosulphuric acid* (A., 1931, 600) is confirmed, since dissolution of HgO in an aq. solution of its K salt gives the *K Hg* salt of thiolmethanedisulphonic acid (cf. this vol., 1018): $(SO_3K)_2CH\cdot S_2O_3K + HgO \rightarrow$



J. W. B.

Relation between Kolbe's reaction and hydrogen-ion concentration. VII. H. R. MATSUDA.—See this vol., 1214.

Electrolysis of fused acetates and propionates. G. B. MOORHOUSE.—See this vol., 1213.

Maximum rotations and correlation of disubstituted acetic acids containing a methyl group. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1932, 98, 1—7).—Contrary to those in the series previously investigated (this vol., 365), the max. vals. of $[M]_D$ (given in parentheses) for the acids of the homologous series $CHMeR\cdot CO_2H$ increase progressively towards the left as the size of R is increased. *l*- α -Methyl-*n*-butyric (−18°); *n*-valeric, b.p. 96°/15 mm., $[\alpha]_D^{25} -18.4^\circ$ (−21.4°), *n*-hexoic, b.p. 105°/5 mm., $[\alpha]_D^{25} -18.7^\circ$ (−24.3°), *n*-nonoic, b.p. 115°/1 mm., $[\alpha]_D^{25} -15.9^\circ$ (−27.3°), and *d*-methyl-*n*-dodecoic, b.p. 150°/1 mm., $[\alpha]_D^{25} +12.85^\circ$ (+27.5°), acid, are obtained by resolution of the *dl*-forms. Correlation of the configurations of β -methyl-*n*-hexoic and α -methyl-*n*-valeric acids is afforded by their conversion into the same *d*- α -amino- β -methyl-*n*-pentane, $[\alpha]_D^{25} +4.09^\circ$ (A., 1930, 63). J. W. B.

α - and β -Forms of the higher polybromo-fatty acids (octa- and deca-bromides of behenic acid). H. RUNY (Z. physiol. Chem., 1932, 210, 236—245).—The α - and β -octabromides of the unsaturated acids of brain kephalin are shown to consist of mixtures of isomerides of different solubility and m.p. by re-brominating the Br-free acids derived from each group. In each case mixtures of α - and β -octabromides were obtained differing in the percentage of each group present according to the method of bromination. In between the α (insol.) and β (sol.) groups there are bromides of intermediate solubility, the whole forming a graded series. J. H. B.

Polymerisation and ring formation. XVII. Friedel-Crafts syntheses with the polyanhydrides of dibasic acids. J. W. HILL (J. Amer. Chem. Soc., 1932, 54, 4105—4106).—The polyanhydride (A., 1930, 1558) from adipic acid with C_6H_6 and $AlCl_3$ gives δ -benzoylvaleric acid, m.p. 70—71°, and $\alpha\delta$ -dibenzoylbutane, m.p. 105—106°, according to the equation $[\cdot OC(CH_2)_n CO \cdot O]_x + C_6H_6 \rightarrow (CH_2)_n Bz_2 + {}^x Bz(CH_2)_n CO_2H + {}_i(CH_2)_n(CO_2H)_2$. Similarly, sebacic polyanhydride gives θ -benzoylnonoic acid, m.p. 77—78°, and $\alpha\theta$ -dibenzoyloctane, m.p. 92—93°. This furnishes a convenient method of prep. of ω -benzoylated fatty acids. C. J. W. (b)

Identification test for oxalic acid. E. R. CALEY (Ind. Eng. Chem. [Anal.], 1932, 4, 445).—Only $H_2C_2O_4$ and dihydroxytartaric acid give a ppt. when 1 c.c. of 6*N*-NaOH is added with vigorous shaking to 0.1 g. of the solid in 2 c.c. of cold H_2O . E. S. H.

Reaction between ethyl oxalate and phosphorus pentabromide. V. V. TSCHELINCEV and V. I. ESAFOV (J. Gen. Chem. Russ., 1932, 2, 217—224).— $Et_2C_2O_4$ and PBr_5 react incompletely at atm. pressure, but on heating in an autoclave at 100° for 8—10 hr. some 72% reacts, forming *ethoxalyl bromide*, b.p. 150—152°, PBr_3 , and $EtBr$; PCl_2Br_2

cannot be used in place of PBr_5 . $\text{CBr}_3\cdot\text{CO}_2\text{H}$, HBr , and PBr are produced in side-reactions.

G. A. R. K.

Reduction of unsaturated organic acids at the dropping mercury cathode. L. SCHWABER (Chem. Listy, 1932, 26, 485—489).—Unsaturated carboxylic acids possessing conjugated double linkings, e.g., pyruvic, maleic, fumaric, citraconic, mesaconic, aconitic, cinnamic, and sorbic acids, are readily reduced at a dropping Hg electrode, using a potential of -0.4 to 1.0 volt in acid and -1.2 to -2.1 volt in alkaline solution. Fumaric acid differs from maleic acid in its smaller reduction potential (-1.69 and -1.89 volt, respectively). Citric, malonic, and tartaric acids can be determined polarographically after conversion into the corresponding unsaturated acids.

R. T.

Preparation of glutaconic ester and acid. B. S. GIDVANI (J.C.S., 1932, 2666).—The prep. from Et β -hydroxyglutarate and SOCl_2 in $\text{C}_5\text{H}_5\text{N}$ is described; the ester is hydrolysed by 50% aq. HCl.

F. R. S.

cis-cis-Muconic acid and its oxidation by potassium permanganate. J. BOESEKEN and C. L. M. KERKHOVEN (Rec. trav. chim., 1932, 51, 964—970).—Muconic acid, m.p. 187 — 188° [improved prep. by Farmer's method (J.C.S., 1923, 123, 2540) and by oxidation of PhOH , $o\text{-C}_6\text{H}_4(\text{OH})_2$ or o -benzoquinone with AcO_2H], is the *cis-cis*-modification and on oxidation with KMnO_4 at 0° gives (besides $\text{H}_2\text{C}_2\text{O}_4$) only mesotartaric acid unmixed with any *dl*-form. Such absence of configurational changes during KMnO_4 oxidation confirms Behrend and Heyer's conclusion (A., 1919, i, 521) that muconic acid, m.p. 298° , is the *trans-trans*-form.

J. W. B.

Constitution of the safran dye, crocetin. Synthesis of perhydrobixin ethyl ester and perhydrobixin. P. KARRER, P. BENZ, R. MORE, H. RAUDNITZ, M. STOLL, and T. TAKAHASHI (Helv. Chim. Acta, 1932, 15, 1218—1219).—Perhydrocrocetin, when treated successively with Br and KOH , gives the $\alpha\alpha'$ -dihydroxycarboxylic acid, changed by $\text{MgMe}\cdot\text{Hal}$ to the *ditert*-carbinol, which with $\text{Pb}(\text{OAc})_4$ yields $\beta\alpha$ -diketo- γ -dimethyl-*n*-hexadecane, b.p. 135 — $138^\circ/0.2$ mm. (disemicarbazone, m.p. 168°). Crocetin is, therefore, $(\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{H})_2$. Perhydrobixin (I) gives similarly $\beta\gamma\alpha$ -tetramethyl-hexadecane- $\alpha\pi$ -dialdehyde, b.p. 185 — $190^\circ/0.3$ mm., oxidised to the corresponding dicarboxylic acid, b.p. $220^\circ/0.1$ mm. In accordance with these constitutions, oxidation of tetrahydrocrocetin gives methylsuccinic acid (II), but not succinic acid (III), and of tetrahydrobixin (III), but not (II). Et $_2$ sodiomethylmalonate and $\alpha\gamma$ -dibromopropane give Et $_2$ $\alpha\alpha'$ -dimethyl-*n*-pentane- $\alpha\alpha\alpha'$ -tetracarboxylate, whence the dicarboxylic acid was obtained. Reduction of the ester of this gives the dialcohol; the corresponding dibromide with Et $_2$ sodiomalonate gives Et $_2$ $\gamma\gamma$ -dimethyl-*n*-nonane- $\alpha\alpha\alpha'$ -tetracarboxylate, which was changed to the *K* salt of the acid ester of the corresponding dicarboxylic acid; this on electrolysis gives the di-ester of (I), identified as diamide, m.p. 110.5° , and di-2:4:6-tribromoanilide, m.p. 83° .

R. S. C.

Formation of triacetylacetic ester. K. VON AUWERS (Ber., 1932, 65, [B], 1561—1563).—Et *o*-acetylacetoacetate and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ give 3-methylpyrazol-5-one and Et 3:5-dimethylpyrazole-4-carboxylate in varying ratio. Correspondingly, Et diacetoacetate reacts normally in part and, in part, loses Ac , whilst its *O*-Ac derivative gives essentially Et dimethylpyrazolecarboxylate with, occasionally, methylpyrazolone; Seidel's compound,

$\text{N}:\text{CMe} > \text{C}(\text{Ac})\cdot\text{CO}_2\text{Et}$, m.p. 188° (this vol., 931), is never encountered. On theoretical grounds the existence of Seidel's Et triacetylacetate is doubted and the constitution of the compound, m.p. 188° , is regarded as unproven.

H. W.

Action of sodium ethoxide on itaconic, citraconic, and mesaconic esters. E. H. COULSON and G. A. R. KON (J.C.S., 1932, 2568—2573).—The addition of NaOEt to citraconic, itaconic, and mesaconic esters results in the formation of some 50% of *OEt*-ester at the end of 5 min. and reaches a max. of 80%. The reaction is reversible. The unsaturated ester recovered consists of the two $\alpha\beta$ -forms (citraconic and mesaconic) only, except in the short-time experiments, when a small amount of itaconic acid is obtained. This shows that the 3-C change is more rapid than the addition of EtOH . The *OEt*-acid has been synthesised from Et $_2$ ethane- $\alpha\beta$ -tricarboxylate and $\text{CH}_2\text{Cl}\cdot\text{OEt}$, and is identical with that obtained by Hope's method (J.C.S., 1912, 101, 895). The three isomeric esters are not equilibrated unless EtOH is added.

F. R. S.

[Attempted] synthesis of $\alpha\alpha'$ -diketoadipic acid. H. SUTTER (Annalen, 1932, 499, 47—59).—Addition of $\text{Et}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ to succinyl chloride and anhyd. HCN in Et_2O gives 18% of $\alpha\alpha'$ -diketoadiponitrile, m.p. 98° , which with $\text{NHPh}\cdot\text{NH}_2$ affords succinphenylhydrazide and is hydrolysed by conc. HCl at about 5° to 40% of $\alpha\alpha'$ -diketoadipamide, m.p. 230 — 235° (decomp.) (darkens at 200°). This is hydrolysed by dil. NaOH to a little $\alpha\alpha'$ -diketoadipamic acid, m.p. 152° (decomp.); definite products could not be isolated from acid hydrolysates. Et sodio-oxaloacetate and Br in cold CHCl_3 give Et $\alpha\delta$ -diketobutane- $\alpha\beta\gamma\delta$ -tetracarboxylate, m.p. 83° , which when hydrolysed by dil. HCl affords furan-2:3:5-tricarboxylic acid (I), m.p. 273° (decomp.); treatment of the product from the acid mother-liquors with diazomethane gives a small amount of a substance, $\text{C}_{12}\text{H}_{14}\text{O}_{10}$, m.p. 160° (not sharp). Et sodio-oxaloacetate and $\text{CH}_3\text{Br}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ (II) yield Et β -carbethoxy- $\alpha\alpha'$ -diketoadipate, m.p. 79° , also hydrolysed by dil. HCl or H_2O to (I); hydrolysis with aq. $\text{Ba}(\text{OH})_2$ gives $\text{H}_2\text{C}_2\text{O}_4$. Definite products could not be isolated from (II) and "mol." Ag. Oxidation of $\alpha\alpha'$ -dihydroxyadipic acid with aq. KMnO_4 at 5° gives a little α -hydroxy- α' -ketoadipic acid (as 2:4-dinitrophenylhydrazone, m.p. 213°); with $\text{Br}\cdot\text{H}_2\text{O}$, a compound (2:4-dinitrophenylhydrazone, decomp. 237°) results. Oxidation with O_2 in presence of Cu powder and H_2O gives a little of the diketo-acid (?) [di-(2:4-dinitrophenylhydrazone)]; with H_2O_2 and FeSO_4 , succinaldehyde results.

H. B.

Isolation of hexuronic acid. E. K. NELSON (Science, 1932, 76, 345).—Difficulties encountered in King's method are pointed out. L. S. T.

Polygalacturonic acid diacetate and dinitrate. K. SMOLEŃSKI and W. PARDO (Chem. Listy, 1932, 26, 446—449).—Polygalacturonic acid yields a diacetate, $[C_6H_6O_4(OAc)_2]_n$, and dinitrate, $[C_6H_6O_4(NO_3)_2]_n$, indicating that it contains ≥ 2 OH groups. R. T.

Complex types involved in the catalytic oxidation of thiol acids. M. SCHUBERT (J. Amer. Chem. Soc., 1932, 54, 4077—4085).—Complexes of Fe^{++} with cysteine and thiolacetic acid and its Et ester are prepared in absence of O_2 ; their structures are discussed in detail. The role of these complexes in the catalytic oxidation of SH-acids in presence of Fe salts is indicated and a theory of the mechanism of this catalysis is presented. If an air-free solution of Fe^{++} and twice as many mols. of thiolacetic acid is mixed in H_2 and air-free KOH is added dropwise, a yellow colour soon develops and further slow addition ppts. the yellow salt, $Fe(S\cdot CH_2\cdot CO_2)_2 \cdot 1.5H_2O$; further addition of KOH causes this to dissolve, giving a deep orange to orange-red solution, from which $Fe(S\cdot CH_2\cdot CO_2K)_2$ is isolated; if enough KOH is added, $Fe(OH)_2$ is pptd. The same sequence of changes occurs with cysteine or when Fe is replaced by Co (the colours are different).

C. J. W. (b)

Fission of mercaptal- and mercaptol-acetic acids $[CR'R_2(S\cdot CH_2\cdot CO_2H)_2]$. B. HOLMBERG (J. pr. Chem., 1932, [ii], 135, 57—100).—Ethylidenebis-thiolacetic acid may be determined by addition of $HgCl_2$ or $HgSO_4$, and titration of the acid liberated or (iodometrically) of the Hg compound formed according to the equation $CHMc(SR)_2 + 2HgCl_2 + H_2O = McCHO + 2HgCl\cdot SR + 2HCl$ [or, perhaps, $CHMc(SR)_2 + HgCl_2 + H_2O = McCHO + Hg(SR)_2 + 2HCl$]. Reaction is retarded by the presence of Br^- or I^- , particularly the latter, and is very slow in EtOH; it is rather faster with $HgSO_4$ than with $HgCl_2$. It is generally applicable to compounds of the type $CRR'(S\cdot CH_2\cdot CO_2H)_2$, with the exception of those from CH_2O and phenolic aldehydes, and also to glucose diethylmercaptal (cf. A., 1894, i, 269). Trustworthy results are obtained with the phenolic aldehydes by substitution of $CdSO_4$ for the Hg salt in a solution buffered with $NaOAc$ or $CO(NH_2)_2$ and iodometric titration; this method gives sharper end-points in many other cases, but fails with the derivatives of CH_2O , $CHO\cdot CO_2H$, $CH_2Ph\cdot CHO$, and $CHPh\cdot CH\cdot CHO$. Direct iodometric titration gives consistently high results. The course of reaction may be followed kinetically; it is complicated, but its velocity is governed essentially by the equations $CRR'(S\cdot CH_2\cdot CO_2H)_2 + I_2 + H_2O = (S\cdot CH_2\cdot CO_2H)_2 + CRR'O + 2HI$, and $2I + I' \rightleftharpoons I_3$. The reaction velocity is increased by added $(S\cdot CH_2\cdot CO_2H)_2$, which is therefore responsible for the increase in velocity coeff. as the reaction proceeds. CH_2O displaces other aldehydes from their thiolacetic acid derivatives with formation of $CH_2(S\cdot CH_2\cdot CO_2H)_2$; the reaction is apparently irreversible.

The thiolacetic acid derivatives were prepared by direct condensation with the aldehydes, if necessary

in presence of a little HCl (cf. A., 1888, 479); the following are new: propylidene-, m.p. 74—75°; 3:4-dihydroxybenzylidene-, m.p. 150—151° (decomp. ?); vanillylidene-, m.p. 136—138°; veratrylidene-, m.p. 124—126°; piperonylidene-, m.p. 138—139°; β -phenylethylidene-, m.p. 99—100°; hydrocinnamylidene-, m.p. 110—111°; furfurylidene-, m.p. 108—109°; β -butylidene-, m.p. 109—111°; carboxyisopropylidene-, m.p. 146—147° [from the Et ester, m.p. 99—101° (loc. cit.)], and cyclohexylidene-, m.p. 138—140°, -bisthiolacetic acids. H. A. P.

Identification of aldehydes and primary alcohols by dimethyldihydroresorcinol. C. H. KAO and J. Y. YEN (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 185—188).—The prep. of dimethyldihydroresorcinol (I) is modified. Details are given for the $K_2Cr_2O_7\text{--}H_2SO_4$ oxidation of primary alcohols and condensation of the resulting aldehydes with (I). The alkylidenebisdimethyldihydroresorcinols from the following aldehydes are new, or have been previously assigned incorrect m.p.: Pr^iCHO , m.p. 133.8°; Bu^iCHO , m.p. 104.5°; n -hexaldehyde, m.p. 108.5°; n -heptaldehyde, m.p. 101.7°; n -octaldehyde, m.p. 89.8°; n -nonaldehyde, m.p. 86.3°; n -decaldehyde, m.p. 91.7°. R. S. C.

Distyryl ketone and triphenylmethane. XV. Thermal decomposition of α -alkoxylalkyl chlorides. F. STRAUS and H. J. WEBER [with N. STANCOVICI].—See this vol., 1132.

Oxidation of methylglyoxal to pyruvic acid with molecular oxygen. C. NEUBERG and M. KOBEL (Biochem. Z., 1932, 252, 215—230).—Within the range pH 5.8—8.1 the H sulphite compound of methylglyoxal in aq. solution in presence of phosphate (or, to a smaller extent, in that of borate) takes up O_2 with formation of $AcCO_2H$. At pH 6.8 and 37° the reaction is quant. Free methylglyoxal reacts much more slowly and to a much smaller extent. In Na_2CO_3 solution the reaction also proceeds anaerobically, but the yields of $AcCO_2H$ are poor.

W. McC.

Reactions of methylglyoxal with nitrogen-free compounds. C. NEUBERG and J. BURKARD (Biochem. Z., 1932, 253, 222—224).—Although oxalacetic and acetonedicarboxylic acids do not reduce Fehling's solution and methylglyoxal reduces it only very slightly, mixtures of the acids with the keto-aldehyde in dil. aq. solution reduce it readily. The condensation products responsible for the reduction react with hydrazine derivatives.

W. McC.

Correlation of the Walden inversion with the pinacol and Beckmann changes. J. KENNER (Nature, 1932, 130, 309).—A discussion. L. S. T.

Detection of acetone. R. RAW (J.S.C.I., 1932, 51, 276r).—The condensation of $COMe_2$ and $o\text{--}NO_2\text{--}C_6H_4\text{--}CHO$ (I) to indigotin can be used as a test for small quantities of the former by heating the solution containing $COMe_2$ in an org. solvent, e.g., MeOH or EtOH, with a few crystals of (I) for about 1 min., pouring into an equal vol. of 10% aq. NaOH, and heating for a few min. at 80—90°. Addition of aq. NaOH at the commencement of the test retards the reaction.

Condensation products of propanone; mesityl oxide and derivatives. G. GALLAS and F. G. GONZALEZ (Anal. Fis. Quím., 1932, 30, 645—654).— $\text{CMe}_2\text{Cl}\cdot\text{CHAc}\cdot\text{OH}$ may be prepared by adding mesityl oxide to a solution of HOCl (3% free Cl) and extracting with Et_2O after 24 hr. With primary and *sec.* amines it yields compounds of the type $\text{NHR}\cdot\text{CMe}_2\cdot\text{CHAc}\cdot\text{OH}$; the compound obtained with *isoamylamine* has m.p. 212° ; that with NH_2Ph , m.p. 189° (*Bz* derivative, m.p. 155° ; *oxime*, m.p. about 250°); with NHPr_2 , m.p. 180° ; and with *toluidine*, m.p. 206° ; the *hydrochlorides* of the products obtained with NH_2Et , NH_2Pr , and NH_2Bu have m.p. between 150° and 190° . NH_2Et , NHPhEt , NHPhMe , and NHPhPr formed deep red condensation products which could not be isolated. H. F. G.

Catalytic decomposition of diethyl ketone phenylhydrazone. A. E. ARBUSOV and V. A. ROTERMEHL (J. Gen. Chem. Russ., 1932, 2, 397—398).— $\text{Et}_2\text{ ketone phenylhydrazone}$, b.p. $144^\circ/9\text{ mm.}$, on heating with a trace of ZnCl_2 gives NH_3 and a 69% yield of 3-methyl-2-ethylindole, b.p. $153^\circ/10\text{ mm.}$, m.p. 59.5° (*dipicrate*, m.p. 150.5°). G. A. R. K.

Triacetylmethane. K. VON AUWERS (Ber., 1932, 65, [B], 1634—1636).—Comparison of the optical consts. of triacetylmethane (Birckenbach and others, this vol., 933) with those of the acetate of diacetoacetic ester, ethoxymethyleneacetone, and acetylacetone acetate shows that it is enolised to the extent of at least 75%. Its salts are therefore *O* derivatives. Its presence predominatingly as ketone in H_2O or $\text{HCl}\cdot\text{H}_2\text{O}$ is in harmony with the known ketonising power of these media. H. W.

[Triacetylmethane.] L. BIRCKENBACH, K. KELLERMANN, and W. STEIN (Ber., 1932, 65, [B], 1636—1637; cf. this vol., 933).—In reply to von Auwers (preceding abstract) it is stated that the salts of triacetylmethane (I) are derived initially from the enolic form. Dissolution in H_2O causes extensive hydrolysis into KOH and free (I), which becomes extensively ketonised. The K salt is hydrolysed rapidly, the Ag salt slowly. The contradiction that (I) can be sharply titrated in presence of phenolphthalein, but is completely enolised only by a large excess of KOH , is merely apparent, depending on the widely differing concn. of KOH employed. Conclusions with respect to the constitution of homogeneous (I), particularly on its keto-enolic equilibrium, cannot be based on measurements of its absorption in H_2O . H. W.

Influence of the vicinity of amino-groups on the formation of salts of α -dioximes (oxamide-dioxime). J. V. DUBSKY and A. OKAC (Coll. Czech. Chem. Comm., 1932, 4, 388—399).—Gradual addition of an aq. solution of 3 mols. of oxamide-dioxime (I), $[\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot]_2$ (designated OxH_2), m.p. 204° (lit. 195° and 200°), to a solution of 1 mol. of CuSO_4 in aq. NH_3 gives the salt $\text{Cu}(\text{OxH})_2\cdot 2\text{H}_2\text{O}$ (II), decomp. about 200° , which is completely sol. only in 4 mols. of HCl (0.1*N*), and is thereby converted (mainly) into the tetrammine salt (III), $\text{Cu}(\text{OxH}_2)_2\text{Cl}_2$, decomp. explosively at about 142° [corresponding *dinitrate* (IV), decomp. explosively

at about 128°], which is also prepared from (I) (3 mols.) and CuCl_2 (1 mol.) in dil. HCl . The conversion of (II) into (III) is considered to occur by way of an unstable intermediate formed by addition of 4*HCl* to the NH_2 -groups of (II). Aq. solutions of (I) (3 mols.) and CuSO_4 (1 mol.) afford a complex, $\text{Cu}_2(\text{OxH}_2)_5\text{SO}_4\cdot 4\text{H}_2\text{O}$, decomp. about 158° (slight explosion). (I) and an excess of CuCl_2 give the salt $\text{Cu}(\text{OxH}_2)_2\text{Cl}_2$ (V), decomp. explosively about 169° , also formed in small amount when (II) is dissolved in 0.1*N*- HCl (above), and converted by AgNO_3 into (IV): $2\text{Cu}(\text{OxH}_2)_2\text{Cl}_2 + 4\text{AgNO}_3 \rightarrow 4\text{AgCl} + \text{Cu}(\text{NO}_3)_2 + \text{Cu}(\text{OxH}_2)_2(\text{NO}_3)_2$. Addition of aq. NH_3 to an aq. solution of (V) ppts. a complex, $3\text{CuOx}\cdot\text{Cu}(\text{OH})_2\cdot 6\text{H}_2\text{O}$, decomp. about 196° (slight explosion), also formed from an equimol. mixture of (I) and CuCl_2 (or CuSO_4) in H_2O and aq. NH_3 , in which the $\text{NO}\cdot\text{Cu}\cdot\text{ON}$ group probably occurs. The proximity of the NH_2 to the $\text{N}\cdot\text{OH}$ groups should suppress the basic function of the latter, thereby causing them to react as acids; it should, therefore, be possible to prepare complexes containing the group $\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NO} \end{smallmatrix} \text{M}$.

The salt $\text{Ni}(\text{OxH})_2\cdot 2\text{H}_2\text{O}$ (Tschugaev and Surenjanz, A., 1907, i, 198) is converted by conc. HCl (4 mols.) into the salt $\text{Ni}(\text{OxH}_2)_2\text{Cl}_2$, decomp. about 216° ; the *sulphate* (+4*H* $_2\text{O}$), decomp. about 219° , is similarly prepared. H. B.

Identification of common carbohydrates. W. M. DEHN, K. E. JACKSON, and D. A. BALLARD (Ind. Eng. Chem. [Anal.], 1932, 4, 413—415).—Colour reactions given by many reagents with common carbohydrates are listed so as to form a scheme of identification. Single-test identifications are given for cellulose, starch, glycogen, dextrin, pectin, fructose, mannose, maltose, and rhamnose; other carbohydrates require two or more tests. E. S. H.

Determination of reducing sugars. Application of Shaffer and Hartmann iodometric cuprous titration. G. L. MARSH and M. A. JOSLYN (Ind. Eng. Chem. [Anal.], 1932, 4, 368—371).—Sources of error in the procedure (A., 1921, ii, 417) have been examined and modifications are suggested. E. S. H.

Formation of furfuraldehyde from methylated pentoses. H. G. BOTT and E. L. HIRST (J.C.S., 1932, 2621—2624).— Me_3 derivatives of arabo- and xylo-furanose and -pyranose are decomposed readily by 12% aq. HCl with formation of furfuraldehyde in good yield. The mechanism of the reaction is discussed. F. R. S.

Ribosephosphoric acid from xanthylic acid. II. P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1932, 98, 9—16).—Methylation of the *d*-ribosephosphoric acid (I), $[\alpha]_D^{25} -8.93^\circ$ as its Na salt in H_2O , obtained from xanthylic acid (this vol., 497) by the action of MeI on the Ag salt of its methylriboside, affords *dimethylphosphordimethyl-n-methylriboside*, b.p. $128\text{—}133^\circ/0.1\text{ mm.}$, $[\alpha]_D^{25} -17.2^\circ$, which could not be completely hydrolysed to the methylated ribose. Oxidation of (I) with HNO_3 gave only $\text{H}_2\text{C}_2\text{O}_4$. Reduction of $\text{O} \begin{smallmatrix} \text{CH}(\text{OH})\cdot\text{CH}(\text{OH}) \\ | \\ \text{CH} \end{smallmatrix} \text{CH}(\text{OH}) \text{CH}_2\text{OPO}_3\text{H}_2$ (I) (as its Ba salt) with $\text{H}_2\text{—PtO}_2$ affords an inactive

POCl_3 and PCl_5 in Et_2O at room temp., a quant. yield of *tri-β-diisopropylidene-fructose phosphate*, m.p. 136—137° (*Na* and *K* salts), is obtained; the other compounds are not esterified. The free acid [*cinchonidine*, m.p. 212—213° (decomp.), and *Ag* salts] is hygroscopic. *Me*, m.p. 109°, and *Et*, m.p. 113—114°, *di-β-diisopropylidene-fructose phosphate* are described; on hydrolysis they yield, probably, *Na Et* and *Na Me β-dusopropylidene-fructose phosphates*. H. F. G.

[Preparation of] sugars for microbiological uses. Maltose. A. STEPANOV and A. KUZIN (Khim. Farm. Prom., 1932, No. 2—3, 57—64).—Starch solution (5%) is kept at 37° for 24 hr. with enzyme (0.8%) from malt extract; albumins are coagulated by warming and maltose from the filtrate is purified by recrystallisation. CH. ABS.

3 : 6-Dinitro-2 : 7-dihydroxyfluoran as a reagent for the detection of reducing sugars. M. DOMINKIEWICZ (Rocz. Chem., 1932, 12, 686—692).—2 : 7-Dinitro-3 : 6-dihydroxyfluoran yields with KOH - EtOH an orange K salt, an orange-brown K_2 salt, and a violet K_3 salt; the last two dissociate on dilution with H_2O to yield the K salt. 3 : 6-Dinitro-2 : 7-dihydroxyfluoran (I) gives an orange-brown K_2 salt, which readily dissociates, yielding an orange K salt, reduced to 2 : 7-dihydroxyrhodamine by glucose, fructose, mannose, galactose, arabinose, xylose, lactose, and maltose, but not by sucrose, raffinose, starch, and inulin, or by sorbitol, dulcitol, mannitol, glycerol, glyoxal, glyceraldehyde, CH_2O , HCO_2H , or $\text{H}_2\text{C}_2\text{O}_4$. Reducing sugars are detected by adding (I) to the alkaline solution, when a cerise coloration develops, changing to an intense orange fluorescence on acidification. This method serves for the detection of 0.01275 mg. per c.c. of sugar. R. T.

Reaction of starch with dilute alkali. M. SAMEC [with S. SAZANOW] (Chem. Listy, 1932, 26, 451—454).—The titration curves of amylopectin, amylophosphoric acid, and phosphoric acid all exhibit a series of step-like breaks. The viscosity-c.c. of NaOH curve of amylopectin at first rises to a max. at 0.5 g.-equiv. of NaOH , then falls to a min. at 1 g.-equiv., after which it rises continuously. These observations support the author's theory of the constitution of starch. R. T.

Constitution of cellulose and its derivatives. III. Solid solutions and dyeing. (MILLER) A. DOBRY and J. DUCLAU (Bull. Soc. chim., 1932, [iv], 51, 1172—1177).—Cellulose diacetate is dyed by the following complexes (in aq. solution): Fe^{+++} (I), Co , and Mo thiocyanates; Au bromide (brown) (II); FeCl_3 ; phosphomolybdic acid; Fe nitrososulphide, $\text{Fe}_2\text{K}_2\text{S}_2(\text{NO})_2$ (III). Dyeing of cellulose triacetate, ethylcellulose, and cellophane with (I), cellulose triacetate and ethylcellulose with (II), and ethyl- and benzyl-cellulose with (III), also occurs. Dyeing is considered to be due to the formation of solid solutions; the complexes used are sol. in Et_2O or EtOAc , and the cellulose derivatives which are dyed contain the same groupings. Of the complexes used, (III) only is sol. in PhOMe ; the dyeing of benzylcellulose by (III) supports the solution theory. Cellulose di- and tri-nitrates are not dyed by any of the above

complexes; this may be concerned with the cryst. structure of the nitrates. In accordance with this view, cellobiose octa-acetate is not coloured by crystallisation from an EtOH solution of (I), its Co analogue, or (III); amorphous cellobiose acetates and the micro-cryst. acetates of (probably) cellobiose and higher polymerides are coloured, thus indicating that the constitution of the compounds is only one aspect of the problem. H. B.

Resolution of racemic amines at low temperatures. T. D. STEWART and C. ALLEN (J. Amer. Chem. Soc., 1932, 54, 4027—4039).—The method, which consists in salt formation between amine antipodes and optically active acids at -70° , is standardised with *dl-α*-phenylethylamine and 1-bromo-*d*-camphor-10-sulphonic acid; formation of cryst. salt is necessary for resolution. Success in the resolution appears to depend on a difference between the amine enantiomorphs in their rate of forming salt crystals from supersaturated solutions, rather than on a difference in the solubility of the non-enantiomorphic salts. Attempted resolution of an *as*-substituted amine, $\text{NPhEt-CH}_2\text{Ph}$, failed.

C. J. W. (b)

Action of alkali on ζ -bromo-*n*-hexylamine and η -bromo-*n*-heptylamine. A. MÜLLER and P. KRAUSS (Monatsh., 1932, 61, 219—228).—The action of KOH on ζ -bromo-*n*-hexylamine [hydrobromide, m.p. 142—143° (corr.) (lit., 89—90°)] gives only a little hexamethyleneimine (I), whilst with η -bromo-*n*-heptylamine no heptamethyleneimine is formed (cf. J. Pharm. Soc. Japan, 1928, 48, 72; 534, 368; 557, 688). The primary amines were prepared by the phthalimide route, the following compounds being described: α -bromo- ζ -phthalimido-*n*-hexane, m.p. 57° (corr.); α -bromo- η -phthalimido-*n*-heptane, m.p. 34° (corr.), and heptamethylenediphthalimide, m.p. 129° (corr.). The chloroplatinate of (I) has m.p. 197° (decomp.); the form ($+1\text{H}_2\text{O}$), m.p. 149—150°, could not be obtained. H. A. P.

Racemisation of amino-acids in aqueous solution by acetic anhydride. V. DU VIGNEAUD and C. E. MEYER (J. Biol. Chem., 1932, 98, 295—308).—In extension of previous work (this vol., 753), the Na salts of either the Ac or formyl derivatives of various NH_2 -acids are racemised by Ac_2O and thus are obtained: *acetyl-dl-methionine*, m.p. 114—115° [from *acetyl-l-methionine*, m.p. 111—111.5° (corr.), $[\alpha]_D^{25} -16.1^\circ$; identical with a specimen prepared by Ac_2O - NaOH on the *dl*-parent]; *dl-glutamic acid* (from *acetyl-d-glutamic acid*); *formyl-dl-phenylalanine* [from *formyl-l-phenylalanine* (brucine salt, m.p. 91—93°, $[\alpha]_D^{25} -7.3^\circ$; cf. Fischer and Schoeller, A., 1907, i, 1037) and from *acetyl-d-phenylalanine*, m.p. 172° (corr.), $[\alpha]_D^{25} -51^\circ$ in EtOH (erroneously described by Knoop and Blanco, A., 1925, i, 1208, as the *l*-compound)]; and *acetyl-dl-arginine*+ $2\text{H}_2\text{O}$, m.p. 108—110° (from *d*-compound). According to the conditions *l*-tyrosine with $\text{NaOH-Ac}_2\text{O}$ affords *N*-*acetyl-l*-tyrosine or *diacetyl-dl-tyrosine*, m.p. 167—170° (corr.). Similar attempts to racemise *diacetyl-l*-cystine lead to decomp., whilst no racemisation of *acetyl-l-proline*+ H_2O , m.p. 81—82°, and anhyd., m.p. 116—117° (corr.), could be effected by this method.

The rate of racemisation of acetyl-*d*-glutamic acid decreases with time, 50% being racemised in 0.25 hr. and 100% in 8 hr. No racemisation occurs with free NHAc-acids, but the action is not due to any sp. action of Na ions, since no racemisation occurs when NaCl is added. The determining factor is the p_H val., since racemisation occurs in the presence of NaOAc (inhibited by addition of H_2SO_4) or with C_3H_5N in place of NaOH. J. W. B.

Action of sugar on amino-acids. I. In alkaline media. J. WATANABE (J. Biochem. Japan, 1932, 16, 163—189).—Deamination of glycine, alanine, leucine, glutamic acid, and lysine in alkaline solution is accelerated by glucose, fructose, galactose, and glyceraldehyde, in presence of which formation of NH_3 , CO_2 , and aldehydes occurs. The influence of the sugar is proportional to its rate of decomp. by alkalis, a decomp. which also renders the sugar more reactive towards NH_2 -acids. With the sugar and NH_2 -acid at 100° the reaction is equimol. and irreversible. F. O. H.

Synthesis of ϵ -amino-*n*-heptoic acid. A. MÜLLER and P. KRAUSS (Monatsh., 1932, 61, 206—211).— ϵ -Keto-*n*-heptoic acid, m.p. 33° (corr.), is conveniently prepared by interaction of $CHNa(CO_2Et)_2$ with $COCl[CH_2]_4CO_2Et$ and hydrolysis and decarboxylation of the product. Its phenylhydrazone, m.p. 97° (decomp.), is reduced by Al-Hg in aq. EtOH to NH_2Ph and ϵ -amino-*n*-heptoic acid, m.p. 188° (decomp.) [hydrochloride, m.p. 131° (corr.); chloroplatinate, m.p. 183° (decomp.); Bz derivative, m.p. 92.5° (Me ester, m.p. 68°), and benzenesulphonyl compound, m.p. 100° ; lactam, m.p. 90 — 90.5° (chloroplatinate)]. H. A. P.

Trichloromethyl alkyl urethanes. N. N. MELNIKOV and M. M. VINOKUROV (J. Gen. Chem. Russ., 1932, 2, 484—490).— CCl_3 chloroformate (I) with *p*-nitroaniline (II) in Et_2O yields *s*-dinitrophenylcarbamide (III) and CCl_3N -*p*-nitrophenylurethane (IV), yellow crystals evolving $COCl_2$ and rapidly decomposing in moist air or with boiling H_2O giving (III) and a little (II). (IV) with NaOAc at 150 — 160° gives *p*-nitrophenylacetamide, whilst when heated alone or in CCl_4 on the water-bath it forms *p*-nitrophenylcarbamide, $COCl_2$, and HCl. With MeOH and EtOH it gives the corresponding alkyl urethanes. *Pr*^a, *Bu*^β, and isoamyl *N*-*p*-nitrophenylurethanes have m.p. 116° , 81° , and 98° ; the corresponding dialkyl carbonates were also obtained, b.p. 167° , 186° , and 228° .

$NHPh_2$ and (I) in Et_2O furnish CCl_3N -*di*-phenylurethane (V), m.p. 61° . This on boiling with H_2O gives $NHPh_2$, on heating alone $COCl_2$ and diphenylcarbamyl chloride, and with NaOAc, $NACPh_2$. With alcohols the following alkyl *N*-*di*-phenylurethanes have been obtained: *Me*, m.p. 85° , *Et*, m.p. 84° , *Pr*^a, m.p. 85° , *Bu*^β, m.p. 87° , and isoamyl, m.p. 84° , together with the corresponding alkyl carbonates. G. A. R. K.

Flask for Van Slyke protein analysis. R. PATTON (Ind. Eng. Chem. [Anal.], 1932, 4, 417).

E. S. H.

Constitution of spilanthol, the pungent principle of para cress. M. ASANO and T. KANEMATSU

(Ber., 1932, 65, [B], 1602—1604; cf. A., 1920, i, 654; 1922, i, 505).—Tetrahydropilanthol is converted by 50% HBr at 160° into decolic acid (identified as the *p*-toluidide, m.p. 76 — 77°) and $NH_2Bu^β$ (identified as *p*-toluenesulphonisobutylamide, m.p. 77°). Ozonisation of spilanthol in $CHCl_3$ and decomp. of the ozonide with warm H_2O affords HCO_2H , succinic acid (?), and $PrCO_2H$. The presence of a conjugated double linking is thus established and confirmed by the formation with maleic anhydride of the compound $C_{18}H_{27}O_4N$, m.p. 167 — 168° . Spilanthol is therefore regarded as Δ^8 -decadienisobutylamide. H. W.

Aminobiuret and its formaldehyde derivative. P. P. T. SAH and S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 189—191).—The preps. of biuret, nitrobiuret, and aminobiuret hydrochloride (I) are modified. (I) with aq. CH_2O gives methylenecaminobiuret, m.p. 220° , but reacts only very slowly with a no. of other aldehydes and ketones. R. S. C.

Determination of the thiocyno-group in organic compounds. A. N. PANTSCHENKO and G. S. SMIRNOV (J. Gen. Chem. Russ., 1932, 2, 193—196).—When org. CNS compounds are heated with Na_2S in EtOH the CNS group is quantitatively eliminated as NaCNS and can be titrated, after removal of excess of Na_2S , by Volhard's method. This method is rapid and accurate for compounds of the aliphatic, aromatic, and mixed series. The presence of the CO, CN, or NO_2 groups, as well as of As, N, and S (other than in the CNS group), does not affect the accuracy. M. Z.

Action of the Grignard reagent on aminonitriles. II. T. THOMSON and T. S. STEVENS (J.C.S., 1932, 2607—2612).—Interaction of $R'MgX$ and $NR'_2CHR-CN$ ($R' = Me$) gives NR'_2CHRR'' (I) or $NR'_2CHR-COR''$ (II) and no $(NR'_2)CH-R-CHR-NR''$. The results obtained lead to the rules: (a) When $R=H$ (II) predominates. (b) When R =lower alkyl (II) predominates if R'' =alkyl, and (I) if $R''=Ph$ or CH_2Ph . (c) When $R=Ph$ the main product is (I). When $NR' = C_3H_7N$, (I) and not (II) is formed in all cases. Competition experiments with C_4H_9MgCN and $NC_5H_9-CHMe-CN$ and differing Grignard reagents show that the reaction is sensitive to small constitutional changes. The following are described: *p*-bromophenacylbromide of $NMe_2CHMeCOEt$, m.p. 180 — 181° (decomp.); *Me Pr*^a ketone 2:4-dinitrophenylhydrazone, m.p. 142 — 143° ; CH_2NMe_2 CH_2Ph ketone hydrobromide, m.p. 151 — 153° ; cyclohexyl $NMe_2CH_2CH_2$ ketone *p*-bromophenacylbromide, m.p. 213 — 214° (decomp.); β -dimethylamino- α -phenylpropane methopicate, m.p. 103 — 105° ; CH_2Ph *Et* ketone 2:4-dinitrophenylhydrazone, m.p. 140 — 141° ; propiophenone 2:4-dinitrophenylhydrazone, m.p. 187 — 189° ; α -phenyl- β -piperidinopropanep-*p*-bromophenacylbromide, m.p. 197 — 199° ; and picrates of the following: NMe_2CH_2CN , m.p. 168 — 169° , $NMe_2Pr^a, m.p. 240 — 241° (decomp.), $NMe_2CHMeCOEt$, m.p. 166 — 168° , $NMe_2Bu^β, m.p. 192 — 193° , $NMe_2CHEtCOEt$, m.p. 161 — 163° , $NMe_2CHEtCOPr^a, m.p. 200 — 201° , β -dimethylaminopentane, m.p. 208 — 210° , cyclohexyl $NMe_2CH_2CH_2$$$$

ketone, m.p. 165—167°, $\text{NMe}_2\cdot\text{CHMe}\cdot\text{COBu}^a$, m.p. 118—120°. F. R. S.

Mixed magnesium alkoxides and their molecular compounds. I. Molecular compounds of magnesium iodide alkoxide with benzophenone and other ketones. V. M. TOLSTOPIATOV and B. N. SVERDLOV (J. Gen. Chem. Russ., 1932, 2, 105—127).—The mol. compound $\text{CMe}_3\cdot\text{COMe}\cdot\text{MgMeI}\cdot\text{COPh}_2$ is obtained on addition of COPh_2 to $\text{CMe}_3\cdot\text{COMe}\cdot\text{MgMeI}$ or of $\text{CMe}_3\cdot\text{COMe}$ to $\text{CPh}_2\cdot\text{Me}\cdot\text{OMgI}$; on distillation it yields $\text{CMe}_3\cdot\text{CMe}_2\cdot\text{OH}$ and COPh_2 , with about 5% of $\text{CPh}_2\cdot\text{Me}\cdot\text{OH}$. The compounds $\text{R}\cdot\text{OMgI}\cdot\text{COPh}_2$ ($\text{R}=\text{Me}$, Et , Bu^a , Bu^v), obtained similarly, and $\text{R}\cdot\text{OMgI}\cdot\text{Et}_2\text{O}$ ($\text{R}=\text{Me}$, Et , Bu^v , $\text{CMe}_3\cdot\text{CMe}_2$) are described. R. T.

Dehydrogenation of stereoisomeric dimethylcyclohexanes; contact transformation of the *cis*- into the *trans*-forms. N. D. ZELINSKY and E. I. MARGULIS (Ber., 1932, 65, [B], 1613—1617).—Catalytic hydrogenation of *o*- and *p*-xylene in presence of Os at 50—70° produces the corresponding *cis*-dimethylcyclohexanes, whereas the *trans*-forms result in presence of Ni. In presence of Pt-C, Ni, or Os-asbestos, *m*-xylene affords a mixture of the stereoisomeric forms. Ni as catalyst causes the transformation of *cis*-*o*- and *p*-dimethylcyclohexanes into the *trans*-forms. Dehydrogenation of the *cis*- and *trans*-forms of the dimethylcyclohexanes follows the same course, but it remains undecided whether the change is preceded by isomerisation of the *trans*- into the *cis*-variety. H. W.

Reactions of etherates of aluminium and thallium trichlorides in benzene. L. I. KASCETANOV (J. Gen. Chem. Russ., 1932, 2, 515—523).— TiCl_3 reacts like TiCl_4 (A., 1928, 876), causing condensation of C_6H_6 with alkyl radicals of esters but not with the acid radicals; AlCl_3 reacts more vigorously, causing both radicals of an ester to combine. The following were condensed with C_6H_6 in presence of TiCl_3 : $\text{CH}_3\cdot\text{PhCl}$ or $\text{CH}_2\text{Ph}\cdot\text{OEt}$ to yield $\text{CH}_3\cdot\text{Ph}$ and *m*- and *p*- $\text{C}_6\text{H}_4(\text{CH}_2\text{Ph})_2$; BzCl to COPh_2 ; AcCl to COPhMe ; isoamyl acetate and benzoate, no reaction (?). With C_6H_6 and AlCl_3 , $\text{CH}_2\text{Ph}\cdot\text{OEt}$ gives PhEt , CH_2Ph_2 , *m*- and *p*- $\text{C}_6\text{H}_4(\text{CH}_2\text{Ph})_2$; EtOAc gives PhEt and ethylacetophenone; isoamyl acetate, COPhMe and *p*-diisoamylbenzene; Et valerate, PhEt , ethylvalerophenone (semicarbazone, m.p. 191—192°), and valeric acid; isoamyl benzoate, a hydrocarbon, $\text{C}_{17}\text{H}_{30}$, and a product, b.p. 295—300°, giving terephthalic acid on oxidation; $\text{CH}_2\text{Ph}\cdot\text{OBz}$, CH_2Ph_2 , *m*- and *p*- $\text{C}_6\text{H}_4(\text{CH}_2\text{Ph})_2$ and BzOH , but no COPh_2 . This appears to be the only difference between the Friedel-Crafts reaction and that now described.

G. A. R. K.

Reaction of nitrobenzene. L. PAVOLINI (Riv. Ital. Ess. Prof., 1932, 14, 110—111; Chem. Zentr., 1932, i, 3508—3509).— PhNO_2 in AcOH is reduced by Mg first to azoxybenzene; then under the influence of H_2O and rising temp. this is reduced to NH_2Ph , which reacts with the PhNO_2 and gives azoxybenzene. The presence of 1% of PhNO_2 in PhCHO is readily detected by the production of an orange coloration.

A. A. E.

Reaction between triarylmethyl halides and magnesium phenyl bromide. I. C. S. SCHOEFFLE and S. G. TREFF (J. Amer. Chem. Soc., 1932, 54, 4059—4065).—A theory postulating quinoidation of triarylmethyl halides is advanced to explain the supposedly abnormal reaction of these compounds with MgPhBr . *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CPh}_2\text{Cl}$ and 3 mols. of MgPhBr give about 10% of *p*-chlorotetraphenylmethane, m.p. 227—227.5°, 28% of 4-chloro-4'-phenyltriphenylmethane (I), m.p. 102—103°, and 9% of $\text{CHPh}(\text{C}_6\text{H}_4\text{Ph})_2$. Approx. the same results are obtained with *p*-chlorotriphenylmethyl bromide, m.p. 111—112°. *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CPh}_2\text{Cl}$ and MgPhBr give 13% of *p*-bromotetraphenylmethane, m.p. 245°, 7% of 4-bromo-4'-phenyltriphenylmethane (II), m.p. 82—84°, and 20% of $\text{CHPh}(\text{C}_6\text{H}_4\text{Ph})_2$. *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{COCl}$, Ph_2AlCl_3 , and CS_2 give 63% of 4-chloro-4'-phenylbenzophenone, m.p. 169.5—170.5°, which with MgPhBr affords 4-chloro-4'-phenyltriphenylcarbinol; this did not crystallise readily and was converted into (I) by 57% HI in C_6H_6 . (II) is prepared similarly. *p*- $\text{PhC}_6\text{H}_4\cdot\text{CPh}_2\text{Cl}$ and MgPhBr give 7—10% of *p*-phenyltetraphenylmethane (III), m.p. 197—198°, and 58—70% of $\text{CHPh}(\text{C}_6\text{H}_4\text{Ph})_2$; (*p*-*p'*-diphenylphenyl)-diphenylmethane could not be isolated. 4-Amino-4'-phenyltetraphenylmethane, m.p. 192°, obtained in 92% yield from *p*- $\text{PhC}_6\text{H}_4\cdot\text{CPh}_2\text{Cl}$ and $\text{NH}_2\text{Ph}\cdot\text{HCl}$, is converted by the diazo-reaction into (III). *p*- $\text{PhC}_6\text{H}_4\cdot\text{CPh}_2\text{Cl}$ and NH_2Ph in C_6H_6 give 86% of *N*-phenyl-*p*-diphenylldiphenylmethylamine, m.p. 154—155°; *N*-*p*-diphenylldiphenylmethylamine, m.p. 179.5—180.5°, is prepared from CPh_2Cl and 4-amino-diphenyl. C. J. W. (b)

Bromonitro-derivatives of diphenyl. L. GUGLIAMELLI and M. R. FRANCO (Anal. Assoc. Quím. Argentina, 1932, 20, 8—50).—Bromination of 4-nitrodiphenyl in AcOH yields 4-bromo- and a small amount of 2-bromo-4'-nitrodiphenyl (I), m.p. 102—103° (A., 1927, 236, gives m.p. 82.5°). A 25% yield of (I) is obtained by bromination in H_2O (+ FeCl_3). 4-Bromo-4'-aminodiphenyl yields the following derivatives: benzylidene, m.p. 182—183°; piperonylidene, m.p. 129°; dimethylaminobenzylidene, m.p. 236°; thiocarbamide, m.p. 226°. Reduction of (I) by SnCl_2 yields 2-bromo-4'-aminodiphenyl, m.p. 120—121° (derivatives: *Ac*, m.p. 155—156°; benzylidene, m.p. 126—127°; piperonylidene, m.p. 124°; *p*-dimethylaminobenzylidene, m.p. 183°; thiocarbamide, m.p. 207°), from which 2 : 4'-dibromodiphenyl, m.p. 109°, is prepared. The course of substitution in the diphenyl series is discussed. R. K. C.

Substitution in compounds containing two or more phenyl groups. III. Nitration and bromination of 2 : 4 : 6-trimethyldiphenyl. D. H. HEY (J.C.S., 1932, 2636—2640).—Four methods of prep. of 2 : 4 : 6-trimethyldiphenyl (I), b.p. 275—277°, are described, the most successful being from diazotised NH_2Ph and mesitylene in presence of aq. NaOH , and from nitrosoacetanilide and mesitylene. Nitration of (I) with $\text{HNO}_3\cdot\text{AcOH}$ at room temp. gives 3 : 4'-dinitro- (II), m.p. 120°, and with more conc. acid, 3 : 5 : 4'-trinitro-2 : 4 : 6-trimethyldiphenyl (III), m.p. 216°. A mononitro-product could not be prepared. Oxidation of (II) and (III) yields *p*-

nitrobenzoic acid. (II) is reduced and acetylated to 3:4'-diacetamido-, m.p. 293—294°, and (III) forms with SnCl_4 , 3:5:4'-tri-amino-, m.p. 248°, and with Na_2S , 5-nitro-3:4'-diamino-2:4:6-trimethyldiphenyl, m.p. 194° (brominated to the 3':5'- Br_2 -compound, m.p. 238°). Bromination of (I) affords 3:5:4'-tribromo-2:4:6-trimethyldiphenyl, m.p. 223°.

F. R. S.

Stereochemistry of 2:2'-disubstituted diphenyls. II. Optical resolution of diphenyl-2:2'-disulphonic acid. (Miss) M. S. LESSLIE and E. E. TURNER (J.C.S., 1932, 2394—2396; cf. this vol., 942).— NH_4 salts obtained from distrychnine and dibrucine diphenyl-2:2'-disulphonates showed activity. From the strychnine H salt *strychnine H* d. (+7.5H₂O), m.p. 275—276° (decomp., softens 135°), —8.5°, dl. (+7.5H₂O), m.p. 145° and 265° (decomp.), $[\alpha]_{\text{D}}^{20}$ —11.0°, and l-diphenyl-2:2'-disulphonate (+4H₂O), m.p. 143—145° and 209—210°, $[\alpha]_{\text{D}}^{20}$ —13.8°, are obtained. Racemic and active NH_4 salts are obtained from these, the latter being racemised at 100° in H_2O .

A. A. L.

Chlorination of 1-nitronaphthalene. J. BUFFLE and J. CORBAZ (Arch. Sci. Phys. Nat., 1932, 14, 149—158).—Little HCl is evolved when 1- $\text{C}_{10}\text{H}_7\text{NO}_2$ (0.5 g.-mol.) dissolved in 50 g. of C_6H_6 , PhCl , or CCl_4 is treated with 35.5 g. of Cl_2 during 1 hr. in presence of I (0.635 g.) or FeCl_3 (2—3 g.). When the resulting product is heated in vac., progressive decomp. occurs from 100—105°; HCl and nitrogen oxides are evolved and C_{10}H_8 , $\text{C}_{10}\text{H}_7\text{Cl}$, $\text{C}_{10}\text{H}_6\text{Cl}$, (mixture), and $\text{C}_{10}\text{H}_5\text{Cl}_3$, m.p. 102—103°, are isolated. The initial reaction gives a mixture of chloronitronaphthalenes and chlorides of 1- $\text{C}_{10}\text{H}_7\text{NO}_2$; the chlorides subsequently decompose (when heated) to the above N-free substances. Chlorination during 1.5 hr. affords some tetrachloronitronaphthalene, m.p. 176.5°.

H. B.

Anthracene derivatives. E. DE B. BARNETT (Ber., 1932, 65, [B], 1563—1566).—1:4-, 4:5-, and 2:3-dichloroanthrone, like the 1:5- and 1:8-compounds, are reduced by Zn-HCl to the corresponding dichloroanthracenes. Dianthrils are produced from 2-, 3-, and 4-chloroanthrone. Among dimethylanthrones, the pinacol condensation appears to be hindered only when a Me group is in the *peri* position to CO. Oxidation of anthrones with FeCl_3 to dianthrils appears generally independent of the presence of *Bz* substituents. The following substances are described: 1:1'-dichloro-, m.p. 288°; 3:3'-dichloro-, m.p. 288° after softening; 1:3:1':3'-tetramethyl-, m.p. 284°, and 2:3:2':3'-tetramethyl-, m.p. 310°, -dianthrils; 2:2'-dichloro-, darkens at about 240°; 2:3:2':3'-tetrachloro-, blackens at about 250°; 1:4:1':4'-tetrachloro-, m.p. 275° (decomp.); 2:2'-dimethyl-, m.p. 210°; 3:3'-dimethyl-, m.p. 239° (decomp.); 1:3:2':3'-tetramethyl-, m.p. 193°; 1:4:1':4'-tetramethyl-, m.p. 216°; 2:3:2':3'-tetramethyl-, m.p. 222° (decomp.), -dianthrils.

H. W.

Resin acids. I. Synthesis of phenanthrene hydrocarbons derived from *d*-pimaric acid, and a new route to phenanthrene. J. C. BARDHAN and S. C. SENGUPTA (J.C.S., 1932, 2520—2526).—Condensation of β -phenylethyl bromide and the

K derivative of Et cyclohexanone-2-carboxylate gives Et 2- β -phenylethylcyclohexanone-2-carboxylate, b.p. 184—185°/6 mm. (reduced to the -hexanol-, b.p. 182—183°/3 mm.), hydrolysed to 2- β -phenylethylcyclohexanone, b.p. 154°/6 mm. [semicarbazone, m.p. 179—180° (decomp.)], which is reduced by Na and Et_2O to the -hexanol (I), b.p. 158—160°/6 mm. (phenylurethane, m.p. 115—116°). (I) gives with P_2O_5 , 1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 135°/9 mm. (also obtained from diketooctahydrophenanthrene), dehydrogenated by Se to phenanthrene. 2-Methylphenanthrene, m.p. 54—55° (cf. Haworth, this vol., 608), is similarly prepared; Et 4-methyl-2- β -phenylethylcyclohexanone-2-carboxylate, b.p. 175—178°/3 mm.; 4-methyl-2- β -phenylethylcyclohexanone, b.p. 145—147°/3 mm. [semicarbazone, m.p. 187° (decomp.)], and -hexanol, b.p. 157—160°/6 mm.; 2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 137°/6 mm., are the intermediate products.

2:5-Dimethylbenzyl chloride, b.p. 85—86°/7 mm., is converted into the cyanide, b.p. 115—119°/6 mm., which forms Et 2:5-dimethylphenylacetate, b.p. 114°/4 mm. The ester is reduced by Na to β -2:5-dimethylphenylethyl alcohol, b.p. 110—113°/5 mm., which yields the bromide, b.p. 104—106°/5 mm. 1:4-Dimethylphenanthrene, m.p. 77° (picrate, m.p. 155°), has been obtained from Et 2-(β -2':5'-dimethylphenylethyl)cyclohexanone-2-carboxylate, b.p. 192—194°/4 mm., reduced to the -hexanol-, b.p. 195—198°/4 mm., converted into the corresponding octahydrophenanthrene derivative, b.p. 170—174°/4 mm. Et 4-methyl-2-(β -o-tolylethyl)cyclohexanone-2-carboxylate, b.p. 185—187°/2 mm., is reduced to the -hexanol-, b.p. 195—197°/2 mm., converted into 1:7-dimethylphenanthrene, identical with the product obtained from *d*-pimaric acid.

F. R. S.

Action of aniline on glucose in aqueous solution in presence of acetic acid. C. N. CAMERON and G. H. GUEST (Canad. J. Res., 1932, 7, 237—247).— NH_2Ph and glucose in H_2O react, more rapidly in presence of AcOH, to give a brown amorphous ppt., decomp. 140—146° after darkening at 119°; the reaction is faster in conc. than in dil. solutions. AcOH increases the reactivity of mixtures of NH_2Ph and glucose in H_2O with respect to quinone formation and Selivanov's reaction. It is suggested that there are formed successively glucose- α -anilide, - β -anilide, -anil, and AcCHO or (possibly) an indole derivative.

R. S. C.

Reactions of ω -substituted acetophenone derivatives. III. Comparison of the mechanism of interaction of ω -halogenoacetophenones and of benzyl halides with primary and tertiary bases. J. W. BAKER (J.C.S., 1932, 2631—2636).—The effects of substituents (R —*p*-OMe, *p*-Me, *m*- and *p*- NO_2) on the ϕ -unimol. velocity coeffs. for the reactions $\text{C}_6\text{H}_4\text{R}\cdot\text{CH}_2\cdot\text{Hal} + \text{NH}_2\text{Ph} \rightarrow \text{C}_6\text{H}_4\text{R}\cdot\text{CH}_2\cdot\text{NHPh} + \text{HHal}$ and $\text{C}_6\text{H}_4\text{R}\cdot\text{CH}_2\cdot\text{Hal} + \text{C}_5\text{H}_5\text{N} \rightarrow$

$\text{C}_6\text{H}_4\text{R}\cdot\text{CH}_2\cdot\text{NC}_5\text{H}_5\text{Hal}$ are determined; the reactions are carried out with 10 mols. of the base in *M*/40 solution in 90% EtOH at 30.5°. The above reactions are facilitated by an accession of electrons to the side-chain and they are of the opposite type to those with

$C_6H_4R \cdot CO \cdot CH_2 \cdot Hal$ (this vol., 744); anionisation of the halogen is, therefore, the main factor in determining the velocity. The velocity increases in the order $Cl < Br < I$ when R is const. and is the reverse of the order expected. The factors operating in the above reactions are discussed. *p*-Methoxybenzylpyridinium bromide has m.p. 162—163° (decomp.). H. B.

Reactions of unsaturated compounds. I. Addition of arylamines to cyclohexene and 1:4-dihydronaphthalene. W. J. HICKINBOTTOM (J.C.S., 1932, 2646—2654; cf. this vol., 1124).—1:4-Dihydronaphthalene heated with NH_2Ph and its hydrochloride (hydrobromide, cobaltobromide, or cadmiumbromide) at 300° gives mainly 2-*p*-aminophenyl-1:2:3:4-tetrahydronaphthalene, m.p. 89—90° [hydrochloride; hydrobromide; sulphate; picrate, m.p. 186—188° (decomp.); Ac, m.p. 184—185°, *m*-nitrobenzenesulphonyl, m.p. 168—169°, and phenylthiocarbonyl, m.p. 154—155°, derivatives], together with another primary and a sec. amine (not identified). 2-*p*-Hydroxyphenyl-, m.p. 130—131° (softens at 129°) (lit. 129—130°), and 2-*p*-bromophenyl-1:2:3:4-tetrahydronaphthalenes are prepared by the usual methods; oxidation (CrO_3 -AcOH) of the latter gives *p*- $C_6H_4Br \cdot CO_2H$. cycloHexene. NH_2Ph and $NH_2Ph \cdot HCl$ at 230—250° give *o*-[hydrochloride (+ H_2O); *p*-toluenesulphonyl derivative, m.p. 156—157°] and *p*-aminophenylcyclohexane (*m*-nitrobenzenesulphonyl derivative, m.p. 160—161°) and *N*-cyclohexylaniline [Ac derivative, m.p. 69—70° (lit. 66°); hydrochloride; *p*-toluenesulphonyl derivative, m.p. 141—142° (crystallographic data by E. G. Cox)]. cycloHexene. *p*- $C_6H_4Me \cdot NH_2$, and *p*- $C_6H_4Me \cdot NH_2 \cdot HCl$ at 270—280° afford *N*-cyclohexyl-*p*-toluidine, b.p. 161—161.5°/20 mm., m.p. 42—42.5° (also prepared from *p*- $C_6H_4Me \cdot NH_2$ and cyclohexyl bromide at 130°) [hydrochloride; Ac, m.p. 87—88° (crystallographic data given), *NO*-, m.p. 57—58°, *p*-toluenesulphonyl, m.p. 133—134°, and *m*-nitrobenzenesulphonyl, m.p. 143—144°, derivatives], and 4-amino-3-cyclohexyltoluene, b.p. 167—168°/21 mm. (hydrochloride; Ac derivative, m.p. 136—137°), separable through the differing solubilities of their oxalates in EtOH and H_2O . H. B.

Steric hindrance. VI. J. VON BRAUN and K. WEISSBACH (Ber., 1932, 65, [B], 1574—1580; cf. A., 1931, 1407).—The extent to which *o*-substituted sec. bases react with $CPhCl \cdot NPh$ or $CPhCl \cdot N \cdot C_6H_4Me$ in Et_2O at 25° during 120 hr. according to the equation 2 mols. base + 1 mol. imide chloride = 1 mol. amidine + 1 mol. base, HCl is measured and compared with the amounts of Ac and chloroacetyl compounds of the corresponding primary bases which after equally prolonged action of PCl_5 undergo further change as imide chlorides and with the extent to which the corresponding Me. bases add MeI . The first type of change is more impeded by Me than by halogen, in qual. agreement with the experiments on the Ac derivatives, but reversing the results of the addition of MeI . In the first type of change the difference in the influence of Cl and Br is sharply marked, but this is not the case with the second and third types. In the first type OMe has a smaller influence than Cl or Br and apparently no effect in the remaining types.

o- $C_6H_4Cl \cdot NMe_2$ is converted by β -phenylpropionic acid at about 225° into β -phenylpropion-*o*-chlorophenylmethylamide, b.p. 230—232°/15 mm., hydrolysed by conc. HCl at 130° to *o*-chloromethylaniline, b.p. 95°/14 mm. β -Phenylpropion-*m*-chlorophenylmethylamide, b.p. 239—241°/15 mm., and *m*-tolylmethylamide, b.p. 211—214°/15 mm., similarly afford the corresponding pure sec. bases. *o*- $C_6H_4Cl \cdot NH_2$ is converted into the formyl derivative, which is treated successively with $NaOEt$ and $EtBr$; hydrolysis and nitrosation afford nitroso-*o*-chlorophenylethylamine, b.p. 148—150°/14 mm., reduced by $SnCl_2$ and conc. HCl to *o*-chlorophenylethylamine, b.p. 99°/14 mm. (picrate, m.p. 124°). The formyl compound of *o*- $C_6H_4Br \cdot NH_2$ is transformed by Me_2SO_4 , hydrolysis, and nitrosation into nitroso-*o*-bromophenylmethylamine, b.p. 154—156°/14 mm., and thence into *o*- $C_6H_4Br \cdot NHMe$, b.p. 117°/14 mm. (picrate, m.p. 105°). *o*-Formamidodiphenyl ether, m.p. 100°, is similarly converted into nitrosomethylaminodiphenyl ether, b.p. 198—200°/13 mm., and thence into *o*-methylaminodiphenyl ether, b.p. 170°/13 mm., m.p. 48° (hydrochloride, m.p. 134°; picrate, m.p. 149°). The following benzamides are described: *N'*-phenyl-*N*-*o*-tolyl-*N*-methyl-, b.p. 226—223°(?) /13 mm., m.p. 89° (picrate, m.p. 179°); *N'*-*p*-tolyl-*N*-*o*-tolyl-*N*-methyl-, b.p. 237—239°/12 mm., m.p. 94° (picrate, m.p. 128°); *N'*-phenyl-*N*-*o*-tolyl-*N*-ethyl-, b.p. 227—229°/14 mm., m.p. 76° (picrate, m.p. 76°); *N'*-phenyl-*N*-*o*-chlorophenyl-*N*-methyl-, b.p. 228—230°/13 mm., m.p. 120° (picrate, m.p. 175°); *N*-*o*-chlorophenyl-*N'*-*p*-tolyl-*N*-methyl-, b.p. 242—244°/12 mm., m.p. 116° (picrate, m.p. 209°); *N'*-phenyl-*N*-*o*-chlorophenyl-*N*-ethyl-, b.p. 240°/13 mm., m.p. 123° (picrate, m.p. 177°); *N'*-phenyl-*N*-*o*-bromophenyl-*N*-methyl-, b.p. 245°/13 mm., m.p. 107—110° (non-cryst. picrate); *N*-*o*-bromophenyl-*N'*-*p*-tolyl-*N*-methyl-, b.p. 250°/14 mm., m.p. 103° (picrate, m.p. 204°); *N'*-phenyl-*N*-*o*-anisyl-*N*-methyl-, b.p. 252—255°/13 mm., m.p. 114° (picrate, m.p. 137°); *N*-*o*-anisyl-*N'*-*p*-tolyl-*N*-methyl-, b.p. 252—255°/13 mm., m.p. 106° (picrate, m.p. 168°); *N'*-phenyl-*N*-*o*-phenoxyphenyl-*N*-methyl-, b.p. 275—280°/12 mm., non-cryst. (hydrochloride, m.p. 238°); *NN'*-diphenyl-*N*-methyl-, b.p. 226—228°/13 mm., m.p. 47° (picrate, m.p. 189°); *NN'*-diphenyl-*N*-ethyl-, b.p. 225°/13 mm., m.p. 88° (non-cryst. picrate); *N'*-phenyl-*N*-*m*-tolyl-*N*-methyl-, b.p. 232—234°/13 mm., m.p. 98° (picrate, m.p. 181°); *N'*-phenyl-*N*-*m*-chlorophenyl-*N*-methyl-, b.p. 238—240°/13 mm., m.p. 89° (picrate, m.p. 188°). H. W.

Decomposition of quaternary ammonium hydroxides. J. VON BRAUN and K. HAMANN (Ber., 1932, 65, [B], 1580—1586).—Quant. investigation of the mixture of propenes, $X \cdot C_6H_4 \cdot CH \cdot CH \cdot CH_2Ph$ and $X \cdot C_6H_4 \cdot CH \cdot CH \cdot Ph$, obtained by decomp. of quaternary hydroxides $X \cdot C_6H_4 \cdot CH_2 \cdot CH(NMe_2 \cdot OH) \cdot CH_2Ph$ indicates that the method is suitable for the comparison of the tenacity of H atoms in CH_2 groups in complicated CH_2Ph residues in which the effect of substituents in the C_6H_6 nucleus is not obvious. The mixture of propenes is ozonised and the aldehydes are determined by treatment with dil. H_2SO_4 and $CH_3Ph \cdot CHO$ followed by steam-distillation. It is found, for example, that treatment of n mols. of $PhCHO$ and m mols. of $C_6H_4Me \cdot CHO$ with $n+m$ mols.

of $\text{CH}_3\text{Ph}\cdot\text{CHO}$ yields an aldehyde distillate in which PhCHO and $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ are in the exact ratio $n : m$.

β -Phenyl- α -*p*-methylbenzylpropionyl chloride is converted into the *amide*, m.p. 134° , and thence by NaOMe and Br followed by dil. AcOH into the *urethane*, m.p. 67° , which when distilled with CaO in N_2 affords α -phenyl- γ -*p*-tolyl- β -propylamine, b.p. 191 – $192^\circ/12$ mm. (*hydrochloride*, m.p. 214° ; *picrate*, m.p. 158° ; *Bz* derivative, m.p. 155°). The corresponding *methiodide*, m.p. 164° , when transformed into the hydroxide and decomposed by alkali yields 34% of α -phenyl- γ -*p*-tolyl- Δ^8 -propene and 66% of α -phenyl- γ -*p*-tolyl- Δ^8 -propene. β -Phenyl- α -*m*-methylbenzylpropionamide, m.p. 91° , affords the *urethane* $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Me})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$, m.p. 56° , and α -phenyl- γ -*m*-tolyl- β -propylamine, b.p. 194 – $195^\circ/12$ mm. (*hydrochloride*, m.p. 161° ; *picrate*, m.p. 175° ; *Bz* derivative, m.p. 130°). The corresponding quaternary *iodide*, m.p. 134° , is transformed through the hydroxide into a mixture of 73% of α -phenyl- γ -*m*-tolyl- Δ^8 -propene and 27% of α -phenyl- γ -*m*-tolyl- Δ^8 -propene. *Et* benzyl-*p*-chlorobenzylmalonate, b.p. 245 – $250^\circ/12$ mm., yields the dicarboxylic acid and thence β -phenyl- α -*p*-chlorobenzylpropionic acid, b.p. 220 – $223^\circ/0.2$ mm., m.p. 88° , transformed through the *amide*, m.p. 151° , and *urethane*, m.p. 100° , into α -phenyl- γ -*p*-chlorophenyl- β -propylamine, b.p. 212 – $214^\circ/12$ mm. (*hydrochloride*, m.p. 212° ; *Bz* derivative, m.p. 155°). From the *methiodide*, m.p. 216° , a mixture of 75% of α -phenyl- γ -*p*-chlorophenyl- Δ^8 -propene and 25% of the Δ^8 -propene is obtained. *Et* benzyl-*m*-chlorobenzylmalonate, b.p. 240 – $245^\circ/12$ mm., affords successively the dicarboxylic acid, β -phenyl- α -*m*-chlorobenzylpropionic acid, b.p. 200 – $215^\circ/0.1$ mm., m.p. 71° , the *amide*, m.p. 69° , *methylurethane*, m.p. 99° , and α -phenyl- γ -*m*-chlorophenyl- β -propylamine, b.p. 210 – $213^\circ/12$ mm. (*hydrochloride*, m.p. 204° ; *picrate*, m.p. 178° ; *Bz* compound, m.p. 162°). The *methiodide*, m.p. 196° , affords a mixture of 77% of α -phenyl- γ -*m*-chlorophenyl- Δ^8 -propene and 23% of the Δ^8 -propene. H. W.

Chromability rule concerning azo-dyes derived from hydroxyquinolines and additive rule relating to azo-dyes in general. C. COURTOT and H. HARTMAN (Bull. Soc. chim., 1932, [iv], 51, 1179–1199).—Azo-dyes are prepared by coupling diazotised sulphanilic, metanilic, α -naphthylamine-5-sulphonic, amino-G, amino-R, naphthionic, and anthranilic acids with 3-, 5-, 6-, 7-, and 8-hydroxyquinolines; 2- and 4-hydroxyquinolines do not couple. The colours of the dyes on wool are recorded; the bathochromic effect of the OH group increases as it approaches the N atom. Only those hydroxyquinolines containing a OH group in an α -position of the benzenoid ring (i.e., the 5- and 8-derivatives) confer chromability on their azo-dyes; this is the sixth rule of chromability. The azo-dyes derived from anthranilic acid and 3-, 6-, and 7-hydroxyquinolines are chromable, as are those obtained similarly using β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, and R- and G-acids; in all these dyes the OH and CO_2H groups are both *ortho* to $\cdot\text{N}\cdot\text{N}\cdot$ (such an arrangement confers chromability; this is designated the fifth rule). The only exception to the above rules is the azo-dye from 7-hydroxyquinoline and amino-R-acid;

this dye is chromable. The causes of chromability of azo-dyes are discussed briefly. H. B.

Azo chromophore. IV. J. S. P. BLUMBERGER (Chem. Weekblad, 1932, 29, 454–464).—The idea that the colour of azo-dyes depends on an equilibrium between quinonoid and azoid forms (Hodgson, A., 1929, 1298; 1930, 596, 906) fails to account for the bathochromic effect of the *p*- NO_2 group in *p*-nitrobenzeneazo-*p*-dimethylaniline and the sensitivity of disazo-dyes of the type sulphanilic acid \rightarrow *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2 \rightarrow$ 1 : 4-naphtholsulphonic acid, to alkalis. Similarly, Burawoy's views (A., 1931, 144, 544, 1052) are contrary to the ionogenic properties of these dyes. The light absorption curves and the sensitivity to acids and alkalis of a large no. of mono-azo-dyes are satisfactorily explained on simple polarity relationships between chromophore and substituents (A., 1928, 966; 1931, 721). A *m*- or *peri*- NH_2 group in *o*-hydroxyazo-dyes has an unexpectedly marked effect on shade. In disazo-dyes containing a system of two conjugated chromophores, the additional PhN_2 group has a strong bathochromic effect, which may be greatly reduced or intensified by the position of a SO_3H group in the benzidine mol. On account of the co-ordination between the OH group and the azo-linking, *o*-hydroxyazo-dyes show greater differences in shade etc. than *p*-hydroxy- or *o*- or *p*-amino-azo-dyes. Non-conjugated chromophoric systems have little or no effect, the systems acting independently. Nearly 100 light absorption curves are given. S. C.

Formation of azoxy-, azo-, hydrazo-, and benzidine compounds and the dyes derived from the latter. R. N. SEN and R. SADASIVAM (J. Indian Chem. Soc., 1932, 9, 403–411).—6-Nitrocoumarin is reduced by Zn dust and aq. $\text{EtOH}\cdot\text{NH}_4\text{Cl}$ to 6-amino-coumarin (30%) and 6 : 6'-azoxycoumarin, m.p. $>300^\circ$ (60%); a solution of the latter in aq. NaOH treated with HgO gives 5 : 6'-azoxy-*o*-coumaric acid, decomp. above 270° (*Et*₂ ester, m.p. $>250^\circ$). Reduction of *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ with Zn dust and aq. $\text{EtOH}\cdot\text{NaOH}$ gives *m*-hydrazobenzoic acid, rearranged by HCl to 4 : 4'-diaminodiphenic acid. *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ is similarly reduced to *o*-hydrazophenol, m.p. 148° (*Bz*₂ derivative, m.p. 186°), rearranged to 3 : 3'-dihydroxybenzidine (I), m.p. 160° (*dihydrochloride*, m.p. 144° ; *Bz*₂ derivative, m.p. 180° ; *Br*₂-derivative, m.p. 174°), converted by boiling $\text{AcOH}\cdot\text{NaOAc}$ into the *dimethyl-dibenzoxazole*, m.p. 187° . Dyes (m.p. and shades on cotton quoted in parentheses) are prepared from tetrazotised (I) and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ (150° ; pink), β -naphtholsulphonic acid (decomp. above 250° ; pink), β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ ($>250^\circ$, NPhMe_2 ($>250^\circ$)). 2 : 2'-Dihydroxybenzidine is similarly prepared from *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. Reduction of *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ with Zn dust and aq. $\text{EtOH}\cdot\text{NaOH}$ gives *m*-azobenzyl alcohol, m.p. 117° (*Ac*₂ derivative), or *m*-hydrazobenzyl alcohol, m.p. 263° (*Ac*₂, decomp. above 220° , and *Bz*₂ derivatives); the latter is rearranged to 2 : 2'-*di*-(*hydroxymethyl*)benzidine, m.p. 177° [*Bz*₂, m.p. 233° , *Ac*₂, m.p. $>250^\circ$, and *Br*₂, m.p. $>270^\circ$, derivatives]; dyes by coupling with β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ (deep red on silk), β -naphtholsulphonic acid (deep red), β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ (120°), and NPhMe_2 ($>250^\circ$). *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is

similarly reduced to *o*-hydrazobenzyl alcohol, m.p. 200° (*Ac*₂, m.p. >250°, and *Bz*₂, m.p. 107°, derivatives), rearranged to 3:3'-di(hydroxymethyl)benzidine, m.p. 185° [*Ac*₄, *Bz*₄, and *Br*₂-derivatives, all m.p. >250°; dyes by coupling with β-C₁₀H₇-OH (>250°; bluish-violet on silk), β-naphtholsulphonic acid (red), β-C₁₀H₇-NH₂ (>250°; reddish-orange on silk), NPhMe₂ (>250°; violet on silk)]. The ease of the benzidine rearrangement with the above substituted hydrazobenzenes is OH > CO₂H > CH₂OH; the *m*-are generally transformed more readily than the *o*-compounds.

H. B.

Sensitised photolysis of azo-compounds by zinc oxide. I. FUKUSHIMA, M. HORIO, and M. OHMORI.—See this vol., 1215.

Losses in the production of benzidine bases and the reductive cleavage of aromatic hydrazo-compounds during rearrangement. III. V. A. IZMAILSKI, E. P. RUSTANOVICH, and P. T. SHPUNTE-NOK (Anilinokras. Prom., 1932, 2, No. 3, 10—16).—In the prep. of the hydrazo-compound the formation of NH₂Ph is decreased by carrying out the process in two stages: (1) reduction of PhNO₂ to azoxybenzene with Zn dust in alkaline medium, (2) reduction to hydrazobenzene at 57—65° at low alkali concn., preferably in 3—4% solution with Fe. Extraction of reduction sludge at <100° leads to much decomp. with formation of amines. Reductive decomp. is greater with HCl than with H₂SO₄. It is proposed that the sludge should be extracted at a lower temp. and that the rearrangement be effected without separation of hydrazo-compound from its solution in hydrocarbon. The best solvents are PhCl and liquid C₆H₄Cl₂.

CH. ABS.

Replacement of the diazonium group by chlorine or bromine. H. W. SCHWECHTEN (Ber., 1932, 65, [B], 1605—1607).—The base is diazotised and transformed by HgCl₂ in KCl or by HgBr₂ [or Hg(NO₃)₂] in KBr into the corresponding complex salt, which is collected and dried by COMe₂, MeOH, or Et₂O. Mixed with twice its weight of KCl or KBr it is heated from above in a vertical tube sufficiently strongly to cause complete decomp. of the diazonium salt; sometimes it is advisable to heat so that the halogeno-compound is volatilised. Examples cited are: 2:2'-diamino- to 2:2'-dibromo-diphenyl, m.p. 80—81° (yield 80%) and to 2:2'-dichlorodiphenyl, m.p. 60.5° (yield >80%); *p*-C₆H₄Br-NH₂ to *p*-C₆H₄ClBr, m.p. 66—67° (yield about 85%) [the double salt of C₆H₄Br-N₂Cl and HgCl₂, mixed with KBr gives mainly *p*-C₆H₄Br₂, which is the sole product from C₆H₄Br-N₂Br and HgBr₂ in presence of KCl]; β-C₁₀H₇-NH₂ to 2-C₁₀H₇Br (yield about 65%). The use of complex salts containing SbCl₃ and SnCl₄ is also indicated.

H. W.

Action of ethyl oxalate on *o*-aminophenols. E. PUXEDDU and G. SANNA (Gazzetta, 1932, 62, 558—566).—*o*-NH₂-C₆H₄-OH condenses with EtHC₂O₄ or Et₂C₂O₄ to NN'-bis-*o*-hydroxyphenyloxamide, m.p. 280° (decomp.) (*Ac*₂ derivative, m.p. 201°). Similarly 3-amino-*p*-cresol yields NN'-bis-(4-hydroxy-*m*-tolyl)-oxamide, m.p. 282°, and 4-hydroxy-*m*-tolylloxamic acid, m.p. 170°, resolidifying to 6-methyl-2:3-diketophenmorpholine, form of m.p. 230° (cf. A.,

1931, 747), which is also a product of the condensation. 5-Amino-eugenol with EtHC₂O₄ gives 4-hydroxy-eugenyl-*o*-oxamic acid, m.p. 233—235°, but with Et₂C₂O₄ or C₂O₂Cl₂ the product is 6-allyl-8-methoxy-2:3-diketophenmorpholine.

E. W. W.

Dimorphism of phenacetin [acet-*p*-phenetide]. R. FISCHER and A. KOFLER (Arch. Pharm., 1932, 270, 433—435).—Phenacetin exists in stable, m.p. 134—135°, and metastable, m.p. 128—129°, modifications.

H. B.

Resolution of α-*m*-hydroxyphenylethylmethylamine and preparation of *d*- and *l*-motine (methylurethanes of *d*- and *l*-α-*m*-hydroxyphenylethylmethylamine). J. M. MACDONALD and E. STEDMAN (J.C.S., 1932, 2513—2519).—*dl*-α-*m*-Methoxyphenylethylmethylamine, b.p. 117—118°/15 mm. (hydrochloride, m.p. 152—153°), best prepared from the ethyl bromide and NH₂Me in MeCN, is demethylated (aq. HBr) to *dl*-α-*m*-hydroxyphenylethylmethylamine, m.p. 160°, which is resolved by treatment of its hydrochloride, m.p. 160°, first with aq. NH₄ *d*- and then with NH₄ *l*-bromocamphor-*π*-sulphonate. *d*- and *l*-α-*m*-Hydroxyphenylethylmethylamines, m.p. 171°, [α]_D ±68° in C₆H₅N [hydrochlorides, m.p. 201°, [α]_D ±20° in H₂O; *d*- and *l*-bromocamphor-*π*-sulphonates (hydrated), m.p. about 193°, respectively], are converted by H₂ in presence of PtO₂, MeOH, and aq. CH₂O into *d*-, m.p. 116°, [α]_D +55.8° in EtOH [hydrochloride, m.p. 161°, [α]_D +15.2° in H₂O; methylurethane (=d-motine), m.p. 85°, [α]_D +37° in EtOH [hydrochloride, m.p. 167° (decomp.) (sinters at about 160°), [α]_D +10.6° in H₂O]], and *l*-α-*m*-hydroxyphenylethylmethylamine, m.p. 116°, [α]_D -55.8° in EtOH [hydrochloride, m.p. 161°, [α]_D -15° in H₂O; methylurethane (=l-motine), m.p. 85°, [α]_D -35.7° in EtOH [hydrochloride, m.p. 167° (decomp.), [α]_D -10.2° in H₂O]], respectively. *dl*-α-*m*-Hydroxyphenylethylmethylamine and its methylurethane (=dl-motine) (A., 1929, 692) could not be resolved.

H. B.

Recognition of dithio-*o*-toluidine as 2:2'-diamino-5:5'-ditolyl disulphide. R. CHILD (J.C.S., 1932, 2666).—The identification (cf. Hodgson and France, this vol., 943) was carried out by Child and Smiles (A., 1926, 1243) by a different method.

F. R. S.

Preparation and germicidal properties of *p*-hydroxyphenyl alkyl sulphides. C. M. SUTER and H. L. HANSEN (J. Amer. Chem. Soc., 1932, 54, 4100—4104).—The following sulphides are prepared, generally from SHAr, alkyl bromide, and EtOH-NaOEt: PhSMe, b.p. 58—60°/6 mm.; *p*-OMe-C₆H₄-SMe, b.p. 99°/4 mm.; *p*-OMe-C₆H₄-SEt, b.p. 103°/5 mm.; anisyl Pr, b.p. 110°/5 mm., Bu, b.p. 120°/5 mm., amyl, b.p. 127°/5 mm., and hexyl, b.p. 142°/5 mm., sulphides; *p*-ethoxyphenyl Me, b.p. 98—100°/5 mm., m.p. 19—20°, and Et, b.p. 110—112°/6 mm., sulphides. Anisyl Me, m.p. 119—120°, and Et, m.p. 55—56°, and *p*-ethoxyphenyl Me, m.p. 89—89.5°, sulphones are prepared. The following *p*-hydroxyphenyl alkyl sulphides are prepared from the anisyl derivatives and HBr in AcOH: Pr, m.p. 33—33.5°; Bu, m.p. 36—37°; amyl, m.p. 53—56°; hexyl, m.p. 58—59°. The germicidal

properties of these last sulphides are at a max. towards *B. typhosus* with the Bu and amyl derivatives. The hexyl compound is probably the most effective towards *S. aureus*, since its PhOH coeff. is not much higher than that of the amyl derivative. The at. refraction of S in these compounds is abnormally great.

C. J. W. (b)

Manufacture of nitroaminodiphenyl sulphides. SOC. ANON. DES MAT. COL. ET PROD. CHIM. DE ST. DENIS, and R. LANTZ.—See B., 1932, 974.

Action of gaseous cyanogen on phenols. I. The three dihydroxybenzenes. G. MACHEK (Monatsh., 1932, 61, 87—98).—Gaseous (CN)₂ and aq. pyrocatechol in absence of air give 2 : 3-dihydroxybenzonitrile (I), m.p. 197—198° [3(?) Ac, m.p. 182—184°, and Bz derivatives; the diacyl derivatives could not be prepared]. With excess of Me₂SO₄ and NaOH (I) gives veratrole and a small amount of unidentified substance, m.p. 214—216°, whilst under milder conditions a Me ether seems to be formed, but cannot be isolated. Attempts to hydrolyse (I) to the corresponding carboxylic acid gave only pyrocatechol and unidentified products. Under similar conditions resorcinol and quinol give with (CN)₂ additive compounds, C₆H₆O₂(CN)₂, m.p. 92—94° (decomp.), and 120—121° (decomp.), respectively.

H. A. P.

Styphnic acid. I. Preparation and properties. P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 197—199).—Styphnic acid (modified prep.) with egg-white gives a ppt. of protein styphnate, and is reduced to styphnamic acid in hot, alkaline solution by glucose and by creatinine present in urine. When warmed with PCl₅ it explodes.

R. S. C.

4-Aminoresorcinol and its reactions. N. N. VOROSHCHEV and A. M. GORKOV (J. Gen. Chem. Russ., 1932, 2, 421—432).—4-Aminoresorcinol, prepared by reduction of 4-benzeneazoresorcinol (I), is stable only as hydrochloride (N-Ac compound, m.p. 164—165°; Ac₂, m.p. 113°, and Ac₄ compound, m.p. 106—108°). It can be diazotised in presence of CuCl₂ or NiCl₂; the cryst., explosive product is probably a quinonediazide. An attempted Sandmeyer reaction gave an orange cryst. product, m.p. 126.5—127.5°, probably resorcinolazochlororesorcinol. Resorcinolazoresorcinol can be separated into two forms, both forming brown needles, by crystallisation from AcOH, one giving a cherry-red solution in H₂SO₄ and a reddish-violet one in aq. NH₃, the other brown solutions. Resorcinolazo-β-naphthol, m.p. 192°, gives brownish-red solutions in alkalis and violet ones in aq. NH₃. The Me₂ ether of (I) is reduced to 2 : 4-NH₂·C₆H₃(OMe)₂·HCl (Ac derivative, m.p. 115—116°), oxidised by FeCl₃ to 2-methoxy-3 : 1'-4'-dimethoxyanilino-p-benzoquinone, m.p. 153—154°. 2 : 4-Dimethoxybenzeneazoresorcinol has m.p. 178—179°, and 2 : 4-dimethoxybenzeneazo-β-naphthol, m.p. 148—149°. Benzenediazonium chloride couples with resorcinol Me ether to the Me ether of resorcinoldisazobenzene, m.p. 172—173°, further methylated by Me₂SO₄ and KOMe to the Me₂ ether, m.p. 151°.

G. A. R. K.

Constitution of cholesterol. R. ROBINSON (Nature, 1932, 130, 540—541).—A formula which identifies the cholesterol C skeleton with that of squalene less 3 C atoms has been devised. Cholesterol may be 2 : 6 : 22-trimethyl-(7 : 24)(8 : 22)(12 : 21)(16 : 20)-tetracyclotetracosen-Δ^{16,17}-14-ol. The sec. alcoholic group and the double linking of cholesterol are better moved one position to the left in the graphic formula as usually given.

L. S. T.

Constitution of cholesterol. R. ROBINSON (Nature, 1932, 130, 665—666).

L. S. T.

Dehydrogenation of phytosterols with selenium. H. DIETERLE and A. SALOMON (Arch. Pharm., 1932, 270, 495—501).—Dehydrogenation of sterol acetates proceeds under milder conditions and gives better yields of products than with the sterols themselves.

[With C. COESTER.] Lupcol is dehydrogenated by Se at 230—240° to a compound, C₂₇H₄₄O, m.p. 199—200°, whilst acetyl-lupeol similarly gives lupane, C₂₇H₄₈, m.p. 184—185°, lupene (I), C₂₇H₄₆, m.p. 150—181°, the acetate, m.p. 242—243°, of dihydro-lupeol, m.p. 201° (Ruzicka et al., A., 1929, 932), and a substance, C₂₄H₄₀O, m.p. 207—208°.

[With W. ROSENFELDER.] α-Amyrin benzoate is dehydrogenated (cf. A., 1931, 624) to a hydrocarbon (b.p. 225—250°/11 mm.), C₁₅H₂₀ (picrate, m.p. 133°), and amyranene, C₂₇H₄₆, m.p. 182—183°, which is not identical with (I).

Betulin diacetate is dehydrogenated to (mainly) a compound, C₁₉H₃₂O, m.p. 167.5—168°, and betulin monoacetate, whilst cholesteryl acetate gives β-cholestane but no chrysene.

H. B.

Halogen analogues of adrenaline and ephe-drine. I. ω-3 : 4-Dichlorophenyl-β-amino-ethanol. H. E. GLYNN and W. H. LINNELL (Pharm. J., 1932, 129, 249—250).—o-C₆H₄Cl₂, AlCl₃, and CH₂Cl·COCl give ω-3 : 4-trichloroacetophenone, m.p. 44°, which with NH₃ or with NH₂Me in H₂O or C₆H₆ gives 3 : 4-dichloro-ω-hydroxyacetophenone, m.p. 137°. 3 : 4-Dichloroacetophenone (Roberts and Turner, A., 1927, 975) and amyl nitrite afford the oximino-derivative, m.p. 143°, reduced to 3 : 4-dichloro-ω-aminoacetophenone [hydrochloride (I) resinifies at 255°], and then to the hydrochloride (II) of β-amino-α-3 : 4-dichlorophenylethyl alcohol. The results of a pharmacological examination of (I) and (II) are given.

W. S.

Benzyl alkyl ethers. P. P. T. SAH and M. LEI (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 193—195).—The b.p., n_D, and d at 20° and 25° are recorded for the following benzyl alkyl ethers (prepared from CH₂PhCl, Na alkoxide, and the corresponding alcohol): Me, Et, Prⁿ, Prⁱ, Buⁿ, Buⁱ, and isoamyl.

R. S. C.

Comparative stability of isomerides according to their absorption spectra. Transpositions in the arylglycol series. (MME.) RAMART-LUCAS and F. SALMON-LEGAGNEUR (Bull. Soc. chim., 1932, [iv], 51, 1069—1087).—The dehydration (by heat) of aryl-ethylene glycols to aldehydes or ketones and the trans-formation (by heat) of aldehydes into ketones are studied. The results agree with those predicted from the rules previously proposed (A., 1928, 760) for the

relationship between intramol. transformations and absorption spectra. Thus, hydrobenzoin passes at about 300° into (mainly) $\text{CHPh}_2\cdot\text{CHO}$ but at 450° deoxybenzoin (also formed from $\text{CHPh}_2\cdot\text{CHO}$ at 500°) results; $\alpha\alpha$ -diphenylethylene glycol similarly gives $\text{CHPh}_2\cdot\text{CHO}$ or deoxybenzoin; $\alpha\alpha$ -di-*p*-tolylethylene glycol, m.p. 110° (from Mg *p*-tolyl bromide and $\text{CH}_2\text{OH}\cdot\text{CO}_2\text{Et}$), affords di-*p*-tolylacetaldehyde at 160–190°/0.7–1 mm. or *p*-tolyl *p*-methylbenzyl ketone at 250–450°; β -phenylpropane- $\alpha\beta$ -diol yields $\text{CHPhMe}\cdot\text{CHO}$ at 250–300° or benzyl Me ketone at 550°; β -phenylbutane- $\alpha\beta$ -diol (improved prep. given) furnishes α -phenylbutaldehyde at 300° or benzyl Et ketone at 460°; $\beta\gamma$ -diphenylpropane- $\alpha\beta$ -diol, m.p. 73° (obtained together with a compound, $\text{C}_{22}\text{H}_{22}\text{O}$, m.p. 92°, probably β -phenyl- $\beta\beta$ -dibenzylethyl alcohol, from $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ and benzoylcarbonyl acetate), gives $\alpha\beta$ -diphenylpropaldehyde (semicarbazone, m.p. 120–121°) and a trace of a hydrocarbon, $\text{C}_{15}\text{H}_{12}$, m.p. 167°, at 300° [at 500°, the hydrocarbon is the sole product, and it is obtained similarly from $\alpha\beta$ -diphenylpropaldehyde, Ph β -phenylethyl ketone, or dibenzyl ketone; the hydrocarbon is probably identical with that obtained from 1-phenylindene by Mayer and Sieglitz (A., 1921, i, 554)]. All the experiments are carried out by distilling the glycols at 10–20 mm. or lower) through a tube packed with kieselguhr heated to the requisite temp. Ultra-violet absorption curves of many of the above compounds are given. H. B.

Dehydration of ditertiary acenaphthene glycols. N. MAXIM (Bull. Soc. chim., 1932, [iv], 51, 1147–1151).—3-Bromoacenaphthenequinone (I) and MgEtBr give 3-bromo-7:8-dihydroxy-7:8-diethylnaphthene, m.p. 196°, dehydrated by conc. HCl in AcOH to 3-bromo-7:8-diethylnaphthene (II), m.p. 159°, which is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7\text{--AcOH}$ to (I) and 4-bromonaphthalic anhydride. The colour (orange-red) of (II) is deeper than that of the parent 7:8-diethylnaphthene (A., 1928, 1137). H. B.

Mechanism of hydrolysis of phenyl benzoate in aqueous ethyl alcohol. C. W. GIBBY and W. A. WATERS (J.C.S., 1932, 2643–2646).—The sequence of reactions in the hydrolysis of BzOPh with NaOH in 95% EtOH at 30° is: (i) $\text{EtOH} + \text{NaOH} \rightarrow \text{NaOEt} + \text{H}_2\text{O}$; (ii) $\text{BzOPh} + \text{NaOEt} \rightarrow \text{BzOEt} + \text{NaOPh}$ (rapid); (iii) $\text{BzOEt} + \text{NaOH} \rightarrow \text{NaOBz} + \text{EtOH}$ (slow). The presence of free PhOH in a mixture of BzOPh , NaOH, and EtOH can be detected ($\text{Br}\cdot\text{H}_2\text{O}$; diazo-coupling) in <1 m.n.; BzOEt is isolated in almost quant. yield after 5 min. The rate of hydrolysis of BzOEt by NaOH is decreased greatly by the presence of free PhOH. Hydrolysis in the mixed solvent probably proceeds by ionic additive mechanisms involving OH' , OEt' , and OPh' . H. B.

Action of potassium pyrosulphite on aromatic acid chlorides. Preparation of aromatic anhydrides. I. GASPOPOULOS (Praktika. 1931, 6, 347–353; Chem. Zentr., 1932, i, 3171–3172).—The aromatic acid chloride (1 mol.) is heated in C_6H_6 with a *tert.* base (1 mol.; $\text{C}_5\text{H}_5\text{N}$, NMe_2Ph , quinoline) in presence of excess of $\text{K}_2\text{S}_2\text{O}_5$; the corresponding acid anhydride is obtained in good yield. *p*-Nitrobenzoyl chloride affords the anhydride in 70% yield.

A. A. E.

Action of ammonia and amines on the esters of unsaturated acids. II. Action of ammonia, methylamine, and diethylamine on ethyl cinnamate. K. MORSCH (Monatsh., 1932, 61, 299–308).—Interaction of Et cinnamate and $\text{EtOH}\cdot\text{NH}_3$ at room temp. for 30 weeks gives unchanged ester (42.6%), Et β -amino- β -phenylpropionate (I) (13%), β -amino- β -phenylpropionamide [*H* oxalate, m.p. 171.5° (decomp.)] (12%), and cinnamamide [oxalate, m.p. 160.5–161° (decomp.)] (20.1%); reaction is slower than with liquid NH_3 at room temp. (Stosius and Philippi, A., 1925, i, 918). Liquid NH_3 at 100°/70 hr. gives unchanged ester (35%), (I) (35%), and a mixture of the amides (21.4%). Et cinnamate and $\text{EtOH}\cdot\text{NH}_2\text{Me}$ at room temp. for 14 days afford unchanged ester (32.5%), Et β -methylamino- β -phenylpropionate (32.5%), and β -methylamino- β -phenylpropionmethylamide (about 26%); at 100°/24 hr. the corresponding % are 17.3, 17.8, and about 46. Addition of NH_4Et_2 across the double linking does not occur; there is no reaction at room temp., but at higher temp., both in absence and presence of EtOH, cinnamdiethylamide results. H. B.

β -Thionaphthoic acid and di- β -naphthoyl disulphide. L. SZFERL [with U. DEBSKA] (Chem. Listy, 1932, 26, 444–446).—Na β -thionaphthoate, obtained from Na_2S and β -naphthoyl chloride, yields β -thionaphthoic acid, m.p. 44–45° (K, Ba, Pb, and Ag salts), when treated with HCl, and di- β -naphthoyl disulphide, m.p. 185–186°, when treated with I.

R. T.

Phenanthrene-1-carboxylic acid. L. F. FIESER (J. Amer. Chem. Soc., 1932, 54, 4110).—K phenanthrene-1-sulphonate and $\text{K}_4\text{Fe}(\text{CN})_6$ give 1-cyanophenanthrene, m.p. 128°, oxidised (CrO_3 at 90°) to 1-cyanophenanthrenequinone, m.p. 339°, and hydrolysed by $\text{EtOH}\cdot\text{KOH}$ to the amide, m.p. 284°, of phenanthrene-1-carboxylic acid, m.p. 232–233° (Me ester, m.p. 57°). C. J. W. (b)

Phenolic acids. I. Alkyl salicylates and their 3:5-dinitro-derivatives. P. P. T. SAH and S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 201–204).—For the following esters of salicylic acid *d* and *n*_D at 20° and 25° are recorded, the figures in parentheses being the m.p. of the 3:5-(NO_2)₂-derivatives (prepared by fuming HNO_3 and oleum below 0°): Me; Et (92–93°); Pr^a, b.p. 249–251° (67–68°); Pr^b, b.p. 240–242° (101–102°); Bu^a, b.p. 270–272° (60–61°); Bu^b, b.p. 260–262° (72–73°); isoamyl, b.p. 276–278° (61–62°). The use of 3:5-dinitrosalicylic acid for identification of alcohols is suggested. R. S. C.

Configuration of the mandelic acid from amygdalin and of the active phenylaminoacetic acids. O. LUTZ (Ber., 1932, 65, [B], 1609–1613).—The activity graph of mandelic acid from amygdalin in 0.05*M* solution in presence of 0.05*M*- Na_2MoO_4 and varying amounts of NaOH and HCl, respectively (cf. this vol., 720), shows that it belongs to the *d*-series. The graph of *d*(–)-phenylglycine in presence of varying amounts of NaOH and HCl proves it to belong to the *d*-series; the *l*(+)-acid belongs to the *l*-series.

H. W.

Action of hypochlorous acid on arylidene-cyanoacetic acids. J. A. McRAE and C. Y. HOPKINS (Canad. J. Res., 1932, 7, 248—257).—Aq. NaOCl and the Na salts of *o*-(I) and *p*-(II) methoxybenzylidene-, piperonylidene- (III), and veratrylidene-cyanoacetic acids give the corresponding arylacetic acids. *o*-Chlorobenzylidene-cyanoacetic acid, m.p. 53°, and NaOCl give α -cyano- β -*o*-chlorophenylglycidic acid, m.p. 159°, changed by alkaline H_2O_2 to α -cyano- β -*o*-chlorophenylglycidic acid, m.p. 186°. Indefinite results were obtained with the following cyanoacetic acids: benzylidene-, cinnamylidene-, furfurylidene-, 6-nitropiperonylidene- (m.p. 247°), *o*- (new m.p. 231—232°) and *m*- (m.p. 171°; NH_4 H salt, m.p. 214—215°) (IV) nitrobenzylidene-, and 3-nitroanisylidene- (m.p. 240°). (I) has m.p. 208° (Et ester, m.p. 53°). (III) and NaOBr gave (in one experiment only) (?) α -bromo- β -hydroxy- β -piperonylpropionitrile (not obtained pure), m.p. 106°. 3-Nitroanisaldehyde and hippuric acid give the azlactone, m.p. 206°. (IV) and HCN give a substance, hydrolysed to *m*-nitrophenylsuccinic acid (over-all yield 37%). R. S. C.

Fluorinated amino-acids and their derivatives.

III. Fluorotyrosine and fluorothreonine and nuclear fluorinated β -phenylethylamines. G. SCHIEMANN and W. WINKELMÜLLER (J. pr. Chem., 1932, [iii], 135, 101—127).—3-Fluoro-4-methoxybenzaldehyde, prepared in a crude state by oxidation of 3-fluoro-4-methoxytoluene (I) with $CrOCl_2$ in CS_2 , is condensed with hippuric acid in Ac_2O in presence of NaOAc to give 2-phenyl-4-(3'-fluoro-4'-methoxybenzylidene)-5-oxazolone, m.p. 206.5°. This is hydrolysed by NaOH in EtOH to 3-fluoro-4-methoxy- α -benzamido-cinnamic acid, m.p. 214° (decomp.), which with HI and red P gives dl- α -amino- β -3-fluoro-4-hydroxyphenylpropionic acid [fluorotyrosine] (II), m.p. 276—277° (decomp., rapid heating). Interaction of *o*-fluorophenetole, $Zn(CN)_2$, and dry HCl in C_6H_6 , and hydrolysis of the product gives 3-fluoro-4-ethoxybenzaldehyde, which with hippuric acid in Ac_2O gives 2-phenyl-4-(3'-fluoro-4'-ethoxybenzylidene)-5-oxazolone, m.p. 169°, reduced by HI and P to (II). Nitration of α -amino- β -*m*-fluorophenylpropionic acid, decomp. 262°, reduction of the 4- NO_2 -compound, m.p. 209.5°, thus formed with Sn and HCl, and diazotisation and decomp. of the resulting 4- NH_2 -compound, decomp. >300° (hydrochloride, decomp. >310°), also gives (II).

3-Fluoro-4'-methoxydiphenyl ether, b.p. 161.4—161.6°/14 mm., is prepared by treating quinol Me ether with *m*- C_6H_4BrF and K_2CO_3 in presence of C_5H_5N and Cu-bronze at 180°. It is converted by a modified Gattermann synthesis [$Zn(CN)_2$ -HCl] into 2-fluoro-4-*p*-anisoxylbenzaldehyde, the azlactone, m.p. 155°, from which and hippuric acid in Ac_2O is reduced and demethylated by HI and P in Ac_2O to dl- α -amino- β -2-fluoro-4-*p*-hydroxyphenoxyphenylpropionic acid [fluorothreonine], m.p. 264.5°.

Decarboxylation of (II) in fluorene at 280° gives β -3-fluoro-4-hydroxyphenylethylamine [fluorotyramine] [picrate, m.p. 194° (decomp.)]; *m*-fluorophenylalanine, similarly, gives β -*m*-fluorophenylethylamine (III), b.p. 87°/15 mm. [hydrochloride, m.p. 233°; picrate, m.p. 157°]. *m*-Fluorocinnamic acid, m.p. 166.5°, is prepared from *m*- C_6H_4F -CHO and

$CH_2(CO_2Et)_2$, and is reduced by Na-Hg to β -*m*-fluorophenylpropionic acid, m.p. 46°, b.p. 119.2°/0.4 mm. (oxidised by CrO_3 - H_2SO_4 to *m*-fluorobenzoic acid), the amide, m.p. 96.5°, of which is converted into (III) by NaOBr.

Oxidation of (I) with $Na_2Cr_2O_7$ - H_2SO_4 gives 3-fluoro-*p*-anisic acid, m.p. 207.5° (lit. 204°). The diazonium fluoroborate, decomp. 88°, from 2-methoxy-*m*-toluidine gives on decomp. 3-fluoro-*o*-tolyl Me ether, b.p. 58.6°/19 mm. 5(?) Nitro-3-fluoro-*p*-cresol, m.p. 62.5°, b.p. 120—123°/13 mm., is prepared by nitration of 3-fluoro-*p*-tolyl Me ether. Oxidation with CrO_3Cl_2 in CS_2 of anisyl *p*-tolyl ether and hydrolysis of the product gives tarry materials only. 3-Amino-4-methoxydiphenyl ether, m.p. 71.5°, b.p. 205°/15 mm., prepared by reduction of the NO_2 -compound, gives a diazonium fluoroborate, decomp. 145°, from which only a trace of 3-fluoro-4-methoxydiphenyl ether was obtained. H. A. P.

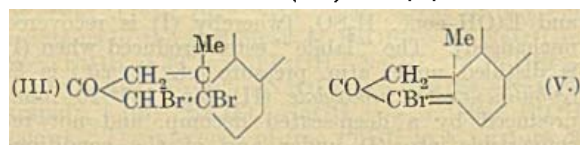
Structure of glutaconic acids and esters.

VII. Derivatives of 3-methylcyclopropane-1:2-dicarboxylic acid. G. A. R. KON and H. R. NANJJI (J.C.S., 1932, 2557—2568).—3-Methylcyclopropane-1:2-dicarboxylic acid and its "normal" ester (Goss *et al.*, J.C.S., 1923, 123, 327, 3342; A., 1925, i, 549) are the Δ^2 -derivatives; ozonolysis of the Et ester (I) gives AcOH, $H_2C_2O_4$, and Et acetyloxaloacetate (pyrazolone, m.p. 230°, from $NHPhNH_2$), whilst reduction (H_2 , colloidal Pd, aq. EtOH) and subsequent hydrolysis affords 3-methylcyclopropane-1:2-dicarboxylic acid, m.p. 147° (cf. *loc. cit.*). Treatment of (I) with EtOH-NaOEt and subsequent dilution with H_2O gives Et 3-ethoxy-3-methylcyclopropane-1:2-dicarboxylate, b.p. 145—146°/11 mm., a little of the ethoxy-acid, m.p. 156° (anhydride, m.p. 49°), and a little quasi-acid enolic product, b.p. 140°/11 mm., which is not isomeric with (I); the "labile" Et 3-methylcyclopropane-1:2-dicarboxylate of Goss *et al.* (*loc. cit.*) could not be obtained by this method, or from Et 2:3-dibromo-3-methylcyclopropane-1:2-dicarboxylate and "mol." K in xylene, or from (I) and EtOH-conc. H_2SO_4 [whereby (I) is recovered unchanged]. The "labile" ester produced when (I) is distilled under atm. pressure (cf. *loc. cit.*) is Et Δ^2 -butinene- $\alpha\delta$ -dicarboxylate (II), b.p. 137°/20 mm., produced by a deep-seated decomp. and not reconvertible into (I) under any of the conditions tried. Reduction (H_2 , colloidal Pd, aq. EtOH) of (II) and subsequent hydrolysis gives adipic acid. Hydrolysis of (II) with 10% HCl affords lævulic acid, whilst aq. MeOH-KOH yields (mainly) β -keto-adipic acid, m.p. 124—125° (decomp.) (which with semicarbazide gives CO_2 and lævulic acid semicarbazone), and a little β -methoxy- Δ^2 -butene- $\alpha\delta$ -dicarboxylic acid, m.p. 186° (decomp.) (formed by addition of MeOH to the acetylenic acid). (II) treated with EtOH-NaOEt does not give a Na derivative (cf. *loc. cit.*); Et β -ethoxy- Δ^2 -butene- $\alpha\delta$ -dicarboxylate, b.p. 155°/15 mm. (free acid, m.p. 161°, hydrolysed by aq. HCl to lævulic acid) (ozonolysis products, $H_2C_2O_4$ and Et succinate), is formed by addition of EtOH. Ozonolysis of (II) gives much unchanged (II), syrupy acidic products, and some impure Et $\alpha\beta$ -diketoadipate (the free acid could not be prepared by

hydrolysis); the latter is oxidised by H_2O_2 to succinic acid and with $\text{NPh}\cdot\text{NH}_2\cdot\text{AcOH}$ affords the *phenylhydrazone*, $\text{NPh}\cdot\text{C}(\text{CO}\cdot\text{C}\cdot\text{N}\cdot\text{NPh})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ m.p. 190° [*phenylhydrazone* ($\text{CO}_2\text{Et}=\text{CO}\cdot\text{NH}\cdot\text{NPh}$), m.p. $225-226^\circ$]. (II), unlike (I), reacts with $\text{EtOH}\cdot\text{conc. H}_2\text{SO}_4$; addition of EtOH probably occurs, but the resulting product has not been characterised.

Me 3-methyl- Δ^2 -cyclopropene-1:2-dicarboxylate (III) and $\text{MeOH}\cdot\text{NaOMe}$ give mainly Me 3-methoxy-3-methylcyclopropane-1:2-dicarboxylate; a Na derivative is not formed. Distillation of (III) under atm. pressure causes very little decomp. H. B.

Constitution of bile acids. XL. *isoDeoxybilianic acid*, *pyroisodeoxybilianic acid*, and *norcholoidanic acid*. H. WIELAND, E. DANE, and L. MAIWEG. XLI. *Pyrocholoidanic acid*. H. WIELAND, E. DANE, and W. SCHONBERGER. XLII. *Chollepidanic acid*. H. WIELAND and K. KRAFT. XLIII. *Degradation of lithobilianic acid*. H. WIELAND, E. DANE, and E. SCHOLZ (Z. physiol. Chem., 1932, 211, 164—176, 177—186, 203—210, 261—274; cf. this vol., 1131).—XL. Bromination of *isodeoxybilianic acid* gives the *monobromo-acid* (I), m.p. 208° (decomp.). Hydrolysis of (I) with $\text{N}\cdot\text{NaOH}$ affords *hydroxyisodeoxybilianic acid* (II), m.p. 205° . Oxidation of (II) did not yield *isocholoidanic acid*, but with $\text{Pb}(\text{OAc})_4$ the *aldehydotetracarboxylic acid*, $\text{C}_{24}\text{H}_{36}\text{O}_9$ (+ H_2O), m.p. 195° (decomp.), was obtained. Bromination of *pyroisodeoxybilianic acid* yields the *monobromo-*, m.p. 198° , and the *tribromo-* (III), m.p. 123° (decomp.), -acids. Hydrolysis of (III) with aq. NaOH eliminates the Br , giving an unsaturated *hydroxydiketocarboxylic acid*, $\text{C}_{23}\text{H}_{32}\text{O}_5$ (IV), m.p. 246° . In boiling $\text{C}_5\text{H}_5\text{N}$ the unsaturated *monobromo-acid* (V), m.p. 205° , is obtained. With NaOH (V) does not yield (IV) but a *keto-enol acid*, $\text{C}_{23}\text{H}_{32}\text{O}_5$, m.p. 190° . Oxidation of (V) with KMnO_4 eliminates one C atom, giving a saturated *diketocarboxylic acid*, $\text{C}_{22}\text{H}_{32}\text{O}_6$, m.p. 191° (decomp.). These changes suggest the constitution shown for (III) and (V):

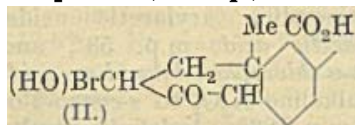


Oxidation of (IV) with alkaline KMnO_4 affords a *tribasic acid*, $\text{C}_{23}\text{H}_{32}\text{O}_9$ (VI), m.p. 224° (decomp.), probably as below.

Thermal decomp. of *norcholoidanic acid* gave a *ketotricarboxylic acid*, $\text{C}_{22}\text{H}_{32}\text{O}_7$ (VII), m.p. 165° ($160^\circ + \text{H}_2\text{O}$) (*Ba* salt, m.p. about 290°), in the formation of which the CO_2H of the side-chain must be involved. With Br in AcOH , (VII) gives *monobromopyroncholoidanic acid*, m.p. $235-240^\circ$ (decomp.), which eliminates Br with $\text{C}\cdot\text{H}\cdot\text{N}$, giving *hydroxypyroncholoidanic acid* (VIII), m.p. 210° (decomp.). Oxidation of (VIII) with CrO_3 in AcOH gives a *tetracarboxylic acid*, $\text{C}_{22}\text{H}_{32}\text{O}_6$ (?), m.p. $150-153^\circ$ (+ $2\text{H}_2\text{O}$).

XLI. In the closed *pyrocholoidanic acid* the CO_2H

group of ring D must be lactonised with ring A. Bromination of the open acid gives a *monobromo-acid* (I), m.p. $219-220^\circ$ (decomp.). NaOH replaces Br by OH giving a *hydroxyketotricarboxylic acid*, $\text{C}_{23}\text{H}_{34}\text{O}_8$ (II), m.p. 219° (decomp.), which readily yields the *lactone* m.p. 238° .



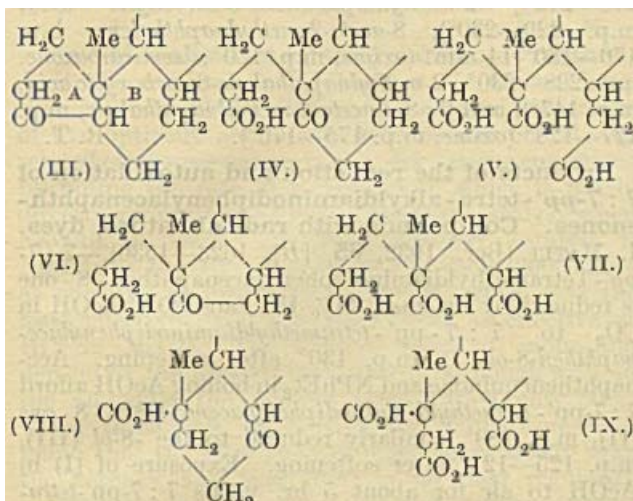
From the crude Et_2O filtrate of the lactone-dicarboxylic acid there was isolated an unsaturated *ketotricarboxylic acid*, $\text{C}_{23}\text{H}_{32}\text{O}_7$, m.p. $285-287^\circ$, which with NaOH yields (II). Bromination of (III) gives the *bromoketolactonedicarboxylic acid*, $\text{C}_{23}\text{H}_{31}\text{O}_7\cdot\text{Br}$ (IV), decomp. at 236° . Dil. aq. NaOH converts (IV) into the *keto-enoltricarboxylic acid*, $\text{C}_{23}\text{H}_{32}\text{O}_8$, m.p. 271° (slight decomp.), also obtained on oxidation of (II) with Fehling's solution or by hydrolysis of *dibromoketotricarboxylic acid*, decomp. at 229° . The closed *pyrocholoidanic acid* gives a *Br-derivative*, m.p. 223° (darkens).

Keto-β-deoxybilianic acid (A., 1931, 841) above its m.p. loses H_2O giving an unsaturated *tricarboxylic acid*, $\text{C}_{24}\text{H}_{34}\text{O}_8$, m.p. $248-250^\circ$ (*Me* ester, m.p. 109°). Mono- or di-bromodeoxybilianic acid with KOH in MeOH affords an unsaturated *ketolactonedicarboxylic acid*, $\text{C}_{24}\text{H}_{32}\text{O}_7$ (V), m.p. $235-240^\circ$ (decomp.) (*Me* ester, m.p. 195°). Reduction of (V) with Zn dust in AcOH and HCl gives a *ketotricarboxylic acid*, $\text{C}_{24}\text{H}_{36}\text{O}_7$, m.p. 210° , differing from ordinary α -deoxybilianic acid probably by epimerism at C_9 .

XLII. *Chollepidanic acid* (I), now formulated as a hexacarboxylic acid, $\text{C}_{24}\text{H}_{34}\text{O}_{12}$, $[\alpha]_D^{25} +38.8^\circ$ in 50% aq. EtOH , is probably choloidanic acid with the Me group at C_{10} replaced by CO_2H . *Pyrochollepidanic acid* (*Me*, ester, m.p. 127°) gives on titration the open pyro-acid (*Me*, ester, m.p. 140°). Thermal decomp. of (I) gave as by-product in addition to *Flaschen-trager's acids* a neutral substance, $\text{C}_{30}\text{H}_{26}\text{O}_2$ (?), m.p. 205° .

XLIII. *Deoxycholic acid* yields an *Ac* derivative, m.p. $112-115^\circ$ (decomp.), which on oxidation with CrO_3 in AcOH gives *12-keto-3-acetoxycholanic acid*, m.p. 197° [*semicarbazone* (I), m.p. $194-195^\circ$ (decomp.)]. With Na in EtOH at $170-180^\circ$, (I) gives the *Na* salt of lithocholic acid (II). Oxidation of (II) with HNO_3 gives lithobilianic acid (III) and *isolithobilianic acid*, m.p. 262° . (III) together with the *allo-isomeride* was also obtained from deoxybilianic acid by the *Kishner-Wolff* method. β -Deoxybilianic acid similarly gives *allolithobilianic acid*. Thermal decomp. of (III) at $280-295^\circ/12\text{ mm.}$ affords the pyro-acid, which on oxidation with KMnO_4 in alkaline solution gives the *ketodicarboxylic acid* $\text{C}_{23}\text{H}_{36}\text{O}_5$ (IV), m.p. 187° . With NaOBr or HNO_3 , (IV) yields the tetracarboxylic acid $\text{C}_{23}\text{H}_{36}\text{O}_8$ (V), (+ EtOAc) m.p. $168-169^\circ$ (decomp.). Thermal decomp. of (V) at $270-290^\circ/\text{vac.}$ gives the *ketodicarboxylic acid* $\text{C}_{22}\text{H}_{34}\text{O}_5$ (VI), m.p. $167-168^\circ$, which then yields on oxidation with alkaline KMnO_4 the tetracarboxylic acid, $\text{C}_{22}\text{H}_{34}\text{O}_8$ (VII) (*Me*, ester, m.p. 75°), identical with the product obtained by Windaus from cholesterol (A., 1909, i, 920). Thermal decomp. of (VII) at 320° gives the *ketodicarboxylic acid* $\text{C}_{21}\text{H}_{32}\text{O}_5$ (VIII), m.p. 168° , which on oxidation with HNO_3 gives the tetracarboxylic acid (IX) (*Me*, ester, m.p. 84°), identical

with Windaus' acid. These reactions are formulated as follows :



To exclude the possibility of a cyclisation of the 1- and 8- CO_2H groups of (V) the acid $\text{C}_{22}\text{H}_{32}\text{O}_9$ (this vol., 614) was reduced by way of the semicarbazone to (VII).

The view that the ring in cholesterol adjoining the OH ring and containing the double linking is the same as that which was regarded as ring II in the bile acids must apparently be abandoned. The suggested form of cholesterol (X), although otherwise unexceptionable, does not explain the degradation of Diels' acid.

J. H. B.

Chemical constitution and rotatory power. Derivatives of chloro- and bromo-benzaldehydes. M. BETTI and P. PRATESI (Atti R. Accad. Lincei, 1932, [vi], 15, 509—513).—The observation that, in the *o*-position, Br increases more than Cl the electronegative character of the Ph in BzOH (cf. Ostwald, A., 1889, 818) is paralleled by the $[M]_D$ vals. of the benzylidene compounds formed by condensing *d*-phenyl-2-hydroxy-1-naphthylmethylamine (I) (cf. A., 1901, i, 611; 1906, i, 950; 1907, ii, 661, 726; 1916, ii, 279; 1921, i, 107) with: PhCHO, +373.1°; *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, -128.4°; *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHO}$, -308.7° (m.p. 157°). In the *m*- and *p*-positions, on the other hand, Cl increases the electronegative character of the Ph in BzOH more than Br does, the dissociation consts. being: BzOH, 0.006; *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$, 0.0137; *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$, 0.0155; *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$, 0.0065; *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$, 0.0093. The vals. of $[M]_D$ for the compounds formed by (I) with the *m*- and *p*-substituted aldehydes are: *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHO}$, +280.9° (m.p. 136°); *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, +255.9°; *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHO}$, +348.1° (m.p. 155°); *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, +282.2°.

T. H. P.

Yield of aromatic substances when lignin hydrochloride is fused with potassium hydroxide. A. WINSVOLD (Cellulosechem., 1932, 13, 158—159).—In reply to Jonas and Freudenberg (cf. B., 1928, 363; A., 1928, 1227; 1929, 915) it is main-

tained that if requisite precautions are taken a yield of >20% of pure aromatic substances can be obtained by fusing lignin hydrochloride with KOH. A. G.

cycloPropane series. cycloPropanone. P. LIPP, J. BUCHKREMER, and H. SEELES (Annalen, 1932, 449, 1—25).— γ -Chlorobutyronitrile and NaNH_2 give some cyclopropanecarboxylamide, m.p. 223.5—224.5°, which with Br and MeOH-NaOMe affords Me cyclopropylcarbamate, b.p. 84—85°/11 mm., m.p. 30—31°, hydrolysed by aq. KOH to cyclopropylamine. Treatment of this with HNO_2 under various conditions gives allyl alcohol. The Ag salt of cyclopropanecarboxylic acid (I) and an equiv. of I at 135° afford (I), its anhydride, and (mainly) slightly impure glyceryl cyclopropanecarboxylate, b.p. 144°/0.04 mm.; the latter is probably formed by way of the cyclopropyl, allyl, and β -di-iodopropyl esters of (I). cycloPropyl Ph ketone and MgPhBr give cyclopropyldiphenylcarbinol, b.p. 150°/3 mm., m.p. 82—83° [Me ether, b.p. 140°/1.5 mm.; bromide, b.p. 138°/1.5 mm., converted by $\text{C}_6\text{H}_5\text{N}$ into N-(cyclopropyldiphenylmethyl)pyridinium bromide, m.p. 128°, and by NPhMe₂ into (probably) a (cyclopropyldiphenylmethyl)dimethylaniline, b.p. 192°/0.3 mm. (sulphate)], which could be dehydrated only to an ether, $\text{C}_{30}\text{H}_{30}\text{O}$, b.p. 250°/0.09 mm., m.p. 112—113° (by KHSO_4 at 180—190°), or polymeric material; the iodide, m.p. 34°, and $\text{C}_6\text{H}_5\text{N}$ give a salt, $\text{C}_{21}\text{H}_{20}\text{NI}$, m.p. 163°, converted by hot aq. NaOH into a little diphenylmethylene-cyclopropane (II), b.p. 110—114°/0.5 mm. (ozonolysis product COPh_2). A polymeric α -diphenylbutadiene is prepared from diphenylallylcarbinol for comparison with (II). Excess of keten with diazomethane in Et_2O -MeOH gives a little cyclobutanone and (mainly) 1-hydroxy-1-methoxycyclopropane, b.p. 45—46°/14 mm. (*p*-nitrobenzoate, m.p. 62—63°), converted by semicarbazide into β -semicarbazidopropaldehydesemicarbazone (III), m.p. 223° (decomp.); 1-hydroxy-1-ethoxycyclopropane, obtained similarly using diazomethane in Et_2O -EtOH, is isomerised by dil. KOH to EtCO_2Et . Evaporation of the reaction mixture from keten and abs. Et_2O -diazomethane in air (not dried) gives 1:1-dihydroxycyclopropane (cyclopropanone hydrate), m.p. 71—72°, which isomerises slowly (more rapidly by the action of hot H_2O or cold KOH) to EtCO_2H , and with semicarbazide gives (III). Evaporation in absence of moisture gives resinous polymeric material. Monomeric cyclopropanone thus appears to exist only in solution. An improved prep. of cyclobutanone (2:4-dinitrophenylhydrazone, m.p. 132—133°) is given (cf. this vol., 161).

[With II. VERBEEK.] Contrary to Dechamps (A., 1930, 585), distillation of Ca succinate gives COMeEt and a little COEt_2 [2:4-dinitrophenylhydrazone, m.p. 151.5° (lit. 156°)], and not COMe₂ and cyclopropanone.

H. B.

Bromophenacyl esters of organic acids. H. LUND and T. LANGVAD (J. Amer. Chem. Soc., 1932, 54, 4107—4108).—*p*-Bromophenacyl tiglate, m.p. 67.9° (all m.p. are corr.), adipate, m.p. 152.6°, chloroacetate, m.p. 103.7°, *m*-hydroxybenzoate, m.p. 176.1—176.4°, *p*-hydroxybenzoate, m.p. 191.3—191.7°, *m*-nitrobenzoate, m.p. 135.4°, *o*-chlorobenzoate, m.p. 107°, *m*-nitrocinnamate, m.p. 178°, *p*-nitrocinnamate, m.p. 191°.

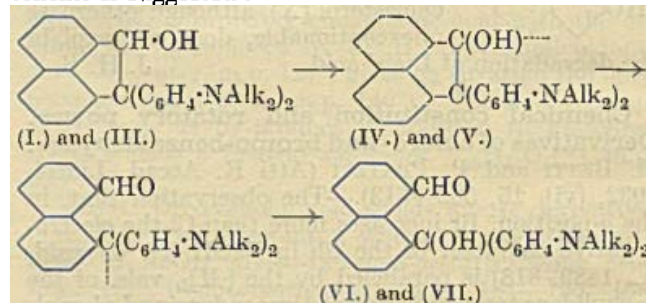
o-methoxycinnamate, m.p. 145°, and *o*-methoxyallacinnamate, m.p. 97.5°, are described. C. J. W. (b)

Steric hindrance in mesitylenic ketones. E. P. KOHLER and R. BALTZLY (J. Amer. Chem. Soc., 1932, 54, 4015—4026).—Study of acetomesitylene (I), dimesityl ketone (II), and dimesityl diketone (III) shows that the two Me groups in the di-*o*-positions affect only those reactions which involve addition to the C atom in direct union with the mesityl group. These Me groups neither promote nor hinder the enolisation of (I), Et 2 : 4 : 6-trimethylbenzoylacetate, and similar substances; neither do they interfere with reactions which involve addition to the O of the CO group. In general, the hindrance is adequate to prevent all additive reactions that involve the α -C atom except reduction, but it may be overcome, in part, by another CO group in the α -position. The enolate of (I), prepared from (I) and MgEtBr in Et₂O, and AcCl give 2 : 4 : 6-trimethylbenzoyldiacetylmethane, m.p. 66—67°, isolated as the Cu salt. Dibenzoyl-2 : 4 : 6-trimethylbenzoylmethane, m.p. 192° (85% yield) (Cu salt), is similarly prepared. *p*-C₆H₄Me·SO₂Cl and the enolate give $\alpha\beta$ -di-2 : 4 : 6-trimethylbenzoylthane, m.p. 138—139°, whilst ClCO₂Et affords the Mg complex, m.p. 147°, of Et 2 : 4 : 6-trimethylbenzoylmalonate; the free ester could not be isolated [Et 2 : 4 : 6-trimethylbenzoylacetate (IV), b.p. 150°/11 mm., resulted from elimination of the Mg]. 2 : 4 : 6-Trimethylbenzoyl chloride and CHNaAc·CO₂Et give Et mesitylcarbonate, b.p. 139—141°/120 mm., and not (IV). (IV) and N₂H₄ in EtOH give 3-mesityl-5-pyrazolone, decomp. 290—300° (4-benzylidene derivative, decomp. 280°). The equilibrium mixture of (IV) contains 24.5% of enol; the EtOH solution contains 27.3%. The enolate of (I) and O₂ give (I); CO₂ apparently reacts, but a carbonated product could not be isolated. 2 : 4 : 6-Trimethylbenzoyl chloride and Mg mesityl bromide give (II), b.p. 200°/2 mm., m.p. 136—137°, which does not react with NH₂OH. Reduction of (II) with Na or Na-Hg and EtOH gives dimesitylcarbinol (V), m.p. 149—150° (benzoate, m.p. 154°), whilst reduction with HI and red P gives dimesitylmethane, m.p. 135°. (II) combines readily with Na in C₆H₆ to form a greenish-blue ketyl which, on hydrolysis, gives an equimol. mixture of (II) and (V); Mg+MgI₂ give a dark purple ketyl which, on hydrolysis, yields the same mixture. Mg mesityl bromide and Et mesitylglyoxylate give a small yield of (III), m.p. 122° (oxime, m.p. 209—210°), which is not reduced by Zn and AcOH, amalgamated Zn and conc. HCl, or by catalytic methods; Zn and EtOH-KOH slowly give mesitylacetomesitylene [2 : 4 : 6-trimethylphenyl 2 : 4 : 6-trimethylbenzyl ketone], m.p. 141°. Na₂O₂ and (III) in dil. MeOH give 2 : 4 : 6-Me₃C₆H₂·CO₂H; (III) does not react with fused KOH or with *o*-C₆H₄(NH₂)₂, but combines with Na, forming a brown Na₂ compound, which with BzCl affords hexamethylisobenzil dibenzoate [$\alpha\beta$ -dibenzoyloxy- $\alpha\beta$ -dimesitylethylene], m.p. 190°. C. J. W. (b)

Ketones of the naphthalene group. Synthesis of acetyl derivatives of 2-methylnaphthalene. K. DZIEWONSKI and M. BRAND (Rocz. Chem., 1932, 12, 693—701).—2-C₁₀H₇Me reacts with AcCl in

presence of AlCl₃ to yield 6-aceto-2-methylnaphthalene, m.p. 70—71° (oxime, m.p. 181°; semicarbazone, m.p. 240—242°; 2-methylnaphthalene-6-carboxylic acid, m.p. 229—230°), 8-aceto-2-methylnaphthalene, b.p. 176—180°/14 mm. (oxime, m.p. 120°; semicarbazone, m.p. 228—230°; 2-methylnaphthalene-8-carboxylic acid, m.p. 147°), and 6 : 8-diaceto-2-methylnaphthalene, m.p. 127—128° (oxime, m.p. 175—176°). R. T.

Products of the reduction and autoxidation of 7 : 7-pp'-tetra-alkyldiaminodiphenylacenaphth- enones. Compounds with radical nature, dyes. I. MATEI (Ber., 1932, 65, [B], 1623—1630).—7 : 7-pp'-Tetramethyldiaminodiphenylacenaphthen-8-one is reduced by Zn dust, 25% HCl, and 20% AcOH in CO₂ to 7 : 7-pp'-tetramethyldiaminodiphenylacenaphthen-8-ol (I), m.p. 130° after softening. Acc-naphthenequinone and NPhEt₂ in boiling AcOH afford 7 : 7-pp'-tetraethyldiaminodiphenylacenaphthen-8-one (II), m.p. 189°, similarly reduced to the -8-ol (III), m.p. 125—127° after softening. Exposure of (I) in AcOH to air for about 5 hr. yields 7 : 7-pp'-tetramethyldiaminodiphenyl-8-aldehydo-1-naphthylcarbinol (VI), m.p. 180° (decomp.), whilst (III) or (V) gives the di-*p*-diethyl compound (VII), decomp. above 160°. Salts of (VI) and (VII) are green basic dyes; (IV) and (V) also dye and are autoxidised on the fibre more rapidly than in solution. The following scheme is suggested :



H. W.

Reducing action of organomagnesium compounds. Action of magnesium cyclohexyl bromide and iodide on benzophenone. A. E. ARBUSOV and I. A. ARBUSOVA (J. Gen. Chem. Russ., 1932, 2, 388—396).—Mg cyclohexyl bromide and CPh₂ give CPh₂ (30.7%), benzhydrol (5.9%), benzpinacene (13.4%), and cyclohexylidenediphenylmethane (I). It is assumed that the first products of the reaction are the free radicals Ph₂COMgBr... (II) and C₆H₁₁... (II). The union of these radicals, followed by dehydration of the *tert*-alcohol formed, gives (I). The union of two radicals (II) gives benzpinacene, whilst reduction of (II) at the expense of (III) gives benzhydrol and cyclohexene (not isolated). CPh₂ could be formed by the oxidation of (II).

With Mg cyclohexyl iodide the products were CPh₂ (16.6%), benzpinacene (21.9%), dicyclohexyl (7.7%), diphenylcyclohexylcarbinol (1.26%), (I) (5.1%), and tetraphenylethane (IV) (3.6%); no benzhydrol was isolated. The mutual oxidation and reduction of

(II) and (III) did not take place; hence the increased yield of benzpinacolone and the formation of dicyclohexyl. The formation of (IV) is difficult to explain.

G. A. R. K.

Rate of enolisation by the polariscopic method. J. B. CONANT and G. H. CARLSON (J. Amer. Chem. Soc., 1932, 54, 4048—4059).—The rates of enolisation of five optically active aryl ketones and one closely related ester were determined under various conditions by noting the rate of racemisation, which is nearly directly proportional to the concn. of catalyst when NaOAlk is used. The most effective catalyst is NaOMe in BuOH; this catalyst is about 2000 times as effective as piperidine in MeOH, which was the least effective base, and 1000 times as effective as HCl in MeOH. The relative rates of enolisation depend on the catalyst and solvent, although with all the alkoxides the relative rates varied only 50%. Using these vals. as a basis for comparison, it is found that the ester enolises much more slowly than the ketones, and that there is no clear regularity between the rate of enolisation and structure of the ketone. The heat of activation of the enolisation is about 14+1 kg.-cal. The free energy of enolisation of the CPhMe derivatives is estimated to be between 5 and 14 kg.-cal. CPhMe and MgBuBr give *phenylmethylbutylcarbinol*, b.p. 129—130°/4 mm., which with MeOH and conc. H₂SO₄ affords *α-phenyl-α-methylamyl Me ether*, b.p. 105—106°/6 mm. This ether and liquid Na-K alloy in Et₂O give (after treatment with CO₂) *α-phenyl-α-methylhexoic acid* (I), b.p. 153°/4 mm. (Me ester, b.p. 115°/2 mm.). Resolution of (I) with quinine gives the *d*-form, [α]_D²⁵ +13.65° in EtOH, the chloride of which with MgPhBr affords *d-α-phenyl-α-methylhexophenone* [Ph *α-phenyl-α-methylamyl ketone*], b.p. 150—152°/0.5 mm., [α]_D²⁵ +30.78° in EtOH. *d-Ph β-phenyl-α-methylethyl ketone*, m.p. 42—43°, [α]_D²⁵ +87.5° in EtOH, is prepared from *d-β-phenyl-α-methylpropionyl chloride* and MgPhBr. *l-CH₂Ph-CHPh-COCl* and Mg mesityl bromide give 1:2:4:6-*trimethylphenyl αβ-diphenylethyl ketone*, m.p. 113—114°, [α]_D²⁵ -8.06° in COMe₂. *d-2:4:6-Trimethylphenyl α-phenylethyl ketone*, m.p. 59—60.5°, [α]_D²⁵ +71.5° in MeOH, is prepared similarly. Tables give the results of the action of NaOBu in BuOH, NaOMe in MeOH, and piperidine in BuOH and in MeOH.

C. J. W. (b)

Fries rearrangement of α-naphthyl esters. H. LEDERER (J. pr. Chem., 1932, [ii], 135, 49—56).—By acting on α-naphthyl esters with AlCl₃ in PhNO₂ at 0—25° both the 2- and 4-ketones are formed; the proportion of the latter increases as the temp. is lowered, but below 0° the reaction is impracticably slow. The acidity of the latter is normal, but that of the former is low, and decreases rapidly as the series is ascended. The following are described: 1-hydroxy-4- and -2-naphthyl Me ketones; *α-naphthyl n-butyrate*, b.p. 182°/15—18 mm., and *phenylacetate*, m.p. 48°, b.p. 232°/15—18 mm.; 1-hydroxy-4-naphthyl *Pr^a ketone*, m.p. 167° (corr.); 1-hydroxy-2-naphthyl *Pr^a ketone*, m.p. 85° (corr.); 1-hydroxy-2-naphthyl *CH₂Ph ketone*, m.p. 94—95° (corr.). CH₂Ph-COCl has b.p. 202° (lit. 180—183°).

H. A. P.

Manufacture of substituted aromatic ketones. SOC. CHEM. IND. IN BASLE.—See B., 1932, 974.

Interconversion of mixed benzoin. E. M. LUIS (J.C.S., 1932, 2547—2550).—*r*-4'-Methoxybenzoin (benzoyl-*p*-anisylcarbinol) and EtOH-KOH at room temp. for 3 days give *r*-4-methoxybenzoin (*p*-anisoylphenylcarbinol), which is unaffected by such treatment; interconversion probably proceeds by way of the αβ-dihydroxy-αβ-diarylethylene. *r*-4'-Dimethylaminobenzoin (I) is similarly converted into *r*-4-dimethylaminobenzoin (II); *p*-dimethylaminobenzil (III) is a by-product. (III) is also formed (to some extent) when (II) is treated with cold EtOH-KOH. (I) [or (II)] heated with EtOH-KOH gives (II), (III), BzOH, and *p*-NMe₂·C₆H₄·CO₂H. Determination of the structure of ketones by fission with EtOH-KOH is not applicable to mixed benzoin.

H. B.

Dehydration of the α-forms of *r*- and (+)-*p*-tolylhydrobenzoin. A. MCKENZIE, R. ROGER, and W. B. MCKAY (J.C.S., 1932, 2597—2604).—*p*-Tolyl benzhydryl ketone, previously obtained (A., 1930, 778) by dehydration of *r*-*p*-tolylhydrobenzoin (α-form) (I) with conc. H₂SO₄ (cf. Koelsch, this vol., 746) and by semipinacolonic deamination of *r*- and (+)-β-amino-αβ-diphenyl-α-*p*-tolylethyl alcohol, is prepared from CHPh₂·CN and *p*-C₆H₄Me·MgBr with subsequent hydrolysis. Dehydration of (I) with H₂C₂O₄ gives *r*-*p*-tolyldeoxybenzoin (Ph *p*-methylbenzhydryl ketone) (II), m.p. 96—97°, synthesised by the following methods: (a) from MgPhBr and *p*-C₆H₄Me·CHPh·CN, m.p. 60—62° (lit. 59°), (b) from desyl chloride, PhMe, and AlCl₃ (cf. Koelsch, *loc. cit.*), (c) from *r*-benzoin, PhMe, AlCl₃, and HCl, (d) from *p*-C₆H₄Me·MgBr and desyl chloride. Dehydration of (I) with conc. H₂SO₄ now gives mainly (II), also formed (probably by way of α-hydroxy-αβ-diphenyl-β-*p*-tolylethylene) by dehydration of (+)-*p*-tolylhydrobenzoin with H₂C₂O₄ or dil. H₂SO₄.

The *r*-*p*-tolyldeoxybenzoin, m.p. 159—160°, obtained by McKenzie and Widdows (J.C.S., 1915, 107, 702) from or (+)-*p*-C₆H₄Me·CHPh·COCl, C₆H₆, and AlCl₃, is now shown to be CPh₂·OH. The original reaction may have given CPh₂·CHPh·C₆H₄Me(*p*), which then underwent scission to CPh₂, which is convertible into CPh₂·OH by way of the peroxide.

H. B.

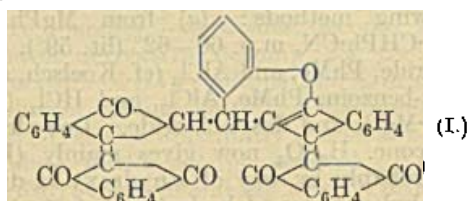
Preparation of reduction products of benzoin. D. A. BALLARD and W. M. DEIN (J. Amer. Chem. Soc., 1932, 54, 3969—3971).—Reduction of benzoin with amalgamated Zn and conc. HCl-EtOH gives 50% of stilbene in 1—2 hr.; amalgamated Sn affords 88% of deoxybenzoin. KI, red P, and conc. HCl, boiled gently for 20 hr., give β-deoxybenzoin pinacolone; Zn and NaOH afford deoxybenzoin, isodidesyl, didesyl, and an unknown compound, m.p. 208°. Details are given.

C. J. W. (b)

Fluorene series. IV. Preparation of 1:2-di-acetylfluorene. K. DZIEWONSKI and A. KLESZCZ (Bull. Acad. Polonaise, 1932, A, 109—114; cf. A., 1931, 622).—Fluorene and AcCl with AlCl₃ in boiling CS₂ give (mainly) 1:2-diacetylfluorene, m.p. 188—190° [diphenylhydrazone, m.p. 250—252°; dioxime, m.p. 252°, which undergoes the Beckmann change (HCl in

Ac₂O-AcOH) yielding the Ac₂ derivative, m.p. 220° (decomp.), of 1:2-diaminofluorene], and small amounts of 2-acetyl- and 2:7-diacetyl-fluorenes. 1:2-Diacetylfluorenone [triphenylhydrazone, m.p. 252° (decomp.)] has m.p. 262°. H. B.

Derivatives of di-indone. Indandionedi-indones and bisdi-indones. M. V. IONESCU and H. SLUSANSCHI (Bull. Soc. chim., 1932, [iv], 51, 1109—1125).—Condensation of indandione (4 mols.) and RCHO (1 mol.) in boiling EtOH-piperidine gives mainly alkylidene- or arylidene-bisdi-indones (for constitution see A., 1928, 422); the following are prepared: *ethylidene*-, m.p. 263°; *propylidene*-, m.p. 265°; *n*-, m.p. 256°, and *iso*-, m.p. 234°; *butylidene*-, *isovalerylidene*-, m.p. 263°; *heptylidene*-, m.p. 256°; *β-phenylpropylidene*-, m.p. 251°; *phenylethylidene*-, m.p. 227°; *furfurylidene*-, m.p. 230°; *o*-, m.p. 295°, *m*-, m.p. 238°, and *p*-, m.p. 251°; *-chlorobenzylidene*-, *o*-, m.p. 289°, *m*-, m.p. 232°, and *p*-, m.p. 232°; *-nitrobenzylidene*-, *o*-, m.p. 256°, and *m*-, m.p. 231°; *-methoxybenzylidene*-, *o*-, m.p. 213°, *m*-, m.p. 272°, and *p*-, m.p. 228°; *-hydroxybenzylidene*-, *veratrylidene*-, m.p. 212°; *2-hydroxy-3-methoxy*-, m.p. 227°; *2-hydroxy-4-methoxy*-, m.p. 225°, and *4-hydroxy-3-methoxy*-, m.p. 219°; *-benzylidene*-, *resorcyldiene*-, m.p. 229°; *asarylidene*-, m.p. 253°; *cinnamylidene*-, m.p. 233°; *p-dimethylaminobenzylidene*-, m.p. 203°. When *o*-OH-aldehydes are used in the above condensation, the arylidenebisdi-indone is accompanied by its anhydro-derivative (as I); the *anhydro-salicylidene*,



m.p. 309°, *2-hydroxy-3-methoxybenzylidene*-, m.p. 296°, *2-hydroxy-4-methoxybenzylidene*-, m.p. 304°, and *-resorcyldiene*-, m.p. >380°, derivatives are thus obtained. By-products in some of the above condensations are the alkyl- or aryl-ideneindandionedi-indones (*loc. cit.*) and arylideneindandiones; the following are isolated: *ethylidene*-, m.p. 278°; *o*-, m.p. 283°, *m*-, m.p. 240°, and *p*-, m.p. 240°; *-nitrobenzylidene*-, and *o*-, m.p. 275°, and *m*-, m.p. 260°; *-methoxybenzylidene*-indandionedi-indones; *m-methoxybenzylidene*-, m.p. 143°, *veratrylidene*-, m.p. 205°, and *asarylidene*-, m.p. 206°, *-indandiones*. *Ethylidenebisindandione*, m.p. 254° (lit. 227°), is also a by-product when MeCHO is used. Indandione (3 mols.) and α -naphthylideneindandione (1 mol.) in EtOH-piperidine give α -naphthylidenebisdi-indone (*loc. cit.*) and α -naphthylideneindandionedi-indone, m.p. 260°. H. B.

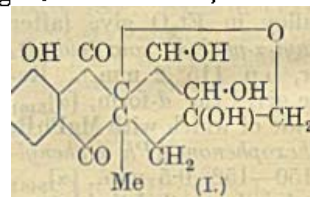
Preparation of chloranil. M. GALLOTTI (Annali Chim. Appl., 1932, 22, 602).—Benzoquinone (108 g.) is dissolved in small portions in 1080 g. of HCl (*d* 1.18). After 20 hr. stirring, 320 c.c. of H₂O₂ (120 vol.) are gradually added below 60°. The pasty mass is stirred for 12 hr., diluted with twice its wt. of H₂O, washed with H₂O on a vac. filter, and dried at 60—70°. Yield, 239 g, m.p. 289—290°.

O. F. L.

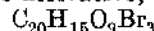
Synthesis of aloe-emodin. P. C. MITTER and D. BANERJEE (J. Indian Chem. Soc., 1932, 9, 375—377).—The *chloride*, m.p. 190°, of 1:8-diacetoxy-anthraquinone-3-carboxylic acid (prepared by oxidation of diacetylchrysophanic acid) is converted by reduction (Rosenmund) and subsequent hydrolysis into 1:8-dihydroxy-3-aldehydeanthraquinone, m.p. 218°, reduced (H₂, PtO₂, FeCl₃, EtOH) to 1:8-dihydroxy-3-hydroxymethylanthraquinone, m.p. 219—220° (corr.), which is identical with natural aloe-emodin. Anthraquinone-2-carboxyl chloride is similarly reduced to the aldehyde and thence to 2-hydroxymethylanthraquinone, m.p. 183°. H. B.

Synthesis of 1:2-benzanthraquinone by thermal dehydration of *o*- α -naphthoylbenzoic acid. M. GALLOTTI and P. GALIMBERTI (Annali Chim. Appl., 1932, 22, 598—600).—Dry *o*- α -naphthoylbenzoic acid (prep. described) is heated for 2 hr. at 130—140°, and then for a few sec. at 170°. The product has m.p. 168—169° after crystallising from AcOH; yield 80%. O. F. L.

Constitution of the aloins. III. R. S. CAHN and J. L. SIMONSEN (J.C.S., 1932, 2573—2582; cf. A., 1930, 609).—It is concluded from new and old analytical and chemical evidence that barbaloin is (I), C₁₆H₁₈O₇ (cf. J.C.S., 1877, 32, 267). The halogenoaloin, previously (*loc. cit.*) designated halogenonorbarbaloin, are true derivatives of (I), and



the tetrahalogenoaloe-emodins obtained on oxidation are *sec.* products. The constitution of the derivative,



is uncertain. (I) gives

by the Purdie method the *Me*₅ ether, m.p. 177—179° after sintering at 175° (2:4-dinitrophenylhydrazone, amorphous; *oxime*, a gum), [α]_D²⁵ -12.05° in CHCl₃, giving, with Br in CHCl₃, HCl and a gum, and oxidised by hot aq. KMnO₄ to *rhein Me*₅ ether. (I) and aq. borax give aloe-emodinanthranol (II) and MeOH (but not arabinose) (cf. Hauser, this vol., 370), and the yield is improved by addition of N₂H₄. Hydrogenation (Pd-C) of (II) in aq. KOH gives *dihydroaloe-emodinanthranol*, m.p. 180° (*K* salt). (II) with boracetic anhydride in warm Ac₂O gives immediately a dark ppt., but (I) reacts much more slowly, owing probably to fission to (II). Hauser's formula for (II) is thus confirmed. (I) and aq. FeCl₃ at 110° give a 75% yield of aloe-emodin. Penta-acetyltribromobarbaloin ("nor" derivative) with CrO₃-AcOH-Ac₂O gives *tetrabromotriacetylaloe-emodin*, decomp. 291—292°, hydrolysed to *tetrabromoaloe-emodin*, m.p. 272° (lit. 264—266°). Tribromobarbaloin *Me*₅ ether ("nor" derivative) and hot piperidine give the phenolic *Me*₅ ether, dimorphic, decomp. 260° after sintering at 250°. R. S. C.

Ramalic acid. G. KOLLER (Monatsh., 1932, 61, 286—292).—The Et₂O extract of *Ramalina pollinaria* contains evernic (I) and ramalic acid (II), C₁₈H₁₈O₇, decomp. 209° (vac.) [Ac₂ derivative, m.p. (vac.) 175° (decomp.) (*Me* ester, m.p. 142°)]. (II) is hydrolysed by cold 30% NaOH in H₂O to orsenillic

and rhizonic acids and is probably identical with obtusatic acid (Asahina and Fuzikawa, this vol., 613). The ramalic acid of Hesse (A., 1898, i, 531) and Zopf (*ibid.*, 89) is either (I) or a mixture of (I) and (II).

H. B.

Estrin. VI. Ring structure of crystalline trihydroxy- and ketohydroxy-estrin. G. F. MARRIAN and G. A. D. HASLEWOOD (J.S.C.I., 1932, 51, 277—283r).—The Me ethers of trihydroxy- (I) and ketohydroxy-estrin (II) give "I vals," close to the theoretical for one double linking when treated with the Rosenmund-Kuhnnehn reagent; the bromides isolated from the reaction mixtures are $C_{19}H_{25}O_3Br$, m.p. 200—203°, and $C_{19}H_{23}O_3Br$, m.p. 191—193°, respectively, showing that the "I vals" are due to substitution and not addition of Br. Clemmensen reduction of (II) gives a phenolic substance, $C_{18}H_{24}O$, m.p. 133—134°, which is insol. in hot aq. NaOH (but forms a Na salt); the existence of the non-reactive "enolic" double linking of Butenandt *et al.* (this vol., 781) is no longer necessary. These results afford fairly conclusive evidence against the presence of a fourth double linking in (I) or (II) (which must be four- and not three-ring compounds). (II) is transformed by AcOH—conc. HCl into a more fusible and probably less acidic compound. Prolonged KOH-fusion of (I) gives a *phenoldicarboxylic acid*, $C_{18}H_{22}O_5$, m.p. 146—147° (turbid), 187—190° (clear), which yields an *Ac* derivative *anhydride*, m.p. 186—190°, and a *Me ether anhydride*, m.p. 172—174°. It is probable that (I) and (II) contain



the annexed ring system. The CO group in (II) is probably in ring 4. Ring 1 or 2 is aromatic (and has a phenolic OH group) in both compounds.

H. B.

Amyrins. II. Products of selenium dehydrogenation. O. BRUNNER, H. HOFER, and R. STEIN (Monatsh., 1932, 61, 293—298; cf. A., 1929, 71; Ruzicka *et al.*, *ibid.*, 932; Dieterle, A., 1931, 624).—Dehydrogenation of α - or β -amyrin (or a mixture) with Se at 280—360° gives sapotalin (1:2:7-trimethylbipthalene), a hydrocarbon, $C_{14}H_{16}$, m.p. 116° (*picrate*, m.p. 156—157°; *stypnate*, m.p. 166°) [probably identical with that obtained by Ruzicka *et al.* (this vol., 517) by dehydrogenation of betulin], a hydrocarbon, m.p. 304—305° (C 93.1, H 6.1%), and a *naphthol*, $C_{13}H_{14}O$, m.p. 156—157° (*benzoate*, m.p. 185°) [probably identical with that described by Ruzicka *et al.* (*loc cit.*)].

H. B.

α -Elemolic and elemolic acids. V. H. LIEB and M. MLADENOVIC (Monatsh., 1932, 61, 274—285).—Acetyl- α -elemolic acid (A., 1931, 960) is hydrolysed by EtOH—NaOEt to α -elemolic acid (I), m.p. 226°, $[\alpha]_D^{20}$ —29.56° in $COMe_2$, which analyses correctly as $C_{30}H_{48}O_3$. (I) is reduced (H_2 , Pd—C, EtOH) to dihydro- α -elemolic acid (II), m.p. 238°, $[\alpha]_D^{20}$ —18.35° in EtOH, and converted by HBr in $CHCl_3$ into bromohydro- α -elemolic acid, m.p. 229°, $[\alpha]_D^{20}$ —15.6° in $COMe_2$, which with MeOH—KOH regenerates (I). The dibromide, m.p. 285°, $[\alpha]_D^{20}$ —8.16° in EtOH, of (I) and MeOH—KOH give bromo- α -elemolic acid, m.p. 283°. Analyses of all the

above compounds support the C_{30} formula. Elemolic acid (III), m.p. 274—275°, $[\alpha]_D^{20}$ —66.85° in $CHCl_3$, affords an oxime, m.p. 236—237° (lit. 230—231°), $[\alpha]_D^{20}$ —112.8° in $CHCl_3$, which, contrary to Bauer and Dimokostoulos (A., 1931, 847), could not be reduced by Na—Hg (or catalytically). Oxidation of (II) with CrO_3 in AcOH gives *dihydroelemolic acid*, $C_{30}H_{46}O_3$, m.p. 293°, $[\alpha]_D^{20}$ —52.4° in $CHCl_3$ (*oxime*, m.p. 249°, $[\alpha]_D^{20}$ —6.16° in $CHCl_3$), identical with the acid (*oxime*, m.p. 231°, $[\alpha]_D^{20}$ —126.1° in $CHCl_3$) obtained by catalytic reduction of (III) [and previously described (this vol., 397) as tetrahydroelemolic acid] and isomeric with the dihydroelemolic acid of Ruzicka *et al.* (this vol., 749).

H. B.

Stereochemical structure. V. Menthyl and bornyl esters of α -keto-acids. R. ROGER and P. D. RITCHIE (Biochem. Z., 1932, 253, 239—265).—The mechanism of asymmetric induction is studied by comparison of the rotations of the menthyl and bornyl esters of α -keto-acids with those of the esters of the corresponding non-ketonic acids. Tables permit comparison of the rotations in different media ($COMe_2$, C_6H_6 , $CHCl_3$, CS_2 , EtOH, and EtOAc) for various wave-lengths (6708—4358 Å.) of such pairs of esters and the influence of temp. and concn. is investigated.

P. W. C.

Oxidation of unsaturated compounds by selenium dioxide. E. SCHENK and E. BORGFARDT (Ber., 1932, 65, [B], 1601—1602; cf. Riley and others, this vol., 833).— SeO_2 in EtOH is added slowly to a boiling mixture of technical α -pinene and EtOH, whereby verbenone, b.p. 97—99°/14 mm. (semicarbazone, m.p. 208—211°), is obtained.

H. W.

Synthesis of camphor. II. Saponification. M. TOMEO (Anal. Fis. Quim., 1932, 30, 679—689).—Crude bornyl acetate gives a yield of borneol, m.p. 180—185°, of only 57.5%, as compared with 96—98.7% from the purified acetate. A 5—10% excess of NaOH is advisable, and refluxing should be continued for 2 hr. at 111°. The product obtained from purified acetate has m.p. 203°; this gives an 85% yield of camphor, compared with 95% from pure borneol. The results are discussed from the technical viewpoint.

H. F. G.

Rotatory powers of substituted camphor-anilic acids and N-phenylcamphorimides. M. SINGH and R. C. BHALLA (J. Indian Chem. Soc., 1932, 9, 363—369).—The following are prepared from camphoric anhydride, NH_2Ar , and NaOAc at 140—145°: 2':4'-dimethyl-, m.p. 220—221°, 3':5'-dimethyl-, m.p. 214—215°, 2':4'-dichloro-, m.p. 200—201°, 2':6'-dimethoxy-, m.p. 137—139°, 3'-methoxy-, m.p. 186.5°, and 3'-ethoxy-, m.p. 168°, -camphoranilic acids; 2':4'-dichloro-, m.p. 62.5°, 2':5'-dimethoxy-, m.p. 111—112°, 3'-methoxy-, m.p. 121—123°, 3'-ethoxy-, m.p. 93—95°, and 2':6'-dimethyl-, m.p. 154—155°, -N-phenylcamphorimides. 4'-Nitro-2'-methoxy-, m.p. 182—184° (lit. 185—186°), 4'-nitro-2'-ethoxy-, m.p. 171—173°, 4'-nitro-2'-methyl-, m.p. 226—228° (lit. 229—230°), and 2'(or 6')-nitro-3'-methyl-, m.p. 139—140°, -camphoranilic acids are obtained by nitration (fuming HNO_3 —AcOH) of the appropriate acids. Vals. of $[M]_D$ for the above

in various solvents are given. Introduction of a second Me in the *m*-position (with respect to the first Me) has little effect on the rotation; 4'-NO₂, 2'-OMe, and 2'-Cl groups cause depression (cf. A., 1931, 626).

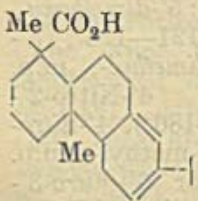
H. B.

Rotatory dispersive power of organic compounds. XX. Rotatory dispersion and circular dichroism of camphor-β-sulphonic acid in the region of absorption. T. M. LOWRY and (Miss) H. S. FRENCH (J.C.S., 1932, 2654—2658; cf. A., 1930, 135).—The rotatory dispersion of camphor-β-sulphonic acid in H₂O rises rapidly to a max. (2000) at 3090 Å. and falls to a -max. (2450) at 2690 Å. with reversal of sign at 2950 Å. The ordinary absorption rises to a max., ϵ 35, at 2840 Å., and the circular dichroism to a max., $\epsilon - \epsilon_c$ 1.535, at 2900 Å. The ketonic band is thus shown to be composite.

R. S. C.

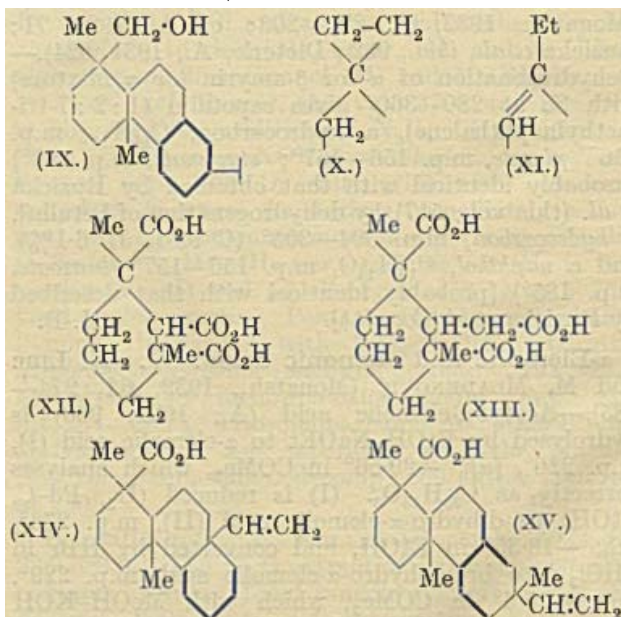
Polyterpenes. LXXII. Oxidations with perbenzoic acid and dehydrogenations with selenium in the amyrin series. L. RUZICKA, H. SILBERMANN, and P. PIETH. **LXXIII. Addition of maleic anhydride to abietic acid and *d*-pimaric acid.** L. RUZICKA, P. J. ANKERSMIT, and B. FRANK. **LXXIV. Oxidation of methyl *d*-pimarate and dihydro-*d*-pimarate with perbenzoic acid.** L. RUZICKA and B. FRANK. **LXXV. Carbon skeleton of abietic and *d*-pimaric acids.** L. RUZICKA, G. B. R. DE GRAAFF, and H. J. MÜLLER (Helv. Chim. Acta, 1932, 15, 1285—1289, 1289—1294, 1294—1299, 1300—1303; cf. this vol., 948).—LXXII. Hydrogenation of β-amyrilene gives dihydro-β-amyrilene (I), m.p. 84—85°, new $[\alpha]_D +83^\circ$ in C₆H₆, and an *isomeride*, m.p. 92—93°, $[\alpha]_D +77^\circ$ in C₆H₆. Dihydro-α-amyrilene has new $[\alpha]_D +74^\circ$ in C₆H₆. Use of EtOAc for purification led to isolation of purer, and some new, oxides produced by the action of BzO₂H on substances of the amyrin series. β-Amyrin oxide, C₃₀H₅₀O₂, has new m.p. 201—202°. β-Amyrilene gives a *dioxide*, C₃₀H₄₈O₂, m.p. 199—201° after sintering. (I) affords a *monoxide*, C₃₀H₅₀O, m.p. 126—127°. A mixture of α- and β-amyrin with Se under certain conditions affords the substituted naphthol, C₁₃H₁₄O, m.p. 153—154°, obtained from betulin (this vol., 517) and sapotalin.

LXXIII. Me abietate and maleic anhydride at 160° give an additive compound (II), C₂₅H₄₄O₅, m.p. 214—215°, $[\alpha]_D -26^\circ$ in CHCl₃, hydrolysed by KOH-EtOH to the *anhydride-carboxylic acid* (III), C₂₄H₃₂O₅, m.p. 227—228°, $[\alpha]_D -25^\circ$ in CHCl₃, the Me₃ ester, m.p. 113° after sintering, of which is shown by its *R* to contain one ethylenic linking. (II) gives an impure Me₂ Et ester, b.p. 220°/0.35 mm. Et abietate (IV) gives a similar additive compound, which affords a Me₂ Et ester, b.p. 212°/0.3 mm.; the portion of (IV) which did not react yielded an *Et abietate*, (V), +2EtOH, m.p. 62—63°, and anhyd., m.p. 66—67°. American colophony and maleic anhydride afford (III) directly, $[\alpha]_D -28^\circ$. *d*-Pimaric acid reacts abnormally. The above reactions indicate the annexed formula for abietic acid, although isolation of (V) shows the natural acid to be a mixture of isomerides.



LXXIV. Previous results (A., 1928, 425) with *d*-pimaric acid and BzO₂H (VI) are confirmed. (VI) adds on about 1.6 atoms of O to Me *d*-pimarate, m.p. 69—70°, in CHCl₃ at 12° to yield a *dioxide*, amorphous, b.p. 199—205°/2 mm. Me dihydro-*d*-pimarate (VII), m.p. 79—80°, $[\alpha]_D +18.7^\circ$ in C₆H₆ (modified prep.), reacts with 2 mols. of (VI) at 12° in CHCl₃ to give a mixture, b.p. 170—175°/0.15 mm., of mono- and di-oxide, from which on distillation a 50% yield of an *isomeride*, m.p. 54—55°, $[\alpha]_D +52^\circ$ in C₆H₆, of Me *d*-pimarate was obtained. This yields an *isomeride*, m.p. 215—216, $[\alpha]_D$ about +60° in EtOH, of *d*-pimaric acid, and, when hydrogenated (PtO₂) in AcOH, an ester, hydrolysis of which gives a new *dihydropimaric acid*, m.p. about 189—192°, which is still unsaturated [C(NO₂)₄]. (VII) reacts, however, with only 1 mol. of (VI) at -10° to give in one experiment an unstable *oxide*, m.p. 103—104°, and in a second experiment an isomeric, stable *oxide*, m.p. 118—119°, which with AcOH and a drop of H₂SO₄ is dehydrated to yield *d*-pimaric acid, m.p. 186—188°. The dehydrogenation of (VII) at 12° and the formation of two oxides at -10° are abnormal and cast doubt on the utility of (VI) as a reagent in the polyterpene series.

LXXV. Methylpimanthrenequinone (from *d*-pimarol) or methylretenequinone (from abietinol) with KMnO₄ gives hemimellitic and diphenyl-2:3:2':4'-tetracarboxylic acids. Methylretene (VIII) and K₃Fe(CN)₆ give phenanthrene-1:7-dicarboxylic acid. These reactions indicate that (VIII) and methylpimanthrene are 1-ethyl-7-isopropyl- and 7-methyl-1-ethyl-phenanthrene, respectively, and the substances are re-named *homoretene* and *homopimanthrene*, respectively. The following compounds are assigned new formulæ: abietinol (IX); methylabietin (re-named homoabietin) (XI), formed from (IX) by a pinacolin change by way of (X); the tricarboxylic acids, C₁₁H₁₆O₆ and C₁₂H₁₈O₆, from abietic acid and *d*-pimaric acid, (XII) and (XIII), respectively;



d-pimaric acid (XIV) or (XV), of which (XIV) is more probable, since tetrahydro-*d*-pimaric acid and

Se give only pimanthrene, whereas (XV) would be expected to yield also 4-methyl-7-ethylphenanthrene. (XIV) and (XV) can be built up from an irregular chain of isoprene units. The lines in heavy type indicate the possible positions of the ethylenic linkings.

R. S. C.

2-Chloro-5-methylfuran and 5-nitro-2-methylfuran. H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1932, 54, 4108—4110).— N_2H_4 -NaOEt reduction of 5-chlorofurfuraldehyde gives 36% of 2-chloro-5-methylfuran, identical with the decarboxylation product of 5-chloro-2-methyl-3-furoic acid; it does not react with Mg. Reduction of 5-nitrofurfuraldehyde gives 5-nitro-2-methylfuran.

C. J. W. (b)

Allylio systems in furan. H. GILMAN and R. A. FRANZ (Rec. trav. chim., 1932, 51, 991—995).—Mg 2-furyl iodide gives furfuryl alcohol, Et furoate, and furfuraldehyde with CH_2O , $ClCO_2Et$, and HCO_2Et , respectively.

J. W. B.

2:4-Dimethylfuran-3-aldehyde. T. REICHSTEIN and H. ZSCHOKKE (Helv. Chim. Acta, 1932, 15, 1105—1110).—2:4-Dimethylfuran-3-carboxylic acid (I) (modified prep.), m.p. 125—126°, b.p. 131°/12 mm., and $SOCl_2$ give the acid chloride, b.p. 78—79°, yielding with HCN and C_5H_5N in Et_2O at -15° 2:4-dimethylfuran-3-carboxylic acid (II), b.p. 91°/11 mm., which with Zn dust and AcOH gives the OH-nitrile, whence aq. K_2CO_3 affords 2:4-dimethylfuran-3-aldehyde (III), b.p. 73°/11 mm. (semicarbazone, m.p. 168°). (II) is polymerised by cold, conc. HCl and unchanged by dry HCl-SnCl₂ in Et_2O . The oxime, m.p. 74—76°, b.p. 105—110°/11 mm., with Ac_2O gives the nitrile, b.p. 66°/11 mm., hydrolysed by KOH-EtOH to (I). The acid chloride of (I) and NH_2Ph in Et_2O give the anilide (IV), m.p. 135—136°, which with PCl_5 (1 mol.) in warm PhMe yields the chloroimide, b.p. 132°/0.7 mm., changed by anhyd. SnCl₂ and dry HCl in Et_2O into the oily anil, which with 2N- H_2SO_4 rapidly affords (III). When (IV) is heated with a large excess of PCl_5 and reduced, it yields an aldehyde, $C_7H_7O_2Cl$, m.p. 42°, which may be 5-chloro-2:4-dimethylfuran-3-aldehyde, since it gives a stable semicarbazone, m.p. 189°, or 2-chloromethyl-4-methylfuran-3-aldehyde, since with boiling $AgNO_3$ it ppts. $AgCl$. (III) is unstable to NaOH and differs from furan- α -aldehydes in forming a normal anil with NH_2Ph , AcOH. All m.p. are corrected.

R. S. C.

Synthesis of two trimethylfurans and of trimethylfurfuraldehyde. T. REICHSTEIN, H. ZSCHOKKE, and W. SYZ (Helv. Chim. Acta, 1932, 15, 1112—1118).—Et $\alpha\beta$ -diacetyl-*n*-butyrate and boiling 10% H_2SO_4 give Et 2:4:5-trimethylfuran-3-carboxylate, b.p. 100—105°/12 mm. (94.5% yield), and a little of the corresponding acid (I), m.p. 131—132°, which with Cu chromite and boiling quinoline affords 2:4:5-trimethylfuran (II), b.p. 114°/720 mm., 51.5°/12 mm. Et acetonedicarboxylate, Me α -chloroethyl ketone, and NH_3 in Et_2O give a 10.7% yield of Et, 2:3-dimethylfuran-4-carboxylate-5-acetate, b.p. about 110—115°/0.2 mm., hydrolysed by KOH-MeOH to the corresponding dicarboxylic acid, m.p. 211° (decomp.), which at 220—250° gives CO_2 and (I). The hydrazone, m.p. (crude) 52° (changed by warm AcOH

to an azine), of 2:4-dimethylfuran-3-aldehyde with NaOMe at 200° affords 2:3:4-trimethylfuran, b.p. about 54—55°/57 mm., which with HCN and HCl in Et_2O at -15° gives 3:4:5-trimethylfurfuraldehyde, m.p. 31—32°, b.p. 68°/0.3 mm., oxidised (Ag_2O -NaOH) to 3:4:5-trimethyl-2-furoic acid, m.p. 185° (decomp.), and yielding, by way of the hydrazone, 2:3:4:5-tetramethylfuran (III), m.p. about -30° , b.p. 44°/12 mm. (III) prepared by Willstätter's method (A., 1914, i, 286) is not pure. "Dimethylketopentene" is probably 5-methyl-2-ethylfuran, and not (II) (cf. loc. cit.); similarly, "methylvinic acid" is probably 2-methyl-5-ethylfuran-3-carboxylic acid, not (I), and "methylmethronic acid" is 2-methylfuran-3-carboxylic acid-5- α -propionic acid.

R. S. C.

Synthesis of 2-isopropylfuran and 5-isopropylfurfuraldehyde. T. REICHSTEIN, H. ZSCHOKKE, and G. RONA (Helv. Chim. Acta, 1932, 15, 1118—1124).—2-Furyl Me ketone or Et furoate and MgMeI give 2-furyldimethylcarbinol, m.p. about 11—12°, b.p. 62°/11 mm., dehydrated by boiling Ac_2O to give a poor yield of 2-isopropenylfuran (I), b.p. below about 30°/70 mm., a dimeride, b.p. 75°/0.3 mm., and a substance, b.p. 140—180°/0.3 mm. Hydrogenation (PtO_2) of (I) in Et_2O affords 2-isopropylfuran (II), b.p. about 40°/60 mm., yielding 5-isopropylfurfuraldehyde, b.p. 86—87°/11 mm. (semicarbazone, m.p. 167°), oxidised by Ag_2O to 5-isopropyl-2-furoic acid, m.p. 66—67°. Et β -keto- γ -methylvalerate and $\alpha\beta$ -dichloroethyl ether in Et_2O and aq. NaOH give in poor yield Et 2-isopropylfuran-3-carboxylate, b.p. 92°/12 mm., and Et β -isobutyroxyeronate. The former ester yields the corresponding acid, m.p. 79°, which with Cu chromite and boiling quinoline gives (II). Et sodiomalonate and Et β -2-furylacrylate give Et, 6-2-furylpropane- $\alpha\gamma\gamma$ -tricarboxylate, b.p. 162—165°/0.7 mm., hydrolysed to the corresponding acid, which at the m.p. (158°) or when distilled yields β -2-furylglutaric acid, decarboxylated to (II) best with Cu chromite and boiling 6-naphthoquinoline.

R. S. C.

Abnormal reaction of furfuryl halides with potassium cyanide. T. REICHSTEIN and H. ZSCHOKKE (Helv. Chim. Acta, 1932, 15, 1124—1127).—2-Furylmethylcarbinol (I), b.p. 65.5—66.5°/11 mm., PBr_3 , and C_5H_5N in pentane at -15° give an unstable solution of the corresponding chloride, which with aq. KCN yields 5-ethyl-2-furonitrile, b.p. about 68—70°, hydrolysed by KOH-MeOH to 5-ethyl-2-furoic acid (II), m.p. 94—95°, also prepared from 5-ethylfurfuraldehyde and Ag_2O -NaOH. (I), C_5H_5N , and $SOCl_2$ give a similar unstable solution, whence (II) was obtained. 2-Furyldimethylcarbinol, PBr_3 , and C_5H_5N in C_5H_{12} at -20° give a very unstable solution, giving with KCN a very poor yield of a neutral oil, b.p. about 80°/12 mm. The halides could not be isolated.

R. S. C.

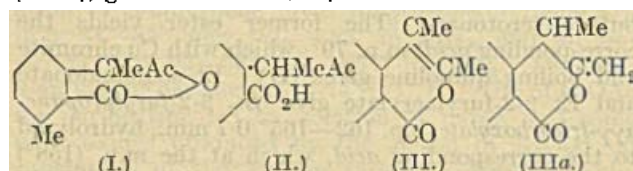
Synthesis of 2:6-diethyl- and 2:6-di-*n*-propyl- γ -pyrones. S. S. DESHPANDE (J. Indian Chem. Soc., 1932, 9, 303—308).—Dehydropropionylacetic acid (improved prep. given; cf. von Pechmann and Neger, A., 1893, i, 398) and boiling HCl (d 1.19) give 2:6-diethyl- γ -pyrone, b.p. 126°/7 mm., m.p. 10° [hydrochloride, m.p. 77—78°; chloroplatinate, m.p. 188° (decomp.); picrate, m.p. 110°; mercuri-

chloride, m.p. 72° (decomp.), converted by conc. aq. NH_3 at 130° into 2:6-diethyl-4-pyridone (+ H_2O), m.p. 65–66° [hydrochloride (+ H_2O), m.p. 76–78°; chloroplatinate, m.p. 203° (decomp.)]. Acetonedicarboxylic acid, PrCOCl , and a little conc. H_2SO_4 give carboxydehydro-n-butyrylacetic acid,

$\text{PrCO}\cdot\text{CH}\langle\text{CO}\text{---}\text{O}\rangle\text{CPr}$, m.p. 80°, the K salt, m.p. 164°, of which when heated with H_2O and then acidified (AcOH) affords dehydro-n-butyrylacetic acid, b.p. 140–144°/4 mm., m.p. 16°. This is converted (as above) into 2:6-di-n-propyl- γ -pyrone, b.p. 136°/5 mm. [picrate, m.p. 61°; chloroplatinate, m.p. 162–164°; mercurichloride, m.p. 88–89° (decomp.)]. 2:6-Di-n-propyl-4-pyridone [monohydrate, m.p. 62°; hydrochloride (+ H_2O), m.p. 96–98°; chloroplatinate, m.p. 204°] has b.p. 210–215°/12 mm., m.p. 85–88°.

H. B.

Congo copal oil. 3-Acetyl-3:7-dimethylphthalide. L. WESTENBERG and J. P. WIBAUT (Rec. trav. chim., 1932, 51, 1004–1007).—The lactone of the methyl ketone (I) (A., 1931, 484, where it is erroneously given the structure $\text{C}_6\text{H}_4\langle\text{CO}\text{---}\text{O}\rangle$) obtained by oxidation of 1:2:5-trimethylnaphthalene, is converted by HI (d 2.0) and red P into the isocoumarin derivative (III) or (IIIa), m.p. 135°, converted by NaOH - MeOH and subsequent acidification with HCl into the keto-acid (II), m.p. 108° (oxime, m.p. 150°), which by treatment with HI (d 2.0), gives H_2O and (III).



Determination of Br addition to (III)
1.37 atoms Br per mol. lactone instead of

Paenol derivatives: a case of bromine displacement. J. SHINODA, D. SATO, and M. KAWAGOE (J. Pharm. Soc. Japan, 1932, 52, 91–94).—Nitration of paenol gives the 5- NO_2 -derivative (cf. Adams, A., 1919, i, 160), converted by standard methods into the 5- NH_2 , m.p. 113–114°, 5-OH, m.p. 166–167°, 5-Cl, m.p. 154–155°, and 5-Br, m.p. 172–173° (I) (cf. A., 1897, i, 221), -derivatives; the last-named is converted by Ac_2O at 180° into 6-bromo-7-methoxy-3-acetyl-2-methyl-1:4-benzopyrone, m.p. 190–191°, and under milder conditions into the acetate, m.p. 90–91°. Oxidation of the Me ether of (I) with KMnO_4 gives 5-bromo-2:4-dimethoxybenzoylformic acid, m.p. 170–171° (oxime, m.p. 164–166°), further oxidised by H_2O_2 to 5-bromo-2:4-dimethoxybenzoic acid, m.p. 193–200°. Nitration of (I) (cf. Adams, loc. cit.) gives a mixture of the 3- NO_2 -derivative, m.p. 125–126° {3- NH_2 -compound, m.p. 109–110° [hydrochloride, m.p. 215° (decomp.)]}, and 6-bromo-5-nitropaenol (II), m.p. 125–126°, the Br having been displaced by the NO_2 group. The 5- NH_2 -derivative, m.p. 135° (hydrochloride, m.p. 205–206°), corresponding with (II), gave 6-bromopaenol, m.p. 133–134° (III)

[phenylhydrazone, m.p. 192–193° (decomp.); Me ether, m.p. 52–53°; acetate, m.p. 125°; 5-bromo-7-methoxy-3-acetyl-2-methyl-1:4-benzopyrone, m.p. 178–179°], when replacement of its NH_2 group by OH was attempted. Oxidation of (III) with $\text{K}_2\text{S}_2\text{O}_8$ gives a bromohydroxyphaenol, m.p. 164–166°. H. A. P.

O-Methylation of quercetin. J. A. ANDERSON (Canad. J. Res., 1932, 7, 283–284).—Freudenberg's method gives penta- (I) and tetra-methylquercetin in the proportions 2:1 (cf. this vol., 167). Modification of the method gives an 84% yield of (I). R. S. C.

Yellow colouring matter of Khapli wheat, Triticum dicocci. II. Constitution of tricetin. J. A. ANDERSON (Canad. J. Res., 1932, 7, 285–292; cf. A., 1931, 1426).—Khapli wheat contains H_2O -sol. substances (also present in six other varieties), possibly glucosides of tricetin (I), and small amounts of (I) (modified prep.), m.p. 288° after softening at 278° (also obtained from Marquis wheat leaves in smaller yield). The Ac_3 derivative of (I) by Freudenberg's method gives the Me_3 ether (II), m.p. 192–193°, hydrolysed by KOH - EtOH to O-trimethylgallic acid (III) and 2-hydroxy-4:6-dimethoxyacetophenone. Phlorogheicol Me_3 ether (modified prep.) is converted into 2-acetoxy-4:6-dimethoxyacetophenone. Phloracetophenone, 3:4:5-trimethoxybenzoic anhydride, and the Na salt of (III) at 175° yield a little 5:7-dihydroxy-3':4':5'-trimethoxyflavone (IV), m.p. 269–270°, and much 3-(3':4':5'-trimethoxybenzoyl)-5:7-dihydroxy-3':4':5'-trimethoxyflavone, m.p. 203–204.5° (Ac_5 derivative, m.p. 189–191°) [hydrolysed by aq. KOH to (IV)]. The Ac_2 derivative, m.p. 160–162°, of (IV) gives by Freudenberg's method the Me_2 ether, identical with (I), whilst HI and AcOH demethylate (IV) to 5:7:3':4':5'-pentahydroxyflavone (V), decomp. above 330°, the Ac_5 derivative of which is identical with that of (I). (I) is thus proved to be (IV). Many of the data of Badhwar *et al.* (this vol., 621) regarding (IV) and its derivatives are corrected.

R. S. C.

Dye from acacia wood. K. BRASS and H. KRANZ (Naturwiss., 1932, 20, 672–673).—The dye (I) from *Gleditsia monosperma* is identical with that from *Robinia pseudacacia* (II) (cf. B., 1932, 760), since both yield Ac - and (MeO)₅- (III) derivatives, m.p. 224° and 148°, respectively. (I), $\text{C}_{15}\text{H}_{10}\text{O}_7$, +1 or 2 H_2O and anhyd., is 3:3':4':5'-tetrahydroxyflavonol, since (a) (III) with KOH - MeOH gives gallic acid Me_3 ether and fisetol Me_2 ether, and (b) gallaldehyde Me_3 ether and paenol give 3:3':4':5'-tetramethoxyflavonol, m.p. 194°, yielding (III) when methylated. (II) contains also a substance, which gives an Ac derivative, m.p. 141°.

R. S. C.

Plant dyes. XLII. Isomeric carotenes and their relations to vitamin-A. P. KARRER, K. SCHOPP, and R. MORF. XLIII. Carotenoids of flowers. P. KARRER and A. NOTTHAFT. XLIV. Reactions of gossypol. P. KARRER and E. TOBLER. XLV. Constitution of diglucosidic anthocyanins. P. KARRER and G. DE MEURON (Helv. Chim. Acta, 1932, 15, 1158–1165, 1195–1204, 1204–1212, 1212–1217; cf. this vol., 976).—XLII. The mother-liquors (A) from α - and β -carotene

contain a third *carotenoid* (not obtained pure), an oil, adsorbed by Al_2O_3 and desorbed therefrom by 90% MeOH (not by ligroin), with absorption max. in CS_2 at 482 and 453 $\text{m}\mu$; it has no vitamin activity. (A) contained also α -carotene, m.p. 172° , absorption max. at 510 and 476 $\text{m}\mu$; since it has $[\alpha]_D^{25} +130^\circ$, carrots must contain also inactive α -carotene, and the rotation is, therefore, no measure of the carotene content of a prep. *iso*-Carotene (I) (modified prep.), $\text{C}_{40}\text{H}_{56}$, m.p. 192 – 193° (corr.), with cold alkaline KMnO_4 gives $\alpha\alpha$ -dimethylglutaric (II), $\alpha\alpha$ -dimethylsuccinic, and (probably) succinic acids, with hot KMnO_4 and CrO_3 -8 and 6 mols. of AcOH , respectively, with O_3 in CCl_4 - AcOH (I) but not COMe_2 , geronic or isogeronic acid, and is hydrogenated (PtO_2) in AcOH to $\text{C}_{40}\text{H}_{80}$. (I) thus probably contains only one ring, which differs from the β -ionone ring in the position of the ethylenic linking. The β -ionone ring is considered to be essential for vitamin-A activity.

XLIII. The following carotenoids, occurring mainly as esters, were isolated from the flowers named: xanthophyll from *Calltha palustris*, *Trollius europaeus*, *Ranunculus arvensis*, and *Tragopogon pratensis* (I); violaxanthin from (I), *Laburnum*, and *Sinapis officinalis*; zeaxanthin (II) from *Senecio Doronicum*; and lycopene from *Dimorphoteca aurantica*. Carotenoids are not confined to yellow flowers. The name "phytoxanthin" is proposed for carotenoids containing O and 40 C atoms, whilst the name xanthophyll is retained for the substance, $\text{C}_{40}\text{H}_{56}\text{O}_2$, obtained from green leaves. The following esters of (II) were prepared: $(\text{EtCO}_2)_2$, m.p. 142° ; $(\text{Pr}^n\text{CO}_2)_2$, m.p. 132° ; $(\text{Bu}^n\text{CO}_2)_2$, m.p. 125° ; *di-n-hexoate*, m.p. 117 – 118° ; and *di-n-heptoate*, m.p. 107° .

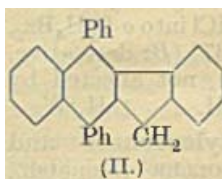
XLIV. Gossypol (I) (modified prep. from cotton-seeds), m.p. 199° , gives a *quinoxaline* derivative, m.p. 298° after sintering and decomp., and is, therefore, an α -diketone or, more probably, an *o*-quinone. It is phenolic, gives an Ac_6 derivative (II), but two of the OH groups titrate as acids and two are characterised by resistance to hydrolysis when esterified. With 40% NaOH at 100° (I) gives HCO_2H (2 mols.) and *apogossypolic acid*, $\text{C}_{28}\text{H}_{30}\text{O}_6$ (Ac_6 derivative; no CO group). With O_3 under certain conditions (I) gives *gossypolic acid*, $(\text{C}_{12}\text{H}_{14}\text{O}_4)_x$ (x =probably 2), m.p. 241° , shown by colour reactions to be an α -OH-acid, yielding with CH_2N_2 in Et_2O *methylogossypolate*, $[\text{C}_{12}\text{H}_{12}\text{O}_2(\text{OMe})_2]_x$, m.p. 142° , which is hydrolysed by $2N$ -KOH-MeOH to *methylogossypolic acid*, m.p. 225° . The *dihydrazone*, m.p. about 285° , of (I) with NaOEt at 180° gives a substance, $\text{C}_{30}\text{H}_{34}\text{O}_6\text{N}_2$, decomp. from 170° , containing the grouping $\text{CH}_2\text{:C:N:NH}_2$. (I) is not a glucoside and does not give MeCl or EtCl with conc. acids.

XLV. When an anthocyanin is treated with H_2O_2 , the excess of H_2O_2 destroyed by Pt -black, and the glucoside-ester hydrolysed either by NHPh-NH_2 , or by NH_3 , the sugar from position 3 is liberated and can be identified as osazone. Subsequent treatment with HCl hydrolyses the glucoside at position 7 and allows this sugar component to be identified. Results with paeonin, cyanin, monardin, and hirsutone are in agreement with the conclusions of Robinson (this vol., 1140). Violanin, however, gives the osazone of a polysaccharide in the first stage. R. S. C.

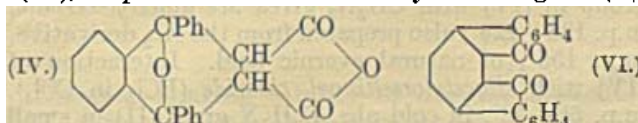
Synthesis of chromones. III. Condensation of β -naphthol with ethyl alkylacetoacetates. D. CHAKRAVARTI (J. Indian Chem. Soc., 1932, 9, 389–392; cf. this vol., 519).— β - $\text{C}_{10}\text{H}_7\text{:OH}$, $\text{CHAcMe}\cdot\text{CO}_2\text{Et}$, and conc. H_2SO_4 give a little 3:4-dimethyl-1:2- β -naphthapyrone, m.p. 127° ; with P_2O_5 as the condensing agent, 2:3-dimethyl-1:4- β -naphthapyrone, m.p. 130° , results. β - $\text{C}_{10}\text{H}_7\text{:OH}$ does not condense with Et α -ethyl- and -*n*- and -*iso*-propyl-acetoacetates in presence of H_2SO_4 ; the use of P_2O_5 gives 2-methyl-3-ethyl-, m.p. 117° , 2-methyl-3-propyl-, m.p. 95° , and 2-methyl-3-isopropyl-, m.p. 131° , 1:4- β -naphthapyrone, respectively. These results agree with the generalisation previously made (*loc. cit.*). The course of the Pechmann and Simonis reactions depends on both the phenol and the ester. 2-Styryl-3-methyl-, m.p. 186° , -3-ethyl-, m.p. 183° , -3-propyl-, m.p. 168° , and -3-isopropyl-, m.p. 187° , 1:4- β -naphthapyrones have been prepared. H. B.

Condensation of 2:5-diphenyl-3:4-benzofuran with unsaturated compounds. I. R. WEISS and A. BELLER. II. 1:4-Diphenylnaphthalene and derivatives. R. WEISS and A. ABELES [with E. KNAPP] (Monatsh., 1932, 61, 143–146, 162–168).

I. Addition of 2:5-diphenyl-3:4-benzofuran (I) to Et cinnamate occurs readily in EtOH , best under the influence of HCl , and gives *Et* 1:2:4-triphenylnaphthalene-3-carboxylate, m.p. 138 – 140° . This was not hydrolysable by ordinary methods, and with HI and PhOH gives 1:4-diphenyl-2:3-benzofluorene (II), m.p. 199° , or, with conc. H_2SO_4 , 1:4-diphenyl-2:3-benzofluorenone (III), m.p. 208° . (II) is identified by synthesis by addition of (I) to indene, and is oxidised by CrO_3 in AcOH to (III).



II. Interaction of (I) with maleic anhydride in xylene gives 1:4-diphenyl-1:4-oxido-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride (IV), m.p. 270 – 274° , converted by HCl in AcOH (with loss of H_2O) into 1:4-diphenylnaphthalene-2:3-dicarboxylic anhydride (V), m.p. 275° , and by cold conc. H_2SO_4 into 1:2:3:4-dibenzoylenenaphthalene (VI), m.p. 295 – 297° . The anhydride ring of (V)

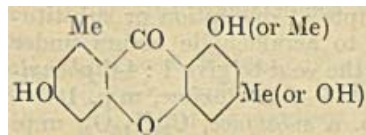


resisted all other attempts at disruption or substitution. Addition of (I) to acetaldehyde occurs under the influence of HCl in the cold to give 1:4-diphenyl-2-naphthaldehyde, m.p. 146 – 148° (oxime, m.p. 187 – 191°), at higher temp. a substance, $\text{C}_{22}\text{H}_{16}\text{O}_2$, m.p. 163 – 166° [not (VII)], is formed. The aldehyde is oxidised by KMnO_4 in aq. COMe_2 to 1:4-diphenyl-2-naphthoic acid (VII), m.p. 223 – 225° (*Me* ester, m.p. 163 – 165°), and a little 1:4-diphenylnaphthalene (VIII), m.p. 135 – 137° (NO_2 -derivative, m.p. 163 – 165°) (definitely different from the substance described as such by Franssen, A., 1925, i, 1146). Distillation of the Na salt of (VII) with KOH in N_2 gives (VIII) and a little 2-phenyl-3:4-benzofluorenone,

m.p. 189°, the latter of which was synthesised for comparison from the chloride of (VII) (SOCl_2) by action of AlCl_3 in CS_2 . H. A. P.

$\alpha\alpha'$ -Substituted $\beta\beta'$ -benzo- $\alpha\alpha'$ -dihydrofurans. II. F. SEIDEL and O. BEZNER (Ber., 1932, 65, [B], 1566—1574; cf. A., 1929, 73).—*o*-Cyanotriphenylmethane in Et_2O is converted by MgPhBr at room temp. into *o*-benzoyltriphenylmethane (I), m.p. 88°, which does not react with $\text{NHPh}\cdot\text{NH}_2$ in AcOH or with molten $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$. It is oxidised to diphenylphthalide (II) and yields a 2 : 4-dinitrophenylhydrazone, m.p. 218—220° after softening at 200°. It differs completely from 2 : 2 : 5-triphenyl-3 : 4-benzodihydrofuran, m.p. 120°, which does not react with 2 : 4-dinitrophenylhydrazine, and evidence of mutual interconvertibility is not obtained. The prep. of *o*-hydroxy-2 : 2 : 5-triphenyl-3 : 4-benzo-2 : 5-dihydrofuran (III), m.p. 121°, from (II) and MgPhBr , from *o*-dibenzoylbenzene, and from (I) and Br is recorded. (I) and *o*-benzoyltriphenylcarbinol (IV) are related as ring-chain tautomers. Reduction of (I) from each source by HCO_2H affords 2 : 2 : 5-triphenyl-3 : 4-benzo-2 : 5-dihydrofuran. With 2 : 4-dinitrophenylhydrazine (I) affords the diazine $\text{C}_6\text{H}_4\cdot\text{CPh}_2\text{N}=\text{N}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, m.p. 245—247° (or $+1\text{C}_6\text{H}_6$, m.p. 77°, and $+1\text{EtOH}$, m.p. 160—163°). Attempts to synthesise (IV) from *o*-cyanobenzophenone, m.p. 86.5°, and MgPhBr lead to 1-hydroxy-1 : 3-diphenylisoindole, converted by conc. HCl into *o*- $\text{C}_6\text{H}_4\text{Bz}_2$, and the imine of (IV), m.p. 135—137° (Bz derivative, m.p. 240° after softening at 225°), not affected by boiling $2\text{N}\cdot\text{HCl}$ or $2\text{N}\cdot\text{NaOH}\cdot\text{EtOH}$. H. W.

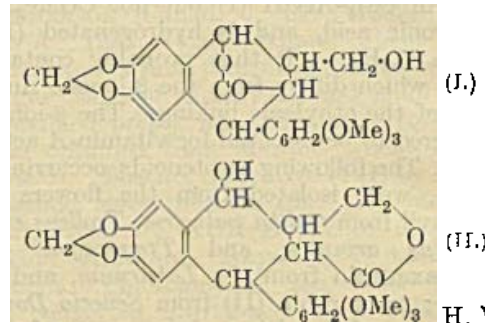
Synthesis of methyl diacetylevernate and tetra-acetylglyrophorate. G. KOLLER (Monatsh., 1932, 61, 147—161).—Gyrophoric acid (I) readily gives an Ac_4 derivative, decomp. 231°, converted by CH_2N_2 into its Me ester (II), m.p. 202°, energetic alkaline hydrolysis of which gives only orcinol. Hydrolysis of (I) with cold 30% NaOH gives lekanoric (III) and orsellinic acids. The Me ester, m.p. 157° (CH_2N_2), of triacetyl-lekanoric acid (Ac_3O and $\text{C}_5\text{H}_5\text{N}$), readily gives the corresponding Ac_2 (IV), m.p. 149—150°, and Ac , m.p. 167°, derivatives on incomplete hydrolysis by alkali. Methylation of the free OH group in (IV) with CH_2N_2 gives Me diacetylevernate, m.p. 128—129°, also prepared from the Ac_2 derivative, m.p. 155°, of natural evernic acid. Interaction of (IV) with diacetylorsellinoyl chloride (PCl_5 in CCl_4), m.p. 56—58°, in cold abs. $\text{C}_5\text{H}_5\text{N}$ gives (II) in small yield, thus confirming the structure assigned to (I) by Asahina (this vol., 851). Thermal decomp. of (I) or (III)



give orcinol and dihydroxydimethylxanthone, m.p. 260° (annexed formula), also formed by distillation of (III) with Ac_2O . H. A. P.

Eosin B. W. C. HOLMES, C. G. MELIN, and A. R. PETERSON (Stain Tech., 1932, 7, 121—127).—The absorption spectra of the two known dibromodinitrofluoresceins have been determined. Commercial eosin B is impure. H. W. D.

Podophyllin. W. BORSCHÉ and J. NIEMANN (Ber., 1932, 65, [B], 1633—1634).—In reply to Spath and others (this vol., 1137) it is stated that podophyllomeronic acid is 6 : 7-methylenedioxy-2-methylnaphthalene-3-carboxylic acid, since it can be converted through phyllomeronic acid (6 : 7-dihydroxy-2-methylnaphthalene-3-carboxylic acid) and phyllomerol (6 : 7-dihydroxy-2-methylnaphthalene) into 2-methylnaphthalene. These observations and the isolation of 4 : 5-methylenedioxy- ω -3' : 4' : 5'-trimethoxyphenylphthalide by the oxidative degradation of podophyllin acid establish the constitutions (I) and (II) for podophyllotoxin and picropodophyllin respectively.



Podophyllin. II. W. BORSCHÉ and J. NIEMANN (Annalen, 1932, 499, 59—76).—Oxidation of podophyllomeronic acid (I) (this vol., 618) [Br_2 -derivative, m.p. 359° (Me ester, m.p. 233—234°)] with HNO_3 (d 1.4) gives 6-nitrotoluene-2 : 4 : 5-tricarboxylic acid (II), m.p. 232—233° (Me_3 ester, m.p. 95—96°), whilst oxidation with alkaline KMnO_4 at 100° (bath) affords toluene-2 : 4 : 5-tricarboxylic acid, m.p. 212—215° (Me_3 ester), which is nitrated to (II). Boiling KMnO_4 converts (I) into pyromellitic acid. (I) heated with quinoline and Cu-bronze gives podophyllomerol (6 : 7-methylenedioxy-2-methylnaphthalene), m.p. 129—129.5° (picrate, m.p. 133—134°), whilst fusion with KOH and a little Zn dust at 280—325° affords phyllomeronic acid (III) (6 : 7-dihydroxy-2-methylnaphthalene-3-carboxylic acid), m.p. 243—244° [Me ester, m.p. 186—187°; Me_2 ether (IV), m.p. 223—225° (Me ester, m.p. 125—126°); Ac_2 derivative, m.p. 220° (previous sintering); Br_2 -derivative, m.p. 265° (decomp.) (previous darkening) (Me_2 ether Me ester, m.p. 127—129°)], which when heated with $\text{Ba}(\text{OH})_2$ gives phyllomerol (6 : 7-dihydroxy-2-methylnaphthalene), m.p. 161—162° [Me_2 ether, m.p. 98—100° (picrate, m.p. 120—121°), obtained similarly from (IV)]. Zn dust distillation of (III) gives $2\cdot\text{C}_{10}\text{H}_7\cdot\text{Me}$. (I) is 6 : 7-methylenedioxy-2-methylnaphthalene-3-carboxylic acid. Oxidation of podophyllin acid with cold alkaline KMnO_4 gives $\text{H}_2\text{C}_2\text{O}_4$, picropodophyllin, a lactone, $\text{C}_{18}\text{H}_{16}\text{O}_7$, m.p. 218—221°, and substances, m.p. 195—200° and 210—213°; the last is methylated (CH_3N_3) to a compound, $\text{C}_{20}\text{H}_{15}\text{O}_7$, m.p. 166—167°. Oxidation at 100° (bath) gives 3 : 4 : 5-(OMe) $_3\cdot\text{C}_6\text{H}_2\cdot\text{CO}_2\text{H}$, $\text{H}_3\text{C}_2\text{O}_4$, and two aldehydo- or keto-acids, $\text{C}_{12}\text{H}_{14}\text{O}_6$ (2 : 4-dinitrophenylhydrazones, m.p. 200—201° and 176—177°). Picropodophyllin and podophyllotoxin (see preceding abstract), heated with $\text{MeOH}\cdot\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ give podophyllhydrazide, m.p. 155—160° (decomp.). H. B.

Synthesis of aldehydes in the furan series.
III. Dicyclic furan substances, difuryl and difurylmethane. T. REICHSTEIN, A. GRUSSNER, and H. ZSCHOKKE (Helv. Chim. Acta, 1932, 15, 1066—1074; cf. this vol., 166).—Furoylacetic acid and di- β -chloroethyl ether in Et_2O and aq. NaOH give 2 : 2'-difuryl-3-carboxylate (I), b.p. 86—98°/0.5 mm. (21% yield), and sometimes a neutral substance, b.p. 52°/0.5 mm.; the latter gives a Na salt and is possibly a lactone. The acid obtained by hydrolysing (I) with quinoline and Cu chromite at 160—200° gives difuryl (66.6% yield), b.p. 63—64°/11 mm., which with HCN and HCl in dry Et_2O at -15° gives 2 : 2'-difuryl-5-aldehyde, b.p. 91—94°/0.4 mm., m.p. 54° (semicarbazone, m.p. 221°), oxidised by Ag_2O to 2 : 2'-difuryl-5-carboxylic acid, m.p. 154°. A dialdehyde could not be obtained, activity of the second furan ring being decreased by the negatively substituted ring attached directly to it. 2-Bromofuran and activated Cu-Mg (modified prep.) in Et_2O give the Grignard reagent, which with furonitrile gives 2 : 2'-difuryl ketone, m.p. 34°, b.p. about 110°/0.5 mm. (decomposed by N_2H_4 in EtOH at 180° and unchanged at 150°), reduced by Na and EtOH to 2 : 2'-difurylmethane (II), m.p. about -30°, b.p. 78°/12 mm., also obtained in poor yield from Mg 2-furyl bromide and furfuryl chloride. (II) with HCN and HCl in Et_2O at -15° gives 2 : 2'-difurylmethane-5 : 5'-dialdehyde, m.p. 118—119°, b.p. about 165°/0.5 mm. [disemicarbazone, decomp. about 260°; dioxime, m.p. about 185—187° (decomp.)], decomposed by dil. alkali with colour changes. All m.p. are corrected.

R. S. C.

Stereoisomeride of 2 : 3 : 5 : 6-tetrachlorodioxan. W. BAKER (J.C.S., 1932, 2666—2667).—Chlorination of dioxan gives, besides "2 : 3-dichlorodioxan," a new 2 : 3 : 5 : 6-tetrachlorodioxan, m.p. 101°, nearly quantitatively hydrolysed to glyoxal.

R. S. C.

Synthesis of difuryl- and dithienyl-acryloylmethane. W. LAMPE, S. ROZENBLUMÓWNA, and A. KESSEL (Chem. Listy, 1932, 26, 454—458).— β -Furylacryloyl chloride (I) condenses with Et sodioacetate to yield Et β -furylacryloylacetate, m.p. 50—52°, which on heating eliminates CO to give β -furylacryloylacetone (II), m.p. 62—64°. The Na salt of (II) condenses with (I) to yield di- β -furylacryloylacetone, m.p. 98—100°, which on hydrolysis eliminates AeOH to yield di- β -furylacryloylmethane (III), m.p. 128—130°. The corresponding thienyl compounds, prepared analogously, are : β -thienylacryloyl chloride, m.p. 128—129°, Et β -thienylacryloylacetate, m.p. 65°, β -thienylacryloylacetone, m.p. 86—87°, di- β -thienylacryloylacetone, m.p. 107—108°, and di- β -thienylacryloylmethane (IV), m.p. 182—184°. (III) and (IV) are substantive yellow dyes for cotton. Solutions of (III) give max. absorption for λ 4128 Å., of (IV) for λ 4228 Å., as compared with 3780 Å. for the corresponding Ph derivative.

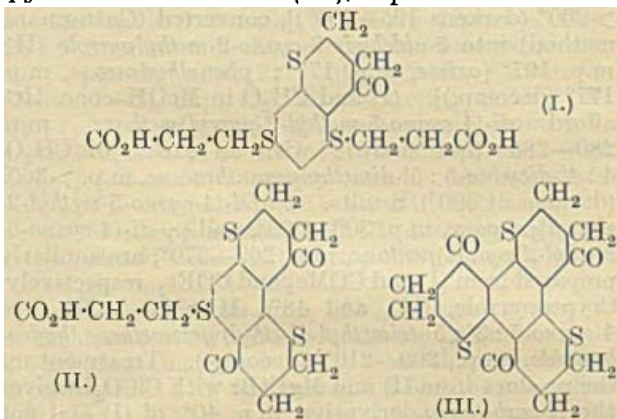
R. T.

New synthesis of diphenylene sulphide. H. W. SCHWECHTEN (Ber., 1932, 65, [B], 1608—1609).—The tetrazotised solution of 2 : 2'-diaminodiphenyl is treated with K hexathiocyanochromate. The pptd. complex salt is dried with MeOH and Et_2O . When heated with twice its wt. of KCl it yields a

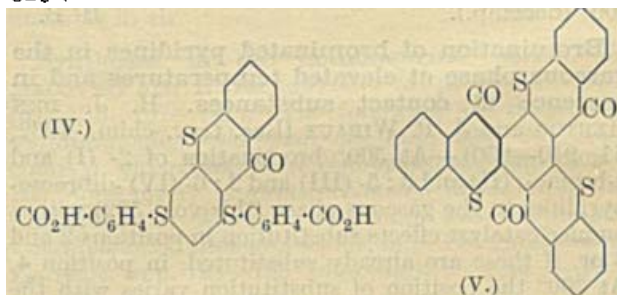
mixture of diphenylene sulphide and disulphide, from which the former is isolated by distillation over Cu-bronze or the latter by crystallisation from MeOH.

H. W.

Thiophenols. Thiochromanone and thioxanthone [derivatives]. V. BELLAVITA (Gazzetta, 1932, 62, 655—663).—The Na salt of $s\text{-C}_6\text{H}_4(\text{SH})_3$ (A., 1909, i, 791) reacts with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ to form benzene-1 : 3 : 5-tri- β -thiopropionic acid, m.p. 171—172°, which with warm conc. H_2SO_4 yields thiochromanone-5 : 7-di- β -thiopropionic acid (I), m.p. 216°, 5 : 6-thiopyranonothiochromanone-7- β -thiopropionic acid (II), m.p. 224—225°, and 5 : 6 : 7 : 8-bisthiopyranonothiochromanone (III), m.p. above 320°. The



same Na salt reacts with diazotised anthranilic acid to form benzene-1 : 3 : 5-tri- α -thiobenzoic acid, m.p. 300°, which with hot conc. H_2SO_4 yields thioxanthone-1 : 3-di- α -thiobenzoic acid (IV), m.p. above 320°, and 1 : 2 : 3 : 4-bis-(2' : 3')-thiochromononothioxanthone (V), m.p. above 320°.



E. W. W.

Electron-sharing ability of organic radicals.

VI. 2-Substituted pyrrolines and pyrrolidines. D. F. STARR, H. BULBROOK, and R. M. HIXON (J. Amer. Chem. Soc., 1932, 54, 3971—3976; cf. this vol., 167).—The general method (A., 1931, 849) of prep. of 2-substituted pyrrolines is improved. 2-p-Tolylpyrroline, b.p. 125—132°/6—8 mm., m.p. 60—61° (picrate, m.p. 185—186°), reduced to 2-p-tolylpyrrolidine, b.p. 128—130°/8—10 mm., 141—144°/23—25 mm. [picrate, m.p. 173° (lit. 150°)]; 2-cyclohexylpyrroline, b.p. 114—116°/22—24 mm. (picrate, m.p. 117°), reduced to 2-cyclohexylpyrrolidine, b.p. 84—87°/7—9 mm., 214—221° [chloroaurate, m.p. 105—106°; the m.p. (153°) of the picrate reported by De Jong and Wibaut (A., 1930, 479) could not be confirmed], and 2-benzylpyrrolidine, b.p. 129—

131°/17—19 mm., 150—153°/44—46 mm. (*picrate*, m.p. 136—137°), are described. Dissociation consts. are reported as follows: 2-ethyl-, 6.09 ($-\log K_p$); 2-benzyl-, 6.92; 2-*p*-tolyl-, 6.41; 2-phenyl-, 7.12—7.27, and 2-cyclohexyl-pyrroline, 6.05; 2-*p*-tolyl-, 4.00; 2-benzyl-, 3.64, and 2-cyclohexyl-pyrrolidine, 3.20. If the criteria for measuring chemical affinity are observed, the polar properties of any group may be expressed as a mathematical function of the electron-sharing ability of the attached radical. C. J. W. (b)

3-Cyano-2-methylpyrrole. W. H. STRAIN (Annalen, 1932, 499, 40—46).—Et $\alpha\beta$ -dichloroethyl ether and diacetonitrile in aq. NH_3 give 3-cyano-2-methylpyrrole (I), m.p. 133° [4:5- Br_2 -derivative, decomp. >200° (darkens 195—200°)], converted (Gattermann method) into 5-aldehydo-3-cyano-2-methylpyrrole (II), m.p. 197° [oxime, m.p. 177°; phenylhydrazone, m.p. 177° (decomp.)]. (I) and CH_3O in MeOH—conc. HCl afford di-(4-cyano-5-methyl-2-pyrrolyl)methane, m.p. 280—285° (not sharp); with an excess of CH_3O , 4:4'-dicyano-5:5'-dimethylpyranthracene, m.p. >360° (darkens at 300°), results. $\beta\beta$ -Di-(4-cyano-5-methyl-2-pyrrolyl)propane, m.p. 300—305°, and $\gamma\gamma$ -di-(4-cyano-5-methyl-2-pyrrolyl)pentane, m.p. 269—270°, are similarly prepared from (I) and COMe_2 and COEt_2 , respectively. Cryptopyrrole, (II), and 48% HBr in AcOH give 4-cyano-5:3':5'-trimethyl-4'-ethylpyrromethene hydrobromide, m.p. 209—210° (decomp.). Treatment of the product from (I) and MgEtBr with ClCO_2Et gives the *N*-carbethoxy-derivative, m.p. 40°, of (I) and not Et 3-cyano-2-methylpyrrole-5-carboxylate, m.p. 127°, which is obtained by dehydration of the oxime, m.p. 178° (not sharp), of Et 3-aldehydo-2-methylpyrrole-5-carboxylate with Ac_2O — KOAc . Hydrolysis of the product from (I) and SO_2Cl_2 in Et_2O with H_2O gives some 4:5-dichloro-2-aldehydo-3-cyanopyrrole, m.p. 200° (decomp.). H. B.

Bromination of brominated pyridines in the gaseous phase at elevated temperatures and in presence of contact substances. H. J. DEN HERTOG and J. P. WIRAUT (Rec. trav. chim., 1932, 51, 940—950).—At 500° bromination of 2- (I) and 3-bromo-, (II) and 3:5- (III) and 2:6- (IV) dibromopyridines in the gaseous phase (this vol., 522) with a pumice catalyst effects substitution in positions 2 and 6 or, if these are already substituted, in position 4. At 300° the position of substitution varies with the catalyst (given in parentheses), being 3- and 5- with FeBr_2 and 2- and 6- with Cu_2Br_2 . Thus at 500°, (II) gives 2:5-di- (25%) and 2:3:6-tri-, m.p. 82° (25%; also from 2:6- Br_2 -compound) (36% unchanged); (III) affords 2:3:5-tri- and 2:3:5:6-tetra-, m.p. 102—103° (also from 2:6-compound) (50% unchanged); whilst (IV) gives 2:4:6-tri-, m.p. 107° (28%) (60% unchanged), -bromopyridine. At 300° (I) gives 2:5-di- and 2:3:5-tri- (FeBr_2) or 2:6-di- (27%) and penta-, m.p. 209.5—210° (Cu_2Br_2 ; 66% unchanged); (IV) gives 2:3:6-tri- (30%) and 2:3:5:6-tetra- (5%) (FeBr_2 ; 42% unchanged); whilst (III) gives 2:3:5-tri- (22%) (Cu_2Br_2 ; 53% unchanged) -bromopyridine. No differential contact action is observed when $\text{C}_5\text{H}_5\text{N}$ itself is brominated at 300° [(II) and (III) formed], probably owing to the much greater formation of carbonaceous matter

which coats the catalyst and destroys its sp. action. Interaction of $\text{C}_5\text{H}_5\text{N}$ and Br at 250° without a contact substance gives, in addition to (III), 3:5-dibromo-4-aminopyridine, m.p. 168—169°, identical with the compound obtained by Fischer and Riemerschmied (A., 1883, 923) from pyridine-3-sulphonic acid and erroneously described as a dibromopyridine. With Cu_2Br_2 at 350° is obtained, also, a dibromopyridine, m.p. 88—88.5° (not 2:5-derivative), whilst from the product previously obtained by bromination of $\text{C}_5\text{H}_5\text{N}$ (*loc. cit.*) is isolated 3:4:5-tribromopyridine, m.p. 100—102°. The various bromination products and their physical properties are summarised.

J. W. B.

2-Methylhexamethyleneimine. A. MÜLLER and P. KRAUSS (Monatsh., 1932, 61, 212—218).—The 2-methylhexamethyleneimine (Bz derivative, b.p. 185—187°/13 mm.) of Gabriel (A., 1909, i, 493) is proved by direct comparison to be different from 2-ethylpiperidine, and identical with the product of reduction of α -amino-*n*-heptolactam (this vol., 1239) with Na and EtOH . Its PhSO_2 derivative is oxidised by aq. KMnO_4 to α -benzenesulphonamido-*n*-heptonic acid (*loc. cit.*). The ready formation of the 7-membered ring seems to be favoured by the α -Me group. The reduction product of phenyl α -amino-*n*-amyl ketone (Gabriel) differs markedly from α -benzylpiperidine, thus confirming the cyclic structure (2-phenylhexamethyleneimine) originally assigned.

H. A. P.

Electrolytic preparation of isoindolines. E. W. COOK and W. G. FRANCE (J. Physical Chem., 1932, 36, 2383—2389).—*iso*Indolines are prepared by electrolytic reduction of methylphthalimidine, phthalimidine, methylphthalimide, and phthalimide. *N*-Amino-*iso*indoline is prepared similarly from *N*-nitroso-*iso*indoline. Variations in the yields obtained with different electrodes are attributed to the H_2 overvoltages and probable differences in selective activation of the depolariser by the metals.

R. H. C. (b)

Indolenines. V. Addition of acyl halides to indolenines. H. LEUCHS, G. WULKOW, and H. GERLAND (Ber., 1932, 65, [B], 1586—1593; cf. A., 1929, 704).—The additive nature of the reaction between indolenines and acyl chlorides is established by experiments in the absence of H_2O and alkali. 3:3-Dimethylindolenine, ($\text{C}_{10}\text{H}_{11}\text{N}$)₂ (I), and BzCl quantitatively yield the non-isolated 2-chloro-1-benzoyl-3:3-dimethylindoline, transformed by H_2O into 2-hydroxy-, m.p. 202—204° (yield 93%), by NaOMe into 2-methoxy-, m.p. 71—72° (74%), by NH_3 — MeOH into 2-amino-, m.p. 116°, and by AgOBz into 2-benzoyloxy-, m.p. 147—148°, -1-benzoyl-3:3-dimethylindoline; with AgOAc it gives the 2-*OAc*-derivative, m.p. 156—157°. (I) and AcCl yield a resinous product identified by transformation into 2-hydroxy-, m.p. 118°, and 2-amino-, m.p. 78—80°, -1-acetyl-3:3-dimethylindoline. With $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ (I) yields 2-chloro-1-*p*-nitrobenzoyl-3:3-dimethylindoline, m.p. 147—148° (or $+\text{C}_6\text{H}_6$, m.p. about 143° after softening at 105°), converted by boiling H_2O into the corresponding 2-*OH*-compound, m.p. 167—169° (or $+\text{C}_6\text{H}_6$, m.p. 165—167° after softening), and by ClCO_2Et into the resinous 2-chloro-1-carbethoxy-3:3-

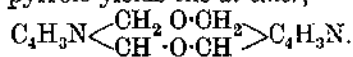
dimethylindoline, whence 2-hydroxy-1-carbethoxy-3:3-dimethylindoline, m.p. 84°. 2-Bromo-1-m-bromobenzoyl-3:3-dimethylindoline, m.p. 114–115° (vac.), is obtained from m-bromobenzoyl bromide, b.p. 156°/38 mm. β -Phenyl- α -benzylpropionamide, m.p. 129°, is transformed by MgPhBr in Et₂O into Ph β -phenyl- α -benzylethyl ketone, m.p. 78°; the *phenylhydrazone*, m.p. 92–94°, is transformed by ZnCl₂ in EtOH at 105° into 2-phenyl-3:3-dibenzylindolenine, m.p. 123–125°, in poor yield. 2-Methyl-1-hydrindonephenylhydrazone is converted by boiling 12N-HCl into the non-cryst. 3:2:0-benzylene-3-methylindolenine (II) (non-cryst. *hydrochloride*; *picrate*, m.p. 146°), transformed by Ac₂O and NaOAc at 100° into 2-acetoxy-1-acetyl-3:2:0-benzylene-3-methylindoline, m.p. 122°, from which the corresponding 2-OH-, m.p. 199°, and 2-NH₂-, m.p. 137°, compounds are derived. 2-Chloro-1-benzoyl- (corresponding 2-OH-derivative, m.p. 177°) and 2-chloro-1-p-nitrobenzoyl- (corresponding 2-OH-compound, m.p. 197°) 3:2:0-benzylene-3-methylindoline are described. The product derived from BzCl and 3:2:0-benzylene-3-ethylindolenine (III) is converted into the corresponding 2-hydroxy-1-benzoyl-, m.p. 145–146°, and 2-benzoyloxy-1-benzoyl-, m.p. 179°, 3:2:0-benzylene-3-ethylindolines. 2-Hydroxy-1-p-nitrobenzoyl-, m.p. 156–157°, and -1-benzenesulphonyl-3:2:0-benzylene-3-ethylindoline, m.p. about 120°, or +C₆H₅, m.p. 83–87° (decomp.) after softening at 77°, are derived from the non-cryst. additive compounds of (III) and p-NO₂-C₆H₄-COCl and PhSO₂Cl, respectively. (III) and AcCl give a non-cryst. substance identified by conversion into 2-hydroxy-, m.p. 160°, 2-acetoxy-, m.p. 125°, 2-amino-, m.p. 138°, -1-acetyl-3:2:0-benzylene-3-ethylindoline.

2-Phenyl-1-hydrindone is best obtained by rapid dissolution of $\alpha\beta$ -diphenylpropionic acid in H₂SO₄ and treatment of the mixture with ice. The acid monohydrate is transformed by PCl₅ (1.2 mols.) or SOCl₂ into the anhydride and a compound, C₂₀H₂₂O₂, m.p. 238°, converted by MeOH-NH₃ at 100° into $\alpha\beta$ -diphenylpropionamide and regarded as a derivative of 1:3-cyclobutanedione.

2-Chloro-1-benzoyl-3:2:0-benzylene-3-phenylindoline, m.p. 169–170° (corresponding 2-OH-compound, m.p. 192–193°), is derived from 3:2:0-benzylene-3-phenylindolenine (IV) and BzCl. Similarly from (IV) are derived 2-chloro-, m.p. 185–186°, and 2-hydroxy-, m.p. 198–200°, -1-p-nitrobenzoyl-3:2:0-benzylene-3-phenylindoline. 3-Phenylindolenine appears to react with difficulty or not at all with PhSO₂Cl; the non-cryst. additive product with AcCl is hydrolysed to 2-hydroxy-1-acetyl-3:2:0-benzylene-3-phenylindoline, m.p. 184°.

H. W.

Syntheses of pyrrolic and indolic alcohols. Q. MINOIA (Gazzetta, 1932, 62, 844–854).—Trioxymethylene, or better gaseous CH₂O, in Et₂O converts Mg indole into 3-indolylcarbinol, m.p. 158° (Ac derivative, m.p. 95°), together with bis-3-indolylmethyl ether; Mg 2-methylindole yields 2-methyl-3-indolylcarbinol, m.p. 205–206° (Ac derivative, m.p. 140–142°), and bis-(2-methyl-3-indolylmethyl) ether. Mg pyrrole yields the *di-ether*,



4 R.

E. W. W.

Action of nitrous acid on amines of the indole series. N. I. PUTCHIN and N. P. DAVYDOVA (J. Gen. Chem. Russ., 1932, 2, 290–296; cf. A., 1931, 629).—3-Indolylmethylamine sulphate (I) when treated with Ba(NO₂)₂ gives quinoline, whilst 2-methyl-3-indolylmethylamine (II), which cannot form the intermediate cyclic complex, affords di-(2-methylindolyl)-ethane. Indolealdoxime and Ac₂O give the *acetate*, m.p. 154°, reduced (H₂ and PtO₂) to the amine, isolated as (I); (II) is similarly prepared from 2-methylindolealdoxime (*acetate*, m.p. 149–150°).

G. A. R. K.

Aminotetrahydroquinolines. I. E. BALABAN (J.C.S., 1932, 2624–2626).—Reduction of the corresponding NO₂-compounds gives the following *quinoline* derivatives: 5-amino-6-methoxy- (*picrate*, m.p. 225°); 8-amino-6-methoxy- (I) [*hydrochloride*, m.p. 228°; *picrate*, m.p. 221° (decomp.)]; 6-amino-8-methoxy- (II), m.p. 169° after sintering at 165° (lit. 168°) (*picrate*, m.p. 224° after softening); 8-amino-7-methoxy- (III), m.p. 108° [*picrate*, m.p. 226° (decomp.)]; 5-amino-8-methoxy-, m.p. 156° (*picrate*, m.p. 126°). Reduction with Sn-HCl-EtOH affords 5-amino-6- and -8-methoxy-1:2:3:4-tetrahydroquinoline [*dihydrochlorides*, +H₂O, m.p. 247° (decomp.) and +0.5H₂O, m.p. 258–260° (decomp.)], respectively; *dipicrate* of the former, m.p. 147°. Similar reduction of 2-chloro-6-nitro-4-methylquinoline gives a little di-6-amino-4-methyl-1:2:3:4-tetrahydroquinoline [*dipicrate*, m.p. 173° (decomp.)]. 8-Methoxyquinoline and fuming HNO₃ at 0° give the 5-NO₂-compound [*nitrate*, +H₂O, m.p. 177° (effervescence)], whilst 7-methoxyquinoline gives the 8-NO₂-compound, m.p. 178° [*nitrate*, m.p. 155–156° (effervescence)], and a little ?-NO₂-compound, m.p. 200°. Reduction of (I), (II), and (III) gives coloured solutions, but no tetrahydro-base. The free tetrahydroquinolines are unstable in air.

R. S. C.

Syntheses in the homoneurine series. E. MACOVSKI and E. RAMONTIANU (J. pr. Chem., 1932, [ii], 135, 137–141).—The following are described: *pyridiniumallyl chloroplatinate*, m.p. 200–201° (decomp.); *quinoliniumallyl chloroplatinate*, m.p. 208–209° (decomp.); *isoquinoliniumallyl iodide*, m.p. 78° (impure), and *chloroplatinate*, m.p. 175° (decomp.); 2-methylquinoliniumallyl iodide, m.p. 196°, and *chloroplatinate*, m.p. 194–195° (decomp.).

H. A. P.

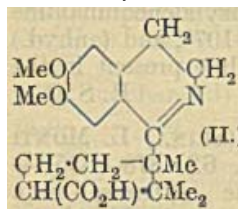
Reaction of quinoline and benzaldehyde. W. M. CUMMING and J. G. GILLAN (J.C.S., 1932, 2666).—The base, m.p. 99–100°, obtained by Cumming *et al.* (this vol., 155) is benzylidenequinaldine [*hydrochloride*, m.p. (+H₂O) 106–107°, and (anhyd.) 221–221.5°], formed from quinaldine present in the quinoline.

R. S. C.

Quinoline derivatives. II. (SIGNA) L. MONTI and G. VERONA (Gazzetta, 1932, 62, 878–885).—8-Hydroxy-5(?)-quinolylmethylamine [*picrate*, m.p. 195° (decomp.)] is obtained as the *hydrochloride* by the action of HCl on its Bz derivative (A., 1905, i, 247), which with NaOH gives a green *polymeride*, also obtainable from 8:8'-dihydroxy-5:5'-diquinolylmethane (A., 1913, i, 990). The *hydrochloride* and *picrate*, m.p. 185–187° (decomp.), of 6-hydroxy-?

quinolylmethylamine are similarly prepared from its Bz derivative, m.p. 231—232° (from $C_6H_5N \cdot OH$ and $OH \cdot CH_2 \cdot NHBz$), which with KOH gives 6':6-di-hydroxy-1:1-diquinolylmethane, m.p. >300° (hydrochloride; Ac_2 derivative, m.p. 203—204°). The latter is not obtained by the action of CH_3O on 6-hydroxyquinoline in H_2SO_4 , which gives 6: ω -methylenedioxy-1-methylquinoline, $C_9H_5N \cdot \begin{smallmatrix} O-CH_2 \\ | \\ CH_2-O \end{smallmatrix}$, m.p. 119° (picrate, m.p. 216°). 2-Hydroxy-6-methoxy-4-methylquinoline (this vol., 402) with $OH \cdot CH_2 \cdot NHBz$ yields 2-hydroxy-6-methoxy-4-methyl-1-quinolylmethylbenzamide, m.p. 280—282°. E. W. W.

Synthesis of isoquinoline derivatives. II. K. S. NARANG, J. N. RAY, and S. S. SILOOJA (J.C.S., 1932, 2510—2513; cf. A., 1931, 1168).—1-Methylnorhydrastinine (I), $o\text{-NO}_2 \cdot C_6H_4 \cdot CHO$, and NaOEt in EtOH give 1- o -nitrostyrylnorhydrastinine, m.p. 132°, but other aldehydes do not condense. (I) and MeI give 1-methylhydrastinium iodide, m.p. 257°, which with Al-Hg, hot H_2O , and a little HCl affords 1-methyldihydrohydrastinine (hydrochloride, m.p. 221°; picrate, m.p. 192—193°). β -3:4-Dimethoxyphenylpropiono- β -piperonyl ethylamine, m.p. 146°, and $POCl_3$ in PhMe at 110° afford 1- β -3':4'-dimethoxyphenylethylnorhydrastinine, m.p. 90°, the methiodide, m.p. 196°, of which is reduced by Al-Hg to 1- β -3':4'-dimethoxyphenylethyl dihydrohydrastinine, m.p. 101°. β -Piperonylpropiono- β -3':4'-dimethoxyphenylethylamide, m.p. 149°, with PCl_5 in $CHCl_3$ gives 6:7-dimethoxy-1- β -piperonylethyl-3:4-dihydroisoquinoline, m.p. 75.5° (hydrochloride, m.p. 187—188°), the methiodide, m.p. 175°, of which is reduced to the tetrahydroisoquinoline derivative, m.p. 101° (picrate, m.p. 137°). The following were prepared by similar methods: β -piperonylpropiono- β -piperonylethylamide, m.p. 135°; 1- β -piperonylethylnorhydrastinine (best by $POCl_3$), m.p. 105° (methiodide, m.p. 229°); 1- β -piperonylethyl dihydrohydrastinine, an oil (picrate, m.p. 102°); 6:7:3':4'-tetramethoxy-1- β -phenylethyl-3:4-dihydroisoquinoline, m.p. 94° (picrate, m.p. 129°; methiodide); 6:7:3':4'-tetramethoxy-1- β -phenylethyl-2-methyl-1:2:3:4-tetrahydroisoquinoline, an oil (picrate, m.p. 166°). β -Piperonylethylamine, phthalic anhydride, and a little NaOAc at 150—160° give phthal- β -piperonylethylimide, m.p. 140°, and β -piperonylethylphthalamic acid, m.p. 143°; the acid with PCl_5 in hot $CHCl_3$ yields 6:7-methylenedioxy-1-phenyl-3:4-dihydroisoquinoline-2'-carboxylic acid, m.p. 175°. β -3:4-Dimethoxyphenylethylcamphoramic acid and $POCl_3$ in PhMe at 110° give 6:7-dimethoxy-1-(3'-carboxy-1':2':2'-trimethylcyclopentyl)-3:4-dihydroisoquinoline (II), m.p. 65° (evolution of CO_2 at 85°). The methiodide, m.p. 259°, of veratrylidene- β -piperonylethylamine, m.p. 78°, with Ag_2O in aq. EtOH gives an oily base (picrate, m.p. 179°), not identical with 1-3':4'-dimethoxyphenyl dihydrohydrastinine. R. S. C.



Formation of heterocyclic nuclei containing iodine, nitrogen, and oxygen. L. MASCARELLI (Mem. Accad. Italia, 1932, 3, Chim., No. 2, 5—15).—

A review of the reactions by which diphenyleneiodonium, carbazole, and diphenylene oxide derivatives are formed from 2:2'-disubstituted Ph_2 derivatives with elimination of one of the substituents.

R. K. C.

Naphthenic acids from petroleum. F. VON PILAT and J. REYMAN [with H. MORAWSKI, F. ROSENKRANZ, and C. ZEMBAL] (Annalen, 1932, 499, 76—83; cf. von Braun, A., 1931, 1396).—The naphthenic acids from Potok petroleum are esterified (EtOH-HCl), fractionated, and the fractions (a) b.p. 95—170°/3 mm. and (b) 170—220°/3 mm. reduced (Na-EtOH) to the corresponding alcohols (a) b.p. 100—168°/2 mm. (composition $C_{11}H_{22}O$) and (b) 168—200°/3 mm. ($C_{17}H_{34}O$). Condensation of the corresponding bromides with $CHNa(CO_2Et)_2$ and treatment of the resulting esters with $CO(NH_2)_2$ and EtOH-NaOEt gives (a) barbituric acids, $C_{15}H_{24}O_3N_2$, m.p. 208—211°, and $C_{16}H_{26}O_3N_2$, m.p. 218—220°, and (b) a barbituric acid, $C_{22}H_{38}O_3N_2$, m.p. 173—177°. The naphthenic acids from the illuminating oil fraction of the above petroleum similarly afford a barbituric acid, $C_{15}H_{24}O_3N_2$, m.p. 187—188°; an isomeride, m.p. 194—195°, and an analogue, $C_{18}H_{30}O_3N_2$, m.p. 201—202°, are similarly obtained from the same fraction of a Czechoslovakian oil. When Et naphthenates are reduced with Na and 96% EtOH in "benzine," a preponderance of glycols results. H. B.

Variation with p_H of ultra-violet spectra of some six-membered heterocyclic compounds. G. FLORENCE, J. ENSELME, and M. POZZI (Compt. rend., 1932, 195, 614—615).—The increase in the absorption of diethyl-, ethylbutyl-, and diallyl-malonylcarbamide in passing from p_H 2 to p_H 6 and 9 is ascribed to enolisation. Uric acid probably has an enolic structure, and its strong absorption increases only slightly with p_H . The increased absorption of phenylethylmalonylcarbamide is related to electropositive nuclei. The decrease of absorption of diketopiperazine with increasing p_H is probably due to hydrolysis. A. C.

Thermal decomposition of azines. L. B. HOWARD and G. E. HILBERT. Thermal decomposition of benzaldazine under 1000 atmospheres pressure of nitrogen, hydrogen, and ammonia [with R. WIEBE and V. L. GADDY] (J. Amer. Chem. Soc., 1932, 54, 3628—3641).—The products of the pyrolysis of benzaldazine (I), anisaldazine, o -chlorobenzaldazine, p -tolualdazine (II), hydroanisamide, tri- o -chlorohydrobenzamide (III), and benzoinhydrazone (IV) are given. Lophine [2:4:5-triphenylglyoxaline] (V) or its corresponding derivative is obtained from (I), (II), (III), and (IV). (V) is probably derived from (I) by way of benzaldimine, the intermediate existence of which is supported by the fact that pyrolysis of the mixed azine of PhCHO and fluorenone gives 9-imino fluorene. $CH_3Ph \cdot NH_2$ or $(CH_2Ph)_2NH$ when heated at 300° yields (V) and tetraphenylpyrrole (VI), but in presence of stilbene only (VI) is obtained. The azines of $COPh_3$ and $COPhMe$ and the mixed azine of $COPh_2$ and fluorenone are more stable to heat than the above aldazines and tend to eliminate PhCN rather than N. The pyrolysis

of (I) is little affected by 1000 atm. of H_2 or N_2 ; with NH_3 the reaction is complex. H. A. B. (b)

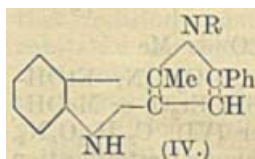
Condensation products of pyrroles with acetaldehyde, acetone, and phorone. H. FISCHER, A. SCHORMULLER, and R. E. WINDECKER (Annalen, 1932, 498, 284—296).— $\alpha\alpha$ -Di-(4-carbethoxy-3:5-dimethyl-2-pyrrolyl)ethane and Br (1 or 2 mols.) in the cold give 4:4'-dicarbethoxy-3:5:3':5'-tetramethylpyrromethene hydrobromide; with 3 mols. of Br, 5-bromo-3:4'-dicarbethoxy-4:3':5'-trimethylpyrromethene results (probably by fission of the intermediate methine linking and formation of Et 5-bromo-2:4-dimethylpyrrole-3-carboxylate). MeCHO reacts with 3-propionyl-2:4-dimethyl- and 3-acetyl-2-methyl-4-ethyl-pyrroles in EtOH—conc. HCl to give $\alpha\alpha$ -di-(4-propionyl-3:5-dimethyl-2-pyrrolyl)ethane, m.p. 180°, and $\alpha\alpha$ -di-(4-acetyl-5-methyl-3-ethyl-2-pyrrolyl)ethane, m.p. 248°, respectively. Cryptopyrrole and hæmopyrrolecarboxylic acid with hot Ac_2O and AcOH afford acetylcryptopyrrole, m.p. 112°, and acetyl hæmopyrrolecarboxylic acid, m.p. 171°, respectively; all attempts to condense these with 2-unsubstituted pyrroles failed. Cryptopyrrole, $COMe_2$, and cone. HCl give 88-di-(3:5-dimethyl-4-ethyl-2-pyrrolyl)- $\beta\zeta$ -dimethyl- Δ^8 -heptadiene, m.p. 148°, also obtained using mesityl oxide or, better, phorone in place of $COMe_2$; opsopyrrole similarly gives an O-containing product, m.p. 110°. Cryptopyrrolecarboxylic acid similarly affords 88-di-(3:5-dimethyl-4- β -carboxyethyl-2-pyrrolyl)- $\beta\zeta$ -dimethyl- Δ^8 -heptadiene, m.p. 177°; the 4:5-dimethyl-3- β -carboxyethyl isomeride (Me_2 ester, m.p. 110°) has m.p. 280°. Hæmopyrrolecarboxylic acid, paracetaldehyde, and HBr—AcOH give a compound, $C_{22}H_{48}O_5N_3$, m.p. 283° (decomp.) (darkens at 280°), whilst Et 2:4-dimethylpyrrole-3-carboxylate, EtCHO, and EtOH—conc. HCl afford $\alpha\alpha$ -di-(4-carbethoxy-3:5-dimethyl-2-pyrrolyl)propane, m.p. 139°.

Fusion of 5:5'-dibromo-4:4'-dimethyl-3:3'-di- β -carboxyethylpyrromethene hydrobromide (I) and 5-bromo-3:4'-dicarbethoxy-4:3':5'-trimethylpyrromethene give coproporphyrin (spectrum) and traces of (probably) deuteroporphyrin and dicarbethoxydi- β -carboxyethylporphyrin. 4:4'-Dicarbethoxy-3:5:3':5'-tetramethylpyrromethene hydrobromide and (I) fused with succinic-methylsuccinic acids afford 5:8-dicarbethoxy-1:4:6:7-tetramethyl-2:3-di- β -carboxyethylporphyrin (corresponding Me_4 ester, m.p. 282°). 5-Carbethoxy-3:3'-dimethyl-4-ethyl-4':5'-di- β -carboxyethylpyrromethene hydrobromide, m.p. 145° (from 3-methyl-4:5-di- β -carboxyethylpyrrole-2-carboxylic acid, 2-formyl-3-methyl-4-ethylpyrrole-5-carboxylic acid, and 40% HBr in AcOH), and Br in AcOH give 5-bromo-3:3'-dimethyl-4-ethyl-4':5'-di- β -carboxyethylpyrromethene hydrobromide (II), m.p. 203° (decomp.), which when fused with 5-bromo-4-carbethoxy-3:4':5'-trimethyl-3'-ethylpyrromethene hydrobromide (III) affords a little mesoporphyrin [formed by self-condensation of (II)] and a dicarbethoxyporphyrin [from (III)].

Di-(5-carboxy-4-methyl-3-ethyl-2-pyrrolyl)methane, $COMe_2$, and 40% HBr give a compound, m.p. 120—122° (darkens at 105°), brominated to a substance, darkens from 170° and decomp. slowly, which with EtOH— NH_3 affords a base, $C_{28}H_{34}N_3Br_4$, m.p. 115°,

converted by 10% MeOH—KOH into a compound, $C_{13}H_{24}O_6N_2$, m.p. 106°. H. B.

Chemotherapy. Attempts to find antimalarials. II. Pyrrolindoles. J. S. AGGARWAL, A. U. QURESHI, and J. N. RAY (J. Amer. Chem. Soc., 1932, 54, 3988—3992; cf. A., 1931, 743).— α -Benzoyl- $\beta\beta$ -diacetylene (I), prepared by a modification of March's method (A., 1901, i, 596), is accompanied by a little $\alpha\gamma$ -dibenzoyl- $\beta\beta$ -diacetylpropane (II), m.p. 125°. The following *N*-aryl derivatives of 3-acetyl-5-phenyl-2-methylpyrrole are obtained from (I) and the requisite NH_2Ar : Ph, m.p. 101° (phenylhydrazone, m.p. 162°; piperonylidene, m.p. 164°, and salicylidene, m.p. 192° [hydrochloride, m.p. 135° (decomp.)], derivatives); o-, m.p. 95°, m-, m.p. 142°, and p-tolyl (III), m.p. 150° [corresponding phenylhydrazones, m.p. 126° (decomp.), 156°, and 167—168°, respectively]; o-, m.p. 152°, and p-anisyl, m.p. 124° (phenylhydrazones, m.p. 174° and 185°, respectively); o-ethoxyphenyl, m.p. 100°; α -, m.p. 128°, and β -naphthyl, m.p. 140° [phenylhydrazone, m.p. 152° (decomp.)]; o-, m.p. 170° (phenylhydrazone, m.p. 182°), m-, m.p. 136° (phenylhydrazone, m.p. 158°), and p-nitrophenyl, m.p. 115°. Of the above phenylhydrazones, only those from the Ph, m- and p-tolyl, and p-anisyl derivatives are



converted (by heating with $ZnCl_2$) into pyrrolindoles (IV), m.p. 221°, 220—221°, 224°, and 228°, respectively. (III) and piperonal in EtOH—KOH give a compound, $C_{28}H_{23}O_5N$, m.p. 132°.

$\alpha\beta$ -Dibenzoyl- α -acetylene (V) and CH_2BzBr give (II), which with NH_2Ph affords 4:4'-diacetyl-1:2:6-triphenyl-1:4-dihydropyridine, m.p. 130°, oxidised by NaOBr to $CHBr_3$. (V) and NH_2Ph give a pyrrole, m.p. 134° (phenylhydrazone, m.p. 174°), analogous to the above; o-, m-, and p- $C_6H_4MeNH_2$ similarly afford pyrroles, m.p. 150°, 156°, and 142°, respectively. Some of the above compounds have antipyretic properties and are toxic to paramecium.

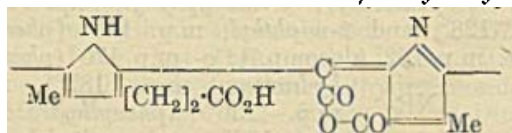
C. J. W. (b)

The cyanines. E. PRINCEVALLE (L'Ind. Chimica, 1932, 7, 1350—1357).—A review.

2- α - and 2- β -Pyridylbenziminazole. A. LEKO and G. VLAJINATZ (Bull. Soc. Chim. Yougoslav, 1932, 3, 85—89).—The Ag salts of 2- α - (A) and 2- β -pyridylbenziminazole (B), and the double salts A, $CuCl_2$ and B, $CuCl_2 \cdot 2H_2O$ are described. R. T.

Chlorophyll. XXIV. Phæopurpurin 18 and its identification with phylloporpurin; chlorin *p*- and preparation of chlorin *e* trimethyl ester. H. FISCHER, W. GOTTSCHALDT, and G. KLEBS. XXV. Chlorophyll *b*. I. II. FISCHER, F. BROICH, S. BREITNER, and L. NUSSLER. XXVI. Complex iron salts of chlorophyll-porphyrins and -purpurins. H. FISCHER and H. K. WEICHMANN. XXVII. Phæophorbide *a*, chlorin *e*, and chlorophyll *a*. H. FISCHER and H. SIEBEL (Annalen, 1932, 498, 194—227, 228—267, 268—283; 499, 84—108).—XXIV. Phæopurpurin 18 (I), prepared essentially by Conant and Moyer's method (A., 1930, 1299), is $C_{33}H_{34}O_5N_4$ (cf. loc. cit.), m.p. 270—280° (decomp.), and is esterified (CH_2N_2 in $Et_2O-C_5H_5N$)

to a Me ester (II), $C_{34}H_{36}O_5N_4$, m.p. 260° (previous sintering). When the Et_2O solution obtained during the prep. of (I) is treated with CH_2N_2 , a Me₃ ester, $C_{36}H_{42}O_6N_4$, m.p. $264-267^\circ$ (not sharp) (not depressed by phylloporphyrin Me ester), is obtained: the isolation of (I) (as crystals) involves anhydride formation. The conversion of phaeophorbide *a* into (I) by $PrOH-KOH$ in $Et_2O-C_5H_5N$ is accompanied by loss of 1 C atom as HCO_2H . (I) is degraded by hot HCO_2H to pyrroporphyrin, by $HI-AcOH$ at 55° or $HBr-AcOH$ at 150° to rhodoporphyrin (III), by $HBr-AcOH$ at 50° to rhodoporphyrin- γ -carboxylic acid anhydride (IV), and by hot $AcOH$ to (IV). (II) and $HBr-AcOH$ at 50° give (III) (mainly) and (IV). (IV) is also formed when (I) or (II) is heated to $265-275^\circ$. (I) heated with $Na_2CO_3-C_5H_5N$ gives rhodoporphyrin- γ -carboxylic acid (V), indicating that (I) contains the partial structure (A); (V) is formed by way of (IV) (which also contains structure A). Hydrolysis of (I)



with 25% $MeOH-KOH$ in $Et_2O-C_5H_5N$, $EtOH-Ba(OH)_2$, conc. HCl saturated with Et_2O , or $MeOH-HCl$ gives chlorin *p₆* [Me₃ ester (VI), $C_{36}H_{42}O_6N_4$, m.p. 236° , also obtained on attempted esterification ($MeOH-HCl$, Me_2SO_4 -alkali) of (II) and by the action of excess of CH_2N_2 on (I) in $MeOH-C_5H_5N$], which is degraded by HI to (III), by $Na_2CO_3-C_5H_5N$ to a small amount of a porphyrin (Me ester, m.p. 256°) similar to (V), and by hot HCO_2H to pyrroporphyrin, (III), a chlorin, and (I). (VI) is converted by HI into (V), by $HBr-AcOH$ into (III) and (IV), and by conc. H_2SO_4 into a little (II). Treatment of (I) with piperidine in C_5H_5N gives an unstable chlorin, whilst phaeoporphyrin *a₅* similarly affords an additive compound, $C_{36}H_{38}O_5N_4 \cdot C_5H_{11}N$ (Me ester, m.p. 263° , formed by esterification with CH_2N_2).

Phaeophorbide *a* warmed with 1% $NaOH$ in a current of air gives the unstable ψ -chlorin *p₆* [when the residue from its Et_2O solution is heated at 100° for some time (I) results] [Me₃ ester, $C_{36}H_{42}O_6N_4$, m.p. 225° , degraded ($HI-AcOH$) to an ester, $C_{36}H_{40}O_6N_4$, m.p. 240° , similar to but not identical with the Me ester of (V)] and a mixture of phaeophorbide *a* and decarboxylated phaeophorbide *a*, which is degraded ($HI-AcOH$) to (III), phylloerythrin, and phaeoporphyrin *a₅*; similar results are obtained using Na_2CO_3 , $NaHCO_3$, or aq. NH_3 in place of $NaOH$. Phaeophorbide *a* warmed with 1% $NaOH$ in N_2 gives a substance [degraded ($HI-AcOH$) to phylloerythrin] spectroscopically identical with it; other products formed are chlorin *e*. (degraded to chloroporphyrin *e₅*) and a small amount of a purpurin (converted by $Na_2CO_3-C_5H_5N$ into a chlorin which is degraded by $HI-AcOH$ to phylloerythrin). Phaeophorbide *a* (or methylphaeophorbide *a*) treated with $Et_2O-CH_2N_2$ in $MeOH-C_5H_5N$ gives a good yield of chlorin *e* Me₃ ester.

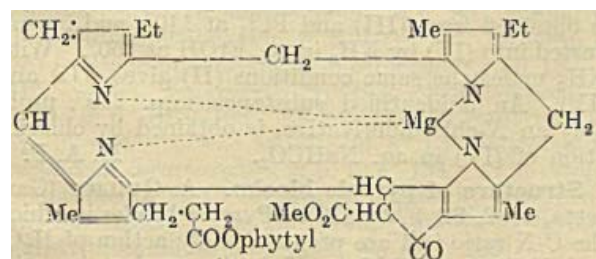
[With E. Plotz.] The purpurin obtained from methylechlorophyllide and $PrOH-KOH$ is identical with (I) [spectrum; conversion (as above) into (IV) and (V)].

XXV. An improved method of separating phaeophorbide *a* and *b* (I) from the hydrolysis products of phaeophytin is described. Hydrolysis of (I) with aq. $Ba(OH)_2$ gives rhodin *g* (II), which contains 3 CO_2H groups, gives Me₃ esters, $C_{37}H_{40}O_7N_4$, m.p. 265° ($MeOH-HCl$) and 253° (Me_2SO_4) [neither of which depresses the m.p. (251°) of the Me₃ ester (CH_2N_2) prepared by Treibs and Wiedemann (A., 1929, 941)], affords a condensation product, $C_{74}H_{78}O_{12}N_{10}$, with $o-C_6H_4(NH_2)_2$, is converted by fusion with succinic acid into phyllo- and pyrro-porphyrins, and is degraded by $HBr-AcOH$ at 180° to rhodo- and phylloporphyrins and deoxophylloerythrin [the last two compounds are also formed similarly from (I)]. (II) heated with $N_2H_4 \cdot H_2O$ in $NPhMe_2$ gives small amounts of two chlorins; in $EtOH$, a chlorin, $C_{31}H_{35}O_5N_4$, and an uncharacterised rhodin result. (II) and hot HCO_2H give rhodo- and phylloporphyrins and rhodinoporphyrin *g_a*, $C_{32}H_{34}O_5N_4$ [Me ester, m.p. 231° (semicarbazone; haemin), converted by $MgMeI$ into a compound, $C_{35}H_{42(44)}O_5N_4$, m.p. 212° , spectroscopically identical with phylloporphyrin]; the latter is converted by $HBr-AcOH$ at 140° into phylloporphyrin, by $MeOH-KOH$ and MgO in C_5H_5N into a rhodin and phyllo- and pyrro-porphyrins, and by oleum (15% SO_3) into a rhodin. Methylphaeophorbide *b* and (I) [which is a (mono) Me ester] are degraded by $HI-AcOH$ to phaeoporphyrin *b₇* (III), $C_{35}H_{38}O_5N_4$ [oxime; haemin: Me ester (CH_2N_2), m.p. 262° Me₃ ester ($MeOH-HCl$), m.p. 245°], which contains a CO_2Me group, is degraded by $HBr-AcOH$ or by $MeOH-KOH$ in $C_5H_5N-MgI_2$ to rhodoporphyrin, and with $MgMeI$ gives a compound, $C_{40(41)}H_{50(52)}O_4N_4$, m.p. 248° , and a porphyrin, m.p. 268° (spectroscopically identical with phaeoporphyrin *a₅*). (III) is converted by boiling HCO_2H into the Me ester (oxime) of phaeoporphyrin *b₅* [formed from (III) and 40% $MeOH-KOH$] (oxime; haemin: Me₃ ester, $C_{34}H_{36}O_5N_4$, m.p. 235° , which with $MgMeI$ gives a porphyrin, m.p. 234° , spectroscopically identical with the compound from rhodoporphyrin Me₃ ester and $MgMeI$), which is degraded by 5% $NaOMe$ in C_5H_5N at 160° to pyrro- and rhodo-porphyrins [also formed with phylloporphyrin by similar treatment of (III)]. Oxidation of (I) with $CrO_3-H_2SO_4$ gives methylethylmaleimide and $H_2C_2O_4$, indicating the presence of a CO group in the $\cdot CH_2 \cdot CH_2 \cdot CO_2H$ side-chain, whilst reduction affords small amounts of haemopyrrole and its carboxylic acid. (I) and $MgMeI$ give (after decomp. and treatment with CH_2N_2) a compound, $C_{38}H_{45}O_6N_4$. (I) heated at $240-250^\circ$ in N_2 eliminates approx. 1 mol. of CO_2 ; (II) at $290-300^\circ$ similarly affords CO_2 (approx. 2 mols.) and pyrroporphyrin. (I) is hydrolysed by 10% $MeOH-KOH$ in C_5H_5N to (II); with Na and $PrOH$ in N_3 , a substance, m.p. 228° , results (in one case only). (II) and 25% $PrOH-KOH$ in C_5H_5N give a substance [Me ester, $C_{37}H_{42}O_7N_4$, m.p. 245° , spectroscopically identical with (II)]; with 40% $MeOH-KOH$ and O_2 , a substance (Me ester, $C_{33}H_{36}O_5N_4$, m.p. 277°) similar to ψ -verdoporphyrin is formed. Methylphaeophorbide *b* and $EtOH-NH_3$ at 130° give a compound, $C_{35}H_{40}O_6N_6$, the methiodide of which when heated with KOH affords NH_2Me . Alternative structures are suggested for (I) and (II).

XXVI. Complex Fe salts (haemins) (m.p. quoted

in brackets) of the following are prepared: chlorophyllin e_6 and its Me_3 ester [260°]; phaeoporphyrin a_5 [decomp. 300°] and its Me_2 ester [305–306° (decomp.)]; phaeoporphyrin a_5 oxime [above 300°]; phyloerythrin oxime (also formed by oximation of phyloerythrin haemin); phaeoporphyrin a_7 Me_3 ester [291° (decomp.)]; dimethylphaeopurpurin a_7 [210° (decomp.)]; phaeopurpurin 18 Me ester. The effect of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ on the spectra of these haemins in C-H-N and other solvents is recorded. Short treatment of phyloerythrin haemin with $\text{MeOH-KOH-C}_5\text{H}_5\text{N}$ gives a chlorin-like compound and a substance, which when freed from Fe by the $\text{Fe}(\text{OAc})_2\text{-HCl}$ method, affords phyloerythrin and rhodoporphyrin- γ -carboxylic acid (I); more prolonged treatment gives (after removal of Fe) a little (I), some rhodoporphyrin, and (mainly) the green anhydride of (I).

XXVII. Chlorin e_7 and cold MeOH-HCl give a Me_2 ester (I), probably $\text{C}_{36}\text{H}_{40}\text{O}_7\text{N}_4$, m.p. 214° (corr.) (*Cu* salt), reduced (HI-AcOH) to chloroporphyrin e_5 and converted slowly by cold MeOH-HCl into chlorin e Me_3 ester (II), also obtained from (I) and chlorin e_7 by esterification with CH_3N_3 or $\text{Me}_3\text{SO}_4\text{-alkali}$. All the specimens of (II) are $\text{C}_{37}\text{H}_{42}\text{O}_6\text{N}_4$ and are all reduced (HI-AcOH) to chloroporphyrin e_5 . Chlorin e_7 and diazoethane in $\text{Et}_2\text{O-C}_5\text{H}_5\text{N}$ give chlorin e Et_3 ester, $\text{C}_{40}\text{H}_{48}\text{O}_6\text{N}_4$, m.p. 149°, also reduced to chloroporphyrin e_5 . Short hot alkaline hydrolysis of (II) gives chlorin e , $\text{C}_{34}\text{H}_{36}\text{O}_6\text{N}_4$, which has the same spectrum and HCl no. as chlorin e_7 but is reduced (HI-AcOH) to chloroporphyrin e_5 . Similar hydrolysis of phaeophorbide a gives chlorin e , verdoporphyrin, and a phaeophorbide-chlorin mixture (reduced by HI to phyloerythrin and rhodoporphyrin), whilst hydrolysis with aq. $\text{Ba}(\text{OH})_2$ in air or N_2 gives chlorin e , deoxypyrrhophaeophorbide a (formed as the main product by hydrolysis with 5% KOH), and a chlorin-like substance (reduced by HI to mainly rhodoporphyrin). These substances and some purpurin are obtained by hydrolysis of methylphaeophorbide a with 8% $\text{Ba}(\text{OH})_2$, whilst ethylchlorophyllide is hydrolysed by 33% MeOH-KOH to chlorin e and rhodin g . The structures of (II), chloroporphyrin e_5 Me_3 ester, phaeophorbide a , and chlorophyllide a are discussed. Chlorophyll a is best represented as:

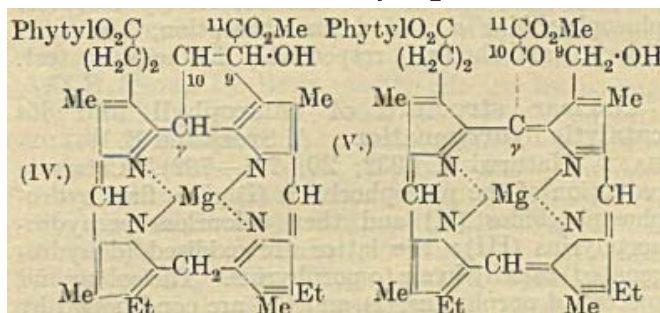


H. B.

Mechanism of the phase test and the constitution of chlorophyll a and b . A. STOLL and E. WIEDEMANN (*Helv. Chim. Acta*, 1932, 15, 1128–1136).—Allomerisation of chlorophyll consists solely in oxidation at C9, CH-OH to CO or $\text{CH}_2\text{-OH}$ to CHO with chlorophyll a and b , respectively (cf. this vol., 174, 756), and takes place in the alkaline medium of the phase test. Phaeophorbide a (I) is rapidly allomerised by I in AcOH at room temp.; the product (II) gives a

negative phase test, but has almost the same absorption as (I). (I) readily gives a characteristic *Bz* derivative in the cold, but no oxime; (II) gives an oxime in the cold, but no *Bz* derivative. Oximation of methylchlorophyllide and phaeophytin (this vol., 756) is preceded by allomerisation. Phaeoporphyrin a and phyloerythrin, which have a CO group at C9, are derivatives of allomerised chlorophyll a . Careful treatment of (I) with HI-AcOH yields *proto*phaeoporphyrin a (III), cryst., which is autoxidisable, gives a yellow phase test, and has an absorption almost identical with that of phaeoporphyrin a_5 ; it is supposed that a perhydro-compound is first formed, which is then dehydrogenated both in the nucleus (thus destroying the chlorin nature of the product) and at C9 by the liberated I. (III), solid or in solution, oxidises (with loss of phase) to phaeoporphyrin a_5 , which yields an oxime, and in the phase test gives chloroporphyrin e_6 smoothly. Careful allomerisation of (I) with alkali gives solutions of a substance with the properties of a chlorin e Me ester, no hydrolysis taking place. The generalisation is made that transformation of chlorophyll derivatives into substance of chlorin nature by alkali consists in oxidation of C9 and subsequent ring-opening, followed in vigorous treatment by hydrolysis of the Me ester group. Chlorophyll a is, therefore, (IV).

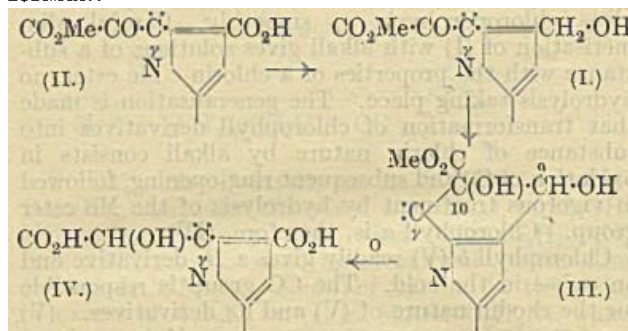
Chlorophyll b (V) readily gives a *Bz* derivative and an oxime in the cold. The CO group is responsible for the rhodin nature of (V) and its derivatives. (V) and rhodins contain the grouping $\text{C}(\gamma)\text{-C}(10)\text{-C}$; thus, phaeophorbides of the b series with RMgAlk pass into the a series by conversion of the CO group into $\text{C}(\text{OH})\text{Alk}_2$ and reduction of the nucleus. Phaeophorbide b (VI) is allomerised by I in AcOH . Both (V) and its allomerisation product give rhodin g Me ester when cautiously treated with alkali. The formation of feebly basic products with 6 or 7 O atoms in the a and b series, respectively, is caused by addition of O. (V) with HI-AcOH gives *proto*phaeoporphyrin b (VII), which gives a yellow phase-test and does not give an oxime, and is therefore formed by wandering of a H atom from C9 to C10 and change of CO to C-OH . (V), therefore, does not contain the isocyclic "side-ring." (VII) with alkali gives *rhodin*porphyrin g_7 . Allomerised (V) is changed back to (V) by reduction; the spontaneous reaction, $\text{CH-OH}(9) \rightarrow \text{CO}$, is thus reversible and may play a part in plant metabolism. Treatment of chlorophyll with alkali causes first dehydrogenation at C9,



rearrangement of the conjugated ethylenic linkings, and fission of Mg-N auxiliary valencies, thus causing

the "brown phase," followed by further reaction of the CO group and return of the valencies to the original condition, thus restoring the chlorophyll spectrum. (V) is given the formula shown. R. S. C.

Constitution of chlorophyll and the formation from it of the fundamental dicarboxylic acids. A. STOLL and E. WIEDEMANN (Helv. Chim. Acta, 1932, 15, 1280—1285; cf. preceding abstract).—Benzoylphæophorbide *a* is stable to dehydrating agents, e.g., I-EtOH. Phæophorbide *b* oxime (I) with MgMeBr gives a green Mg complex salt, changed to (I) by dil. acids. Rhodin *g* (II) readily gives an oxime, the absorption of which closely resembles that of phæophorbide *b* oxime (II). Change of phæophorbide *b* to (II) by alkali and to protophæoporphyrin *b* (III) by acid is represented by the partial formulæ:



(III) gives no oxime and a yellow phase test, and has an absorption almost identical with that of protophæoporphyrin *a*, from which it differs only in having an OH group at C10. The change of (I) to (III) is the first transformation of series *b* into series *a*. Rhodinporphyrin *g*₇ is phæoporphyrin *a*₇ and is allotted formula (IV). Fischer's formula for this substance is incorrect [since (IV) does not give an oxime] and is now assigned to rhodin *g*. In agreement with the hypothesis of reduction of the CHO group, phæophorbides *a* and *b* with KOH-MeOH in the presence of a little aq. Na₂S₂O₄ are hydrolysed, but not oxidised at C9, and unchanged chlorophyllides or phæophorbides can be recovered after a considerable time by dilution and extraction with Et₂O, whereas without Na₂S₂O₄ such recovery is possible only within a few seconds. The alcoholic dicarboxylic acids thus obtained are named *nor-phæophorbide a* and *b*; they give yellow and red phases, have acid nos. 9 and 13, closely resemble phæophorbides *a* and *b* in absorption, and give chlorin *e* and rhodin *g*, respectively, in the phase test. R. S. C.

Nuclear structure of chlorophyll and its catalytic hydrogenation. A. STOLL and E. WIEDEMANN (Naturwiss., 1932, 20, 791—792).—Catalytic reduction of the phæophorbides (I) gives first hydrophæophorbides (II) and then colourless perhydrophorphyrins (III); the latter are oxidised (dehydrogenated) rapidly in air to porphyrins. The colour and spectra of porphyrins, (I), and (II) are conditioned by a continuous conjugation of double linkings. All known porphyrins contain two superfluous double linkings; one of these (nuclear) disappears during the

change porphyrins → (I), the other during (I) → (II). The conjugation is abolished during the production of (III). Formulæ are assigned to chlorophyll *a* and *b* which are supported by the above results; that of *a* contains one O less than that of *b* and has an additional ring (between C₉ and C₁₀).

Bilirubinoid colouring matters. IV. Dehydrobilirubin. R. LEMBERG (Annalen, 1932, 499, 25—40).—Mild reduction of uteroverdin Me ester (I), most probably C₃₅H₃₈O₆N₄, m.p. 209° (all m.p. are corr.) (cf. this vol., 627), with HI-AcOH gives bilirubic acid, showing that uteroverdin is dehydrobilirubin. The EtOH mother-liquors from the prep. of bilirubin (from gallstones) contain dehydrobilirubin Me₂ ester (II), m.p. 214—215°, which is identical with (I); (II) is also formed (by dehydrogenation) when gallstones are heated with AcOH. Whilst methylethylmaleimide is obtained by HNO₃-oxidation of dehydromesobilirubin (glucobilin) ester (Fischer *et al.*, this vol., 627) (also prepared by oxidation of mesobilirubin with FeCl₃ in AcOH, subsequent removal of Fe with alkali, and esterification), it is not produced by similar oxidation of (I) or (II). (II) is also prepared by oxidation of bilirubin with FeCl₃ in AcOH (or MeOH-HCl) (as above). The constitution of (I) is discussed (cf. A., 1930, 488; *loc. cit.*). H. B.

Reaction of 1:4-dichlorophthalazine with sodium azide. R. STOLLE and H. STORCH (J. pr. Chem., 1932, [ii], 135, 128—136).—1:4-Dibromo- (I), m.p. 162°, and 1-bromo-4-hydroxy-phthalazine, m.p. 273°, are prepared from 1:4-dihydroxyphthalazine and PBr₅ at 95—160°. (I) or the corresponding Cl₂-compound gives with NaN₃ in abs. EtOH at the b.p. 4-azido-1:2-tetrazolophthalazine, N₃C<C₆H₃<N=N>N

(II), m.p. 152°, the structure of which follows from the removal of one N₃ group only by NaOH with formation of 4-hydroxy-1:2-tetrazolophthalazine (III), m.p. 258° (decomp.) (Ag salt; Ac derivative, m.p. 165°; O-Me ether, m.p. 211°; Et ether, m.p. 187°), and its conversion into 4-amino-1:2-tetrazolophthalazine, m.p. 305° (IV) (Ac₂ derivative, decomp. 260°), by heating at 200° in tetrahydronaphthalene. The corresponding 4-Cl-compound, m.p. 195° (decomp.), is obtained from (III) and PCl₅ at 140°, and is converted into (IV) by NH₃ in aq. EtOH at 150°. With NH₃ under the same conditions (II) gives (III) and (IV). An unidentified substance, m.p. 249°, probably an N-chloro-derivative, is obtained by chlorination of (IV) in aq. NaHCO₃. H. A. P.

Structure of pyrrole blacks. A. QUILICO (Gazzetta, 1932, 62, 822—839).—Pyrrole blacks in which the C/N ratio is 4 are prepared. By action of H₂O₂ and Fe⁺⁺⁺ on C₄H₄N in H₂O the product has the formula C₄₀H₄₄O₂₀N₁₀, and loses H₂O and CO₂ when heated. In presence of AcOH the product has the formula C₄₀H₄₀O₁₈N₁₀; with CH₂N₂ this gives a product C₅₀H₅₆O₁₄N₁₀. In alkali the blacks are sol. before methylation, insol. after. Action of Br on C₄₀H₃₄O₁₅N₁₀ yields a product C₄₄H₃₀O₂₆N₁₀Br₁₀ and NH₄ tetroxalate. E. W. W.

Dioximes. XCIII, XCIV. G. PONZIO. XCV. M. MILONE. XCVI. G. LONGO (Gazzetta, 1932,

62, 854—859, 860—868, 868—873, 873—877).—XCIII. Action of POCl_3 on the β form of amino-phenyl- and p -tolyl-glyoximes yields 5-amino-3-phenyl-1:2:4-oxadiazole, m.p. 153—154° [hydrochloride, m.p. 165° (decomp.)]; *Ac* derivative, m.p. 183—184°, which is hydrolysed to the 5-OH-compound, and converted by HI into $\text{NH}_2\cdot\text{CPh}\cdot\text{NH}$, and 3- p -tolyl-1:2:4-oxadiazole, m.p. 221—222° (*Ac* derivative, m.p. 173—174°). The α forms of the above, and the α or β forms of $\text{HON}\cdot\text{CPh}\cdot\text{C}(\text{NHPh})\cdot\text{NOH}$ and $\text{HON}\cdot\text{CBz}\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}$ give only 1:2:5-oxadiazoles.

XCIV. 4-Benzamido-3-benzoyl-1:2:5-oxadiazole treated with $\text{KOH}\cdot\text{EtOH}$ loses the 3-Bz grouping, and then isomerises into cyano-*N*-benzoylformamid oxime, m.p. 138—140° (*Ac* derivative, m.p. 140°), which is converted by boiling H_2O into 3-cyano- and 3-carbamido-5-phenyl-1:2:4-oxadiazole. 4-Benzamido-3- p -toluoyl-1:2:5-oxadiazole, m.p. 149—150°, gives the same products.

XCV. The velocity of hydrolysis of Ac_2 and Bz_2 derivatives of glyoxime and its Me, Me_2 , and MeEt derivatives is studied. *Dibenzoylglyoxime* has m.p. 139°.

XCVI. The β (but not the α) forms of chloroglyoxime react with KCN in Et_2O , giving β -cyano-glyoxime, m.p. 131° (decomp.) [*Ni* salt; Ac_2 , m.p. 145—146°, and Bz_2 , m.p. 185—186° (decomp.) derivatives]. This is converted by NH_2OH in MeOH into aminotrioxime (α -amino- $\alpha\beta\gamma$ -trioximinopropane), m.p. 147—148° (decomp.), which with Ac_2O gives 4-amino-3-acetoximinomethyl-1:2:5-oxadiazole, m.p. 157—158°, hydrolysed (NaOH) to the 3-oximinomethyl compound, m.p. 187—188°. E. W. W.

Interaction of α - p -carbethoxyphenyl- γ -alkylthiocarbamides with bromine: effect of the isobutyl group on hydrotribromide formation in 1-alkylaminobenzthiazoles. R. F. HUNTER and E. R. PARKEN (J. Indian Chem. Soc., 1932, 9, 357—361).— α - p -Carbethoxyphenyl- γ -methylthiocarbamide, m.p. 147—148°, from $p\text{-CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NCS}$ and NH_2Me in EtOH , and Br in CHCl_3 give the hydrotribromide, m.p. 137—138° (decomp.), of *Et* 1-methylaminobenzthiazole-5-carboxylate, m.p. 169° (free acid, m.p. 298°; *Ac* derivative, m.p. 174°). α - p -Carbethoxyphenyl- γ -ethylthiocarbamide, m.p. 89°, similarly gives the hydrotribromide, m.p. 103—104° (decomp.), of *Et* 1-ethylaminobenzthiazole-5-carboxylate, m.p. 150—151°, whilst α - p -carbethoxyphenyl- γ -isobutylthiocarbamide, m.p. 107—108°, affords the hydrotribromide, m.p. 92—94° (softens at 90°), of *Et* 1-isobutylaminobenzthiazole-5-carboxylate, m.p. 133—134°. The esters are obtained from the hydrotribromides by treatment with aq. H_2SO_4 . The Bu^i group appears to favour hydrotribromide formation (cf. A., 1927, 263).

H. B.

Echitamine in *Alstonia* barks. J. A. GOODSON (J.C.S., 1932, 2626—2630).—The following percentages of total alkaloids and echitamine (I), respectively, occur in the species of *Alstonia* bark named; *angustiloba* (II) (Malaya), 0.17, 0.04; *congensis* (III) (Gold Coast), 0.38—0.56, 0.18—0.34; (Nigeria) 0.11—0.12, 0.03—0.04; (Cameroons) 0.18, 0.09; *constricta* (Australia) 0.40, 0; *Gilletii* (Belgian Congo), —, 0.21; *macrophylla* (Philippines) 0.99, 0; *scholaris* (IV)

(Belgian Congo) —, 0.04, (India) 0.16—0.27, 0.08—0.10, (Philippines) 0.28—0.40, 0.20—0.31; *spatulata* (Malaya) 0.06, 0.03; and *villosa* (Australia) 1.61, 0. (II) and (IV) yield also small amounts of echitamidine. $\text{C}_{20}\text{H}_{26}\text{O}_3\text{N}_2$, m.p. (+ H_2O) 135° after softening at 127° and (anhyd.) 244° (decomp.), $[\alpha]_D^{25}$ —515° in EtOH [picrate, m.p. 226—227° (decomp.)]; hydrochloride, m.p. (+4 H_2O) 105° after softening at 75° and (anhyd.) 179° (decomp.), $[\alpha]_D^{25}$ —473° in H_2O ; hydrobromide, m.p. (+2 H_2O) 114° after softening at 105° and (anhyd.) 181° (decomp.), $[\alpha]_D^{25}$ —422° in H_2O ; hydriodide, m.p. (+3 H_2O) 110° and (anhyd.) 182° (decomp.), $[\alpha]_D^{25}$ —389° in H_2O ; sulphate, m.p. (+11 H_2O) 87° after softening at 73°, and (anhyd.) 169° (decomp.), $[\alpha]_D^{25}$ —362° in H_2O ; abnormal OMe and NMe analyses indicate the presence of a NMe but not a OMe group. (II) and (IV) contain a lactone, now named C, obtained previously (A., 1925, i, 1166) from (III), whilst (IV) contains also an isomeric lactone S, $\text{C}_9\text{H}_{14}\text{O}_3$, m.p. (+ H_2O) 80—84° and (anhyd.) 107° (*Ac* derivative, m.p. 86—90°), $[\alpha]_D^{25}$ +142.5° in $\text{N}\cdot\text{H}_2\text{SO}_4$, 143.3° in H_2O , 97.9° in $\text{N}\cdot\text{NH}_3$, and 60.1° in $\text{N}\cdot\text{NaOH}$. Lactone C has $[\alpha]_D^{25}$ +50.6°, 50.6°, 65.3°, and 94.1°, respectively, in these solvents. Both lactones contain one fully reduced ring and a saturated side chain or chains. (I) and hot aq. NaOH (1 equiv.) give MeOH and demethylechitamine, reconverted into the hydriodide and *Me* sulphate, m.p. 253° (decomp.), of (I) by hot MeI and cold Me_2SO_4 , respectively; the ester nature of (I) is thus confirmed. The HCl salt of (I) and MeOH form an additive compound (1:1), m.p. 277° (decomp.), $[\alpha]_D^{25}$ —52° in H_2O . R. S. C.

Demethylation of narcotine and vitamin-C. J. BRUGGEMANN (Z. physiol. Chem., 1932, 211, 231—240).—Narcotine was demethylated in stages in order to obtain methylornarcotine. This was not obtained cryst. and the products were antiscorbutically inactive (cf. Rygh *et al.*, this vol., 310). J. H. B.

Microchemical identification of alkaloids. F. AMELINK (Pharm. Weekblad, 1932, 69, 1121—1123).—Prostigmine (dimethylcarbamate ester of *m*-hydroxyphenyltrimethylammonium methosulphate) does not react visibly with PtCl_4 , but when NaI is added a characteristic cryst. ppt. forms; the sensitivity is 0.1%. $\text{K}_4\text{Fe}(\text{CN})_6$, picric acid, and HgCl_2 also yield ppts., but the first reaction is the most useful. Various other reactions of the alkaloid are described.

H. F. G.

Use of hydrobromic acid in the characterisation of arylarsinic acids. G. SCHUSTER (Compt. rend., 1932, 195, 611—614).—Replacement of the AsO_3H_2 group by Br is readily effected by boiling HBr (*d* "1.75") (cf. A., 1931, 105), which converts *o*- and *p*-nitrophenyl-, *p*-aminophenyl-, *p*-chlorophenyl-, phenyl-, *o*-tolyl-, *p*-tolyl-, and 2-nitro-3-hydroxyphenyl-arsinic acids into *o*- $\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{NO}_2$ (86%), *p*- $\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{NO}_2$ (88%), *p*- $\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{NH}_2$ (72%), *p*- $\text{C}_6\text{H}_4\cdot\text{ClBr}$ (91%), PhBr (40—42%), *o*- $\text{C}_6\text{H}_4\cdot\text{MeBr}$ (45%), *p*- $\text{C}_6\text{H}_4\cdot\text{MeBr}$ (52%), and 5:6-dibromo-2-nitrophenol (?) (83%), respectively. Poor yields resulting from similar treatment of phenyl- and 4-nitrophenyl-dichloroarsines are greatly improved by using the corresponding arsinioxides. A. C.

Trypanocidal action and chemical constitution. XIII. Arylthioarsinites from cysteine and glutathione. A. COHEN, H. KING, and W. I. STRANGWAYS (J.C.S., 1932, 2505—2510; cf. this vol., 408).—Reduction of Me phenylglycine-*p*-arsinite (SO₂ method) gives *N*-phenylglycine-*p*-arsin oxide Me ester, solid, which with conc. aq. NH₃ at -10° gives *N*-phenylglycineamide-*p*-arsin oxide (I), cryst., changed by warm 3% AcOH into tri(phenylglycineamide)arsine, m.p. about 225° (decomp.), which with I yields the oxide, effervescence at about 160°. (I) and aq. cysteine hydrochloride (II) afford di-(β-amino-β-carboxyethyl) *N*-phenylglycineamide-*p*-thioarsinite (III), +1.5H₂O, crvst., $[\alpha]_{5461}^{20} +9.3^\circ$ in *N*-HCl, whilst glutathione (IV) yields similarly di(glutathionyl) *N*-phenylglycineamide-*p*-thioarsinite, amorphous. Tryparsamide and (II) give an inseparable mixture of cystine and (III), changed by cold, conc. 16% HCl to cystine and tricysteinyarsine. *N*-Phenylglycine-*p*-dichloroarsine and MeOH-HCl give phenylglycine Me ester, whilst reduction [also of (I)] in acid solution similarly removes As. Reduction of 4-acetamido-2-hydroxyphenylarsinic acid gives the corresponding arsin oxide, cryst., +0.5H₂O, which with (II) yields di-(β-amino-β-carboxyethyl) 4-acetamido-2-hydroxyphenylthioarsinite, +2.25H₂O, gelatinous, and with (IV) the corresponding di(glutathionyl) compound (V), amorphous. 4-Amino-2-hydroxyphenylarsinic acid, however, loses As when reduced in acid solution, and with (II) (4 mols.) gives tricysteinyarsine. 3-Amino-4-hydroxyphenylarsinic acid, when reduced, yields 3-amino-4-hydroxyphenyl-dichloroarsine hydrochloride, cryst., which with (II) gives di-(β-amino-β-carboxyethyl) 3-amino-4-hydroxyphenylthioarsinite, m.p. 237—238° (decomp.) [lit. 225—227° (uncorr.)]; the arsin oxide with (IV) gives the di(glutathionyl) compound, a syrup. Dithioacetic acid, when reduced with Zn dust and 3*N*-HCl at 35—40° and then condensed with tryparsamide, affords di(carboxymethyl) phenylglycineamide-*p*-thioarsinite. The above condensation products are toxic to *Trypanosoma equiperdum*, (V) being extremely effective. R. S. C.

Organo-arsenic compounds. I, II. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1932, 9, 371—373, 393—401).—I. The following are prepared by alkaline coupling of the diazotised aminocoumarins with (?)sulpho- α -naphthylarsinic acid (Hill and Balls, A., 1922, i, 1080): coumarin-6-, m.p. 185° (decomp.), 7-methylcoumarin-6-, decomp. 235° (shrinks at 168°), 4:7-dimethylcoumarin-6-, m.p. 204° (decomp.), 1:2- α -naphthapyrone-6-, shrinks at 170°, and 4-methyl-1:2- α -naphthapyrone-6-, m.p. 162° (decomp.), -azo-(?)sulpho- α -naphthylarsinic acids.

II. The following are prepared by the Bart method: xanthone-3-arsinic acid, m.p. > 335°; 8-nitroxanthone-1-arsinic acid, m.p. > 330° (from 8-nitro-1-aminoxanthone, m.p. 205—207°, prepared by reduction of 1:8-dinitroxanthone with SnCl₂ and EtOH-conc. HCl); 7-nitroxanthone-2-arsinic acid (I), m.p. > 340° (from 7-nitro-2-aminoxanthone, m.p. 264—265°); bromonitroxanthonearsinic acid, m.p. 258—260° (decomp.) [from the bromonitroaminoxanthone, m.p. 143—145°, obtained by reduction (EtOH-NH₄HS)

of bromodinitroxanthone]; ψ -1:8-isonaphthoxazone-3-arsinic acid, m.p. 225—227° (decomp.) [from 3-amino- ψ -1:8-isonaphthoxazone, m.p. 270°, obtained by reduction (EtOH-NH₄HS) of the 3-NO₂-derivative, m.p. 228—230°, which is prepared from 3:6-dinitrocoumarin, glycerol, and conc. H₂SO₄ at 135—170°]; xanthoquinoline- β -arsinic acid, m.p. > 345° (shrinks at 315°) [from β -aminoxanthoquinoline, m.p. 276—278°, prepared by reduction (EtOH-NH₄HS) of the NO₂-compound]. (I) is reduced by FeSO₄ and aq. NaOH to 7-aminoxanthone-2-arsinic acid, m.p. > 347° (Ac derivative, m.p. > 340°). H. B.

Arsenic derivatives of indazole. E. PŁAZEK and E. NEYMANÓWNA (Rocz. Chem., 1932, 12, 706—714).—Indazole-6-arsinic acid, m.p. 206—208°, produced, together with other unidentified products, by adding Na₃AsO₃ to diazotised 6-aminindazole, yields indazole-6-arsin oxide (I), decomp. > 170°, on treatment with SO₂, bis-6-arsenindazole, decomp. > 240°, on reduction, and indazole-6-arsenious disulphide on treatment with H₂S; indazole-6-thioarsin oxide, m.p. 170°, is obtained from H₂S and (I). Indazole-7-, m.p. 222—225°, -5-, solid at 340°, and -4-arsinic acid, m.p. 242°, 7-, decomp. 170°, 5-, m.p. 286°, and 4-arsenindazole oxide, decomp. 250°, bis-7-, m.p. 216°, and bis-5-arsenindazole, unstable, are prepared analogously to the above compounds. Indazole-6- and -4-arsinic acids are much stronger acids than are the -7- and -5-compounds. R. T.

Ring fission of heterocyclic arsenic derivatives. G. A. RAZUVAYEV and M. M. KOTON (J. Gen. Chem. Russ., 1932, 2, 529—533).—The fission of various As derivatives with HCl in CCl₄ under pressure, with or without addition of AsCl₃, has been examined. 10-Chloro-, 10-chloro-2:7-dimethyl-, 10-chloro-1:2-benzo-, and 10-chloro-3:4-benzo-9:10-dihydrophenarsazines are the most easily decomposed, then chlorophenoxarsine, and finally diphenylencchloroarsine. The fission of arsenic acids proceeds most readily in acid solution, whilst alkalis retard the change. Phenarsazinic acid is the most easily decomposed, then diphenylencarsinic acid, phenoxarsinic acid being the most stable but less so than acyclic acids (diphenylarsinic acid). G. A. R. K.

Phosphonium compounds with an asymmetric phosphorus atom. G. KAMAY (J. Gen. Chem. Russ., 1932, 2, 524—528).—PPhEt₃, when heated with CH₃PhCl in CO₂ gives CH₃Ph.PPhEt₂Cl, m.p. 194—195°, which decomposes when heated in CO₂ to PPhEt₂, CH₃Ph.PPhEt (I), and PPh(CH₃Ph)₂ (II). (I) with Ac-CH₃Cl in CO₂ gives phenylbenzylethylacetonylphosphonium chloride, syrupy, and with phenacyl bromide phenylbenzylethylphenacylphosphonium bromide, m.p. 166—169° decomposed by boiling H₂O into COPhMe and phenylbenzylethylphosphine oxide. (II) with EtBr gives phenyldibenzylethylphosphonium bromide, m.p. 170—171°. The first two salts yielded only irresolvable bromocamphorsulphonates. G. A. R. K.

Elimination of metallic tin from tin tetraphenyl. M. M. KOTON (J. Gen. Chem. Russ., 1932, 2, 345—347).—SnPh₄ heated at 250° with H₂ at 50 atm. does not decompose; at 275° 6.3% decom-

poses to yield Sn and C_6H_6 , whilst at 350° 71.4% decomposes. With Pr^sOH , $CH_3Ph \cdot OH$, or tetralin the products are similarly C_6H_6 and Sn. R. T.

Application of thallium in organic chemistry.
VII. Chelate rings. R. C. MENZIES and E. R. WILTSHIRE (J.C.S., 1932, 2604—2606; cf. A., 1931, 1280).—Dialkylthallium halides and $TlOEt$ in C_6H_6 give solutions of the corresponding dialkylthallium ethoxides, from which the appropriate diketones ppt. the following compounds: *dipropyl-* (m.p. 181°) and *dibutyl-* (m.p. $138-139^\circ$) *thallium acetylacetonate*; *Tl dipropionylmethane*, m.p. 70° , *dimethyl-* (m.p. 121°), *diethyl-* (m.p. 116°), and *dipropyl-dipropionylmethane*, m.p. 89° ; *dimethyl-* (m.p. 162°) and *diethyl-propionylacetonate*, m.p. 147° . These compounds form a graduated series, the stability and insolubility in H_2O falling from the $TlBu_2$ compound, which resembles Cu or Be compounds, to Tl acetylacetonate, which approaches the Na and K compounds. The m.p. of the Me compounds are abnormal. R. S. C.

Racemisation. XI. Action of alkali on polypeptides. P. A. LEVENE and R. E. STEIGER (J. Biol. Chem., 1932, 98, 321—332).—Glycine anhydride, NaOH, and *l*- α -bromoisohexoyl chloride afford *l*- α -bromoisohexoylglycylglycine, m.p. $130-132^\circ$, $[\alpha]_D^{25} -36.4^\circ$ in H_2O , which with aq. NH_3 gives *d*-leucylglycylglycine (I), $[\alpha]_D^{25} -49.4^\circ$ in H_2O . (I) is similarly converted successively into *l*- α -bromoisohexoyl-*d*-leucylglycylglycine, m.p. 190° (corr.) (decomp.), $[\alpha]_D^{25} -5.64^\circ$ in EtOH, *d*-leucyl-*d*-leucylglycylglycine (II), $[\alpha]_D^{25} -8.6^\circ$ in $C_5H_5N-H_2O$; *chloroacetyl-d*-leucyl-*d*-leucyl-*d*-leucine, m.p. $198-199^\circ$ (decomp.), $[\alpha]_D^{25} +71.2^\circ$ in EtOH (from $CH_2Cl-COCl$ and the tripeptide), gives *glycyl-d*-leucyl-*d*-leucyl-*d*-leucine (III), $[\alpha]_D^{25} +82.3^\circ$ in $N-NaOH$. The hydrolysis and racemisation of (II) and (III) by $N-NaOH$ for 8 days at 25° were quantitatively studied, the loss of optical activity under these conditions being 19 and 23%, respectively, i.e., considerably > that observed (4%) with the parent tripeptide *d*-leucyl-*d*-leucyl-*d*-leucine (A., 1931, 1430). Hydrolysis of (II) and (III) with 20% HCl at 100° was also studied. J. W. B.

Union of bio-colloids. VIII. M. Z. GRYNBERG and S. KISIEL (Biochem. Z., 1932, 253, 146—151).—If the aggregation of the colloid (gelatin) is prevented by heating, no binding of uric acid occurs. The amount of binding varies greatly with the substance (egg protein, ovalbumin, birch charcoal) used and with the $[H^+]$. Between p_H 6.5 and 7.5 the degree of binding increases, but it is only partly dependent on the degree of dissociation of the acid and decreases at higher p_H . Uric acid does not combine with fats or lipins. W. McC.

Serinephosphoric acid obtained on hydrolysis of vitellinic acid. F. A. LIPMANN and P. A. LEVENE (J. Biol. Chem., 1932, 98, 109—114).—Vitellinic acid (I) (A., 1906, i, 913) with 0.25*N*-NaOH yields a dephosphorylated polypeptide (II). Acid hydrolysis of (I) and (II) yields 17.3 and 17.9% of NH_3 , respectively, of which >25% originated in the amide N of the polypeptide. Hydrolysis of (I) with 2*N*-HCl, followed by suitable technique, gives rise to *Ba serinephosphate*,

$BaO_2 \cdot PO \cdot OCH_2 \cdot CH(NH_2) \cdot CO_2H$, and the *Ba* salt, $[BaO_2 \cdot PO \cdot OCH_2 \cdot CH(NH_2) \cdot CO_2]_2Ba$, $[\alpha]_D^{25} +8.2^\circ$.

F. O. H.

Clupein. V. K. FELIX, K. INOUE, and K. DIRR (Z. physiol. Chem., 1932, 21, 187—202; cf. this vol., 954).—From the products of tryptic digestion of clupein there were isolated as flavianates or picrates five dipeptides: arginylarginine (*dipicrate*, decomp. 185° and then 275°), arginylloxypoline (*flavianate*, decomp. about 240°), and dipeptides of arginine with alanine (*picrate*, decomp. 250°), serine (*picrate*, decomp. 225°), and valine (*flavianate*, decomp. 250°). Free arginine was also found. J. H. B.

Micro-determination of carbon. Improvements in Nicloux' method. P. L. KIRK and P. A. WILLIAMS (Ind. Eng. Chem. [Anal.], 1932, 4, 403—404).—A modified technique is recommended (cf. A., 1927, 436). E. S. H.

Determination of fluorine and boron in organic compounds. D. J. PFLAUM and H. H. WENZKE (Ind. Eng. Chem. [Anal.], 1932, 4, 392—393).—The substance is oxidised with Na_2O_2 , $KClO_3$, and sucrose in a Parr S bomb. The product is dissolved in H_2O and boiled with NH_4Cl to permit the determination of F^- by pptn. as CaF_2 . Excess of Ca^{++} is removed from the filtrate by means of 4*N*-NaOH, and H_3BO_3 is then determined by the mannitol method. E. S. H.

Determination of organic compounds by oxidation with chromate mixture. V. MICHL (Časopis Českoslov. Lék., 1932, 12, 57—68; Chem. Zentr., 1932, ii, 257).—AcOH is completely oxidisable only by long boiling with $K_2Cr_2O_7$ and H_2SO_4 after addition of $AgNO_3$; even in presence of $AgNO_3$, certain alkaloids cannot be determined by this method. Substances which afford EtCHO as intermediate product require more $Cr_2O_7^{--}$ than is calc. A. A. E.

Determination of lactic acid. H. LIEB and M. K. ZACHERL (Z. physiol. Chem., 1932, 211, 211—216).—A simplified apparatus for determining $OH \cdot CHMe \cdot CO_2H$ is described. Absorption of MeCHO is facilitated by passing the gas stream through a sintered glass plate. J. H. B.

Iodometric determination of glucose. M. I. NAKHMANOVICH, S. L. BERMAN, and B. O. LYUBIN (Nauk. Zapsiki Tzuk. Prom., 1931, 14, 453—482).—The buffer solution (0.2*M*- $NaHCO_3$ - Na_2CO_3) is replaced by 0.1*N*-NaOH (25 c.c.). CH. ABS.

Detection and determination of sucrose by means of invertase. V. ESTIENNE [with J. TRUS-SART and G. JUBLOU] (Bull. Assoc. anc. Étud. Louvain, 1932, 32, 6—14; Chem. Zentr., 1932, i, 3236—3237).—Stable invertase solution is prepared by treating press yeast (25 g.) with H_2O (150 c.c.) for 7—14 days until acid to litmus, filtering through kieselguhr, and keeping in presence of toluene in a brown bottle. For the determination of sucrose 50 c.c. of a solution are treated with 2 c.c. of invertase solution, 5 drops of 20% AcOH, and 5 drops of toluene in a closely stoppered flask kept over-night at $53-55^\circ$; the invert sugar is determined by Bertrand's method. A. A. E.

Determination of glucose and maltose in aqueous solution and in broth and peptone solutions. M. L. SMITH (Biochem. J., 1932, 26, 1459—1466).—Shaffer and Hartman's method has been adapted. S. S. Z.

Colour reaction for lecithin, phytin, and phytosterol. H. KÜHL (Pharm. Zentr., 1932, 73, 625—629).—Phytosterols, phytins, and lecithins give similar Salkowski-Hesse reactions. Tests are given to differentiate between Et_2O , light petroleum, C_6H_6 , and COMe_2 extracts of soya-bean meal with regard to their reactions to H_2SO_4 and alcoholic NaOH . A. C.

Detection of inositol and of phytinates. A crystalline barium phytinate. F. FISCHLER and F. H. KÜRZEN (Biochem. Z., 1932, 254, 138—147).—Inositol and the Ca, Ba, Mg, and Na salts of its phosphoric acids (also phytin and phytinates) yield characteristic colours when treated with H_2SO_4 after oxidation with BaO_2 and/or Na_2O_2 . A cryst. Ba phytinate, $\text{C}_6\text{H}_{12}\text{O}_{24}\text{P}_6\text{Ba}_3 \cdot 3\text{H}_2\text{O}$, has been prepared. W. McC.

Pine-shaving reaction of furan [derivatives]. T. REICHSTEIN (Helv. Chim. Acta, 1932, 15, 1110—1112).—Only mono-substituted furan derivatives give a green colour in the pine-shaving test (modified technique); more highly methylated derivatives give red colours with pine shavings and with Ehrlich's reagent, indistinguishable from those given by pyrrole

derivatives. Tetramethylfuran gives slowly a red colour with pure filter-paper. Shavings stained green and red (or reddish-violet) become nearly blue and violet, respectively, when washed with H_2O . Rules cannot be laid down for the colour to be expected. R. S. C.

Microchemical reactions of loretine. C. VAN ZIJP (Pharm. Weekblad, 1932, 69, 1191—1197).—The reactions of loretine (2-iodo-1-hydroxyquinoline-4-sulphonic acid) with some 50 inorg. compounds are described. Zn yields a characteristic ppt., and with Ca, Sr, and Ba orange needles are formed, whilst the Mg derivative is colourless. The reagent may be employed to detect adulteration of ZnO and white lead with chalk, and the presence of CaCO_3 in MgCO_3 ; in the examination of dolomite; and for the detection of Zn in vegetable matter. H. F. G.

Colorimetric determination of histidine. E. JORPES (Biochem. J., 1932, 26, 1507—1511).—Hanke and Koessler's application of the Pauli reaction for the colorimetric determination of histidine gives very unsatisfactory results. By modifying the technique it is, however, possible to obtain reproducible figures. S. S. Z.

Determination of arginine. E. JORPES and S. THOREN (Biochem. J., 1932, 26, 1504—1506).—The Sakaguchi reaction (addition of α -naphthol and hypobromite) is used. S. S. Z.

Biochemistry.

Carbon dioxide in the blood; influence of carbon dioxide pressure, and determination of alkali reserve. M. LORA Y TAMAYO (Anal. Fis. Quim., 1932, 30, 664—672).—The Nieloux and Van Slyke methods for determining CO_2 in blood yield results which agree to within about 2%. The alkali reserve of five samples of blood saturated with CO_2 at pressures between 20 and 70 mm. has been determined. At pressures >40 mm. it may vary by up to 3% from the val. obtained at 40 mm., whilst at lower pressures the variation may be 5%. H. F. G.

Effects of salts and $[\text{H}^+]$ on the oxygen dissociation constant of the haemocyanin of *Busycon carniculatum*. A. C. REDFIELD and E. N. INGALLS (J. Cell. Comp. Physiol., 1932, 1, 253—275).—In solutions of KCl , NaCl , MgCl_2 , and K phosphate the equilibrium between purified haemocyanin and O_2 follows the law of mass action on the assumption that the various groups combining with O_2 react independently. Addition of CaCl_2 alters the shape of the O_2 dissociation curve. Changes in cause salt formation with certain of the acid or basic groups of the protein and the affinity of the salts for O_2 differs from that of the original protein. No relationship is apparent between the O_2 dissociation const. and the degree of ionisation of the haemocyanin mol. as a whole. A. G. P.

Spectrophotometric determination of certain blood-pigments. G. B. RAY, H. A. BLAIR, and C. I. THOMAS (J. Biol. Chem., 1932, 98, 63—83).—A

theoretical revision of the spectrophotometry of blood-pigments is followed by a description of its application to the determination of total pigment, O_2 content and capacity, and content of carboxy- or met-haemoglobin, or reduced haemoglobin in 0.05 c.c. of blood. F. O. H.

Cyanohaematin standard for the Sahli haemoglobinometer. R. D. BARNARD (J. Lab. Clin. Med., 1932, 17, 824—825).—Cryst. haemin is dissolved in 1% NaCN ; the final dilution of the blood sample is made with 1% NaCN . CH. ABS.

Oxyhaemoglobin reduction in living tissues, particularly in human skin. L. NICOLAI (Pflüger's Archiv, 1932, 229, 372—384; Chem. Zentr., 1932, i, 3305—3306).—The reduction is shown by a photometric method to be unimol.; the half-val. period *in vitro* is 8 sec. A. A. E.

Oxidation potential of the haemoglobin-methaemoglobin system. J. B. CONANT and A. M. PAPPENHEIMER, jun. (J. Biol. Chem., 1932, 98, 57—62).—The mid-point of the oxidation-reduction potential curve, determined by the direct electrochemical method (A., 1931, 40), gives a val. for E_0 of 152 ± 5 mv. for p_{H} 7.0, in good agreement with the spectrophotometric method (A., 1928, 315). The val. for n in the electrochemical equation lies between 1 and 2.5, and hence the oxidation of haemoglobin cannot be represented by the simple equation $\text{Hb}_4 \cdot 4\text{e}^- \rightarrow \text{MHb}$, unless some auxiliary assumptions are made. F. O. H.

Characterisation of blood spots and determination of their origin. R. MARCILLE (Ann. Chim. Analyt., 1932, [ii], 14, 433—445).—An account of the methods employed for the detection of traces of blood. M. S. B.

Simultaneous enumeration of blood platelets and reticulocytes. W. DAMESHEK (Arch. Int. Med., 1932, 50, 579—589).—Red cells, platelets, and reticulocytes are counted on the same slide after staining with an anticoagulating solution of brilliant-cresyl-blue. The abs. figure is then obtained after a red-cell count has been made. The normal platelet count by this method varies between 400,000 and 700,000 per cu. mm. The experimental error lies between 10,000 per cu. mm. for very low, and 70,000 per cu. mm. for normal, counts. H. G. R.

Protein component of the erythrocyte membrane or stroma. E. JORPES (Biochem. J., 1932, 26, 1488—1503).—This protein (stromatin) differs in its N, arginine, and histidine contents from haemoglobin and globin. It also differs from fibrin or globulin in its content of tyrosine and tryptophan. The protein of the membrane or stroma amounts to about 4% of the total protein of the normal erythrocytes. S. S. Z.

Determination of blood-proteins by acid acetone. J. RACE (Biochem. J., 1932, 26, 1571—1584).—The serum-albumin and -globulin are pptd. with $\text{CCl}_3\text{CO}_2\text{H}$ and the albumin is extracted with acidified COMe_2 , the globulin being insol. in this solvent. The process gives comparable results with those obtained by Howe's method (Na_2SO_4 pptn.) for normal sera and plasmata, but gives lower figures for globulin in pathological specimens. Howe's method gives in the case of COMe_2 extraction low globulin results; with pathological specimens more accurate figures are obtained by the acid COMe_2 method. Experiments with pure proteins and varying concns. of COMe_2 or EtOH suggest a change in the physical properties (surface tension) of the solvent at about 30 vol.-% concn. Blood-albumins from man, sheep, ox, and horse are entirely sol. in acid COMe_2 but ovalbumin is insol. The solubility of the various proteins is determined by the rate of denaturation and coagulation in acid. S. S. Z.

Action of phenylhydrazine on blood-protein. S. LÁNG (Z. ges. exp. Med., 1932, 80, 637—639; Chem. Zentr., 1932, i, 3194).—In dogs injection of $\text{NHPh}\cdot\text{NH}_2$ increases the plasma-protein and the quantity of globulin, but not parallel with the fall in the no. of erythrocytes. A. A. E.

Comparison of the Wu and Kjeldahl methods of serum-protein determination. L. R. TUCHMAN and H. SOBOTKA (J. Biol. Chem., 1932, 98, 35—41).—The method of Wu (A., 1922, ii, 406) is unsatisfactory when the serum-proteins are < 6%. Thus in oedema the tyrosine contents of the albumin and globulin fractions appear to be increased and decreased respectively. F. O. H.

Precipitation and protection of vanadic acid by serum-proteins. E. BOYLAND (Biochem. J., 1932, 26, 1383—1390).—Serum-albumin is pptd. by vanadic, molybdic, or tungstic acid, which form negative

lyophilic semicolloidal solutions in low concns., but not in higher concns., since in the latter case protection occurs and a stable positive colloid is formed. Serum-globulin causes pptn. in all available concns. between p_H 3.0 and 5.3. If euglobulin is added to an amount of albumin great enough to cause protection when a poly-acid is added alone, pptn. will occur. The globulin will, however, remain in solution if excess of albumin is present. The amount of globulin which a definite amount of albumin can protect increases with the acidity of the solution. S. S. Z.

Albumin and globulin contents of serum under various conditions. V. HENRIQUES and U. KLAUSEN (Biochem. Z., 1932, 254, 414—433).—Breathing a mixture of 50% CO_2 and 50% O_2 did not affect the albumin and globulin fractions of dog's serum. The changes in the serum-albumin and -globulin contents, respectively, are after poisoning with P decreases of 45% and 1—4%, after ligation of the bile duct decrease of 47% and increase of 17%, and after bleeding decreases of 30 and 47%. In comparable experiments, changes of albumin and globulin fractions are much greater in the lymph of the thoracic duct than in the blood itself. P. W. C.

Isoelectric point of serum-globulin as determined by cataphoresis. F. O. HOWITT and E. B. R. PRIDEAUX (Proc. Roy. Soc., 1932, B, 112, 24—27).—The cataphoresis of ox serum-globulin in presence of colloidal Au was determined over a range of p_H 2.8—9.6. A zone of insolubility of p_H 4.5—6.5 and an isoelectric point of approx. p_H 5.4 were indicated. F. O. H.

Osmotic pressure, mol. wt., and stability of serum-albumin. N. F. BURK (J. Biol. Chem., 1932, 98, 353—377).—The mol. wt. of cryst. horse serum-albumin, determined by osmotic pressure measurements, is 74,600 in aq. buffered solution at the isoelectric point, p_H 4.8, 76,000 in $(\text{NH}_4)_2\text{SO}_4$ solution, and 74,700 in 75% glycerol solution. In conc. urea solution, in which the albumin undergoes denaturation, the mol. wt. was 73,000, whilst the same val. was obtained for the heat-denatured protein dissolved in conc. urea solution. Denaturation therefore does not appreciably alter the mol. wt. Ovalbumin, denatured by urea and in 6.66M-urea solution, has a min. osmotic pressure at p_H 5.8, corresponding presumably with its isoelectric point, but the isoelectric point of the urea-denatured protein, estimated from the max. flocculation in aq. buffer solution, is at p_H 4.8—4.9, so that the more alkaline isoelectric point of the protein in urea solution is probably due to the effect of urea in the medium. W. O. K.

Determination of phenols in blood. J. GARCÍA BLANCO and F. COMESAÑA (Anal. Fis. Quím., 1932, 30, 690).—The plasma (2 c.c.) is diluted to 10 c.c., and protein is removed by adding 0.67N- H_2SO_4 (1 c.c.) and Na tungstate solution. To 6 c.c. of the filtrate are added 1 c.c. of HCl (5—10%) and 1 c.c. of NaNO_2 solution (1%), and after heating to b.p. and cooling, 2 c.c. of aq. NH_3 (10%) are added. The yellow coloration is compared with that given by a 0.0005% PhOH solution. The PhOH content of

samples of rabbits' blood varied between 1 and 2.5 mg. per 100 c.c. of plasma. H. F. G.

Determination of solids in blood and plasma. S. BALACHOVSKI and F. GINSBURG (Biochem. Z., 1932, 254, 47—49).—The blood (0.5—2.0 c.c.), to which an anticoagulant may be added, is dried at 100° to const. wt. in a shallow dish made of Al or Sn foil. W. McC.

Concentration and distribution of potassium in the serum and cells in the blood of normal unanæsthetised dogs. A. R. MCINTYRE (J. Biol. Chem., 1932, 98, 115—120).—For 10 dogs the content of the serum averaged 21.54 mg. per 100 c.c. and that of the cells 27.04 mg. per 100 g. The ratio K_s/K_c is 0.557 ± 0.16 when the vals. are expressed in millimols. per kg. of H_2O . F. O. H.

Comparative determinations of the calcium contents of various blood-constituents. A. HEIDUSCHKA and H. SCHMIDT-HEBBEL (Biochem. Z., 1932, 253, 336—346).—Determinations of Ca by the $KMnO_4$ titration method in serum and plasma gave comparable results both when the non-deproteinised fluid and its ash were used. Uranyl acetate as protein precipitant gave the most accurate results. Determinations on the ultrafiltrates of serum and plasma show that 30 and 50%, respectively, of the total Ca is retained by the protein on the filter. Using whole blood, the results of determinations in the ash are comparable with those on the directly hæmolyzed blood, but $CCl_3 \cdot CO_2H$ must replace uranyl acetate as deproteinising agent and the excess of this acid must be removed from the filtrate by evaporation to dryness. Hirudin, liquid, and germanin may be employed to prevent clotting without interference with Ca pptn. Oxalates and NaF cannot be used, but citrate gives fairly good results. Blood-corpuscles contain amounts of Ca only determinable spectroscopically. P. W. C.

Serum-calcium and the kidneys. J. CHEYMOL and A. QUENQUAUD (Compt. rend. 1932, 195, 682—684).—In dogs, the serum-Ca of the renal vein is on an average 5% < that of the carotid. Ablation of the kidneys causes an average elevation of 10% in the serum-Ca. A. L.

Determination of small quantities of iodine in blood. E. N. ALLOTT, J. A. DAUPHINEE, and W. H. HURLEY (Biochem. J., 1932, 26, 1665—1671).—An improved colorimetric and a titrimetric method are described. In the former the blood is dried with KOH at 150° in a Ni basin, ashed at 500°, the ash first extracted with H_2O and then with EtOH. After removing the solvent, the contents are taken up in H_2O , the I is liberated with $NO_2 \cdot SO_3H$, and determined by comparing with standards. It is possible to recover KI added to blood quantitatively. As little as 2×10^{-6} g. of I, added as *p*-iodobenzoic acid, is determined. In the titrimetric method details of the extraction, oxidation to HIO_3 , and titration are given. S. S. Z.

Determination of iodine in blood. E. WIDMANN (Biochem. Z., 1932, 254, 223—228).—The blood, dried at 80°, is ignited at 500—550° in an electric furnace (cf. Schwaibold and Harder, this vol., 102), any I

which is not trapped by KOH being absorbed in CS_2 . Normal human blood contains about 0.032 mg. of I per 100 c.c., but no inorg. I, thyroxine, or di-iodo-tyrosine. W. McC.

Comparative investigation of the iodine content of blood with dry and moist ashing. W. MÖBIUS (Biochem. Z., 1932, 253, 275—278).—Tables show the I contents of the whole blood and serum of a no. of patients, the determinations being carried out by both the Pfeiffer and the Fellenburg methods. The former method always gives results considerably higher than the latter. P. W. C.

Apparatus for micro-determination of blood-cholesterol. R. L. DUTTON (Lancet, 1932, 223, 787—788). L. S. T.

Determination of lipin-phosphorus in blood. A. KARSSSEN and C. R. VAN WERING (Biochem. Z., 1932, 253, 427—430).—Determinations of lipin-P by the Baumann (A., 1924, ii, 58, 498) and Whitehorn (A., 1925 i, 95) methods gave reproducible results with an error of <1%. P. W. C.

Determination of bilirubin in blood-serum. M. PICKENS and L. BAUMAN (J. Lab. Clin. Med., 1932, 17, 820—821).—For clinical determinations a solution of $Fe(CNS)_3$ in Et_2O is used as a standard. CH. ABS.

Urobilin compounds. VII. Artificial urobilinæmia. I. M. OSHIMA (Japan. J. Gastroenterol., 1932, 4, 41—51).—Urobilin injected intravenously into rabbits disappears from the blood within 0.5 hr.; it is converted into urobilinogen and excreted in the bile. Urinary urobilin is affected only by large injections. The liver does not convert bilirubin into urobilin. CH. ABS.

Formation of ammonia in blood. J. HELLER and A. J. KLISZECKI (Biochem. Z., 1932, 253, 300—312).—Two processes are concerned in the formation of NH_3 by sheep's and horse's blood, the first being associated with the serum and the second with the corpuscles, the latter occurring during hæmolysis. The first process yields 0.5 mg. per 100 c.c. of NH_3 -N in 24 hr. at room temp. and in 7—8 hr. at 39° and is inhibited by borate, whilst the second process, which is also inhibited by borate, yields 1.0—1.2 mg. of NH_3 -N per 100 c.c., corresponding closely with the content of adenine nucleotide (25—28 mg. per 100 c.c.). P. W. C.

Van Slyke's method of determination of ketonic substances applied to small volumes of blood and urine. S. H. NANAVUTTY (Biochem. J., 1932, 26, 1391—1396). S. S. Z.

Changes in composition of cow's blood at the time of calving and a comparison of the blood of the calf with that of its dam. W. GODDEN and W. M. ALLCROFT (Biochem. J., 1932, 26, 1640—1646).—There is a rise in the blood-sugar at the time of parturition, followed by a fall to a low level maintained for at least 1 week. Serum-Ca falls either just at or within 24 hr. of calving and returns to normal within 4 or 5 days. A sharp fall in inorg. P just prior to calving invariably indicates the onset of labour. The blood of the calf at birth has higher levels of

blood-sugar, serum-Ca, inorg. P, non-protein-N, and a lower Cl level, than that of its dam. S. S. Z.

Blood-esterase. R. TSUJI (Pflüger's Archiv, 1932, 229, 344—353; Chem. Zentr., 1932, i, 3307).—The decomp. of acetylcholine and the vagus substance is attributed to blood-esterase. Adrenaline *in vitro* arrests the ability of the serum to cause fission of tributyrin and acetylcholine. Adrenaline or choline *in vivo* causes a slight reduction in ester fission. A. A. E.

Loss of mitogenetic radiation by blood (a) on keeping *in vitro*, (b) after irradiation with ultra-violet light. A. M. KARPAS and M. N. LANSCHINA (Biochem. Z., 1932, 253, 313—317).—In hæmolyzed blood after keeping *in vitro* glycolysis occurs and is accompanied by decrease or complete loss of mitogenetic radiation. Irradiation with ultra-violet light is able to replace the effect of the glycolytic enzyme. P. W. C.

Blood glycolysis. I. Sugar and phosphorus relationships during glycolysis in normal blood. II. Blood of infants and children with various diseases. G. M. GUEST (J. Clin. Invest., 1932, 11, 555—569, 571—587).—I. Glycolysis occurs in normal defibrinated blood at 37° at a const. rate (13—16 mg. per 100 c.c. per hr.) until the residual reducing substance is about 20 mg. per 100 c.c. Inorg. P remains const. or falls slightly. When the free sugar has been destroyed, P rises rapidly (at the expense of org. acid-sol. P) to 20—25 mg. per 100 c.c. in the 15th hr. The rise occurs quickly in hypoglycæmic blood following insulin. Addition of glucose or fructose delays the rise.

II. Changes in inorg. P in relation to blood-sugar are markedly altered, especially in gastro-intestinal intoxication and nephritis with acidosis, the P rising immediately. CH. ABS.

Role of hexosephosphoric esters in blood. E. WIDMANN (Biochem. Z., 1932, 254, 221—222).—The incorrectness of the view that hexosephosphoric esters are intermediate products in the glycolysis of hæmolyzed red blood-corpuscles (cf. Roche and Roche, this vol., 956) is established by the author's work (A., 1930, 1312). W. McC.

Effect of arsenate on blood glycolysis. A. E. BRAUNSTEIN (J. Biol. Chem., 1932, 98, 379—384).—Polemical against Morgnliis and Pinto (cf. this vol., 530). W. O. K.

Blood glycolysis. I. Effect of arsenate. S. MORGULIS and S. PINTO (J. Biol. Chem., 1932, 98, 385—387).—A reply (see preceding abstract). W. O. K.

Blood coagulation. II. Influence of antipyretics on blood coagulation and on coagulation components of blood. III. Influence of narcotics. Y. BABASAKI (Folia Pharmacol. Japon., 1932, 14, No. 2, 7—13, 14—19).—II. Antipyrine, pyridone, and Na salicylate retard coagulation and decrease the Ca, thrombin, and fibrinogen. NHAcPh retards coagulation but decreases only Ca.

III. CH₄, chloral hydrate, veronal, luminal, and morphine retard coagulation. The coagulation components are variously affected. CH. ABS.

Regular relation between blood-sugar and -coagulation time. VIII. A. PARTOS (Pflüger's Archiv, 1932, 229, 336—343; Chem. Zentr., 1932, i, 3311).—Stuber and Lang's relation could not be found. The quantity of lactic acid present is not a measure of the glycolysis. A. A. E.

Effect of temperature on hæmolytic systems containing propyl alcohol. A. S. GORDON (J. Exp. Biol., 1932, 9, 336—338).—Arrhenius' equation does not describe the effect of temp. CH. ABS.

Blood effects in the living dog produced by the venom of *Lachesis atrox*. J. VELLARD and M. MIGUELOTE-VIANNA (Ann. Inst. Pasteur, 1932, 49, 445—472).—1 mg. of venom will render 1—2 c.c. of blood incoagulable *in vitro* and it is even more active *in vivo*. Considerable quantities of anti-thrombin are found in the blood soon after the spontaneous coagulation is abolished, and these often persist for 24 hr. after the injection of the venom. This property of the venom is attributed to the action of proteases on the fibrinogen rather than to the antithrombin. During the destruction of the fibrinogen the serum loses its normal hæmolytic power; subsequently it acquires a power > normal by activation of the blood-phosphatides by the venom, and finally it loses all hæmolytic power and becomes strongly anti-complementary. P. G. M.

Heparin and complement formation. H. KOWARZYK (Z. Immunität., 1931, 72, 301—308; Chem. Zentr., 1932, i, 3194).—Addition of heparin inhibits immunohæmolysis, but only at certain concns. of amboceptor; with excess of amboceptor hæmolysis is promoted by heparin. A. A. E.

Determination of proteins by the precipitation reaction. G. L. TAYLOR, G. S. ADAIR, and M. E. ADAIR (J. Hyg., 1932, 32, 340—348).—Cryst. albumin in egg-white and globulin in horse serum were determined, and the results compared with those obtained by other methods. Only antisera prepared against pure proteins (prep. described) should be used. CH. ABS.

Determination of nucleotides in blood and muscle. S. E. KERR and M. E. BLISH (J. Biol. Chem., 1932, 98, 193—205).—The tissue is deproteinised with CCl₃·CO₂H, the filtrate neutralised, and nucleotides are pptd. by UO₂(NO₃)₂ (A., 1923, i, 1255). The ppt. is hydrolysed by 10% H₂SO₄, U is removed by neutralising with 4% NaOH and acidifying with AcOH, and purines are pptd. by Cu(OH)₂, the pptd. material being purified by treatment with NaHSO₃ (cf. A., 1905, ii, 776). The final ppt. is dissolved in 25% HCl and N determined by the Kjeldahl method. Satisfactory results for adenine nucleotide are given for admixtures with adenosine. F. O. H.

Preparation of adenylic and inosic acids. P. OSTERN (Biochem. Z., 1932, 254, 65—70).—Methods by which the acids are obtained in good yield from horse flesh (3.5 g. of adenylic acid and 6 g. of Ba inosate from 10 kg.) are described. W. McC.

Muscle extracts. H. STEUDEL (Z. physiol. Chem., 1932, 211, 253—260).—Neither fish nor ox-flesh of commerce is a suitable source for the prep. of adenylic

acid. $\text{H}_2\text{C}_2\text{O}_4$ was isolated from fresh meat in a yield of 0.14 g. per kg. J. H. B.

Constitution of adenylypyrophosphoric acid. K. LOHMANN (Biochem. Z., 1932, 254, 381—397).—The preps. of adenylypyrophosphoric (I) and of adenylic (II) acids, and also of inosinepyrophosphoric acid (III) from (I) by treatment with HNO_3 are described, the velocity of deamination in the latter case being the same as for (II). Electrotitration of (I) before and after hydrolysis with acid shows that the basicity increases from 4 to 6. The velocities of separation of H_2PO_4 when heated in $N\text{-AcOH}$ at 100° from (I), (III), $\text{H}_4\text{P}_2\text{O}_7$, and HPO_3 are investigated, the velocities with (I) and (III) being approx. the same. Hydrolysis of the nucleoside linking of (I) in 0.1N-HCl at 100° takes place as well as of the H_3PO_4 linking, but more slowly. P. W. C.

Osmotic relations between white and yolk in the hen's egg. J. B. BATEMAN (J. Exp. Biol., 1932, 9, 322—331).—A real osmotic difference exists. The amount of bound H_2O is small in both. Urea dissolves in egg-white and depresses the v.p. Urea and Na lactate, but not glucose, are removed from solution when added to yolk. CH. ABS.

I. Behaviour of proteins on incubation of the hen's egg. II. Production of the proteins of the egg in the hen's ovary and oviduct. III. Keratin of feathers. E. G. SCHENCK (Z. physiol. Chem., 1932, 211, 111—153, 153—160, 160—163).—I. In the various portions of the eggshell, membrane, white, yolk, and embryo, the H_2O , proteins, and constituent NH_2 -acids were determined at various stages of incubation. The changes in composition were followed and a balance was constructed for the total protein, and the amounts of the various components. The composition of the feather-proteins is not const., but follows the changes in the proteins of the embryo.

II. The proteins of the ovaries [globulin (I), albumin (II), nucleoprotein (III)], ripening follicles [(I), (II), (III), vitellin], yolk of the unincubated egg [(I), (II), (III)], oviduct [(I), (II)], and white were determined and compared. From the proteins of the ovaries and oviduct, rich in hexone bases, the yolk-proteins, low in hexone bases, are synthesised, but these again yield proteins rich in hexone bases on incubation.

III. The constituents of the keratin of various types of feathers were determined. The composition depends on that of the tissue from which they are formed. J. H. B.

Specificity of the protein of the pig's alimentary mucous membrane. T. ASAO (J. Biochem. Japan, 1932, 16, 17—47).—The isoelectric point of the protein varies with the position of the mucous membrane, viz., stomach, p_H 4.5—5.3; small intestine, 4.4—5.3; large intestine, 4.1—4.4. Differences also occur in the combination with HCl, NaOH, and Cl', in the permeability to Cl', in the resistance to proteolytic enzymes, and in the chemical constitution. F. O. H.

Cystine and wool production. A. H. H. FRASER and J. A. F. ROBERTS (Nature, 1932, 130, 473).—A

review of available evidence indicates that the cystino (I) content of pasture is too low to be a limiting factor in wool production, that (I) is synthesised in the sheep, and that the content of (I) in wool fibre is not const. (I) may be formed during keratinisation and synthesis of (I) may be a function of the wool follicle itself. L. S. T.

Union of biocolloids. IX. Starch and various proteins. S. BARTUSZEK (Biochem. Z., 1932, 253, 279—287).—The extent of combination of starch with caseinogen is almost independent of p_H between 3.3 and 4.8, is not decreased by addition of salts, and is independent of dilution at p_H 3.3. The union with globulin in absence of salts is detected only on the acid side (up to p_H 5), salts decrease the extent of union at p_H 3.3 and 5 but make union possible at $p_H > 5$, and the union is independent of dilution and non-reversible. Union with albumin is dependent on p_H and is decreased by addition of salts at any p_H ; it is independent of dilution at a $p_H <$ isoelectric point, but is proportional at a $p_H >$ isoelectric point. P. W. C.

Union of biocolloids. X. S. J. PRZYLECKI and W. BIALEK (Biochem. Z., 1932, 253, 288—293).—The equilibrium between glycogen in liver pulp and in solution is investigated by shaking the pulp with solutions of various composition and vol. Samples of liver containing initially 2.68, 4.54, and 8.43%, respectively, of glycogen after treatment with 16 c.c. of solution contained 61.2, 85.6, and 73.8 mg., the concns. of glycogen in the solutions being 0.29, 0.55, and 1.65% and remaining in the pulp 1.53, 2.14, and 1.845%. P. W. C.

Source of amylase in the hen's gizzard. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1932, 253, 383—386).—The mucous membrane of the hen's gizzard is concerned in the formation of amylase. P. W. C.

Variations in the dry weight and iodine content of the thyroid glands of sheep under uniform and varying conditions. M. C. DAWBARN and F. C. FARR (Austral. J. Exp. Biol., 1932, 10, 119—142).—The I content, which varied from 0.096 to 1.26% of the dry wt., is increased under drought conditions, appears to have a seasonal variation, and is not influenced by sex or age (except during the period of growth). Access to I-containing salt-licks leads to only a slight increase in I content. F. O. H.

Chemical assay of thyroid gland. G. MIDDLETON (Analyst, 1932, 57, 603—609; cf. A., 1930, 505).—The previous method is improved by the addition of PhOH in AcOH before the liberation of I. Acid-insol. I is determined directly, after hydrolysis by the method of the B.P. 1932, in the ppt. insol. in acid, using the author's method. T. McL.

Bromine content of the pituitary and its relation to age. H. ZONDER and A. BIER (Klin. Woch., 1932, 11, 759—760; Chem. Zentr., 1932, i, 3192).—The Br content of the human pituitary is normally 15—30 and of other organs 1—2 mg. per 100 g.; the posterior lobe is practically free from Br. In men of 45—60 years the val. is min. (15), whilst in women of the same age it falls to 5. In old age the val. is

low (5) in both sexes, and above 75 years Br is usually undetectable.

A. A. E.

Ether-esters of glycerol, or ether-glycerides of shark-liver oil, *Scymnorhinus lichia*, Bonnat-terre. E. ANDRE and A. BLOCH (Compt. rend., 1932, 195, 627—629).—Chimyl, batyl, and selachyl alcohols do not exist as such in the liver-oil of *S. lichia*. The two remaining OH groups of the glyceryl residue in these alcohols are esterified with fatty acids giving an ether-glyceride. The liver-oil contains hydrocarbons (squalene) 57%, glycerides 21%, and ether-glycerides 21%.

A. C.

Comparison of the body constituents of parasite and host. I. Reserve fat of *Balaninus dentipes*. T. SASAKI (Keijo J. Med., 1932, 3, 184—186).—The fat extracted from the cotyledons of *Castanea pubinervis* closely resembles that from the larvae of *B. dentipes* parasitic on them.

F. O. H.

Nutrition of dermestid beetles. I. Composition and nature of the ether extract of beetles. O. SINODA and M. KURATA (J. Biochem. Japan, 1932, 16, 129—139).—The contents of N and chitin and the nature of the Et₂O extract were investigated in *Dermestes coarctatus* and *D. vulpinus*. The bearing of the data thus obtained on the metabolism of the beetles is discussed.

F. O. H.

Arsenic content of large-mouth black bass (*Micropterus salmoides*, Lacepede) fingerlings. A. H. WIEBE, E. G. GROSS, and D. H. SLAUGHTER (Trans. Amer. Fish. Soc., 1931, 61, 150—163).—Normal domesticated bass contain no As. Vals. for fish from Rock River and the Mississippi and for fish living in As-treated waters are recorded.

CH. ABS.

Structure of dental enamel. IV. Cataphoretic determination of the effects of p_H and electrolytes on the electric charge resident on enamel particles. V. Effects of acidity and alkalinity on the nature of the electric charge resident on particles of tricalcium phosphate. VI. Electroendosmotic determination of the electric charge resident on the enamel pore wall; influence of acidity and alkalinity of the bathing salt solution. VII. Mechanism of production of membrane potentials in the enamel of dogs. VIII. Determination of the isoelectric point of enamel by means of membrane-potential measurements. H. KLEIN (J. Dental Res., 1932, 12, 79—83).

CH. ABS.

Solubility of dental enamel in various buffered solutions. H. C. BENEDICT and F. K. KANTHAK (J. Dental Res., 1932, 12, 277—289).—Dental enamel is more complex than Ca₃(PO₄)₂ (I), but the solubility curves (p_H 2.38—7.80) are similar to those of (I). The enamel is sol. in an alkaline liquid. Saliva is usually saturated with respect to (I).

CH. ABS.

Group-specific substance of horse saliva. K. LANDSTEINER (Science, 1932, 76, 351—352).—An active prep. from horse saliva, obtained by treatment with acid and COMe₂, and fractionation with EtOH, gave a weak biuret reaction and yielded 48.5% of reducing sugar on hydrolysis. A second prep. (ash 3.37%) from saliva adsorbed with kaolin and C

reacted strongly with anti-A immune sera and contained (ash-free) C 44.65, H 6.76, N 7.43%.

L. S. T.

Gastric physiology. Role of duodenal regurgitation in the control of gastric acidity. H. SHAY, A. B. KATZ, and E. M. SCHLOSS (Arch. Int. Med., 1930, 50, 605—620).—Duodenal regurgitation bears no relation to gastric acidity.

H. G. R.

Relation of blood-chlorine to gastric secretion and gastric digestion. I. V. BUCHGALTER (Ark. med. nauk., 1929, 2, 301—309).—Variations are not a measure of gastric function. Atropine, or oral administration of NaCl (10 g.), does not affect blood-Cl.

CH. ABS.

Alteration of stomach chemistry by bromide. T. EPSTEIN (Arch. exp. Path. Pharm., 1932, 168, 57—63).—Br⁻ appeared in the gastric juice of man after oral administration of NaBr. The total and free acid was increased, the p_H was lowered, and the proteolytic action of the juice was greater.

W. O. K.

Influence of the vegetative nervous system on the reaction and buffering power of the bile. T. ITOO (Biochem. Z., 1932, 254, 50—58).—In dogs, section of the splanchnic nerves results in reduced secretion of bile (I) and of bile acids (II) and in reduction of the p_H (III) and alkali reserve (IV) of the bile. If only one of the nerves be cut (I), (II), (III), and (IV) first increase and then decrease to original vals., but are again increased by administration of bile acids. It follows that there is a close relationship between the function of the vegetative nervous system and secretion of (II) in the liver.

W. McC.

Protein constituents and formation of bile acids. L. SCHINDEL (Arch. exp. Path. Pharm., 1932, 168, 38—48).—The excretion of bile acids by dogs with a bile fistula and on a standard diet is increased when protein is administered. Of various NH₂-acids tested, the most active in producing increased secretion of bile acids was aspartic acid. Tryptophan and glucosamine were less active, whilst β -alanine was only slightly active. The effect is probably due to a stimulating action on the liver cells.

W. O. K.

Behaviour of cholesterol and other bile constituents in solutions of bile salts. G. O. SPANNER and L. BAUMAN (J. Biol. Chem., 1932, 98, 181—183).—The solubilities of cholesterol in aq. solutions of Na cholate, glycocholate, taurocholate, anthropeoxycholate, deoxycholate, oleate, and bilirubinate and of lecithin were determined. Dialysis and ultrafiltration indicate that the combination between bile salt and sterol is readily dissociated. The bearing of the results on gallstone formation is discussed.

F. O. H.

Human milk. X. Daily and monthly variations in milk components as observed in two successive lactation periods. B. NIMS, I. G. MACY, H. A. HUNSCHER, and M. BROWN (Amer. J. Dis. Children, 1932, 43, 1062—1076).—The components fluctuate about a level characteristic of the individual and maintained without marked variation

through successive lactation periods. The N decreases rapidly up to the sixth month and then remains const. The total ash and Ca decrease gradually, whilst the P, fat, and total solids decreased during the earlier months, regaining higher vals. during later months. CH. ABS.

Yield and composition of milk with special reference to the influence of climatic conditions and other factors. J. HOUSTON and R. W. HALE (J. Dairy Res., 1932, 3, 294—309).—Correlation data are recorded. The butter-fat yield shows greater variation than that of total milk or of solids-not-fat. The butter-fat and solids-not-fat do not show parallel variation. Solids-not-fat are depressed during the summer months, but seasonal changes in the butter-fat are small. Diurnal changes in the yields of whole milk and of solids-not-fat are independent of temp. A. G. P.

Lactation. I. Variations in properties of milk from individual quarters of a cow. E. O. V. MATTICK and H. S. HALLETT (J. Dairy Res., 1929, 1, 35—49).—In general, the yield, acidity, rennin coagulation time, and fat content varied, milks from the two front quarters being usually similar but differing markedly from milks from the two hind quarters. CH. ABS.

Phosphate fractions of cow's milk and changes in them during spontaneous acidification and during dairy treatment. K. LANG and M. MJETHKE (Biochem. Z., 1932, 254, 484—489).—The distribution of various P fractions of cow's milk (caseinogen-, lipin-inorg., readily and difficultly hydrolysable ester-P) and the behaviour of these fractions during spontaneous acidification, centrifuging, and pasteurising are investigated. None of the usual dairy manipulations seriously affects the P fractions. P. W. C.

Determination of iron in cow's milk and human milk. F. REIS and H. H. CHAKMAKJIAN (J. Biol. Chem., 1932, 98, 237—240; cf. A., 1931, 974).—The Fe content of cow's milk varied from 1.00 to 0.14 mg. per 100 c.c., whilst for human milk the corresponding limits were 0.29 and 0.45 mg. per 100 c.c. W. O. K.

Biochemical activators of milk. I. Relation between reducing power and vitamin-C content of milk. Chemical determination of this content. F. SCHLEMMER, B. BLEYER, and H. CAHN-MANN (Biochem. Z., 1932, 254, 187—207; cf. Tillmans and others, this vol., 658).—The substance (I) in milk which reduces 2:6-dichlorophenolindophenol and can be determined by titration is probably identical with vitamin-C. Great variations (not depending on diet) are found in the amount of (I) in different samples of cow's milk, and the milks of sheep, goats, asses, and camels also differ greatly from each other in this respect. Human milk (especially colostrum) has a higher content of (I) than has cow's milk. Milk kept exposed to air rapidly loses much of its (I), but the loss can be reduced by cooling. Boiling the milk for short periods causes only slight loss. Cu and Ag destroy (I), but Ni, Cr, and Al do not. Chemical and biological examination of milks pasteurised in various ways

indicates that their content of (I) runs parallel with their content of vitamin-C. W. McC.

Antirachitic value of milk from cows fed [with] irradiated yeast. E. T. WYMAN and A. M. BUTLER (Amer. J. Dis. Children, 1932, 43, 1509—1518).—The antirachitic property of the milk is not destroyed by boiling or pasteurisation. CH. ABS.

Influence of vitamins on the lactation of cows. H. POELT (Z. Vitaminforsch., 1932, 1, 289—294).—The feeding of irradiated yeast increases the amount of milk secreted. F. O. H.

Iron and thorium precipitation of biological fluids for sugar and other analyses. A. STEINER, F. URBAN, and E. S. WEST (J. Biol. Chem., 1932, 98, 289—293).—The proteins present in blood, laked blood, cerebrospinal fluid, milk, etc. may be removed by treatment with $\text{Fe}_2(\text{SO}_4)_3$ and BaCO_3 , followed by filtration. The filtrates may be used for determination of sugar. Diluted blood or plasma may be deproteinised by treatment with $\text{Th}(\text{SO}_4)_2$ and BaCO_3 . The filtrates may also be used for creatinine and urea determinations, but the non-protein-N vals. are about 25% < those found in tungstate filtrates. W. O. K.

Effect of urea on glucose determination by the formose reaction. H. W. LARSON (J. Biol. Chem., 1932, 98, 151—156).—The interference by urea in the Kingsbury method for urine-sugar (A., 1927, 1172) is due to the formation of NH_3 . Attempts to inhibit the decomp. of urea by addition of NaCNO and EtOH to the reagent were only partly successful. Thus, whilst the reagent cannot be satisfactorily applied to urine, its use for NH_3 - and urea-free glucose solutions and also for the determination of NH_3 is suggested. F. O. H.

Hippuric acid. I. Determination in urine. II. Determination in blood. III. Permeability to red blood-corpuscles. I. KANZAKI (J. Biochem. Japan, 1932, 16, 105—116, 117—123, 125—128).—I. The protein-free urine (20 c.c.) is acidified with H_2SO_4 , extracted with Et_2O , and the residue after removal of Et_2O washed with petrol to remove BzOH . A hot aq. solution of the residue is then titrated with 0.1N-NaOH.

II. The blood (5—15 c.c.) is deproteinised with H_2WO_4 , and an aliquot of the filtrate freed from lactic acid by KMnO_4 and extracted with Et_2O , the extract being treated as above. Ox blood is practically free from hippuric acid.

III. Hippuric acid is absent from the blood of man, ox, horse, cat, dog, guinea-pig, and rabbit. Oral administration of NaOBz to rabbits is not followed by the presence of hippuric acid in the blood. Rabbit erythrocytes are impermeable to hippurate *in vitro* or injected intravenously. F. O. H.

Direct determination of the titratable acidity of urine: correction for the hydrogen carbonate content. E. E. MARTINSON and N. G. BORODIN (Biochem. Z., 1932, 254, 292—300).—The urine is treated with a known amount of HCl , the CO_2 removed in vac., and the resulting fluid titrated, using a comparator to p_H 7.4 with $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-OH}$

as indicator. On subtracting the amount of HCl a figure is obtained corresponding with the urinary acidity minus H carbonate. Comparison with a control determination without HCl enables the NaHCO_3 content to be calc. P. W. C.

Acid-base equilibrium with inhabitants of the tropics. I. Reaction of the urine, especially of the morning urine, obtained under basal conditions. W. RADSMA, G. M. STREEF, and J. V. KLERKS (Arch. neerland. Physiol., 1932, 17, 444—457).—With Europeans of Batavia, but rarely with the natives, there is a shift of the p_H to the alkaline side in the morning urine and, to a smaller extent, in the night or 24-hr. urine. The change in reaction is accompanied by polyuria. F. O. H.

Relationship between chemical structure and physiological response. III. Factors influencing the excretion of uric acid. A. J. QUICK [with M. A. COOPER] (J. Biol. Chem., 1932, 98, 157—169).—The possibility of a carbohydrate intermediary being essential for the normal excretion of uric acid is discussed. The stimulating action on uric acid elimination of glycerol, AcCO_2H , and various NH_2 -acids is completely inhibited by BzOH and some of its substituted products, and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, i.e., by substances which decrease the excretion of uric acid. The excretion is increased by salicylic acid, cinchophen, neocinchophen, and, to a smaller extent, by $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. Replacement of OH by OMe abolishes the stimulating action of o - and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. The mode of conjugation of these substances is discussed. F. O. H.

Excretion of lead by the kidneys, and the effect thereon of foods and drugs. II. So-called "normal" lead in urine. F. WEYRAUCH and S. LITZNER (Arch. Gewerbepath. Gewerbehyg., 1932, 3, 15—22; Chem. Zentr., 1932, i, 3460).—"Normal" Pb in urine (as found in persons not brought into contact with Pb during their work) is 0.01—0.055 (average 0.02) mg. per litre of 24-hr. urine. A. A. E.

Absorption and excretion of water and salts by the elasmobranch fishes. III. Use of xylose as a measure of the glomerular filtrate in *Squalus acanthias*. R. W. CLARKE and H. W. SMITH (J. Cell. Comp. Physiol., 1932, 1, 131—143).—Xylose excreted by the dogfish is entirely filterable in the plasma and is neither secreted nor reabsorbed by the renal tubules. PO_4''' , Mg'' , and administered creatinine are freely secreted and excretion by filtration is small. The filtered urea is almost entirely reabsorbed from the glomerular filtrate. Thiourea is not so reabsorbed. Secretion of creatinine and possibly of PO_4''' and Mg'' is depressed by phloridzin. A. G. P.

Absorption of mineral constituents of the urine in the avian cloaca. E. KRYSZCZYŃSKI (Bull. Acad. Polonaise, 1931, B, 681—702).—The abs. concns. of Na and Cl and the ratio of these elements to N in the faeces of fasting hens are < those in the urine. Hence any absorption of N compounds in the cloaca must be accompanied by a greater absorption of Na and Cl. Absorption of K, Ca, Mg, and P

is less marked. During starvation absorption of H_2O leads to a urine hypertonic to the blood. F. O. H.

Iron content of normal and calcified aorta. I. H. PAGE and W. MENSCHICK (Arch. path. Anat. Physiol., 1932, 283, 626—630; Chem. Zentr., 1932, ii, 242).—The Fe content is not parallel with the degree of calcification, but the org. P increases with the latter. A. A. E.

Lubricating oils and cancer. J. B. SPEAKMAN and N. H. CHAMBERLAIN (Nature, 1932, 130, 578).—The difficulty experienced in removing mineral oil from wool can be overcome by the addition of polar compounds which reduce the oil- H_2O interfacial tension without increasing adhesion sufficiently to make emulsification difficult. Fatty acids and glycerides are ineffective compared with oleyl alcohol, which brings about ready emulsification in 6% concn. Certain alcohols from lanolin are also effective. Dermatitis and tumours may be due to the difficulty of removing mineral oils from the skin by means of soap solution and the beneficial effect of the addition of lanolin may be due to its emulsifying action. L. S. T.

Lipin content of tumours. M. YASUDA and W. R. BLOOR (J. Clin. Invest., 1932, 11, 677—682).—Malignancy of tumours is associated with larger amounts of neutral fat, cholesterol, and (particularly) phospholipin. CH. ABS.

Changes in the contents of cholesterol and phosphorus compounds of cancer tissue with growth. M. URAMOTO (J. Biochem. Japan, 1932, 16, 69—82).—During the growth of tumours in rats there is an increase in the contents of H_2O , free and combined cholesterol, and inorg. P, whilst those of lipin-, acid-sol. org., and protein-P decrease. The content of N remains practically const., whilst protein is degraded mainly during late growth and then only at the centre of the tumour. F. O. H.

Chemical composition of mouse carcinoma. Effect of varying diet on the composition. B. KELLNER and B. LUSTIG (Biochem. Z., 1932, 254, 214—220).—The content of free and combined carbohydrate of the tumours is affected by the type of diet given, free sugar being found when the diet is rich in carbohydrate. No increase in the lipin content results when the diet is very rich in fat. The type of diet, however, affects the chemical composition of the lipins. W. McC.

Factors affecting the calcium content of the tissues of the carcinoma-susceptible rat. H. C. PITTS and H. R. JOHNSON (Amer. J. Cancer, 1932, 16, 854—862).—Subcutaneous injection of Ca gluconate or parathyroid extract, or administration of small doses of irradiated ergosterol, has no influence on the Ca content of the tissues. Parathyroid extract prevents hypervitaminosis arising from the administration of large doses of irradiated ergosterol. CH. ABS.

Urinary excretion of melanogen by sarcomatous subjects. O. FÜRTH and H. KAUNTZ (Biochem. Z., 1932, 253, 231—238).—The urinary melanogen gives a black FeCl_3 colour, reduces $\text{K}_3\text{Fe}(\text{CN})_6$ strongly and in presence also of FeCl_3

gives Prussian-blue even in great dilutions, does not reduce ammoniacal AgNO_3 , gives a ppt. with $\text{Pb}(\text{OAc})_2$ readily sol. in AcOH , is pptd. from MeOH solution by Et_2O , and is present in the H_2O -sol., EtOH -precipitable Ba salts of the urine. P. W. C.

Proteolysis in tumours. P. RONDONI (Biochem. J., 1932, 26, 1477—1487).—The optimum p_H (4.7) for the proteolytic action of mouse-tumour proteinase on the tumour-proteins varies a little with the age of the tumours. The activity of these enzymes is not > those of some normal organs. Lecithin has a slight and cysteine a more or less pronounced accelerating action on proteolysis. The tumours have a varying content of dipeptidases. Aminopolypeptidases were absent in the one series examined, whilst the livers of the same mice contained them. Treatment of the tumour-bearing mice with lecithin delayed the tumour growth and produced some modification in the enzyme content. S. S. Z.

Metabolism of normal and tumour tissue. VII. Anaerobic conversion of fructose into lactic acid by tumour and adult normal tissues. F. DICKENS and G. D. GREVILLE (Biochem. J., 1932, 26, 1546—1556).—The anaerobic conversion by rat's retina, submaxillary gland, and spleen is negligible and that of kidney and testis is slight. There is a variability amongst tumour tissues in their ability to convert fructose anaerobically, similar to that possessed by embryonic tissues. The velocity of the anaerobic glycolysis and sugar concn. curves as measured in the second hr. during the action of Jensen sarcoma are similar for glucose and fructose. The spontaneous increase in anaerobic fructolysis could not be confirmed with the Jensen sarcoma. S. S. Z.

Phosphorylation in tumour glycolysis. R. WILLHEIM and J. SCHMERLER (Biochem. Z., 1932, 254, 355—363).—In aerobic glycolysis of mouse carcinoma suspended in physiological saline containing sugar and PO_4''' , the inorg. PO_4''' decreases and the PO_4''' readily hydrolysed by acid increases, whilst the reverse is true when glycolysis is inhibited by addition of NaF . P. W. C.

Effect of carotene on glycolytic processes. Blood-glycolysis in cancer. C. WETZLER-LIGETI and R. WILLHEIM (Biochem. Z., 1932, 254, 364—373).—Carotene accelerates yeast fermentation of sugar solutions and glycolysis of defibrinated blood, the acceleration disappearing on addition of KCN . Blood-glycolysis in human cancer is not affected by addition of carotene. P. W. C.

Investigations in enzyme action directed towards the study of the biochemistry of cancer. Activation of pancreatic pro-lipase. D. L. WOODHOUSE (Biochem. J., 1932, 26, 1512—1527).—Gelatin, gum arabic, gum tragacanth, and agar augment the action of lipase in olive oil, but are unable to activate the pro-lipase. Starch, caseinogen, haemoglobin, colloidal ZnS , and a suspension of powdered C have no activating power. On the other hand, a solution of egg-white or colloidal Fe activates the pro-lipase, as also do Pb salts. Na taurocholate has an effect in activating pro-lipase. Pro-lipase from the pancreas is

inert towards cod-liver oil, olive oil, hog lard, and croton oil, but readily decomposes palm oil, chaulmoogra, and coconut oils even when these have been purified. EtOH -pptd. proteins from serum and the remaining residue, as well as that obtained by the pptn. of the serum-proteins by heat, have an activating effect. The activator in the latter case is dialysable. Urine, cerebrospinal and ovarian fluids are potent activators. The serum of cancer patients is just as efficient in activating lipase as is that from normal man and animals. S. S. Z.

[Alleged] inhibitory effect of magnesium salts on the growth of malignant tumours. A. A. ASHOUR (J. Egypt. Med. Assoc., 1932, 15, 740—744).—Egyptian soil contains no excess of Mg and cancer is not abnormally rare in Egypt. Hence the view that excess of Mg in the soil, H_2O , and food-stuffs reduces the incidence of cancer is not supported. W. O. K.

Analysis of teeth, roots, and crowns affected by pyorrhoea alveolaris and dental caries. II. Phosphorus and magnesium. L. I. KAUSHANSKY (Dental Cosmos, 1932, 74, 468—473).— Mg in the entire tooth and the crown is high in pyorrhoea and caries; in the roots it is normal in caries but high in pyorrhoea. In all cases the crowns contain less Mg than the roots. In the entire tooth, crown, and roots the P content falls in the order caries, pyorrhoea, normal. CH. ABS.

Phosphorus metabolism. IV. Phosphorus of saliva with special reference to dental caries. G. E. YOUNGBURG (J. Dental Res., 1932, 12, 267—275).—Normally, and in nephritis and dental caries, 96% of the saliva- P is present as inorg. PO_4''' , the rest being combined with mucin. Vals. of inorg. P are: normal 17.50, nephritis 17.54, dental caries 18.13 mg. per 100 c.c.; apparently it plays no part in dental caries, increases slightly with age, and varies appreciably during the day and from day to day. CH. ABS.

Vitamin factor in dental caries. W. A. OSBORNE (Nature, 1932, 130, 630).—A discussion. The high incidence of caries in Australia indicates that the vitamin factor in the production of caries is unduly emphasised. L. S. T.

Significance of urinary "proteose" in idiopathic epilepsy. R. L. H. MINCHIN (Brit. Med. J., 1932, ii, 97—98).—The "proteose" isolated from the urine of epileptics (cf. Lancet, 1930, ii, 231) gives negative Millon, biuret, and xanthoproteic reactions and is of no marked significance in the production of fits. F. O. H.

Plasma-phosphatase in dairy cows suffering from fluorosis. P. H. PHILLIPS (Science, 1932, 76, 239—240).—The plasma-phosphatase increases practically in proportion to the level of F intake; it appears to be a good index of the degree of fluorosis in cattle. L. S. T.

Variations in the iodine content of the blood in hyperthyroidism and non-toxic goitre. E. C. DODDS, W. LAWSON, and J. D. ROBERTSON (Lancet, 1932, 223, 608—611).—Blood- I can be separated into two fractions by EtOH -extraction (cf. A., 1929,

595). The insol. fraction is increased in cases of toxic goitre and may be reduced by oral treatment with I. This fall is not necessarily associated with a reduction in the toxicity and the basal metabolic rate; the EtOH-insol. fraction is not a measure of the toxic secretion of the thyroid. L. S. T.

Mineral alkalinity and iodine content of goitrous tissue. M. SAEGESSER (Biochem. Z., 1932, 254, 475—478).—Simultaneous determinations are made of the EtOH-sol. and -insol. fractions of thyroid tissue in cases of goitre and unsuccessful attempts made to correlate them with the ash alkalinity and the Ca and P contents. P. W. C.

Calcium carbonate gallstones and calcification of the gall bladder following cystic-duct obstruction. D. B. PHEMISTER, A. G. REWBRIDGE, and H. RUDSILL (Ann. Surg., 1931, 94, 493—576).—Obstruction by gallstones leads to deposition of CaCO_3 in the gall bladder and on the stones. CH. ABS.

Blood-lactic acid in hepatic disease. A. M. SNELL and G. M. ROTH (Proc. Staff Mtgs. Mayo Clinic, 1932, 7, 288—289).—Abnormally large increases are reported. CH. ABS.

Bilirubin. VII. So-called direct and indirect diazo-reactions and their application to the determination of bilirubin. W. KERPPOLA and E. LEIKOLA (Acta med. Scand., 1931, 76, 479—490; Chem. Zentr., 1932, i, 2980).—The "direct reaction," as given in sera of static icterus, indicates the presence of alkali-bilirubin. Bilirubin in 0.1N- Na_2CO_3 is immediately coloured pink by the reagent, and brown on further addition. A. A. E.

Inflammation. VIII. Inhibition of fixation by urea. Mechanism of fixation by the inflammatory reaction. V. MENKIN (J. Exp. Med., 1932, 56, 157—172).—A conc. solution of urea dissolves fibrin. Injection into the peritoneal cavity of urea solution with or after an inflammatory irritant partly or wholly prevents local fixation of foreign substances introduced subsequently, this fixation being primarily due to mechanical obstruction caused by a fibrin network and thrombosed lymphatics. CH. ABS.

Ketosis. II. Comparative ketolytic action of glucose, galactose, fructose, and sucrose. H. J. DEUEL, jun., M. GULICK, and J. S. BUTTS (J. Biol. Chem., 1932, 98, 333—351).—In man with ketosis induced either by fasting or by an exclusive protein-fat diet, the acetoneuria is more efficiently reduced by administration of galactose (I) than by an equal quantity of glucose (II). The protein-sparing action is also greater in the case of (I) than of (II). Sucrose and fructose appear to be intermediate in anti-ketogenic activity between (I) and (II). W. O. K.

Excretion of carbohydrate in urine in diseases other than diabetes. Relation of the excretion to the carbohydrate of blood. B. LUSTIG and M. LOBL (Biochem. Z., 1932, 254, 208—213).—The amount of carbohydrate excreted in human urine does not vary greatly with varying pathological conditions (apart from those of diabetes). It is affected by the type of food consumed and by individual factors, but not by body temp. (fever). No

relationship can be traced between the carbohydrate content of the blood of diseased persons and that of their urine. W. McC.

Electrolyte distribution and the acid-base equilibrium in the serum in cases of nephritis and nephritic acidosis. C. H. GREENE, E. G. WAKEFIELD, M. H. POWER, and N. M. KEITH (Biochem. J., 1932, 26, 1377—1382).—In some cases there was a reduction in total base. Ca was reduced in several cases, usually associated in part with reduction in the serum-proteins and perhaps in part with the retention of PO_4''' and SO_4'' . There was no accumulation of undetermined org. acids. Cl' was normal in the majority of cases. There was an accumulation of PO_4''' and SO_4'' , which play an appreciable part in the production of acidosis. The changes in HCO_3' depend on the balance between the opposing effects of loss of Cl' on the one hand and the loss of base and retention of PO_4''' and SO_4'' on the other. Usually the HCO_3' is decreased. S. S. Z.

Mechanism of nephrotic cedema. R. F. LOEB, D. W. ATCHLEY, D. W. RICHARDS, jun., E. M. BENEDICT, and M. E. DRISCOLL (J. Clin. Invest., 1932, 11, 621—639).—Quant. differences between normal and nephrotic patients regarding excretion etc. following ingestion of KCl, NH_4Cl , and NaCl are recorded. CH. ABS.

Kidney weight, body size, and renal function. E. M. MACKAY (Arch. Int. Med., 1932, 50, 590—594).—In man renal function, as measured by the ratio urinary urea rate: blood-urea concn., and kidney wt. are both directly proportional to the body surface. H. G. R.

Urea clearance test as an index of renal function. III. Bright's disease. IV. Urea clearance test in relation to other tests of renal function. M. BRUGER and H. O. MOSENTHAL (Arch. Int. Med., 1932, 50, 544—555, 556—568).—III. A clearance val. > 75% of normal usually indicates no impairment of renal function, whilst vals. < 50% always imply decreased renal efficiency. In Bright's disease with definite impairment of renal function, moderate exercise is without influence on the urea clearance.

IV. The test usually demonstrates impairment of renal function before the urea, uric acid, or creatinine is increased in the blood, although occasionally cases of early renal insufficiency may show an elevation of blood-uric acid first. H. G. R.

Phosphatide-fatty degeneration of brain, liver, and spleen in Niemann-Pick disease. II. E. EPSTEIN and K. LORENZ (Z. physiol. Chem., 1932, 211, 217—230; cf. A., 1931, 115).—Various constituents of the brain, liver, and spleen in a case of Niemann-Pick disease were determined. The liver showed a heavy accumulation of Et_2O -sol. as compared with EtOH-sol. lipins. Extracted N and P were particularly augmented. The liver showed the highest % of lecithin. The free cholesterol: cholesteryl ester ratios for brain and liver were 19:1 and 64:1, respectively, the normal vals. being 1:56:1 and 3:6:1. This total phosphatide content of liver and spleen was about 10 times the normal. J. H. B.

Cerebrospinal fluid in paralysis. K. TAKENO (Arb. Med. Univ. Okayama, 1932, 3, 31—36).—Albumin and globulin increase and, as indicated by N content, their constitutions differ from those of the serum constituents. In paralytic cerebrospinal fluid N is high; purine-N is 13.15%. CH. ABS.

Mineral metabolism during pregnancy and lactation. II. K. U. TOVERDD and G. TOVERUD (Biochem. J., 1932, 26, 1424—1434).—The clinical appearance of two puppies each with Ca and P deficiencies during foetal life and during the lactation period, but one receiving cod-liver oil and the other deprived of it after weaning, was the same. There was a lowering of Ca, P, and Mg in both cases. The histological examination showed, however, that the animal not receiving cod-liver oil was rachitic.

S. S. Z.

Acid-base equilibrium in abnormal pregnancy. D. M. KYDD, H. C. OARD, and J. P. PETERS (J. Biol. Chem., 1932, 98, 241—251).—In six cases of eclampsia, there occurs, as compared with normal pregnancy, a considerable lowering of CO_2 of the blood, accompanied by an elevation of the total base, Cl' , and undetermined acids of the serum, whilst the proteins are reduced during convulsions. The acidosis is probably the effect, rather than the cause, of convulsions. In six cases of vomiting of pregnancy, blood-cell vol. and serum-protein content were high, the CO_2 content was low, and the undetermined acids were increased. Cl' was either normal or low, and the p_{H} was unchanged. The amount of HCl in the vomitus was < the total base and never contained free HCl. In oedematous patients with impaired kidney function, the serum-protein content was reduced as compared with normal pregnancy, whilst the other results showed no significant change.

W. O. K.

Acid-base balance disturbance of pregnancy. V. C. MYERS, E. MUNTWYLER, and A. H. BILL (J. Biol. Chem., 1932, 98, 253—260).—Polemical against Kydd *et al.* (preceding abstract). The decrease in blood- CO_2 content during normal pregnancy is probably caused primarily by hyperventilation.

Alleged alkalosis in pregnancy. D. M. KYDD and J. P. PETERS (J. Biol. Chem., 1932, 98, 261—266).—Polemical against Myers *et al.* (preceding abstract).

W. O. K.

Alleged alkalosis in pregnancy. V. C. MYERS, E. MUNTWYLER, and A. H. BILL (J. Biol. Chem., 1932, 98, 267—268).—A reply.

W. O. K.

Early acidosis in acute eclamptic nephritis and the concentration and dissociation constants of the acids produced. K. HOESCH (Zentr. inn. Med., 1932, 53, 484—490; Chem. Zentr., 1932, i, 3312).—Up to about 25% of the acid is lactic; only small amounts of fatty acids are concerned, whilst P_2O_5 , AcOH, and hydroxybutyric acid do not take part. Possibly the increase in acidity is due to aromatic OH-acids.

A. A. E.

[H⁺] of blood of psychotics. R. H. HURST (Biochem. J., 1932, 26, 1536—1541).—There is no significant difference between the p_{H} of arterial

and venous blood of schizophrenics and of normal subjects, whether in the resting condition or in the early stages after alkali ingestion. As a result of exercise the schizophrenic has a blood- p_{H} < that of the normal for a given lactic acid content. S. S. Z.

Rickets in rats. XIII. Effect of various levels and ratios of calcium to phosphorus in the diet on the production of rickets. XIV. A diet which demonstrates the effect of the acid-base content on the production of rickets and also causes idiopathic tetany. H. B. BROWN, A. T. SNOHL, E. E. CHAPMAN, C. S. ROSE, and E. M. SHURWEN (J. Biol. Chem., 1932, 98, 207—214, 215—224).—XIII. With a const. ratio of Ca : P, a diet deficient in vitamin-D becomes decreasingly rachitogenic as the salt content is raised. At a given level of Ca (or P) rickets becomes increasingly severe as the ratio Ca : P increases, until the ratio exceeds 12 : 1, when the opposite occurs and the animals fail to gain wt. and die early. In all cases the blood-Ca is 10—11 mg. per 100 c.c., whilst the inorg. serum-P decreases as Ca : P increases for every level of Ca in the diet, and with const. Ca : P the serum-P increases with increase in the total salt. The rachitogenic properties of most of the standard diets may be correlated with the above findings.

XIV. In a series of diets deficient in vitamin-B, the rachitogenic effect is more marked with an acid than with a neutral or basic diet when the Ca : P ratio is kept const. When this ratio was 2.5, only rats on the acid diet developed mild rickets, whilst when it was 4.0 all diets produced severe rickets. The acid-base content of a diet is therefore a distinct although secondary factor in its power of producing rickets, the Ca : P ratio being more important. Evidence of latent idiopathic tetany was found in rats with mild healing rickets.

W. O. K.

Phosphatase content of the cartilage of normal and rachitic rats. W. FABISCH (Biochem. Z., 1932, 254, 158—169).—Examination of the rates of hydrolysis of Na glycerophosphate and Na hexosediphosphate by preps. of the cartilage from normal and rachitic rats and from rats recovering from rickets after administration of irradiated ergosterol shows that the phosphatase content of the cartilage is the same in all cases.

W. McC.

Iodine in cod-liver oil. F. E. CHIDESTER, A. L. ASHWORTH, G. A. ASHWORTH, and I. A. WILES (Nature, 1932, 130, 544—545).—The I in cod-liver oil appears to play an important role in the prevention of rickets.

L. S. T.

Blood-lipase, -diastase, and -esterase in multiple sclerosis. L. A. CRANDALL, jun., and I. S. CHERRY (Arch. Neurol. Psych., 1932, 27, 367—374).—A lipase capable of splitting olive oil appeared in 78% of cases of multiple sclerosis, 80% of cases of liver disease, and 7.6% cases of other disease. High diastase vals. were found in 47.6, 75, and 8.3% (controls), respectively. Blood-esterase showed no significant changes.

CH. ABS.

Basal metabolism of Australian aborigines. H. S. H. WARDLAW and W. J. LAWRENCE (Austral. J. Exp. Biol., 1932, 10, 157—165).

Bioluminescence. I, II. K. HAYASI and M. OKUYAMA (Okayama Igakkai-Zasshi, 1929, 41, 185—187, 270—272).—The effects of various treatments on the luminescence of the luminescing organ of the firefly were studied. Luminescence disappears at a partial O_2 pressure < 0.025 atm., increasing proportionally to the partial pressure up to 1 atm., and being max. at 15 atm. CO and HCN have no effect. O_2 is also necessary for, and HCN has no effect on, the luminescing gland of *Cypridina hilgendorfi*, Muller; this active substance is not a fat or a lipid, but is partly conc. by fractional pptn. with EtOH. The luminescence reaction does not belong to the peroxidase or glutathione systems. Acids and alkalis prevent luminescence of the luminescent bacteria of the sword fish; again HCN has no effect.

CH. ABS.

Effect on tissue respiration of salts of organic acids. B. KISCH (Biochem. Z., 1932, 253, 347—372).—The respiration of various tissues of ox, pig, dog, cat, and rat shows a small increase (20—30%) on addition of salts of the lower fatty acids, the increase being greater with the straight- than with the corresponding branched-chain acids. HCO_2Na is inactive. $OH\cdot CHMe\cdot CO_2H$ and $AcCO_2H$ with most tissues have little effect, but with heart muscle and retina cause a large increase (+100% to 500%), the latter acid being more effective. The respiration of normal kidney tissue is inhibited by 0.02—0.01M-pyruvate. Glucose exerts its greatest action on the respiration of heart and striated muscle and on the retina.

P. W. C.

Effect of methylglyoxal on tissue respiration. B. KISCH (Biochem. Z., 1932, 253, 373—376).—The respiration of kidney, retina, diaphragm, liver, and Jensen sarcoma is considerably inhibited by high concns. of $AcCHO$ and is either little affected or slightly increased by low concns. The inhibition is greatest with kidney tissue. The respiration only of heart tissue is increased by 0.01M- $AcCHO$ (30—160%).

P. W. C.

Optimum p_H for the respiration of various tissues. B. KISCH (Biochem. Z., 1932, 253, 377—378).—A table summarises the Q_{O_2} vals. in Ringer's solution for diaphragm, heart, liver, kidney, retina, and tumour tissue of rat, ox, dog, and cat. The optimal p_H of respiration was the same for different tissues of the same animal, with rats at p_H 7.2—7.5, ox 7.2, and cat 7.5—7.8.

P. W. C.

Influence of the salts of organic acids on the respiration of tumours. II. B. KISCH (Biochem. Z., 1932, 253, 379—382).—The respiration of Jensen sarcoma, in contrast with normal, tissue is not increased by salts of fatty acids. With lactate the respiration of fresh tissue is unaffected, but of older tissue is increased. It is also increased by pyruvate. The respiration of the tissue in Ringer's solution falls away more quickly than in this solution containing lactate or pyruvate.

P. W. C.

Energy changes and exchange of phosphoric acid esters in muscle extract. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1932, 253, 431—461).—The heat of hydrolysis of creatinephosphoric acid is 12,000 g.-cal. per mol. and of adenylypyrophosphoric

acid 33,000 g.-cal. per mol. (8000 g.-cal. for separation of NH_3 and 25,000 g.-cal. for hydrolysis of $H_4P_2O_7$). Addition of adenyly- and inosine-pyrophosphoric acid to inactive extracts results in phosphagen synthesis; addition of adenylic acid causes synthesis of adenylypyrophosphate. Examples of the energy exchanges involved in these processes are given and discussed.

P. W. C.

(a) Energy exchange of the kidney. (b) Pharmacological effects on the rate of perfusion and of the energy exchange of the kidney. H. GLASER, D. LASLO, and A. SCHURMEYER (Arch. exp. Path. Pharm., 1932, 168, 139—161, 175—189).—(a) In the dog the energy exchange of the kidneys is usually between 5% and 10% of that of the whole animal, but may exceptionally amount to $> 20\%$. Only about 1% of the energy exchange of the kidney is required to carry out the osmotic work performed in the formation of urine from the blood, and the O_2 consumption does not, in fact, bear any relation to this osmotic work. The same kidney shows marked and unaccountable variations. Intravenous administration of hypertonic $NaCl$, Na_2SO_4 , NH_4Cl , $(NH_4)_2CO_3$, and acid phosphate produces an increase in O_2 consumption not apparently directly related to the effect on secretory activity. The R.Q. tends to rise with a fall in the total metabolism.

(b) When hypertonic $NaCl$ or glucose is administered to a dog the blood-flow through the kidney increases, but the O_2 consumption of the organ does not increase proportionately. The smaller increase in blood-flow which is produced by NH_4Cl and Na_2SO_4 is accompanied by a more than proportionate rise in O_2 consumption. Cantharides or $HgCl_2$ reduces the blood-flow, the reduction in O_2 consumption being less in proportion. Glucose raises the perfusion rate of the poisoned kidney practically to the normal and the O_2 consumption simultaneously increases. With adrenaline the blood-flow is reduced, but the effect on the O_2 consumption is inconst., as it sometimes remains unaltered and sometimes falls.

W. O. K.

Influence of halogen salts on tissue metabolism. I. Influence of sodium halides on the respiration and glycolysis of kidney tissue. R. IWATSURU, N. HOSODA, and Y. NAKAI (Biochem. Z., 1932, 254, 301—321).—The effect of gradual replacement of the $NaCl$ of Ringer's solution by $NaBr$, NaI , and NaF on tissue metabolism is investigated. Br^- accelerates respiration and inhibits glycolysis. Mean replacement by NaI leads to an increase, min. and complete replacement to a decrease, of respiration. Min. replacement by $NaBr$ accelerates, and mean or complete replacement inhibits, glycolysis. NaF in min. concn. accelerates respiration and increases glycolysis and in greater concn. decreases respiration and completely inhibits glycolysis.

P. W. C.

Differences of oxidation and reduction properties of tissues with sex. II. S. KAGIYAMA (J. Biochem. Japan, 1932, 16, 99—104).—The oxidative power of rabbit skeletal muscle, as indicated by the O_2 consumption and the distribution of oxidase granules in the fibres, is greater in the male than in the female.

F. O. H.

Effect of dietary deficiencies on phospholipin metabolism. B. R. MONAGHAN (J. Biol. Chem., 1932, 98, 21—33).—A decrease in the rate of growth of rats due to any type of dietary deficiency is accompanied by a decrease in the phospholipin content of the tissues, the degree of unsaturation remaining unchanged. Whilst the results uphold the conception of phospholipins acting as intermediaries in fat metabolism, no support is given to the theory representing them as indispensable constituents of the protoplasm. F. O. H.

Ergosterol resorption in the laying hen. R. SCHONHEIMER and H. DAM (Z. physiol. Chem., 1932, 211, 241—245).—The eggs of hens receiving 50 mg. of ergosterol daily showed an increase of 0.15 mg. (50%) in the ergosterol content of the yolk. J. H. B.

Resorption of unirradiated ergosterol. Determination of ergosterol. W. MENSCHICK and I. H. PAGE (Z. physiol. Chem., 1932, 211, 246—252).—An improvement in the method of ergosterol determination, whereby amounts $> 0.1\%$ can be determined with an error $> 20\%$, is described. The feeding of ergosterol to hens increases the ergosterol content of the eggs by 40—50%, beginning on the 4th day after commencement of the dose. J. H. B.

Effect of bile acids on carbohydrate metabolism. XIX. Synthesis of glycogen by the liver after administration of phosphates of different p_H values. S. FUJITA (Arb. Med. Univ. Okayama, 1932, 3, 154—162).—Parenteral or oral administration of phosphates of p_H 7.504 increases the synthesis of glycogen from glucose by the liver. It is further increased by cholic acid so long as the p_H of the phosphates is below 8.054; above this val. the synthesis by cholic acid decreases. The corresponding increase and decrease vary with the mode of administration of the phosphates. CH. ABS.

Pentose metabolism. I. Rate of absorption of *d*-xylose and formation of glycogen in the organism of the white rat after oral administration of *d*-xylose. II. Pentose content of tissues after oral administration of *d*-xylose. M. M. MILLER and H. B. LEWIS (J. Biol. Chem., 1932, 98, 133—140, 141—150).—I. Xylose was absorbed from the gastrointestinal tract more slowly than glucose (cf. A., 1926, 429). Over a 3-hr. period the rate of absorption of xylose increased. Absence of liver-glycogenesis indicated that xylose, unlike glucose, is not utilised.

II. The tissues were deproteinised with $\text{CCl}_3\text{CO}_2\text{H}$ and pentoses determined in the filtrates (A., 1926, 1283). The contents of the liver, kidney, and blood, but not that of the muscle, were increased, whilst no change occurred in the content of reducing substances other than pentoses in any tissue. Oral administration of glucose had no effect on the pentose content of the tissues investigated. F. O. H.

Liver-glycogen and excretion of nitrogen in the fasting dog after administration of xylose. H. MAGENDANTZ (Biochem. Z., 1932, 254, 170—175).—Xylose (20—25 g. per day), administered to fasting dogs, is not converted into glycogen in the

liver, but leads to decrease in the amount of N excreted, and hence to reduction in the amount of protein degraded in the organism. W. McC.

Lactose in nutrition. O. L. KLINE, J. A. KEENAN, C. A. ELVEHEIM, and E. B. HART (J. Biol. Chem., 1932, 98, 121—131).—Addition of lactose, but not of maltose or of citric acid, to a basal rachitic diet increases the absorption of Ca, bone formation, and acidity of the intestinal tract in young chicks; growth, however, is subnormal. These beneficial effects of lactose are enhanced by addition of vitamin-D to the diet, whilst the rate of growth is improved. F. O. H.

Effect of disappearance of sexual activity on creatine metabolism. F. LASCH (Z. ges. exp. Med., 1932, 81, 314—320; Chem. Zentr., 1932, i, 3455).—In the child excretion of injected creatine is quant., whilst in the senile it is partial. In aged persons the blood-creatinine is normal, but the total creatinine (creatinine + creatinine) is lower than in middle age. A. A. E.

Tryptophan metabolism. III. Rate of absorption of *l*- and *dl*-tryptophan and tryptophan derivatives from the gastrointestinal tract of the rat. C. P. BERG and L. C. BAUGUEN (J. Biol. Chem., 1932, 98, 171—180).—The rates of absorption observed gave the following descending order: acetyl-*dl*-tryptophan, acetyl-*l*-tryptophan, *l*-tryptophan, *dl*-tryptophan, *dl*-tryptophan Et ester, and *l*-tryptophan Et ester. No enzymic destruction of the Ac derivatives occurs prior to absorption. F. O. H.

Influence of relative vitamin value of milk on growth, digestion, and nitrogen and mineral metabolism in calves. E. G. SVESHNIKOVA (Zap. Leningrad Selsk. Choz. Inst., 1929, 7, 120—142).—Addition of cod-liver oil to the ration increases the vitamin-D content of the milk, but reduces the fat content; it depresses the utilisation of the fat in the feed. The vitamin content of the milk did not affect the rate of digestion or the N or mineral metabolism of calves. CH. ABS.

Nutritional requirements of trout and composition of the entire trout body. C. M. MCCAY, A. TUNISON, M. CROWELL, D. K. TRESSLER, S. P. MACDONALD, J. W. TITCOMB, and E. W. COBB (Trans. Amer. Fish. Soc., 1931, 61, 58—82).—The min. protein requirement is $> 14\%$ of the total cal. Administration of CaCO_3 , bone meal, and NaCl is advantageous; trout fed low protein levels supplemented with inorg. mixtures grow more rapidly, but die sooner, than controls. Factor H is destroyed when dry diets are stored in air. Analyses of variously fed trout were performed. Trout secure sufficient Ca for bone formation from meat diets rich in P and poor in Ca. CH. ABS.

Acid-base metabolism of a normal child on diets that increase in fat content. C. A. WEYMULLER and S. RATNER (Amer. J. Dis. Children, 1932, 43, 1092—1100).—The blood of a normal boy maintained on a ketogenic diet shows a fall in p_H and HCO_3^- , a rise in Cl, and the appearance of ketone substances = 5.7 c.c. of 0.1N- β -hydroxybutyric acid.

The excretion of PO_4 , Cl, SO_4 , and total fixed acid and base was increased. Approx. 82% of the org. acids in the urine was present as ketonic substances.

Ch. Abs.

Relative values of meals from oily and white fish for growth and calcification. J. C. KERNOT and N. E. SPEER (Biochem. J., 1932, 26, 1435—1440).—Fat-free meal prepared from oily fish induces better growth in rats than white fish meal. It also promotes better calcification of the bones. S. S. Z.

Influence of bile acids on calcium metabolism. V. Faecal calcium and phosphoric acid during administration of bile acids and adrenaline to normal and splanchnicotomised dogs. I. OKII (J. Biochem. Japan, 1932, 16, 217—235).—Administration of cholic acid decreases whilst that of adrenaline increases the faecal Ca and PO_4 of normal dogs. Splanchnicotomy also produces a decrease but weakens the action both of adrenaline and of cholic acid, which, in this connexion, are therefore related to the autonomic nervous system.

F. O. H.

Urinary excretion of inorganic phosphate in fasting with particular reference to the effect of exercise. A. G. MULDER, I. E. PHILLIPS, and M. B. VISSCHER (J. Biol. Chem., 1932, 98, 269—279).—During fasting, the urinary excretion of P usually increases during the first few days, the total P excretion exceeding that attributable to the protein metabolised. Exercise during fasting results in an initial rise in P excretion, followed by a fall so low as to reduce the total P excretion during a 4-hr. period of exercise to < the resting level.

W. O. K.

Oestrous cycle in rats on a manganese-free diet. E. R. ORENT and E. V. MCCOLLUM (J. Biol. Chem., 1932, 98, 101—102).—Rats fed on a Mn-free diet or on cow's milk supplemented with Cu and Fe exhibit normal oestrous cycles. Growth on the milk diet is below normal, a deficiency corrected by the addition of 0.5 mg. of Mn per 100 c.c.

F. O. H.

Significance of iron in the diet. III. F. REIMANN and F. FRITSCH (Z. klin. Med., 1932, 120, 16—39; Chem. Zentr., 1932, ii, 83).—Treatment with Fe-rich food (liver) alleviates Fe-sensitive anaemia. There is no important difference between food-Fe and FeCl_2 . The food-Fe is converted into Fe^{II} in the gastro-intestinal canal, chiefly in the stomach with the aid of HCl and enzymes. Only 25—33% of the total food-Fe is so converted, and only Fe^{II} can be resorbed.

A. A. E.

Action of Ferrum reductum. II. F. REIMANN and F. FRITSCH (Z. klin. Med., 1931, 117, 304—320; Chem. Zentr., 1932, i, 3197—3198).— Fe^{II} compounds are formed (chiefly by the HCl) in the gastro-intestinal canal and resorbed. The amount of FeCl_2 formed cannot be calc. from the HCl secreted and Fe administered, since large quantities of Fe accelerate dissolution. Therapeutically active quantities of Fe^{II} are also formed in the intestine. Peroral administration of Fe can be replaced by that of Fe^{II} compounds. The quantity of Fe^{II} compounds formed from Fe depends on the velocity of passage through

the stomach and intestine, as well as on the gastric acidity.

A. A. E.

Iron deficiency. H. NAKAMURA (Keijo J. Med., 1932, 3, 230—249).—Methods for the prep. of Fe-free food materials are described. Mice on a diet with cod-liver oil or butter-fat as the sole source of vitamins and containing Fe survive 1—2 weeks longer than those on a similar but Fe-free diet.

F. O. H.

Action of copper in iron metabolism. C. A. ELVEHJEM and W. C. SHERMAN (J. Biol. Chem., 1932, 98, 309—319).—The addition of pure Fe to the milk diet of anaemic rats has no effect on haemoglobin, but increases the total Fe content of the liver from vals. as low as 0.1 mg. up to 1.0 mg. per 1 g. of dry tissue, whilst the Fe content of the spleen is also increased. Inorg. Fe is stored in the liver more efficiently than is org. Fe in the form of haematin. When the Fe is replaced by Cu, blood regeneration takes place, and the Fe content of the liver, but not of the spleen, decreases. When Cu as well as Fe is added to the diet, increase in haemoglobin takes place, and no increase in the Fe content of the liver is observed, until the Fe intake exceeds 0.3 mg. per day.

W. O. K.

Body desiccation. T. TAKAI (J. Biochem. Japan, 1932, 16, 49—68).—Rats fed on a diet containing excess protein and deficient in salts suffer a greater loss in body-wt. on withdrawal of H_2O than rats on a normal diet. A diet rich in fats tends to prolong life on a H_2O -free diet. With desiccation the oxidase activity and the cysteine, pyrophosphate, and hexosephosphate contents of the tissue decrease, whilst the phosphagen and inorg. PO_4 levels are unchanged.

F. O. H.

Role of fat in development of the chicken. B. KONOPACKA (Bull. Acad. Polonaise, 1931, B, 643—648).—Development of the hen's egg in the ovary and through successive stages of the embryo up to hatching has been studied by the application of microchemical staining methods.

H. G. R.

Development of silkworm eggs. A. AKAO (Keijo J. Med., 1932, 3, 250—261).—Variations in the total wt. and in the content of protein, sugar, total P, cholesterol, phosphatide, and total, non-protein-, purine-, and chitin-N of the eggs, incubated at 25°, were determined and correlated with morphological changes in the embryo.

F. O. H.

Phosphorus metabolism in embryonic life. II. Phosphagen in cephalopod development. J. NEEDHAM, D. M. NEEDHAM, J. VUDKIN, and E. BALDWIN (J. Exp. Biol., 1932, 9, 212—221).—The embryo, but not the yolk, of *Sepia* contains arginine phosphate (max. after 86 days). The inorg. P rises continuously throughout development.

Ch. Abs.

Effect of soap solutions and of varying hydrogen-ion concentration on cell growth in tissue cultures. J. MANGER and A. HOOK (Biochem. Z., 1932, 254, 176—180).—At p_H 5.7, 7.21, and 7.58 the growth of the cells in cultures of embryonic chicken hearts is accelerated by addition of Na oleate, but at p_H 7.94 the salt inhibits the growth. Smallest growth occurs in a neutral medium and

greatest (on the third day) in alkaline medium (p_H 7.94). Growth is also increased, although to a smaller extent, by acid medium (p_H 5.7), especially on the second and third days. W. McC.

Utilisation of proteoses by chicken heart fibroblasts growing *in vitro*. E. N. WILLMER and L. P. KENDAL (J. Exp. Biol., 1932, 9, 149—178).—The presence of plasma, possibly to supply enzymes producing NH_2 -acids, is necessary. A thermolabile substance isolated from Witte's peptone and fibrin digests stimulates the activity and division of cells. CH. ABS.

[Pharmacological] action of derivatives of choline. A. SIMONART (J. Pharm. Exp. Ther., 1932, 46, 157—193).—The muscarine-like action, the contracting action on denervated muscle, and the nicotine action on the blood-pressure of the following derivatives of choline are studied: Ac, Pr, and Bu esters, Me, Et, vinyl, and Bu ethers, α - and β -methylcholine, acetyl- and propyl- α - and β -methylcholine, and β -methylcholine Et ether. Of these, acetyl- β -methylcholine has the greatest clinical usefulness, being more stable than, and as potent as, acetylcholine in lowering the blood-pressure, and having no nicotine-like action on the circulation. A. L.

Action of urine in lowering the blood-pressure. A. BAUER (Arch. exp. Path. Pharm., 1932, 168, 111—120).—Urine contains a depressor substance which is stable to heat and is dialysable and is therefore not identical with "callicrein" (I) (cf. A., 1930, 1069). Its possible relationship to various depressor substances is discussed. (I) could not be detected in plasma. W. O. K.

Complex compound of aminopyrin with strontium sulphosalicylate. H. BERNING (Arch. exp. Path. Pharm., 1932, 168, 206—216).—The compound, $C_4H_4O_6SSr \cdot 2C_{13}H_{17}ON_3$, has stronger antipyretic and respiration-stimulating actions than correspond with its pyrimidine content, but possesses a relatively slight convulsive action. W. O. K.

Harmine. E. ŠVAGR and V. ŠTOLC (Chem. Listy, 1932, 26, 476—479).—Phosphotungstic acid gives a bluish-white ppt. with harmine (I). Reinecke's salt gives a ppt. with (I) in dilutions of $\leq 1 : 200,000$, (I) is best determined in organs by Florence's procedure, titrating the extract with $0.01N-H_2SO_4$, with iodococousin as indicator. Using Florence's method of extraction, 98.9% of (I) present in organs is recovered, as compared with 97.7—101% using the Stas-Otto method. A no. of new colour and pptn. tests for (I) are given. R. T.

Influence of quinine hydrochloride on purine metabolism in hyperthyroidism. T. OGAWA (Folia endocrinol. Japon., 1931, 6, 112—113).—Quinine is antagonistic to thyroid gland in regard to purine metabolism. CH. ABS.

Photobiological sensitisation to ultra-violet rays. F. M. KUEN and P. ROSENFELD (Biochem. Z., 1932, 254, 181—186).—Quinine sulphate and æsculin have no appreciable sensitising effect (measured by degree of hæmolysis produced in blood) to ultra-violet light, but acridine hydrochloride and trypan-flavine sensitise to rays of $\lambda > 302 m\mu$ (especially

365 $m\mu$), although these two substances do not sensitise to visible light. Et chlorophyllide and MeOH extracts of spinach sensitise to rays of $\lambda > 297 m\mu$ (especially 313 and 365 $m\mu$) as well as to visible light, whilst MeOH extracts of *Selaginella* sensitise especially to rays of $\lambda 254 m\mu$. W. McC.

Chronic morphine poisoning in dogs. IV. Excretion of morphine in tolerant and non-tolerant animals. I. H. PEARCE and O. H. PLANT (J. Pharm. Exp. Ther., 1932, 46, 201—228).—A method for the determination of morphine in urine and faeces is described. Whilst the amount of morphine excreted in the urine varies from day to day and depends on the fluid intake of the animal, it is approx. proportional to the dose and $>$ that in the faeces, in which the amounts are nearly const. Of the daily dose approx. 12.5% was excreted, this being greater with small doses than with large. The amounts excreted by tolerant and non-tolerant animals are almost equal; part of a single dose is retained in the body longer than 24 hr. in both cases. A. L.

Nicotine in tobacco smoke. V. L. NAGY (Biochem. Z., 1932, 254, 94—96).—In smouldering cigarettes all the nicotine passes unchanged into the smoke. W. McC.

Mechanism of internal secretory equilibrium. Influence of tobacco smoke on blood-sugar. E. LUNDBERG and S. THYSELIUS-LUNDBERG (Acta med. Scand., 1931, Suppl. 38, 5—65; Chem. Zentr., 1932, i, 3080—3081).—Immediately after the commencement of smoking the blood-sugar rapidly rises to 1.5 times the normal val., to which it falls more slowly during 0.5 hr. The phenomenon is not observed with nicotine-free material. The rise is particularly marked in diabetes. A. A. E.

Drugs employed as antidiabetics in Chinese medicine. VII. Mechanism of the hypoglycaemic action of phellodendronelactone. N. SUGIHARA and S. HIRANO (Keijo J. Med., 1932, 3, 333—339).—Injection of the drug significantly lowers the blood-sugar of normal but not of depancreatized guinea-pigs, pigeons, and rabbits (cf. this vol., 877). Hence this drug increases the secretion of insulin. F. O. H.

Effect of intravenous phosphatide on the sugar excretion of the phloridzinised dog. I. II. PAGE and F. G. YOUNG (Biochem. J., 1932, 26, 1528—1531).—Injection of aq. brain phosphatide emulsion does not appreciably alter the glucose/N ratio of the urine. There is no apparent conversion of fatty acid into sugar. S. S. Z.

Biological assay of digitalis and strophanthus. C. W. CHAPMAN and C. A. MORRELL (J. Pharm. Exp. Ther., 1932, 46, 229—250).—Frogs are used, and the method eliminates seasonal and individual variation. The results of assays are reported, and variations in the animals are discussed. A. L.

Narcosis and oxidations of the brain. J. H. QUASTEL and A. H. M. WHEATLEY (Proc. Roy. Soc., 1932, B, 112, 60—79).—Narcotics inhibit the oxidation by brain tissue of glucose, Na lactate and pyruvate, and, to a smaller extent, of glutamic acid, but not that of Na succinate or *p*-phenylenediamine.

Concns. of narcotics effectively inhibiting oxidation by brain tissue do not influence the respiration of yeast. With narcotics of the same type (e.g., dialkylbarbituric acids) the inhibitive action on brain oxidation is proportional to the hypnotic activity. Brain tissue of mice narcotised by CHCl_3 exhibits a diminished ability to oxidise glucose. A theory of narcosis is advanced. F. O. H.

Percutaneous resorption of narcotics. M. LAZAREV (Arch. exp. Path. Pharm., 1932, 168, 162—170).—When applied to the skin of rabbits in CHCl_3 , EtOH , Et_2O , fat, oil, or H_2O , narcotics are (1) strongly active [e.g., $\text{OH-CMe}_2\text{-CCl}_3$, $\text{CCl}_3\text{-CH(OH)}_2$, $\text{CCl}_3\text{-CHMe-OH}$, $\text{NH}_2\text{-CO}_2\text{Et}$, $\text{CMe}_2\text{-Br-CO-NH}_2$], (2) moderately active (e.g., $\text{CMe}_2\text{Et-OH}$, paraldehyde), or (3) inactive or only slightly active (e.g., barbituric acid derivatives). W. O. K.

Fate of chloral hydrate in the organism. N. E. RENESCU and B. B. OLSZEWSKI (Compt. rend., 1932, 195, 624—626).—The narcotic action of chloral is not due to CHCl_3 formed from it, since the organs of dogs poisoned with chloral hydrate intravenously contain large quantities of the latter, but only traces of CHCl_3 . Chloral is fixed by the brain, liver, kidney, and intestines; its concn. in the blood falls rapidly after injection. The chloral content of the brain is not related to the dose, whilst that of the liver and fat increases with duration of narcosis. Chloral does not survive more than 2—3 months' putrefaction. A. C.

Oxygen consumption of muscles treated with bromoacetate. C. I. WRIGHT (J. Cell. Comp. Physiol., 1932, 1, 225—235).—Sartorius muscles treated with bromoacetic acid or salts sufficient to inhibit lactic acid formation retained 60—70% of their normal resting O_2 consumption. Chemical or electrical stimulation is followed by excessive O_2 consumption proportional to the tension developed. A. G. P.

Effects of monobromoacetic acid on metabolism. K. HIKIJI (Arch. exp. Path. Pharm., 1932, 168, 1—18).—Rabbits to which 15—30 mg. $\text{CH}_2\text{Br-CO}_2\text{Na}$ (1) are administered subcutaneously develop marked oedema and weakness and die after a few days. The gas metabolism is not much affected, but the glycogen content of the muscles is reduced whilst the lactic acid content is unaltered or slightly reduced. Muscle-creatinine falls, whilst a marked creatinuria takes place with no increase in the creatinine output. Phosphagen and muscle-pyrophosphate decrease. The blood-sugar increases a few hr. after administration of the poison. The surviving muscle taken from a rabbit poisoned by (1) has a markedly reduced capacity for work, whilst the production of lactic acid during work is reduced, but does not disappear. W. O. K.

Mechanism of thiocyanate poisoning. K. YAMADA (Arch. exp. Path. Pharm., 1932, 168, 19—31).—In rabbits poisoned for some hr. by KCNS, the glycogen content of the muscles after some hr. has decreased, phosphagen content usually has fallen, and the lactic acid concn. has only slightly changed. Surviving muscles from chronically poisoned animals have a decreased capacity for work. W. O. K.

Effect of age and sex on resistance of Daphnids to mercuric chloride. J. BREUKELMAN (Science, 1932, 76, 302).—In *Daphnia magna* susceptibility to HgCl_2 decreases with age of the animal. Males are more susceptible than females, with the parthenogenetic forms intermediate between the two. L. S. T.

Biology of aluminium. II. H. STEUDEL (Biochem. Z., 1932, 253, 387—394).—Al salts added to the diet of white rats over four generations did not injure reproduction, nor did the animals appear to store Al in the liver, kidney, spleen, or heart. P. W. C.

Influence of -thiol and -sulphoxide on differential growth within the regenerating chela of the Hermit crab (*Pagurus longicarpus*). F. S. HAMMETT and D. W. HAMMETT (Protoplasma, 1932, 16, 253—286).—Regeneration was accelerated by $\cdot\text{SH}$ (in thiocresol) and retarded by $\cdot\text{SO}$ (in Ph_2SO). The role of S equilibrium in cellular differentiation is indirectly the result of the action on cell proliferation. A. G. P.

Inhibition of the concentration of dye in the liver by organic non-electrolytes and organic salts. R. HOBER (Pflüger's Archiv, 1932, 229, 402—421; Chem. Zentr., 1932, i, 3316).—The inhibitory effect of various org. substances on the retention of dyes by the isolated frog's liver perfused with isotonic a.c. dye solution is considered. A. A. E.

Permeability and cytolysis of the sea-urchin egg with regard to some fertilisation problems. W. A. DORFMAN (Protoplasma, 1932, 16, 56—78).—The presence of univalent cations increases and of bivalent cations decreases the permeability of the egg, the relative effects of univalent ions being in the order of the lyotropic series. In still greater concn. cations (especially Al^{+++} and Th^{+++}) bring about coagulation of the cell colloids. A. G. P.

Iodine compounds and fertilisation. IV. Capacity for fertilisation in washed and unripe eggs of *Echinus esculentus* and *E. miliaris*. **V.** Agglutination and chemotaxis of the sperm. **VI.** Physiological properties of extracts of the ovaries and testes of *E. esculentus*. **VII.** Nature of the egg secretions and theory of fertilisation. G. S. CARTER (J. Exp. Biol., 1932, 9, 238—248, 249—252, 253—263, 264—270). CH. ABS.

Influence of small doses of iodine and sulphur and of pituitrin on the liver- and muscle-glycogen. K. MURAS (Folia endocrinol. Japon., 1931, 6, 118).—S causes an increase; I and pituitrin are without effect. CH. ABS.

Iodine content of the blood: its relation to potassium iodide feeding. E. M. MASON (New Zealand J. Sci. Tech., 1932, 14, 32—37).—Changes in the I content of the blood of cows following the feeding of KI are recorded. Max. vals. were attained within 5 hr. of feeding and were proportional to the amount administered. In no case did the calc. total amount of I in the blood approach the quantity ingested. A. G. P.

A new oxidation enzyme and its absorption spectrum. O. WARBURG and W. CHRISTIAN (Bio-

chem. Z., 1932, 254, 438—458).—The enzyme (from bottom yeast) does not dialyse through cellophane and is inactivated at 60°. Aq. solutions are yellowish-red, but on reduction give a colourless leuco-form which reoxidises in air or more quickly on adding methylene-blue. The enzyme can therefore be titrated by methylene-blue and the abs. concn. of the active groups be determined. That part of the respiration of yeast juice insensitive to either CO or HCN is due to the enzyme. The absorption spectra of the oxidised and reduced enzyme solutions are given. P. W. C.

Dehydrogenations by brain tissue. Effects of narcotics. D. R. DAVIES and J. H. QUASTEL (Biochem. J., 1932, 26, 1672—1684).—The dehydrogenating powers of brain tissue (I) of various animals have been studied and the Michaelis consts. determined for a no. of substrates. Velocity-concn. curves exhibit max. above which increase of concn. leads to decreased reduction velocities. Grey matter is three to four times as active as white matter. Glucose, fructose, galactose, and mannitol are activated as H donors by fresh (I). The activations of glucose and fructose are less than those of Na succinate, lactate, and pyruvate. The activations of the sugars disappear more quickly on storage of (I) at 0° or on incubation at 37° than those of Na succinate and glycerophosphate. Exposure of (I) to narcotics results in an elimination of the activation of the sugars, those of Na succinate and glycerophosphate being relatively unaffected. The activations of Na lactate and pyruvate at low concn. are inhibited by the narcotics. The narcotic and Na lactate compete for the same activating enzyme or centre. The former does not inactivate irreversibly the lactic dehydrogenase, but its inhibiting action depends on the concn. of lactic acid present. S. S. Z.

Kinetics of fumarase. K. P. JACOBSON, F. B. PEREIRA, and J. TAPADINHAS (Biochem. Z., 1932, 254, 112—137; cf. this vol., 880).—Fumarase acts as a true catalyst in so far as the enzyme concn., the p_H , and the presence of salts have no effect on the ratio of the components in equilibrium. The equilibrium fumarase \rightleftharpoons *l*-malic acid is true and notably dependent on temp. Fumarase of animal origin sets up a different equilibrium from that of fumarase of vegetable origin. While the equilibrium is being attained the mass action coeff. remains that for a reversible unimol. reaction. When the concn. of substrate is increased the velocity coeff. falls and the reaction velocity is directly proportional to the concn. of enzyme, but there is not complete conformity with the law of mass action. The affinity of liver-fumarase for fumaric acid is twice that for *l*-malic acid. W. McC.

Catalase groups. O. T. ROTINI (Giorn. Chim. Ind. Appl., 1932, 14, 456—461).—Determination of the chemico-kinetic consts. (relative crit. energy, entropy const., etc.) of catalases of org. (animal, bacteria, mould) origin and of inorg. nature renders it possible to classify the catalases. Catalases from blood, liver, fat, *Streptococcus*, *Penicillium glaucum*, and germinated pumpkin seeds appear to be identical, but they differ from those of milk, colostrum, and

lactic acid bacteria. The characteristic relative crit. energy, and hence the nature, of pumpkin-seed catalase is changed on germination of the seeds. Inactivation of blood-catalase by NaNO_3 is regarded as due, not only to diminution of the velocity coeff., but also to variation in the relative crit. energy with a consequent change in the quantic order of the reaction; the same holds for the toxic action of NaCl on the catalase of cow's milk. The toxic action of CN' on blood-catalase shows the revivification observed with colloidal metals and tissue-catalases. The catalase actions of $\text{Fe}(\text{OH})_3$ and MnO_2 are highly activated by small proportions of KCN and NaNO_3 . T. H. P.

Gas burette for catalase apparatus. D. A. PACK (Ind. Eng. Chem. [Anal.], 1932, 4, 393).—The design of the apparatus permits all the chambers containing gas to be immersed in a const.-temp. bath. E. S. H.

Tyrosinase of potato tubers. I. M. ROBERTSON (Proc. Roy. Soc. Edin., 1931—1932, 52, 309—314).—The tyrosinase reaction is unimol. and can be used to distinguish different varieties of potato. Tuber wt., environment, season, or storage does not influence the enzyme activity; this depends on tuber maturity and is affected by the presence of certain diseases. W. R. A.

Quinones as enzyme models. VII. Catalytic deamination of amino-acids in absence of oxygen and with the use of hydrogen acceptors. K. SCHUWIRTH (Biochem. Z., 1932, 254, 148—157; cf. this vol., 1165).—The catalytic deamination of glycine, glycylglycine, and glycyltyrosine (hydroxy-quinol, adrenaline, gallic acid, resorcinol as catalysts) is an aerobic process, but $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ or nitro-anthraquinone can act as substitutes for O_2 (air). Methylene-blue, alloxan, or isatin, however, cannot act thus. The mechanism of the reaction is the same with the H acceptor as with O_2 , but the latter gives much greater yields of NH_3 . W. McC.

Plant amylases. I. Effect of starch concentration on the velocity of hydrolysis by the amylase of germinated barley. C. S. HANES (Biochem. J., 1932, 26, 1406—1421).—The relationship is in close agreement with that predicted by the Michaelis theory. In the case of the initial reaction velocity it is linear over a wide range of enzyme concn. S. S. Z.

Optimal ratio of α - and β -diastase in saccharification of potato starch. W. SYNIEWSKI and S. ZEMINSKI (Biochem. Z., 1932, 253, 266—274).—The ratio is 70 α : 30 β . P. W. C.

Secretion of enzymes. P. ALBERTONI (Rend. R. Accad. Sci. Bologna, 1929—1930, 34, 67—68).—Dog's saliva remains without diastatic action after intravenous injection of takadiastase. Circulation of digestive enzymes does not occur. R. K. C.

Dilatometric investigation of enzymic processes. III. Hydrolysis of α - and β -methylglucoside. P. RONA and N. NEUENSCHWANDER-LEADNER (Biochem. Z., 1932, 254, 322—328).—Tables show the changes in vol. of solutions of α - and β -methylglucosides during hydrolysis with

maltase and emulsin, respectively (cf. this vol. 649).

P. W. C.

Enzymic conversion of synthetic methylglyoxal into lactic acid. K. LOHMANN (Biochem. Z., 1932, 254, 332—354).—Aq. muscle and liver extracts lose their power of converting synthetic AcCHO into $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ on dialysis against dil. salt solutions and on oxygenation in alkaline (NaHCO_3) solution, whilst dry preps. of yeast and of *B. pasteurianum* lose their power on washing with distilled H_2O . The power is, however, regained on adding glutathione. The relationship of the reaction velocity and the glutathione concn., the temp. sensitivity of the enzyme, and the temp. coeff. of methylglyoxalase are investigated. Glutathione is similarly necessary for the conversion of BzCHO . Of the heavy metals ($0.001M$) with glutathione ($0.002M$) Cu, Ag, and Hg inhibit almost completely, whilst Fe, Mn, Ni, Co, Zn, and Pb do not inhibit. The effect of Cu is abolished by larger amounts of glutathione. Aldehydemutase does not require glutathione as does glyoxalase. The breakdown of glycogen into $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ also occurs in the absence of glutathione.

P. W. C.

Action of co-enzyme. III. Activation of lactic acid formation in muscle extracts by various forms of adenosinetriphosphoric acid. H. K. BARRENSCHEEN and K. MÜLLER. IV. Activation of the dismutation of aldehyde. H. K. BARRENSCHEEN and K. BRAUN. V. Chemistry of adenosinetriphosphoric acids. H. K. BARRENSCHEEN and W. FILZ (Biochem. Z., 1932, 253, 408—413, 414—421, 422—426).—III. The adenosinetriphosphoric acid obtained by the $\text{AcOH}\cdot\text{NaNO}_2$ method activates $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ formation in extracts free from or poor in co-enzyme more strongly than does the triphosphoric acid directly extracted from muscle.

IV. Dismutation of MeCHO in liver extracts is activated by co-enzyme, but not by muscle-adenosinetriphosphoric acid, whereas in muscle extracts poor in or devoid of co-enzyme, cozymase is not and the triphosphoric acid is considerably active. Hexosediphosphate in muscle extracts increases the rate of disappearance of MeCHO enormously, and glucose, glycogen, dihydroxyacetone, glyceraldehyde, and lactate but not AcCHO cause a fleeting activation which is increased by the triphosphoric acid.

V. See this vol., 1064.

P. W. C.

Alleged decarboxylation of pyruvic acid by liver. G. GORR and J. WAGNER (Biochem. Z., 1932, 254, 5—7).—In sterile mixtures liver preps. produce COMe_2 , but no MeCHO from AcCO_2Na . W. McC.

Production of acetoacetic acid by liver. G. GORR (Biochem. Z., 1932, 254, 8—11; cf. preceding abstract, and Embden and Oppenheimer, A., 1912, ii, 1075).—The enzymic production of COMe_2 from AcCO_2H by liver preps. does not depend on the presence of CaSO_3 and these preps. produce no COMe_2 from Na formate, acetate, propionate, *n*-butyrate, *n*-valerate, fumarate, succinate, *dl*-lactate, or *d*-alanine. The activity of the preps. varies greatly with the species of animal from which they are obtained and with its state of nourishment. The

COMe_2 produced is entirely derived from $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$; MeCHO is not an intermediate product. From EtOH or MeCHO under the same conditions no $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ is produced.

W. McC.

Animal carboglycase. G. GORR (Biochem. Z., 1932, 254, 12—14).—Preps. of heart-muscle produce acetoin from AcCO_2Na . If sulphite is present MeCHO is produced, but practically no acetoin.

W. McC.

[Formation of] diacetyl and acetoin by the action of pepsin on milk. I. W. CIUSA (Annali Chim. Appl., 1932, 22, 594—597).—The formation of these substances is not peculiar to rennin, but has been found in small amounts by steam-distilling a mash of peas and artichokes. By the action of pepsin on milk they are obtained in quantities up to 0.0087%. In this case they are formed by the sp. action of pepsin on some milk protein, not caseinogen.

O. F. L.

Pepsin. A. HEIDUSCHKA and J. FORSTER (Arch. Pharm., 1932, 270, 419—423).—The activity of pepsin is decreased by various antipyretics, narcotics, xanthine derivatives, and antiseptics, but not by a no. of alkaloids and tinctures, sucrose, or gum arabic. The depression of activity is not proportional to the concn. of the drug added, but is relatively great with small additions.

R. S. C.

Formation of enterokinase from a precursor in the pancreas. J. PACE (Biochem. J., 1932, 26, 1566—1570).—The crit. increment of the process precursor—enterokinase (I) is 9500 g.-cal. per mol. The precursor-like dipeptidase is adsorbable by $\text{Fe}(\text{OH})_3$, from which both can be eluted, (I) being ultimately formed in the elution. The presence of glycine does not affect the rate of formation of (I).

S. S. Z.

Influence of bile acids on the digestion of nucleins. I. Digestion of nucleic acid by intestinal juice. T. KURAMOTO (J. Biochem. Japan, 1932, 16, 141—152).—Bile acids (cholic, taurocholic, and glycodeoxycholic) in low concns. accelerate and in high concns. inhibit the hydrolysis of nucleic acid by dog's intestinal juice to an extent characteristic of each acid.

F. O. H.

Urease. III. Action of fluoride on urease. IV. Action of sodium tungstate on urease. A. RUCHELMANN (Biochem. Z., 1932, 253, 294—299, 254, 479—483).—III. In the reaction of urease on urea, added NaF unites with both substrate and enzyme; it affects the velocity of hydrolysis of carbamate, the action being more energetic in strongly buffered solutions (cf. this vol., 777).

IV. A table and curves show the inhibiting effect of Na_2WO_4 on the action of urease.

P. W. C.

Action of dyes on enzymes. III. Urease. J. H. QUASTEL (Biochem. J., 1932, 26, 1685—1696).—Most basic dyes, especially of the CHPh_3 series (I), are toxic, whilst acidic dyes are inert, towards urease. The toxicity of compounds such as Janus-green or neutral-red increases, and that of (I) diminishes, with increased purification of the enzyme. A substance is present in soya bean which enhances greatly the toxicity of the basic CHPh_3 dyes towards purified

urease. This is present in soya-bean oil and is confined to the unsaturated glycerides, linseed oil being particularly effective. Urea, α -NH₂-acids, sarcosine, C₂H₄(NH₂)₂, NH₂Me, NHMe₂, N₃H₄, and NH₂OH protect urease from the toxic action of dyes. NMe₃, betaine, urethane, methyl- and diethyl-carbamide, oxamic acid, etc. are without effect. Glycine combines reversibly with urease. The dissociation const. of the urease-glycine complex has been determined. The combining group of the protective substances is either a basic NH₂- or NH-group. Combination of α -NH₂-acids, basic amines, etc. takes place reversibly at acidic or negatively-charged groups which constitute either wholly or partly the active centre of urease. Basic dyes appear to combine with these groups irreversibly. Urea is combined at these groups, activation of the mol. then occurring.

S. S. Z.

Inactivation of lipase in dairy products by traces of heavy metal salts. W. L. DAVIES (J. Dairy Res., 1932, 3, 254—263).—The presence of heavy metal salts (up to 25 p.p.m.) inhibited the action of lipase in butter prepared from unpasteurised sweet cream. Of the metals examined Cu was the most active, Fe, Ni, Co, Mn, and Cr being less effective, and Sn and Al without action. The acidity produced during lipase activity was accompanied by fat peroxides in directly proportional amounts. The latter are associated with the free oleic acid formed.

A. G. P.

Hydrolysis by phosphatase of stereoisomeric diarylphosphoric acids. F. VON BRUCKE (Biochem. Z., 1932, 253, 470—481).—The extents of hydrolysis respectively of K *o*-, *m*-, and *p*-ditolyl-phosphate using takaphosphatase (I) at p_H 6.5 for 5 days are 100, 100, and 28%, using (I) at p_H 4.3 for 5 days are 82, 97, and 83%, using pig's liver-phosphatase at 6.5 for 5 days are 5.9, 84.8, and 81.5%, using pig's kidney-phosphatase for 8 days are 52.7, 84.9, and 66%, and using rabbit's kidney-phosphatase for 20 days are 11.1, 32.5, and 28.3%.

P. W. C.

Action of bone-phosphatase on the esters of phosphoric acid of the blood. E. J. KING (Biochem. J., 1932, 26, 1697—1703).—At p_H 9, the optimum [H⁺] for the enzyme, bone-phosphatase liberates about $\frac{1}{4}$ of the total acid-sol. P of the neutralised acid extract of the pancreas. At or near p_H 7 a somewhat larger proportion was hydrolysed during 24 hr. With acid extracts of liver, kidney, and muscle the p_H effect is not so marked, max. hydrolysis taking place at p_H 7—9. In the case of blood the esters of H₃PO₄ contained in CCl₃·CO₂H extracts consist of at least two fractions. One is hydrolysed by bone-phosphatase at p_H 9, whilst the other is hydrolysed preferentially at a p_H near neutrality. Both fractions are almost completely hydrolysed at or near neutrality during 2 days at 37.5°.

S. S. Z.

Adenosinetriphosphatase of liver. H. K. BARRENSCHEEN and S. LANG (Biochem. Z., 1932, 253, 395—407).—The enzyme reacting with adenosinetriphosphoric acid (I) shows a p_H optimum at 8.2—9 and a temp. optimum of 37°. The enzyme is very sp. and does not react with pyrophosphate or glycerophosphate and the hydrolysis curve up to 50%

hydrolysis is approx. linear. Embden's adenylic acid is dephosphorylated by the triphosphatase (II) and (I) is hydrolysed by bone-phosphatase at p_H 9.4 to a slight extent. (II) is inhibited by F⁻, CN⁻, and inorg. PO₄^{'''} but accelerated by cysteine and SO₄^{''}. In contrast with bone- and kidney-phosphatase, (II) is inhibited by Mg⁺⁺.

P. W. C.

Influence of bile acids on glycerophosphatase. III. H. TAKATA (J. Biochem. Japan, 1932, 16, 83—97).—Cholic acid inhibits the hydrolysis of β -glycero- or hexosemono-phosphoric acid by rabbit bone-phosphatase and, to a smaller extent, that by liver- or kidney-phosphatase. The inhibition of bone-phosphatase may also be achieved by subcutaneous injection of cholic acid into guinea-pigs. Obstruction of the bile duct in rabbits also results in a decreased phosphatase content of the liver and kidney, whilst *in vitro* addition of cholic acid to these tissues still further diminishes the phosphatase activity. The influence of this inhibition on the urinary excretion of PO₄ is discussed.

F. O. H.

Growth and enzymic activity of *Saccharomyces cerevisiae* in presence of sodium and potassium cations. I. NOVI (Rend. R. Accad. Sci. Bologna, 1929—1930, 34, 74—75).—Growth of brewer's yeast is retarded by >0.5% of NaCl, but is accelerated by up to 2% of KCl. Glycolysis by cultures heated to 100° is increased by NaCl up to 5% or by KCl up to 1%, but is retarded by greater concn. of KCl.

R. K. C.

Action of organic compounds on alcoholic fermentation. II. Olefinic compounds. E. MAMELI and A. MOSSINI (Giorn. Chim. Ind. Appl., 1932, 14, 450—455).—In small proportions, saturated org. compounds may have an accelerating, a retarding, or zero effect on the rate of fermentation (measured by the CO₂ evolved in 3 hr.). Unsaturated compounds (naphthenes, terpenes, halogen derivatives, alcohols, aldehydes, ketones, phenol derivatives, acids, salts), however, always accelerate the fermentation, the effects being > those of the corresponding saturated compounds. Taking the rate for the control fermentation as 100, the max. rates obtained were, with PrOH 104.1, EtCHO 113, CH₃:CH·CH₂:OH 106.7, CH₃:CH·CHO 117.5, CH₃Ph·CH₂:OH 103.1 and CH₃Ph·CHO 108.1. The accelerating influence of a C:C compound is > that of the corresponding C:O compound.

T. H. P.

Formation of malic acid in alcoholic fermentation in presence of asparagine and aspartic acid. E. GLAMM and M. NITZSCHE (Biochem. Z., 1932, 253, 318—335).—Fermentation by yeast of sugar in pure solution did, but in presence of NH₄ salts did not, give malic acid (I), whilst fermentation with addition of 0.3—0.5% of asparagine always gave an amount of (I) equal to 1/10 of the asparagine. With addition of 0.3—0.5% of aspartic acid, only traces of (I) were formed, although almost all the aspartic acid disappeared. Addition of the mono-amide of (I) did, but of succinic acid did not, give rise to (I). Asparagine either added or formed from yeast-protein appears to be the source of (I).

P. W. C.

An enzyme, in yeast, which oxidises alcohol. F. WINDISCH (Naturwiss., 1932, 20, 673).—When the solution is sufficiently aerated, yeast converts EtOH into AcOH. Since AcOH-bacteria contain also desmolytic enzymes (cf. A., 1930, 447), the physiological criteria of yeast and AcOH-bacteria are no longer sp.

R. S. C.

Amidases of yeast. G. GORR and J. WAGNER (Biochem. Z., 1932, 254, 1—4).—Brewers' and bakers' yeasts and also *Torula utilis* contain asparaginase, but do not liberate NH_3 from urea, $\text{HCO}\cdot\text{NH}_2$, oxamide, succinamide, or NH_2Bz . *Torula*, however, liberates NH_3 from NH_2Ac , $\text{Et}\cdot\text{CONH}_2$, and lactamide. The amount of NH_3 produced from asparagine by dried *Torula* is 300% greater than that produced by the fresh material. With the other amides on which *Torula* acts the increase produced by drying is much smaller.

W. McC.

Physiological behaviour and enzymic hydrolysis of ureidolactose and ureidomaltose. E. HOFMANN (Biochem. Z., 1932, 253, 462—469).—Emulsin and the enzymes of certain lactose-fermenting yeasts (*S. fragilis*, Jorgensen, *S. Kefir*) hydrolyse lactoseureide with the same velocity and to the same extent as they hydrolyse lactose, the products being *d*-galactose and *d*-glucoseureide. Maltoseureide is similarly decomposed without severing the ureide linking. *Aspergillus oryzae* will not grow on solutions containing lactoseureide and inorg. salts, but *Mucor javanicus*, *A. niger*, and *S. fragilis* readily grow and utilise the galactose part of the mol. without attacking the remaining glucoseureide.

P. W. C.

Influence of organic substances on the growth of *Aspergillus niger*. L. E. KIESSLING and A. SCHMIDT (Arch. Pflanzenbau, 1932, 9, 293—305).—Under conditions adopted in determinations of assimilable K in soils by means of *A. niger*, the growth of the organism is markedly affected by the presence of org. plant constituents. In soil-free cultures, additions of filter-paper shreds, washed peat, powdered barley roots, etc. considerably increased the wt. of mycelium produced.

A. G. P.

Citric acid production by *Aspergillus niger*. N. PONGES (Amer. J. Bot., 1932, 19, 559—567).—With a strain of *A. niger* isolated from soil, a high sugar content (15—20%) in the medium was necessary for max. production of citric acid (I). With 5% of sugar (I) was utilised by the organism as an energy source and accumulation was small. NaNO_3 , as the N source, was more favourable than NH_4NO_3 or NH_4Cl to formation of (I). Fe and Zn were essential for the rapid growth of the organism and for the production of (I). The latter did not accumulate in aerated media.

A. G. P.

Biological conversion of glucose into glucosone. T. K. WALKER (Nature, 1932, 130, 582).—Glucosone is produced when the fully-developed mycelium of a mould belonging to the *flavus* section of the *flavus-oryzae* group of *Aspergilli* acts on 5% aq. glucose in presence of a small amount of PhMe at 27—28°.

L. S. T.

Biochemistry of micro-organisms. XXIV. Metabolic products of the *Penicillium brevi-*

compactum series. P. W. CLUTTERBUCK, A. E. OXFORD, H. RAISTRICK, and G. SMITH (Biochem. J., 1932, 26, 1441—1458).—From twelve species or strains of this series mycophenolic acid ($\text{C}_{17}\text{H}_{20}\text{O}_6$) (I) and the following cryst. products were isolated from the medium in which they were grown: $\text{C}_{10}\text{H}_{10}\text{O}_5$, m.p. 145—153°; $\text{C}_{10}\text{H}_{10}\text{O}_6$, m.p. 193—203°; $\text{C}_{10}\text{H}_{10}\text{O}_7$, m.p. 125—135°; $\text{C}_8\text{H}_8\text{O}_6$, m.p. 188—190°. *P. stoloniferum*, Thom, and *P. Biourgeianum*, Zaleski, gave no (I), but in the first case considerable amounts and in the second case small amounts of the other metabolic products, whilst the third species, *P. aurantio-griseum*, Dierckx, var. *Poznaniensis*, Zaleski, gave none of these products. After keeping cultures over long periods in artificial cultivation (20 years) the power of forming (I) but not the products of smaller mol. wt. is lost.

S. S. Z.

Agar-digesting bacteria. H. E. GORESLINE (Science, 1932, 76, 255).—Three new species which can digest agar are described. *Achromobacter pastinator* liquefies agar media and uses carbohydrates as sources of C; *Pseudomonas lacunogenes* softens agar and often utilises carbohydrates, cysteine, asparagine, aspartic acid, tyrosine, alanine, glutamic acid, NH_4 succinate, and peptone as sources of C or N, and $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , and NH_4 phosphate as sources of N when glucose is present; *P. segne* also softens agar, has the same action on carbohydrates as *P. lacunogenes*, but is unable to utilise any of the above compounds, except peptone, as sources of N.

L. S. T.

Degradation of methyl alcohol, formaldehyde, and formic acid by living and killed acetic acid bacteria. D. MÜLLER (Biochem. Z., 1932, 254, 97—101; cf. A., 1931, 1192).—MeOH and CH_3O in low concn. are almost completely converted into CO_2 and H_2O by living *B. Pasteurianum*. Higher concns. (0.25—0.50%) of CH_3O and HCO_2H are only incompletely oxidised by the bacteria. The killed bacteria oxidise MeOH (with production of CH_3O , but not of HCO_2H) and CH_3O incompletely, but not HCO_2H . It is concluded that alcoholdehydrase, aldehydease, and an enzyme which is very sensitive towards COMe_2 and decomposes HCO_2H , partake in the degradation of MeOH.

W. McC.

Oxidases of killed acetic acid bacteria. III. Behaviour of the bacteria towards oxygen and quinone as hydrogen acceptors. D. MÜLLER (Biochem. Z., 1932, 254, 102—111; cf. A., 1931, 1192).— Pr^0OH is dehydrogenated by killed AcOH bacteria when either O_2 or benzoquinone is present as H acceptor, O_2 having 25—30% of the activity of quinone. Even if the activity of the preps., which is almost as great as that of the living bacteria, varies greatly the ratio $\text{COMe}_2\text{-O}_2$: COMe_2 -quinone is const. This ratio cannot be altered by washing the bacteria with H_2O nor by pptg. with $\text{EtOH-Et}_2\text{O}$, and these treatments affect their activity towards the acceptors in the same degree. The temp. of destruction of alcoholdehydrase is 54.5° with both acceptors. It follows that the alcoholdehydrase of the bacteria can utilise O_2 as acceptor without the intervention of an O_2 carrier (cf. Tamiya and Tanaka, A., 1931, 656). Benzoquinone as acceptor is much

less sensitive to the inhibiting action of HCN than is O_2 . Killed bacteria are less sensitive to HCN than are living. In the absence of HCN the amount of $COMe_2$ produced corresponds with that of O_2 absorbed, but when 0.1M-HCN is present only 67–74% of the calc. amount of $COMe_2$ is produced. W. McC.

Products of decomposition of sugar by beriberi bacteria. Isolation of methylglyoxal, and its physiological action. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1931, 7, 763–768).—Mg hexosediphosphate afforded $AcCHO$ (I) in 73.5% of the theoretical yield from 8.73% of hexosediphosphate decomposed. (I) was not obtained from sucrose or fructose. Oral administration of (I) to pigeons did not accelerate avitaminosis-B. CH. ABS.

Lipins of tubercle bacilli. XXIX. Polysaccharides in tubercle bacilli. H. DUMONT and R. J. ANDERSON. XXX. S. LUDEWIG and R. J. ANDERSON (Z. physiol. Chem., 1932, 211, 97–102, 103–110; cf. this vol., 307).—XXIX. Polysaccharides from human and avian tubercle bacilli were isolated by pptn. with basic Pb acetate. Mannose, *d*-arabinose, and inositol were isolated from the former and mannose and inositol from the latter polysaccharide. By acetylation of the polysaccharide of avian tubercle bacilli and hydrolysis of the *Ac* derivative, m.p. 118–120°, it was obtained almost free from N and P. The analysis of the purified material corresponds with a trisaccharide (2 mols. of mannose, 1 mol. of inositol).

XXX. From the crude polysaccharide of human tubercle bacilli after addition of basic Pb acetate, a purer product was obtained by addition of aq. NH_3 . By acetylation and hydrolysis of the *Ac* derivative, m.p. 85–86°, $[\alpha]_D^{25} +64^\circ$ in MeOH, a product free from P and containing only traces of N was obtained. On hydrolysis the purified product gave small amounts of inositol and reducing sugars consisting of 27% of *d*-mannose and 33% of *d*-arabinose + *d*-glucose. Probably other substances (acids) are present in the non-reducing portion. J. H. B.

Lipins of tubercle bacilli. XXXI. Composition of the acetone-soluble fat of the timothy bacillus. M. C. PANGBORN, E. CHARGAFF, and R. J. ANDERSON (J. Biol. Chem., 1932, 98, 43–55).—The fat (cf. A., 1931, 526; this vol., 197) contains no glycerides and only traces of volatile fatty acids, whilst the unsaponifiable matter (27%) is an unsaturated oil free from sterols. The saturated acids consist mainly of palmitic acid and the unsaturated acids are principally C_{16} members. A saturated acid, $C_{18}H_{36}O_2$, isomeric with stearic acid and similar to tuberculostearic acid, is the main constituent of the liquid fatty acids. F. O. H.

Bacterial synergism. Formation by *B. typhosus* or *B. coli anaerogenes* from mannitol of an intermediate substance from which Morgan's bacillus produces gas. J. G. THOMAS (J. Hyg., 1932, 32, 385–395).—The mixture of gases formed by synergic action differs in $H_2:CO_2$ ratio from that obtained with the glucose-fermenting organism alone on glucose or by *B. coli* on mannitol. The intermediate production of formate is suggested. CH. ABS.

Effects of ammonia, of the fatty acids, and of their salts on the luminescence of *B. fischeri*. S. E. HILL (J. Cell. Comp. Physiol., 1932, 1, 145–159).— NH_3 rapidly penetrates and kills the bacteria. NH_4Cl penetrates the cells slowly and eventually causes cytolysis. HCl and NaOH enter only after the destruction of the cell surface. Below p_H 3.5 fatty acids are more toxic than HCl of the same p_H . With a given p_H the destruction of luminescence by the fatty acids increased in the series valeric to formic. The rates of penetration of the free acids and their NH_4 and Na salts increased with the mol. wt. Cytolysis occurring in certain ranges of p_H in 0.5M solutions of the NH_4 salts of the fatty acids increased with the mol. wt. and results from the penetration of mol. NH_3 and fatty acid. A. G. P.

Electric charge of bacterial antigens. L. OLITZKI (J. Immunol., 1932, 22, 251–256).—The H-antigen (I) of *B. proteus* X.19 carries a negative charge at p_H 12.0–4.4 and the O-antigen (II) at p_H 12.0–3.4. By cataphoresis of whole bacteria at p_H 4.0 large amounts of pure (II) are obtained at the positive pole. By cataphoresis of bacterial extracts at p_H 4.0 (II) is completely removed, leaving pure (I) in the middle vessel. CH. ABS.

Welch-Fraenkel bacillus; toxins and antitoxins. S. SHIRAIISHI (Japan. J. Exp. Med., 1931, 9, 613–618).—A true toxin, thermolabile, non-dialysable, and strongly antigenic, and an "acute" toxin, thermostable, dialysable, and non-antigenic (histamine or -like), are present, together with a haemolysin. The true toxin appears to be species-sp., but considerable differences between strains exist. CH. ABS.

Purification and concentration of diphtheria toxoid by means of electrodialysis. L. REINER (J. Immunol., 1932, 22, 439–443).—[H] at the end of dialysis is approx. p_H 3.9, apparently optimal for pptn. of the toxoid. The yield of toxoid was 30–40%; by pptn. with acid it is <10%. CH. ABS.

Purification of Shiga dysentery toxin. S. HOSOYA, S. TERAOKA, and S. TAKATA (Japan. J. Exp. Med., 1932, 10, 97–99).—Removal of toxin from culture filtrates by adsorption, followed by extraction and purification by dialysis, leads to a very potent material giving only a weak ninhydrin reaction. CH. ABS.

Dissociation of the specific protein precipitate of antipneumococcus horse serum and comparison with a protein isolated by chemical means from immune serum. L. D. FELTON (J. Immunol., 1932, 22, 453–467).—After heating in 0.85% NaCl, with or without Na_2CO_3 , the relation protection:N was approx. the same in ppt. and supernatant fluid of the pneumococcus carbohydrate-protein complex. The sol. sp. substance was dissociated from the protein by Ca or Sr phosphate. Protein obtained by dissociation from type I contained 14.9% N, and from type II 15.2% N. In three preps. by the Zn method the N content was 15.3–15.7%. CH. ABS.

Purification of concentrated antitoxins. T. D. GERLOUGH and W. WHITE (J. Immunol., 1932, 22, 331–350).—The potency and amount of protein

in the isoelectric ppts. of diphtheria and tetanus antitoxins varied with the age, previous treatment of the antitoxin, and conductivity of the dialysed solution. Heating the plasma renders the subsequent isoelectric purification of the concentrates more effective for the removal of P-bearing materials. After removal of isoelectric protein from tetanus and diphtheria antitoxins, and especially after electrodialysis, the potencies of the fractions pptd. at lower concns. of $(\text{NH}_4)_2\text{SO}_4$ were increased.

CH. ABS.

Bacterial endotoxin. Search for a specific intracellular toxin in *S. pullorum*. J. H. HANKS and L. F. RETTGER (J. Immunol., 1932, 22, 283—314).—The cell bodies contain a relatively thermostable poison; the toxic principle is stable at p_H 3.0—12.0, is unaffected by direct sunlight during 24 hr., and is destroyed by prolonged action of pepsin and trypsin. It is not dialysable through parchment, and can be pptd. by $(\text{NH}_4)_2\text{SO}_4$ or AcOH-EtOH . Sp. agglutinin antibodies result from its injection.

CH. ABS.

Effect of some chemical factors on survival of purified vaccine virus. H. YAOI and H. KASAI (Japan. J. Exp. Med., 1931, 9, 619—625).—Most of the substances tested, including H_2O_2 , were toxic. Glycerol (50%) and phenol (0.5%) are preservatives.

CH. ABS.

Biological properties of cerebrospinal fluid. A. C. MARIE (Ann. Inst. Pasteur, 1932, 49, 429—434).—The fixed virus of rabies loses much of its virulence when incubated at 38° with physiological saline for 4 hr. If the saline is replaced by cerebrospinal fluid or dialysed serum the virulence is maintained and infected animals show symptoms on the 6th—8th day. Similar results are recorded with tetanus toxin.

P. G. M.

Protein-free suspensions of viruses. IV. Antigenic properties and serological reaction of protein-free suspensions of phage. I. J. KJIGLER and L. ORITZKI (Brit. J. Exp. Path., 1932, 13, 237—248).—The pure phage is a definite antigenic entity. Union of phage and antibody is accelerated by raising the temp. and by addition of complement. Reaction between phage and sp. antibody appears irreversible. The phage antibody is associated with the globulin fraction of the serum.

CH. ABS.

Purification of bacteriophage. S. HOSOYA, K. NAGASE, and T. YOSHIZUMI (Japan. J. Exp. Med., 1932, 10, 101—111).—Pptn. with Zn salts is followed by removal of Zn and dialysis; the non-dialysable residue is conc. by evaporation at low temp. Active phages, giving no protein reactions, were obtained for *Eb. typhi* and *S. dysenteriae*. Lytic activity is destroyed by org. solvents and by some metallic salts. The bacteriophage is probably a non-living agent.

CH. ABS.

Bacteriophages of the root nodule organisms. S. V. DESAI (Indian J. Agric. Sci., 1932, 2, 138—156).—The medium used for the isolation of the bacteriophage should contain little or no sugar; the virulence of the isolated bacteriophage is enhanced in a medium containing 0.5% of sugar. Small amounts of KNO_3 or $(\text{NH}_4)_2\text{SO}_4$ which assist isolation are adverse to the

enhancement of virulence. The optimal p_H for bacteriophage action was p_H 7.6—8.2. CH. ABS.

Structures produced in blood-agar by electric currents between gold and platinum electrodes. I. W. A. G. VAN EVERDINGEN and J. IDZERDA. II. J. IDZERDA and W. A. G. VAN EVERDINGEN (Biochem. Z., 1932, 254, 59—64, 88—93; cf. this vol., 969).—I. Zones similar to those produced by Hg , H_2O_2 , and streptococci are produced in the medium when electric currents are passed between Au or Pt electrodes embedded in it. At the anode the mechanism by which the zones are produced is identical with that caused by the agents named.

II. The changes in the resistance of the erythrocytes to which are due the formation of the zones produced at the anode when an electric current is passed between Au or Pt electrodes are caused by a process of oxidation taking place in an acid medium. The changes can be imitated *in vitro* with the help of H_2O_2 .

W. McC.

Changes of resistance of blood-corpuscles in blood-agar under the influence of streptococci, mercury, and hydrogen peroxide. G. WOKER (Biochem. Z., 1932, 254, 410—413).—The formation of ring structures in blood-agar cultures by streptococci, H_2O_2 , and Hg as described by Brown and by Idzerda and Everdingen (this vol., 969) is discussed.

P. W. C.

Effect of heat on sugar solutions used for culture media. M. L. SMITH (Biochem. J., 1932, 26, 1467—1472).—Autoclaving at 15 lb. pressure causes hydrolysis of maltose to glucose and slow destruction of the latter with production of acid. This change is accelerated by the presence and increasing concn. of $\text{PO}_4^{'''}$. Heating for 1 hr. at 100° causes a similar change in the sugar equiv. to 20 min. autoclaving under 15 lb. excess pressure. S. S. Z.

Nitrogen content of certain proteins. M. L. SMITH, A. M. BROWN, and C. GROSS (Biochem. J., 1932, 26, 1473—1476).—The N content of certain proteins derived from diphtheria toxin and from diphtheria and other sera when determined by the micro-Kjeldahl method varies from 13.57 to 14.64% (average 14.18%).

S. S. Z.

Germicidal activity of alkyl sulphur ethers. E. MILLER and R. R. READ (J. Amer. Chem. Soc., 1932, 54, 4113).—The germicidal activity of $\text{SALK-C}_6\text{H}_4\text{-OH}$ increases with increase in the size of the alkyl group and reaches a max. at Bu. A rise in the temp. (of the bacterial examination) raises the max. to higher members of the series. The isoalkyl ethers have lower PhOH-coeffs. than the n-alkyl derivatives. The O-ethers, $\text{OR-C}_6\text{H}_4\text{-SH}(?)$, of PhSH are probably much less active than the corresponding S-ethers of PhOH.

C. J. W. (b)

Evolution of hormones. D. L. THOMSON (Nature, 1932, 130, 543).—A discussion. L. S. T.

Adrenal cortical extracts and sex changes. F. G. YOUNG and H. W. BENHAM (Nature, 1932, 130, 700—701).—Swingle and Pfiffner's extract of "Eucortone" had no effect on the sexual functions of male or female mice. (Eucortone keeps completely adrenalectomised cats alive for long periods.) In view

of the contrary findings of other authors, it is suggested that the adrenal cortex may secrete two distinct hormones. L. S. T.

Influence of the cortex of the suprarenal capsule on purine metabolism. T. OGAWA (Folia endocrinol. Japon., 1931, 7, 5—6).—Feeding adrenal cortex (0.25 g. per kg. per day) to dogs led to a marked decrease in the purine-N excreted. CH. ABS.

Effect of adrenaline on lipin excretion. E. HILL and A. E. KOEHLER (J. Biol. Chem., 1932, 98, 185—192).—Administration of adrenaline (0.02 mg. per 100 g. body-wt.) to rats fed on a diet poor in fats results in a definite increase in the faecal lipins. F. O. H.

Carbohydrate balance sheet for the adrenalinised fasting rat killed in the recovery period. M. L. LONG and F. BISCHOFF (J. Biol. Chem., 1932, 98, 85—91).—The muscle- and urine-lactic acid, the urine-sugar, and the total and fermentable carbohydrate of the muscles, liver, and organs other than the liver were determined in fasting rats which had received either 0.02 or 0.10 mg. of adrenaline per 100 g. body-wt. and also in non-adrenalinised control animals. The balance sheet thus obtained shows that only 30—40% of the carbohydrate lost from the peripheral tissues is accounted for by a gain in liver-carbohydrate or urinary sugar. Of the total fermentable carbohydrate of the whole body of the control rats, 82 and 76% are accounted for in the rats receiving respectively 0.02 and 0.10 mg. of adrenaline. F. O. H.

Hexosemonophosphate content of mammalian muscle. I. Experiments on rats injected with adrenaline. D. J. BELL (Biochem. J., 1932, 26, 1601—1605).—It is confirmed that the injection of adrenaline and insulin raises the percentage of hexosemonophosphate in rat muscle (this vol., 199). Amputation and freezing of the whole limb of the animal prior to the removal of the muscle for analysis yields equally satisfactory results with the method of dissection from the living animal. S. S. Z.

Influence of protein amino-acids on adrenaline hyperglycaemia. S. MINAMI and H. NISHIYAMA (Folia Pharmacol. Japon., 1932, 14, No. 2, 200—234).—Glycine, tryptophan, cystine, and glutamic acid (I), when injected (with adrenaline) into rabbits, cause hyperglycaemia, whilst histidine (II), leucine (III), and phenylalanine (IV) produce hypoglycaemia. Alanine (V) has little effect. (III) and (IV) decrease adrenaline hyperglycaemia, whilst (I), (II), and (V) do not affect it. The action of combinations of NH_2 -acids is < that of the individual acids. CH. ABS.

Influence of insulin and adrenaline on hippuric acid synthesis. T. Koyasako (Folia endocrinol. Japon., 1931, 6, 110—111).—Insulin alone has no effect on urinary hippuric acid; it diminishes the increase caused by glucose. After injection of BzOH , insulin promotes and adrenaline retards hippuric acid synthesis. CH. ABS.

Crystalline insulin. XVI. Action of ammonium hydroxide and of iodine on insulin. H. JENSEN, E. SCHOCK, and E. SOLLERS (J. Biol. Chem., 1932, 98, 93—99).—Insulin is partly inactivated by

0.5*N*- and *N*- NH_3 on treatment for 6 days at room temp. Subsequent treatment with acid does not reactivate the hormone; this is contrary to Witzemann and Livshis (A., 1924, i, 448), whose results are explained by the apparent decrease in activity of aq. NH_3 solutions injected subcutaneously, a loss due to tissue adsorption. 1 mg. of insulin is inactivated by 0.3 c.c. of 0.1*N*-I, a quantity much smaller than that absorbed in the course of 17 hr. The inactivation by I is probably due to oxidation of the cystine S-S linking. F. O. H.

Crystalline insulin. XVII. Hydrolysis products of insulin. H. JENSEN and O. WINTERSTEINER (J. Biol. Chem., 1932, 98, 281—287).—Re-examination of the hydrolysis products of insulin (cf. this vol., 972) gives no evidence for the presence of aspartic or hydroxyglutamic acids, or glycine, the presence of proline and valine being doubtful. A tentative distribution of the NH_2 -acids in cryst. insulin is: tyrosine 12%, cystine 12%, glutamic acid 21%, leucine 30%, arginine 3%, histidine 8%, lysine 2%. J. W. B.

Insulin. I. Cataphoresis of insulin alone and in presence of glucose; the question of an insulin-glucose reaction *in vitro*. F. O. HOWITT and E. B. R. PRIDEAUX (Proc. Roy. Soc., 1932, B, 112, 13—24).—Using colloidal Au (0.01%) as an indicator of the migration (cf. A., 1930, 159), the cataphoresis of insulin was determined in buffer solutions of p_{H} 2.7—9.6. Under these conditions the protein exhibits a zone of insolubility of p_{H} 4.5—6.5 and an isoelectric point of p_{H} 5.4. Insulin behaves cataphoretically as a chemical entity. Simple addition of glucose (0.1%) or incubation with glucose at 37° for 24 hr. does not influence the velocities for reactions < p_{H} 8: this confirms the non-existence of an insulin-glucose reaction *in vitro* at the reaction of the blood. With greater alkalinity and at room temp. such a reaction occurs and is emphasised by incubation at 37°. Incubation of insulin (0.02%) at 37° and p_{H} 8—9 for 24 hr. is followed by a change in the ζ -potential of the insulin micelle without any concomitant appreciable change of physiological activity. F. O. H.

Insulin dosage and blood-sugar changes. E. L. SCOTT and L. B. DOTTI (Arch. Int. Med., 1932, 50, 511—537).—The relative drop in blood-sugar for doses between 1/16 and 1/2 unit per kg. body-wt. of rabbits is proportional to the logarithm of the dose, blood samples being drawn 30 min. after the injection. There is no evidence that extremely small doses do not have the full expected effect, nor is the response affected if the dose is not administered > once a week or for a longer period than 20 months. Diet may influence the concn. of blood-sugar, but does not affect the relative changes after insulin. H. G. R.

Does insulin contain a specific antigen? P. BARRAL and J. ROUX (Compt. rend. Soc. Biol., 1931, 106, 292—293; Chem. Zentr., 1932, ii, 82).—Experiments on the sensitisation of guinea-pigs to anaphylactic shock suggest that insulin contains a sp. antigen. A. A. E.

Attenuating effect of blood on action of thyroid juice in fowls. E. GIACOMINI (Rend. R. Accad. Sci. Bologna, 1929—1930, 34, 99—109).—The deplum-

ation and depigmentation caused in fowls by large doses of ox-thyroid press-juice dried at 55–60° are less intense when the juice has been mixed before drying with dried ox, sheep, horse, pig, or fowl blood, or has been mixed in a paste with dried blood and H₂O and again dried. R. K. C.

Respiratory metabolism in infancy and childhood. XIV. Effect of thyroid therapy on metabolism of protein in normal infants. L. E. WEYMULLER, T. C. WYATT, and S. Z. LEVINE (Amer. J. Dis. Children, 1932, 43, 1544–1551).—The calorogenic action appears to be due to accelerated combustion of fat and carbohydrate as well as of protein, and not to excessive combustion of protein. CH. ABS.

Comparison of anti-diuretic and oxytocic potencies of commercial pituitary extracts. F. WOKES (Pharm. J., 1932, 129, 241).—The two activities of these extracts are not consistently related. W. S.

Distribution of fat and glycogen after the subcutaneous injection of extracts of the posterior pituitary gland. A. HYND and D. L. ROTTER (Biochem. J., 1932, 26, 1633–1639).—Subcutaneous injection of pituitrin (I) into carbohydrate-fed rats produces effects on the liver- and muscle-glycogen similar to those obtained with pitressin (II) (this vol., 885). On the other hand, (I) is much less efficient than (II) in producing an infiltration of fat into the liver. An artificial mixture of equal parts by vol. of (II) and pitocin inhibits fatty infiltration, and the increase in liver-glycogen is greatly depressed. The effects produced by the several extracts vary with the interval elapsing after the injection. S. S. Z.

Pituitary and sleep. H. ZONDEK and A. BIER (Klin. Woch., 1932, 11, 760–762; Chem. Zentr., 1932, i, 3192–3193).—Distribution of Br in the brain is changed during sleep. In dogs (somnia sleep) the medulla contained 0.61–0.64 mg. Br per 100 g. (normally 0.38–0.41). In animals killed during sleep the pituitary contained 5–7 (normally 15–30) mg. Br per 100 g. Intravenous injection of tetrabromodeiodothyroxine (man, 1 mg.; dog, much larger doses) produces languor and sleep. The Br-containing pituitary extract is more active, the amount of Br thus injected being 0.25 mg. NaBr (20 mg.) was inactive. A. A. E.

Standardisation of male sexual hormone by means of the comb-growth reaction. J. FREUD, P. DE FREMERY, and E. LAQUER (Pflüger's Archiv, 1932, 229, 763–786; Chem. Zentr., 1932, i, 3192).—The cock unit is the smallest dose which, when given during 4 days subcutaneously or intramuscularly in oil (2×0.5 c.c. daily), produces by the fifth day a 15% increase in comb growth. Larger doses are not proportionally more effective than small ones. Standardisation by means of the conen.-activity curve is rejected. No fixed relation was observed between the reactions of cocks and rats; rats require the simultaneous administration of menoformone. A. A. E.

Vitamins. E. ABDERHALDEN (Med. Klinik, 1932, 28, 466; Chem. Zentr., 1932, i, 2969).—It is suggested that foodstuffs contain only precursors of vitamins,

these being converted into the active vitamins after resorption. The relation between vitamins and hormones is discussed. A. A. E.

Quantity of vitamin-A present in the human liver. L. K. WOLFF (Lancet, 1932, 223, 617–620).—Data for 957 specimens of human liver are recorded and indicate that 16% of the population of the Netherlands have sub-normal vitamin-A reserves. In chronic diseases this proportion increased to 24.2%, indicating a connexion between vitamin-A and certain chronic diseases. In embolism, pregnancy, whooping-cough, syphilis III and IV, chronic nephritis, and enteric fever vals. below the average were found. The vitamin-A reserves of the newly-born fall much below the mean. L. S. T.

Vitamin-A reserves of the human liver in health and disease. T. MOORE (Lancet, 1932, 223, 669–674).—The vitamin-A reserve varies widely even among healthy subjects dying from accidental causes, but can be used to give a "normal" val. In cases of diabetes which had received dietetic treatment, vitamin-A reserves were much above this val., but tended to be below the normal in org. heart diseases, non-tuberculosis respiratory diseases, org. kidney diseases, and in septicæmias and certain septic conditions. Vitamin-A should not be regarded as a positive anti-infective agent, indiscriminate in action. L. S. T.

Vitamin-A content of the liver in puerperal sepsis. H. N. GREEN (Lancet, 1932, 223, 723–726).—Low vitamin-A reserves were found in puerperal sepsis even after administration of large doses of the vitamin. L. S. T.

Determination of vitamin-A in cod-liver oils: biologically, chemically, physically, with a statistical examination of the results. II. Intensity of absorption at 328 mμ and biological activity of vitamin-A. K. H. COWARD, T. J. DYER, and R. A. MORTON (Biochem. J., 1932, 26, 1593–1600; cf. A., 1931, 1196).—In re-testing of old oils, the blue val. of the unsaponifiable fraction again gave better agreement with the biological val. of the oil than did the blue val. of the oil itself. This difference was not found with freshly-prepared oils. S. S. Z.

Vitamin-A deficiency in castrated male rats. M. M. SAMPSON and V. KORENCHESKY (Biochem. J., 1932, 26, 1542–1545).—There is no essential difference between normal and castrated rats in respect to the effects of vitamin-A-deficient diets on them. H. W. D.

Administration of ferrous iodide and linoleic acid to rats deprived of vitamin-A. L. L. REED, L. B. MENDEL, and H. B. VICKERY (Science, 1932, 76, 300–301).—Contrary to Chidester and co-workers (Anat. Rec., 1930, 47, 304) the administration of FeI₂ and linoleic acid, alone or in combination, is ineffective as a cure for xerophthalmia, as a growth stimulant, or as a preventive of infection or renal disturbance in rats deprived of vitamin-A (cf. this vol., 972). L. S. T.

Effects of A- and B-avitaminosis on the bones and teeth. P. E. SIMOLA (Biochem. Z., 1932, 254,

245—250).—Anatomical, histological, and X-ray examination of the bones and teeth of rats suffering from *B*-avitaminosis (I) and receiving diets said to cause scurvy, gives no support to the view of Kollath that scurvy is thus caused. The changes produced in the bones of rats by *A*-avitaminosis are very similar to those produced by (I), but in their teeth (I) only causes notable pathological changes.

W. McC.

Fat metabolism with special reference to nutrition on diets devoid of fat. E. GREGORY and J. C. DRUMMOND (*Z. Vitaminforsch.*, 1932, 1, 257—287).—Whilst the view that "scaly tail" in rats is due to an ill-balanced diet is confirmed, no support is forthcoming for the theory that the condition is due to an inadequate supply of linoleic acid (I) or other related unsaturated acids (A., 1929, 853; 1930, 810). The condition is relieved by increasing the intake of vitamin-*B* complex. That the liver-fat of animals fed on a fat-free diet contains considerable amounts of (I) or some very similar fatty acid indicates the ability of the animal to synthesise (I). Omission of vitamin-*B*₁ or -*B*₂ from fat-containing diets gives results indicating the non-existence of a "sparing" action of fats on vitamin-*B* (A., 1929, 852, 1203). Analytical data for the fatty material of the faeces of rats on a fat-free diet are given.

F. O. H.

Photochemical synthesis of vitamin-*B*₁. B. C. GUHA and P. N. CHAKRAVORTY (*Nature*, 1932, 130, 741).—Adenine sulphate, but not guanine chloride, has been activated into vitamin-*B*₁ by ultra-violet radiation.

L. S. T.

Assay of vitamins-*B*₁ and -*B*₂ as influenced by coprophagy. N. B. GUERRANT and R. A. DUTCHER (*J. Biol. Chem.*, 1932, 98, 225—235).—The faeces of rats on a diet deficient in vitamin-*B*₁ or in -*B*₂ were as potent sources of these vitamins as were the faeces of rats on a complete diet, even after a prolonged period on the deficient diet. Vitamins-*B*₁ and -*B*₂ are apparently synthesised in the animal organism.

W. O. K.

Co-enzyme and co-carboxylase content of rats suffering from *B*-avitaminosis. P. E. SIMOLA (*Biochem. Z.*, 1932, 254, 229—244).—No appreciable change occurs in the co-enzyme content of the livers and brains of rats when their food is deprived of vitamin-*B*, but since the co-carboxylase content of these organs decreases as a result of this deprivation and since the administration of co-carboxylase has a favourable effect in *B*-avitaminosis, there may be a relation between this enzyme and the vitamin-*B* complex.

W. McC.

Antiscorbutic vitamin. III. O. RYGH and A. RYGH (*Z. physiol. Chem.*, 1932, 211, 275—284; cf. this vol., 310).—On a vitamin-*C*-free diet guinea-pigs cease to excrete glycuronic acid (I) in the urine. Although (I) alone added to the diet does not prevent scurvy, in conjunction with methylornarcotine (II) it maintains the animals in full health. A cryst. prep. of the hydrochloride of (II) was obtained from the products of hydrolysis of narcotine with cone. HCl for 40 hr. at 60°. The activation of narcotine by

irradiation is now regarded as due to inefficient cooling.

J. H. B.

Narcotine as the alleged precursor of vitamin-*C*. R. L. GRANT, S. SMITH, and S. S. ZILVA (*Biochem. J.*, 1932, 26, 1628—1632).—Narcotine could not be detected in unripe or partly ripe oranges. Attempts to prepare an antiscorbutic fraction by extraction of neutralised lemon-juice with H₂O-free Et₂O failed. The administration of methylornarcotine obtained by demethylation of narcotine under various conditions to guinea-pigs on a scorbutic diet failed to modify the development or character of the ensuing scorbutic symptoms and the experimental animals died in the usual time of typical scurvy.

S. S. Z.

Non-specificity of the phenol-indophenol reducing capacity of lemon-juice and its fractions as a measure of their antiscorbutic activity. S. S. ZILVA (*Biochem. J.*, 1932, 26, 1624—1627).—There is no parallelism between the reducing capacity and the antiscorbutic activity.

S. S. Z.

Experimental scurvy. XIV. Blood-fatty acids and -lipins of guinea-pigs fed on a vitamin-*C*-free diet. XV. Changes in the blood of guinea-pigs fed on a vitamin-*C*-free diet. S. OHATA (*J. Biochem. Japan*, 1932, 16, 191—206, 207—215).—XIV. Scurvy is accompanied by an increase of blood-fatty acids (I) and -phospholipins. The cholesterol level (II) remains fairly const. except in severe scurvy, when it decreases. The ratio (II) : (I) is proposed as a criterion of the degree of scurvy for vitamin-*C* investigations in guinea-pigs.

XV. The H₂O content and the time of coagulation are increased, the serum-proteins are unchanged, while the following factors are decreased to varying degrees: viscosity, red cell and platelet counts, and the contents of haemoglobin, fibrinogen, thrombin, and cephalin.

F. O. H.

Determination of vitamin-*D* by means of its growth-promoting property. K. H. COWARD, K. M. KEY, and B. G. E. MORGAN (*Biochem. J.*, 1932, 26, 1585—1592).—The growth response is graded to the dose of vitamin-*D* administered, that of the bucks being greater than that of does. Logarithmic equations express the responses of the bucks and does, respectively. Tests of the same substances by the line test and by the growth method give identical results. There is an indication that the rat's need for vitamin-*A* is greater than its need for vitamin-*D*.

S. S. Z.

Vitamin-*D* potency of egg-yolk from irradiated hens. G. H. MAUGHAN and E. MAUGHAN (*Brit. J. Phys. Med.*, 1932, 7, 137—138).—Ultraviolet irradiation of hens increases the vitamin-*D* content of the egg-yolk.

W. O. K.

Free fatty acids in cod-liver oil and vitamin-*D*. O. SCHULTZ (*Z. Vitaminforsch.*, 1932, 1, 287—289).—Six samples of oil containing from <1 to 20% of free fatty acids were tested for vitamin-*D* (I) on rats over a period of 2 years. The loss in potency was the same (approx. 30%) for all the oils, indicating that the free fatty acid content does not influence the stability of its (I). With the exception of bleaching,

no method of commercial prep. influences the (I) content. F. O. H.

Fertility of bees and vitamin-E. L. HILL and E. F. BURDETT (Nature, 1932, 130, 540).—Experiments on the fertility of rats indicate that the secretion ("royal jelly") from the pharyngeal glands of the bee contains an amount of vitamin-E which is absent from honey and pollen. L. S. T.

Action of weak electric currents on chlorophyll assimilation in *Elodea canadensis*. F. GÓRSKI (Bull. Acad. Polonaise, 1931, B, 85—101).—In all normal cases the assimilation of chlorophyll decreases gradually during the 2 hr. required for an experiment. This gradual decrease is unaffected by the passage of weak electric currents in solutions of various salts, with the exception of $(\text{NH}_4)_2\text{SO}_4$, which delays it. P. G. M.

Starch synthesis in the variegated leaves of *Pelargonium*. A. G. CHAPMAN and W. H. CAMP (Ohio J. Sci., 1932, 32, 197—217).—Starch synthesis normally does not occur in the non-green portion of the leaf of *P. hortorum*, but occurs if the leaf is placed in (preferably 0.5M) glucose solution. Under normal greenhouse conditions green tissue contains approx. twice as much sugar as non-green tissue. The p_{H} val. or temp. is not the limiting factor of starch synthesis. CH. ABS.

Mannose and the first sugar of photosynthesis. H. F. CLEMENTS (Plant Physiol., 1932, 7, 547—550).—Mannose was not detectable in leaves of numerous plants. Glucose and fructose are probably produced simultaneously as the initial sugars of the photosynthetic process. A. G. P.

Mechanism of the action of light and other factors on stomatal movement. G. W. SCARFF (Plant Physiol., 1932, 7, 481—504).—All movements of stomata are associated with reversible transformations of carbohydrates and changes of p_{H} in the guard cells, the latter being largely dependent on the pressure of CO_2 in the immediate environment of the guard cells. Closure of stomata is associated with CO_2 pressure. A. G. P.

Carbohydrate and nitrogen metabolism in the celery plant as related to premature seeding. H. PLATENIUS (New York [Cornell] Agric. Exp. Sta. Mem., 1932, No. 140, 66 pp.).—The accumulation of carbohydrate in growing celery plants was considerably influenced by temp., the starch and sugar contents increasing on transferring plants to a higher temp. During the growing season the total N and carbohydrate contents declined at similar rates. Exposure of young plants to low temp. increased the proportion of protein and decreased that of sol. N. Temp. did not appreciably affect the synthesis of NH_2 -acids. There was an inverse relationship between the variations of NO_3^- and NH_2 -N and, less consistently, between NH_2 - and protein-N. The NH_3 content was low throughout growth. Premature seeding can be induced in young plants of low carbohydrate content if exposed to low temp., but does not necessarily occur in plants of high carbohydrate content exposed to medium to high temp. The C:N ratio of the plants was higher in the later stages of

growth and was the result of morphological changes. The tendency to seed production is probably unconnected with nutritional factors. A. G. P.

Composition of current and previous season's branch growth in relation to vegetative and reproductive responses in *Pyrus malus*, L. W. THOMAS (Plant Physiol., 1932, 7, 391—445).—The proportions of glucose and sucrose in the current season's growth decreased rapidly during the active season and increased again later. Trees receiving NaNO_3 had higher contents of the simple sugars than did unmanured trees in which the inhibition of invertase activity was marked. The starch cycle in the wood lagged behind that in the bark. Swelling of buds was associated with a lowered N content of the bark, especially in trees receiving N. In unmanured trees starch accumulation was high until the autumn, but where NaNO_3 was applied the starch content diminished rapidly as growth proceeded. The effect of varied fertiliser treatments on starch and total available carbohydrate contents was in the order $\text{N-P-K} < \text{N-P} < \text{N-K} < \text{N} < \text{P-K} < \text{P} < \text{control}$. Starch utilisation was controlled mainly by the N concn. in the tissues, but was also accelerated by increased K and P concns. resulting in fruit bud formation. The ratio carbohydrate:N is a sensitive index of the physiological balance and was affected by fertiliser treatments in the order $\text{N-P-K} < \text{N-P} < \text{N-K} < \text{P-K} < \text{P} < \text{control}$. Applications of N and K increased the absorption of P by the trees. Variations in the ratios starch : P_2O_5 and available carbohydrate : P_2O_5 indicated that P favoured an accelerated respiration only if a sufficiency of P and K was present. Fertilisers affected the moisture content of the tissues in the order $\text{N-P-K} > \text{N-P} = \text{N} > \text{N-K} > \text{P-K} > \text{P} > \text{control}$ and the ash constituents in the order $\text{N-P-K} > \text{N-P} > \text{N-K} > \text{P-K} > \text{N} > \text{P} > \text{control}$. A. G. P.

Relation of age and seasonal conditions to composition of root, petiole, and leaf blade in rhubarb. C. W. CULPEPPER and J. S. CALDWELL (Plant Physiol., 1932, 7, 447—479).—The total-solid content of leaf blades decreased rapidly from the emergence of the leaf and reached a stationary val. when growth ceased. In the petioles the decline in total solids during rapid elongation was followed by an increase later in the season. The EtOH-sol. and -insol. solids of leaves and petioles declined steadily through the growing period, but increased later in the petioles. The leaf mesophyll and petioles were practically free from starch throughout growth and their sugar contents were small. Acid-hydrolysable polysaccharides in leaves and petioles varied only to small extents, the % contents being low throughout growth. The titratable acidity of leaves and petioles increased during vigorous growth and subsequently declined. In all stages the petioles were the more acid. Nitrates occurred in small amounts in young leaves and increased considerably after growth was completed. A. G. P.

Influence of nutritive conditions of seeds and cuttings on the development of the roots. M. E. REID (IX Int. Hort. Cong., 1930, Rep. Proc., 165—169).—The amount of synthesised carbohydrate is important. In addition to furnishing material for

respiration and cell growth, carbohydrates may assist in the formation of other types of nutritive compounds.

CH. ABS.

Changes in the enzyme content of seeds and fruits. N. N. IVANOV (Biochem. Z., 1932, 254, 71—87).—The enzyme (catalase, lipase, peroxidase, urease, invertase, amylase) content of seeds and fruits (peas, barley, wheat, soya bean, pumpkin) frequently indicates the degree of physiological ripeness, often decreasing as that degree increases, but geographical and climatic factors as well as the strain of plant used and its chemical composition also affect the content. During artificially accelerated ripening with the aid of low concn. of C_2H_4 the decrease in enzyme content with ripeness is followed by an increase.

W. MCC.

Wheat as food and seed. G. TALLARICO (Mem. Accad. Italia, 1931, 3, [Biol. 1], 5—325).—The results of 6 years' (1925—1931) study on qual. graniculture are considered from the static and genetic viewpoints. The caryopsides in their physical, chemical, and biological aspects, and as regards the relation of their vol. to their nutritive val., are discussed. Emphasis is laid on the val. of physiological predetermination, according to which the grain is influenced in its activities by external factors acting during the erit. periods of its existence.

T. H. P.

Relationship between soil and associated plants in the Czerwone Wierchy and Bielskie Tatry districts (Tatra mountains). J. WŁODEK, K. STRZEMIENSKI, and E. RALSKI (Bull. Acad. Polonaise, 1931, B, 103—122).—*Versicoloretum Tatricum* and *Trifidi-distichetum* grow in a soil richer in humus than that required by *Disticho-versicolore-tum*; the first-named requires a soil richer in Ca than the two last. All the plants examined grow in soils which have a reaction varying from strongly acid to mildly alkaline (p_H 3.7—7.1). *Festuca versicolor* and *Sesleria Bielzii* require a soil with relatively high Ca content, in contrast to *Juncus trifidus* and *Sesleria disticha*.

P. G. M.

Effects of physical environment on the physico-chemical properties of plant saps and the relation of these properties to leaf temperature. G. A. GREATHOUSE (Plant Physiol., 1932, 7, 349—390).—Changes in the osmotic pressure of leaf juices with age and exposure to various temp. are recorded and discussed.

A. G. P.

Determination of the isoelectric point of protoplasts. VI. Precipitation by buffer and salt solutions of varying acidity. VII. Retardation of the pulsation frequency of contractile vacuoles. H. PFEIFFER (Protoplasma, 1932, 16, 237—243; 244—252).—VI. Microscopical observations of the pptn. of cell colloids by NaOAc solutions buffered to varying extents or containing NaCNS were in accord with vals. for the isoelectric point determined cataphoretically.

VII. The inhibitory effect of alkaloids increased with falling $[H^+]$ and that of Na salts of org. acids with rising $[H^+]$. Relationships between these observations and the isoelectric point are examined.

A. G. P.

Tobacco. VI. Colloid responsible for the water capacity of tobacco. N. I. GAVRILOV and E. I. GINSBERG (Biochem. Z., 1932, 254, 286—291).—The H_2O capacity of tobacco depends chiefly on substances removed by H_2O at 75° , and to a smaller extent on the H_2O capacity of cellulose. Treatment with C_6H_6 and $CHCl_3$ increases the capacity by removing resinous substances which prevent the diffusion of H_2O into the deeper leaf tissue.

P. W. C.

Wood of Spanish *Pinus sylvestris*. L. LEMMEL (Anal. Fis. Quím., 1932, 30, 601—610).—The work of Wedekind (A., 1931, 941) and others on the phenol- and acetylphenol-lignins has been confirmed. *Pyrogallol-lignin*, m.p. $195-215^\circ$ after sintering at 183° , is dark violet; the *Ac* derivative has m.p. $150-154^\circ$ after darkening at 140° .

H. F. G.

Red colouring matter of *Hiviscus babdariffa*, L. (new glucoside, hiviscin). R. YAMAMOTO and Y. OSIMA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1932, 19, 134—141).—The dried calyx of the fruits of *H. babdariffa* yield to 1.5% HCl-MeOH an anthocyanin, *hiviscin chloride* (I), $+4.5 H_2O$, m.p. 192° (2 g. of pure salt from 1.2 kg.) [corresponding *picrate*, m.p. 185° (decomp.)], hydrolysed by HCl (1 : 1) to cyanidin and a dextrorotatory carbohydrate (*phenylosazone*, m.p. 192° ; *p-bromophenylosazone*, m.p. 162°), shown by colour reactions to be a pentose. Colour reactions, the distribution no., and the $FeCl_3$ test show (I) to be a 3-pentoside.

R. S. C.

Survey of anthocyanins. II. G. M. ROBINSON and R. ROBINSON (Biochem. J., 1932, 26, 1647—1664).

Determination of starch in plant tissues. R. L. SHRINER (Plant Physiol., 1932, 7, 541—546).—The method is based on the conversion of starch by taka-diastase followed by a Cu-iodometric determination of the reducing sugars.

A. G. P.

Nitrogen fixation in the dead leaves from forest beds. C. OLSEN (Compt. rend. Lab. Carlsberg, 1932, 19, No. 9, 36 pp.).—N fixation occurs during the decomp. of oak and beech leaves. Addition of $CaCO_3$ increases the amount of N fixed, which is greatest in the range p_H 6.0—7.7, slight at p_H 5.0—6.0, and ceases at p_H 5.0. The fixed N is retained by the organisms until the total N content of the mass reaches approx. 2.2% (about 1 year), when nitrification begins and further fixation ceases. With hornbeam leaves (1.75% total N) decomp. and NH_3 formation begin early and no fixation occurs.

A. G. P.

Discoloration of oak leaves resulting from magnesium deficiency. C. BLATTNY (Z. Pflanz. Düng., 1932, 26A, 216—218).—Typical forms of leaf discoloration are described.

A. G. P.

Detection of inositol and phytinates. F. FISCHLER and F. H. KURTEN.—See this vol., 1270.

Determination of glucose and maltose. M. L. SMITH.—See this vol., 1270.

Determination of histidine. E. JORPES. **Determination of arginine.** E. JORPES and S. THORÉN.—See this vol., 1270.